SGA WEB MINERAL DEPOSIT ARCHIVE

PRESENTATION NOTES AND SLIDES

TITLE: The Rammelsberg shale-hosted Cu-Zn-Pb sulfide and barite deposit, Germany: Linking SEDEX and Kuroko-type massive sulfides.

Author: Andreas G. Mueller
Consultant, 12a Belgrave Street, Maylands W.A. 6051, Australia. E-mail: andreas@conceptual.net.au

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Summary: The Rammelsberg Cu-Zn-Pb sulfide-barite deposit in the Harz mountain range, northern Germany, was mined almost continuously for more than a 1000 years (968-1988 AD). The mine, located south of the medieval town centre of Goslar, is now a UNESCO world heritage site. The Rammelsberg is a type locality for shale-hosted, sedimentary-exhalative (SEDEX) Zn-Pb-Ag deposits but is unusual because of the high grade (27 Mt at 19% Zn, 9% Pb, 160 g/t Ag) and high copper-gold content (1% Cu, 0.5-1 g/t Au) of the sulfide ore.

The Harz is part of the unmetamorphosed slate belt of the Variscan orogen, formed in the Carboniferous during the collision of the paleo-continents Laurussia and Gondwana. The Rammelsberg deposit occurs in a NE-striking, overturned isoclinal syncline of Middle Devonian calcareous black shale, which is enclosed in sand-banded black shale and structurally overlain by Lower Devonian shelf sandstone. In the structural hanging wall but stratigraphic footwall of the sulfide ore, the black shale is altered to a hard quartz-chlorite-ankerite rock termed Kniest. The tightly folded Kniest wedge spans the entire width of the deposit. Pyrite, arsenopyrite and sphalerite disseminations in the Kniest, and sulfide mantos and spotted zones in the Lower Devonian sandstones define a broad zone of epigenetic footwall mineralization. The high-grade massive sulfide, located in the overturned fold limb beneath the Kniest is strongly deformed, recrystallized to a tectonic banding, and separated into two major lenses by reverse movement of the Kniest mass.

The massive sulfide grades laterally into a fringe of shale-banded ore (2 Mt at 6.5% Zn, 3.5% Pb) and is compositionally zoned, stratigraphically higher sulfide-gangue lenses spreading beyond the lower ones. The lowermost lens consists of low-grade pyrite + Fe-dolomite + quartz, overlain by pyrite + Mn-dolomite with layers of chalcopyrite and sphalerite, and blanketed by gold-rich chalcopyrite-sphalerite-galena ore containing 5-10% Fe-dolomite and barite. The uppermost and most extensive layer consists of silver-rich sphalerite-galena ore with intercalated barite beds. Another two beds of sulfide-poor barite occur stratigraphically above the massive sulfide, separated by about 30 m of black shale. Laterally, the sulfide ore grades into the dolomite-rich ore horizon, marked by beds of felsic tuff and traced in drill holes 3 km to the northwest. The ore horizon contains more metal (13 Mt Zn + Pb) than the deposit itself (7-8 Mt Zn + Pb) defining a huge sedimentary-exhalative dispersion halo. The Kniest feeder system, ore textures, and sulfur isotope ratios suggest vent-proximal deposition of sulfide muds in a brine pool by a reduced, H_2S-bearing fluid discharging at about 300°C. Radiogenic lead and osmium isotope data indicate deep fluid circulation and metal leaching from the thick pile (>1000 m) of Lower Devonian shelf sandstones and from paragneisses in the continental crust below.

Paleogeographic reconstructions of the Middle Devonian show that the Rammelsberg deposit formed at the faulted margin of an euxinic basin, part of the basin-and-ridge topography of a marine back-arc rift located at the southern margin of the Laurussian continent. Spilitized alkali basalt and trachyte/rhyolite, associated with hematite ore and pyrite mineralization on volcanic ridges, indicate high heat-flow and extensive seawater circulation. The plate-tectonic setting is remarkably similar to that of the present northwest Pacific, where the Okinawa Trough and the Sea of Japan represent sediment-filled marine rift basins opened in continental crust behind active arc-trench systems. The Japanese Kuroko volcanogenic massive sulfide deposits display ore grades and sulfide-gangue zones almost identical to those of the Rammelsberg, providing a genetic link between VMS and SEDEX, the two main classes of syn-volcanic and syn-sedimentary sulfide deposits.

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1 INTRODUCTION

These explanatory notes accompany color slides illustrating the regional geology, structure, ore petrology, geochemistry, and Devonian plate-tectonic setting of the Rammelsberg SEDEX deposit in Germany. Both text and slide presentation are available as free-of-charge Web downloads. They are designed as teaching tools for digital projection and the study on-screen. The text explains each slide step-by-step. The references quoted on slides are listed below. Most of the published literature is in German and not easily accessible to the international public. Printed reviews in English are those of Hannak (1981) and Large and Walcher (1999).

The high-grade Rammelsberg deposit has been the focus of research for more than two centuries and, together with the Meggen deposit in Germany, represents one of the type localities of sedimentary-exhalative Zn-Pb-barite deposits. In the late 18th century, vonTrebra (1785) interpreted the ore as a sedimentary bed. As geology developed into an independent natural science, increasingly detailed studies led Schuster (1867), Wimmer (1877), Köhler (1882) and Klockmann (1893) to propose similar syn-sedimentary models (reviewed in Kraume et al. 1955). Lindgren and Irving (1911) interpreted the deposit as epigenetic but recognized the effects of dynamo-thermal metamorphism. Wolff (1913) also advocated an origin by metasomatic replacement. Frebold (1927) and Ramdohr (1928) described remnant gel textures and suggested that the sulfides precipitated from "exhalative" hydrothermal solutions in black-shale basins on the sea floor. The cataclastic and recrystallized ore textures were attributed to deformation during folding and low-grade metamorphism. Further microscopic studies by Ramdohr (1953) and the comprehensive Monographs by Kraume et al. (1955) and Ehrenberg et al. (1954) firmly established the syn-sedimentary origin of both the Rammelsberg and Meggen sulfide-barite deposits. The German term "exhalativ-sedimentär" was translated into English (Carne and Cathro 1982) and, as "sedimentary-exhalative" (abbreviated: SEDEX), became the accepted genetic term for this type of base-metal deposit (Leach et al. 2005).

2 SLIDES DESCRIPTION

2.1 *SGA disclaimer*

2.2 *Title slide*

2.3 *Rammelsberg: Past production and grade*

Mining at the Rammelsberg mountain was first documented in 968 AD and ceased in 1988 after the total removal of the ore in place.

Massive sulfide: The massive sulfide, calculated at a density of 4.3 g/cm^3, amounted to:

<u>Altes Lager (Old Orebody):</u> 7.3±0.3 million metric tons (Sperling and Walcher 1990; p 29)

<u>Altes Lager hanging-wall spur:</u> 0.5 million tons (Sperling and Walcher 1990; p 48)

<u>Neues Lager (New Orebody):</u> 19.3±0.7 million tons (Sperling 1986; p 108)

Average mill-head grades were 1% Cu, 19% Zn, 9% Pb, and 160 g/t Ag based on the ore mined during the five years 1950-1954 (Kraume et al. 1955; p 245), which consisted of 75% Neues Lager and 25% Altes Lager massive sulfide. The average gold grade (1.2 g/t in 1950-54) is probably not representative. Underground assays suggest that the total massive sulfide contained 0.5-1 g/t gold. Sperling and Walcher (1990; p 93) quote "production grades" of 1.0% Cu, 15.5% Zn, and 7.0% Pb.

Shale-banded ore: The measured shale-banded sulfide ore amounted to 2 million metric tons at 0.6% Cu, 6.5% Zn, 3.5% Pb, and 60 g/t Ag (Kraume et al. 1955; p 332-333). Sperling and Walcher (1990; p 93) quote "production grades" of 0.3% Cu, 8.2% Zn, and 4.2% Pb.

The Rammelsberg deposit is classified as SEDEX in the strict sense because it is hosted by and in part interbedded with bituminous black shale and siltstone. The Rammelsberg is distinct from other shale-hosted Zn-Pb-Ag deposits by its exceptionally high grade, as illustrated in the diagram of Zn+Pb percent versus total Zn+Pb metal in selected giant and super-giant deposits (modified from Large et al. 2005). The largest shale-hosted SEDEX deposits (McArthur River, Red Dog, Howard's Pass) contain a "geologic resource" of about 30 million metric tons (Mt) Zn+Pb, compared to 7-8 Mt past production from the Rammelsberg. The "mining resource" at McArthur River (125 Mt at 13% Zn, 6% Pb, 60 g/t Ag) equates to 24 Mt Zn+Pb metal (Large et al. 2005).

Copper and gold are not economic in most SEDEX deposits (e.g. Lydon 1983), and the high grades of the Rammelsberg are emphasized when compared to those of other giants:

Red Dog: <0.1% Cu, gold not reported (Kelley et al. 2004)

McArthur River: 0.2% Cu, 0.005 g/t Au (Huston et al. 2006)

Mount Isa: 0.1% Cu, 0.002 g/t Au (Huston et al. 2006)

Sullivan: 0.033% Cu, gold not reported (Hamilton et al. 1983)

Meggen: 0.03% Cu, <0.1 g/t Au (Ehrenberg et al. 1954)

The classification of Broken Hill as SEDEX is controversial. The deposit may be a distal Zn-Pb skarn, given the absence of black shale in the mine sequence and the Mn-rich calc-silicate gangue of the ore (see discussion of the Cannington deposit in Large et al. 2005).

2.4 *Variscan orogen and Alpine foreland tectonics in Europe*

LEFT: Tectonic map of Europe (modified from Meinhold 1971) showing continent-scale geologic units and the present plate-tectonic setting. The Cenozoic Alpine orogen (red, metamorphic massifs dark red) in south-central Europe, part of the extensive Tethyan belt extending eastward into Turkey and Iran, formed during the collision of the African-Arabian and Eurasian continents leaving the Mediterranean as a remnant ocean basin. Most of Europe is underlain by the Precambrian Baltic craton (Baltica), shown in dark pink where outcropping, in light pink where under thin sedimentary cover, and in yellow where covered by deep sedimentary basins. The craton is bounded to the northwest by the Cambrian-Silurian Caledonian orogen (dark violet), and on all other sides by Devonian-Carboniferous Variscan orogenic belts (green). In Germany and other parts of central Europe, the Alpine orogen overprints parts of the older Variscan one.

RIGHT: Physiographic map of Germany (modified from Schulze 1976) showing the Cretaceous-Tertiary foreland structures north of the Alpine molasse basin and fold belt. The Odenwald (OD), Vosges (VG), Black Forest (BF), and Erzgebirge-Bohemian Massif (EBM) represent outcrops of the interior plutonic-metamorphic Variscan terranes. The Rhenish Massif (RM) and the Harz (HZ) are part of the un-metamorphosed Variscan slate belt. Periodic far-field compressive stress in the foreland of the Alpine orogen caused uplift and exposure of the Paleozoic basement (Ziegler 1987), mainly at reactivated Permo-Carboniferous fault zones (dashed white lines). The fault-bounded Harz block was uplifted at least 2000 m since the Late Cretaceous (Franzke and Zerjadtke 1993). In the German-Polish basin to the north, the basement is buried under 2-8 km of Permian-Mesozoic and thinner Tertiary-Quaternary sediments (light yellow-green). Other Alpine foreland structures include the Tertiary Rhine graben (RG) and associated basaltic volcanoes (VB = Vogelsberg). The area of the geologic map shown next (slide 5) is outlined by a white rectangle.

2.5 *Variscan tectonic zones, Germany*

Generalized geologic map (modified from Engel et al. 1983) showing the un-metamorphosed Devonian-Carboniferous slate belt (Rhenohercynikum), exposed in the Rhenish Massif and in the Harz, and the predominantly metamorphic Variscan terranes to the southeast (Saxothuringikum, Moldanubikum), joined by a suture of greenschist-facies schists termed the Northern Phyllite Zone.

The Rhenish Massif and the Harz mountains, which contain the Meggen (M) and Rammelsberg (R) Zn-Pb-barite SEDEX deposits, consist mainly of Devonian marine sandstones and shales (brown), Devonian-Carboniferous basalt ± trachyte-alkali rhyolite volcanic complexes (green dots), and Carboniferous greywackes (brown). Regional folds are upright, strike northeast, and are vergent to the northwest. The slate-belt succession is largely par-autochthonous and rests on Silurian sediments (grey) and on the Cadomian metamorphic basement (650-550 Ma) of Avalonia, a micro-continent accreted to the Baltic craton in the Lower Silurian. Allochthonous units are the Giessen-Selke nappe (GSN), transported at least 60 km to the northwest from a root zone in the Northern Phyllite Zone, and the Hörre-Acker Zone (yellow).

The greenschists of the Northern Phyllite Zone, metamorphosed at 300°C and 300-600 MPa at ca. 325 Ma, include Devonian shelf sediments and igneous rocks of a Silurian-Devonian magmatic arc. Arc-related Silurian and older Cadomian orthogneisses occur also in the amphibolite-facies (800-900 MPa) Mid-German Crystalline Rise, the main source of detritus accumulated in Rhenohercynian greywackes. Both metamorphic zones are bounded by faults and mark the suture of Avalonia with the rifted continental margin (Amorican Terrane Assemblage) of Gondwana, accreted during collision in the Carboniferous and now represented by the Saxothuringian and Moldanubian terranes.

The Saxothuringian (grey) and Moldanubian terranes (pink) consist of para- and orthogneisses, synforms of Neoproterozoic greywacke, Cadomian granites (540-520 Ma), low-grade Cambrian to Carboniferous volcanoclastic strata (brown), and post-tectonic Carboniferous granite batholiths (red). In the gneiss domes, regional metamorphism progressed from the ultra high-pressure (>2 GPa) eclogite facies at 370-350 Ma, to medium-pressure (700-800 MPa) granulite- and amphibolite facies at 350-340 Ma, to low-pressure (200-300 MPa) greenschist facies at 340-300 Ma during batholith emplacement. Klippe structures (black) indicate regionally extensive metamorphic nappes, now largely eroded. Reviews of the regional geology are in Franke (2000) and Linnemann et al. (2003).

2.6 *Harz mountain range: Geologic map*

Generalized geologic map (modified from Hinze et al. 1998) showing the Variscan basement of the Harz, uplifted during the Late Cretaceous and Miocene-Pliocene at the WNW-trending Harz North Rim Fault against Triassic (pink), Jurassic (light blue), and Cretaceous (light green) platform sediments. To the west, the Harz block is offset by normal faults of the Rhine graben system. To the south, it is unconformably overlain by Lower Permian molasse, comprising red-bed fanglomerates (orange) and andesitic-rhyolitic volcanic rocks (red, X-pattern), and by Upper Permian marine sediments (dark blue, lined). The Rammelsberg deposit is located at the southern end of the town of Goslar (GS). Other towns include Clausthal-Zellerfeld (CZ), Göttingen (GT), Mansfeld (MF) and Sangerhausen (SH), the latter two representing the type locality for the Kupferschiefer Cu-Ag deposits.

The Variscan basement is considered autochthonous west-northwest of the Acker tectonic unit (A), and predominantly allochthonous between the Acker (yellow) and the greenschists of the Northern Phyllite Zone (dark grey). The northwestern Harz consists of Lower Carboniferous greywacke (light grey), Devonian sandstone and shale (brown) in an anticlinorium south of Goslar, and Middle Devonian basaltic spilite (light green, heavy black line), all deformed into upright, NE-trending folds.

The Acker unit (A) is bounded by thrust faults and consists mainly of Lower Carboniferous quartzites (yellow) of exotic Caledonian provenance, while the detritus in greywacke is derived from the Mid-German Crystalline Rise. The Upper Devonian to Lower Carboniferous greywacke (yellow, black dots) east of the Acker is imbricated with thrust-faulted Devonian slates (brown, black ellipses), which contain olistostromes of Silurian rocks. The Middle Devonian Elbingerode (EB) volcanic and limestone complex (dark blue, brick pattern) is interpreted as a tectonic window (Franke 2000). The uppermost structural unit is the Giessen-Selke nappe (GSN) placing Devonian slate over Carboniferous greywacke.

The post-tectonic plutons (red, crosses) and associated dike swarms piercing the folds and nappes are co-genetic to the Permo-Carboniferous volcanic rocks in the molasse basins. They consist mainly of biotite granite and minor diorite-granodiorite. The large Brocken pluton (B) is associated with a norite-gabbro intrusion (olive-green, G-pattern), and encloses a raft of biotite-cordierite paragneiss (black). Detrital zircons record a lower U-Pb intercept age of 500-600 Ma indicating that the gneiss represents uplifted Cadomian basement (Walter et al. 1995). The biotite K-Ar age of the granite (295±2 Ma; Schoell 1986) agrees well with the zircon U-Pb ages (307±3 to 294±3 Ma; Breitkreutz and Kennedy 1999) of Permo-Carboniferous volcanic rocks east and north of the Harz.

2.7 *Devonian Elbingerode volcanic complex*

The Rammelsberg Cu-Zn-Pb deposit is hosted by Middle Devonian Wissenbach black shale, marked by thin beds of felsic tuff. The Elbingerode complex (modified from Wagenbreth and Steiner 1990) overlies Wissenbach shale and represents a shallow-marine volcanic ridge rather than a deep-marine sedimentary environment, contrasting facies of the same rift basin. The complex contains hematite ore and volcanogenic pyrite mineralization.

The 700 m thick volcanic rocks and the up to 500 m thick limestone reef, 18 x 4.5 km in outcrop area, are folded into open ENE-trending anticlines and synclines. The surrounding Devonian shales are tightly folded, displaced by stacked reverse faults, and thrust over the outer parts of the complex (inset cross section). The bimodal volcanic succession comprises basalt and trachyte/quartz trachyte, pervasively altered by seawater to green chlorite-calcite-albite spilites and keratophyres, respectively. Minor keratophyre lavas and quartz-albite cherts are intercalated with Eifelian Wissenbach black shale (grey in block diagram). These are overlain by the Givetian succession (green), composed of two lower units of vesicular spilite pillow lava and lithic lapilli tuff, capped by thin layers of hematite-chlorite ore, and an upper unit of auto-brecciated keratophyre lava overlain by the main iron ore bed (black) and the Givetian-Frasnian limestone reef (blue). The youngest keratophyre contains disseminated, stockwork, and breccia pyrite mineralization (red).

Upper Devonian and Lower Carboniferous shales are absent in the centre of the Elbingerode complex where the limestone reef was emergent (Mucke 1973). They contain crystal tuffs of quartz-biotite rhyodacite and plagioclase latite-andesite, tuffitic quartz-albite cherts, a manganese silicate horizon (up to 10 m thick), and mm-thick chalcopyrite-pyrite layers. The entire reef was covered by Lower Carboniferous greywacke (dot pattern) and by flysch of the Hüttenrode olistostrome (brown).

2.8 *Elbingerode volcanogenic iron ore*

Iron ore mining at Elbingerode dates back to the 10th century AD and ceased in 1970. Total production from all mines is estimated at 25 million metric tons at 25% iron, and present measured and drill-indicated reserves amount to 51 million tons at 23% Fe (Walter et al. 1995; Stedingk et al. 2002). The main hematite bed attains greatest thickness (10-20 m) in the peripheral parts of the volcanic complex, where the upper keratophyre unit and the limestone reef pinch out. The keratophyre flows split the ore horizon into a lower and an upper bed, the latter marking the base of the reef. The upper hematite ore (2-3 wt% Mn) contains concretions of braunite, and manganoan siderite (29 mol% $MnCO_3$) occurs locally in the transition zone to limestone (Lange 1957).

TOP LEFT: Cross section through the Büchenberg iron ore deposit (modified from Wagenbreth and Steiner 1990; location in previous slide), illustrating the folding and faulting of siliceous-calcareous hematite ore (black) at the overturned NNW-limb of the Büchenberg anticline. The ore is underlain by Middle Devonian (Givetian) lapilli tuff of basaltic spilite (green), and is overlain by thin limestone lenses (blue), Lower Carboniferous chert and black shale (violet), greywacke (dot pattern), and shaly melange of the Hüttenrode olistostrome (brown). The Eifelian Wissenbach shale is thrust over the volcanic complex.

BOTTOM LEFT: Cross section through the iron ore (30% Fe) at the 200 m level of the Büchenberg mine, Rotenberg area, looking west (modified from Reichstein 1959). The ore is underlain by pillowed keratophyre (yellow) and interbedded with spilite lapilli tuff (green). Beds of oxide-facies siliceous and calcareous hematite ore (black) alternate with reduced chamosite-silica-siderite ore (red). Secondary magnetite (9-16 vol%), probably related to contact metamorphism of the Brocken granite, is widespread. Pyrite (<1%) occurs in cross cutting veinlets, accompanied by trace chalcopyrite and sphalerite. Cu, Zn, and Pb are locally elevated (100-500 ppm), in particular in magnetite-chamosite ore (Dave 1963).

(A): Königshütte, northwestern end of the village. Thick-bedded Givetian lapilli tuffs of the Elbingerode complex, altered to the spilite assemblage chlorite + albite + calcite ± quartz. Beds of lithic lapilli tuff (10-20 cm) are separated by thin flaser-bedded ash tuff. Beds dip 50° south, a steeply dipping spaced cleavage transects the bedding. The outcrop is 25 m high.

(B): Büchenberg iron ore mine. TOP: Fine-grained hematite ore containing 5-7% calcite in 0.5-3 mm aggregates, 1% black bitumen, and 1% microfossils. Pillar at the bottom of the Gräfenhagensberg glory hole, close to the Herrmann shaft. The matchstick is 3 cm long. BOTTOM: Spilite lapilli tuff collected in the footwall of the iron ore. Fine-grained (0.5 mm) chlorite-albite rock enclosing sparry calcite aggregates (20%). The lapilli contain green chlorite pseudomorphs after prismatic pyroxene (?), and white calcite pseudomorphs after rectangular and hollow-cored feldspar. Level 1 (-55 m), stope close to the Herrmann shaft.

2.9 *Elbingerode volcanogenic pyrite*

Volcanogenic pyrite mineralization is associated with the upper keratophyre unit of the Elbingerode complex. Mining of the limonite gossan in the Grosser Graben open pit 2 km southeast of Elbingerode dates back to 1582, and a production of 330,000 metric tons at 40% Fe, 5% Mn, and 0.3% P is recorded for the period 1914-1924 (Lange 1957). Most of the sulfide ore (13 million metric tons at about 25% pyrite) was mined underground to a depth of 460 m below surface for sulfuric acid production (1945-1990), and 7-8 million tons at 15-20% pyrite remain in place (Stedingk et al. 2002). Representative analyses of massive ore are: 44.6 wt.% S, 0.52% SO_3, 40.5% Fe, 0.40% As, 240 ppm Cu, 160 ppm Zn, 10 ppm Pb, and trace mercury and gold (Lange 1957; Scheffler 1975).

The pyrite forms massive lenses up to 20 m thick, which replace the siliceous-calcareous hematite ore below the limestone reef and the upper part of the keratophyre, grading downward into pyrite-cemented breccia and into crackle-veined keratophyre. Adjacent to pyrite veins, the green-grey keratophyre (33 vol.% orthoclase, 48% albite, 8% quartz, 6-9% chlorite, 1-2% magnetite, 1% calcite; Knauer 1958) is altered to a yellow-grey quartz-sericite assemblage. Chlorite and titano-magnetite are selectively replaced by disseminated pyrite containing elevated nickel (100-150 ppm), vanadium (50 g/t), and titanium (200-600 ppm), the latter two elements probably in sericite and leucoxene inclusions. Blebs of chalcopyrite and sphalerite are enclosed locally (Lange 1957; Mucke 1973).

The sulfur isotope values (per mil $\delta^{34}S$, $\pm 2\sigma$) of keratophyre-hosted pyrite vary little in the flotation feed (n=16; mean: -6.5±0.9, range: -8.3 to -4.0), but show a wide range if underground samples are considered (n=101; mean: -6.6±1.2, range: -28.1 to +30.0). The uppermost massive pyrite is lighter on average (n=14, mean: -11.0±1.2, range: -14.1 to -6.1). Scheffler (1975) interprets these data to imply biogenic sulfur sourced from pyrite leached in Devonian and Silurian shales beneath the volcanic complex. Another explanation, consistent with the magnetite-series nature of the felsic volcanic rocks, is that the negative $\delta^{34}S$ values reflect isotope partitioning between pyrite and an unidentified sulfate, both minerals precipitated in equilibrium from a fluid carrying reduced and oxidized sulfur species. During crystallization, an oxidized magma will exsolve aqueous fluid of a certain H_2S/SO_2 ratio. After cooling to 400°C, the SO_2 reacts with condensed magmatic water and/or entrained seawater to form sulfuric acid and H_2S. At Elbingerode, a moderately acidic fluid generated quartz-sericite alteration and, possibly, deposited anhydrite and gypsum, while the H_2S reacted with iron oxides and silicates in the keratophyre and ironstone to form pyrite. The shift to lighter $\delta^{34}S$ values in the uppermost massive pyrite is consistent with fluid cooling (e.g. Rye 1993).

(A): Elbingerode, Kaltes Tal railway cut. Limonite-stained outcrops of quartz-sericite-pyrite altered keratophyre overlain by thick-bedded grey limestone. The stratigraphic contact (dashed white line) is sharp and quartz-pyrite replacement does not extend into the limestone, indicating that volcanogenic sulfide mineralization pre-dates reef formation.

(B): Elbingerode, Kaltes Tal railway cut. Pyrite-rich breccia ore from an outcrop located a few meters below the limestone contact. Angular fragments of hard silica-sericite altered keratophyre (K) cemented by medium-grained (1-2 mm) pyrite, partly coated by white iron sulfate. The Euro 2-cent coin is 19 mm across.

(C): Red chert from the iron ore horizon below the limestone reef, marked by pinhead-sized globular silica shrinkage structures and by fine schlieren of specular hematite and magnetite. The central part of the chert is bleached grey due to the replacement of the iron oxides by pyrite, and some is recrystallized to white quartz. Both chert and quartz are cut by veinlets filled with coarser (0.5 mm) pyrite. Calcite is absent. Einheit mine level 13 (+102 m MSL, 380 m below surface), sample provided by Jens Kruse. The matchstick is 4 cm long.

2.10 *Goslar: Imperial town in 968 AD*

The Rammelsberg mine is located at the southern end of the town of Goslar, where massive ore of the Altes Lager outcropped on the slope of a valley incised into the Harz mountain range. Goslar became imperial residence during the reign of Otto the Great (936-973 AD) due to the economic importance of the mine. Large amounts of coins, minted from Rammelsberg silver, appeared in Saxony from 968 AD onward. The Otto-Adelheid Pfennig, named after Otto III (983-997 AD) and his grandmother, is one of these coins traced due to their high gold and bismuth contents. In contrast to larger German cities, Goslar was not destroyed by aerial bombardment during World War II and retains many medieval buildings in the town centre.

The Rammelsberg mine closed in 1988 after more than 1000 years of near continuous operation (production data from Walther 1986; Museum Rammelsberg, personal communication 2008). Mining was disrupted during the period 1181-1209, when duke Heinrich the Lion destroyed the smelters at Goslar. Activity was insignificant from 1360 to 1460, when the removal of pillars caused stope collapse, parts of the mine flooded, and when the bubonic plague killed much of the workforce. In 1870, underground stoping shifted from the Altes Lager to the Neues Lager, a blind orebody discovered in 1859. Production increased sharply as the industrial revolution progressed.

2.11 *Rammelsberg mine: World heritage*

The surface buildings and upper underground workings of the Rammelsberg mine are now a museum and a UNESCO world cultural heritage site (www.rammelsberg.de).

(A): Looking east at the Rammelsberg mountain, at the flotation plant for the high-grade sulfide ore (completed in 1936), and at the headframe of the Rammelsberg shaft. Note the Kommunion quarry in Lower Devonian sandstone on the upper slope. The quarry was established in 1767 by Johann Christoph Roeder to provide backfill material for the stopes underground. Roeder, mine director from 1763 to 1810, introduced backfill to avoid the frequent collapse of open stopes and permit the recovery of ore pillars. The narrow drives in the Altes Lager were replaced by throughgoing drives in the footwall slate.

(B): Looking at the power and compressed air plant (completed in 1906), originally coal-fired, and at an LHD Diesel loader from the last mining period (1972-1988).

(C): Looking northwest from the Maltermeister tower of the Rammelsberg mine. The forested area in the foreground is underlain by folded Devonian rocks of the Harz mountain range, uplifted at the Harz North Rim Fault, which is marked by the escarpment visible on the left. The town of Goslar on the right is located on Mesozoic platform sediments.

2.12 *Rammelsberg mine: Water system*

In pre-industrial time, water was both curse and blessing for underground mines like the Rammelsberg. The curse came from groundwater flooding the workings. In the 12th century (ca. 1150 AD), the 1 km long Raths Tiefster tunnel was driven from the nearby valley to the Altes Lager orebody, draining the mine to a level (+295 m MSL) about 100 m below the outcrop. Colorful zinc and copper sulfate sinters cover the walls of this tunnel where it approaches the medieval stopes (left photo). About 400 years later (1486-1585), the 2.6 km long Tiefer Julius Fortunatus Stollen was completed, this tunnel draining the mine down to 255 m above mean sea level (MSL).

Surface water collected in the Herzberg reservoir upstream from the mine provided a blessing in the form of hydropower. Channeled into the workings, this water drove wheels (right photo) to pump groundwater in the shafts up to the drainage tunnel level, a forged steel excenter converting the turning into a pushing motion. Double wheels could turn both ways to hoist the ore. In 1798-1805, Johann Christoph Roeder established a highly efficient water-wheel system underground, which remained in operation until 1909 (Dettmer 2005).

2.13 *Rammelsberg district geology*

District geologic map modified from Kraume (1960). The Altes Lager (AL) and Neues Lager (NL) orebodies (light red), part of an overturned fold limb, are projected vertically. The Rammelsberg shaft and the Richtschacht internal shaft (red dots), and the exploration drives and cross cuts on level 7 (red lines), level 9 (blue lines), and level 12 (green lines) are shown. The dark blue wedge represents the Herzberg water reservoir. The mountain summits are in black.

The fossil-rich Calceola marker shale (light blue), about 60-70 m thick, separates Lower Devonian sandstone (yellow) from the Middle Devonian (Eifelian) black shale of the Wissenbach facies (no color). The folded lithologic units strike N60°E. Close to the summit of the Hessenkopf, Wissenbach shale is thrust over Upper Devonian calcareous shale (brown). The Hessenkopf thrust (HKT) was exposed on the Rammelsberg shaft 7 level and dips 45° southeast (Kraume et al. 1955; p 44). Its exact location south of Goslar is not known. Like the folded lithologic units, the thrust is offset at WNW-trending strike-slip faults, part of a Permo-Carboniferous system including the Harz North Rim Fault (HNRF), which juxtaposes Mesozoic platform sediments (green) and the Variscan basement. Reactivation of this fault during Alpine foreland compression caused periodic uplift of the Harz block from the Late Cretaceous to the Pliocene.

2.14 *Rammelsberg: Structure in cross section*

The generalized NW-SE section, modified from Stedingk and Wrede (in Hinze et al. 1998), shows the massive sulfide orebodies (red) within the overturned syncline defined by Middle Devonian (Eifelian) calcareous upper Wissenbach (no color) and by sand-banded lower Wissenbach black shale (grey). The position of the Hessenkopf thrust (HKT) is approximate. The orebodies, oriented sub-parallel to the HKT, were deformed during reverse faulting subsequent to folding. The Calceola shale is not shown. The Lower Devonian sandstones (yellow) are shaded orange where thin sulfide replacement mantos and disseminated sulfide aggregates are exposed in cross cuts of the mine (dark blue). The Rammelsberg (RB) and Richtschacht (RS) shafts are connected by two adits (HBS = Hängebankstollen, TFS = Tagesförderstrecke).

The Lower Devonian succession, mainly micaceous shelf sandstones and quartzites marked by a marine benthonic fauna (e.g. spiriferida), is more than 1000 m thick (Walther 1986). The Middle Devonian units all show an increase in thickness from outcrops southeast of the mine to drill holes northwest of Goslar: the Calceola shale-limestone sequence increases from 30-40 m to more than 100 m, the sand-banded Wissenbach shale from 60-80 m to more than 200 m, and the calcareous Wissenbach shale from 70-150 m to more than 600 m (Paul 1975). These changes indicate that the deposit is located at the edge of a paleo-basin. The combined Calceola and Wissenbach shales contain at least 24 beds of felsic tuff, used as markers for correlation within the mine (Abt 1958).

(A): Looking east at Lower Devonian sandstone exposed in the Kommunion quarry above the headframe of the Rammelsberg shaft. The sandstone beds are overturned and dip 40° southeast. Middle Devonian Wissenbach black shale is exposed in a large outcrop below the headframe, the slaty cleavage dips southeast into the mountainside.

(B): Outcrop of Wissenbach black shale 70 m up-slope from the Rammelsberg shaft, in the structural hanging wall of the Altes Lager orebody. The slaty cleavage dips about 45° southeast. The lens cap (white arrow) is 5 cm across.

2.15 *Rammelsberg: Cu-Zn-Pb sulfides in sandstone*

Subeconomic base-metal mineralization occurs in the Lower Devonian sandstones forming the structural hanging wall but stratigraphic footwall of the Rammelsberg deposit (see section in Slide 14). Sulfide mantos (5-25 cm thick) peneconcordant to bedding, and zones of disseminated sulfides (≤6 m thick) are exposed in the Kommunion quarry, in the Hängebankstollen adit, and in the 9 level and 12 level cross cuts underground (Kraume 1960; Stedingk 1982). The mantos and zones are folded and the sulfides are fractured.

(A): Kommunion quarry, looking southeast at an excavated sphalerite ± galena manto (at pen), about 15 cm thick, in grey quartzite.

Gangue minerals include ferroan dolomite, chlorite, and minor quartz. The numbers represent samples taken along strike.

(B): Replacement manto, composed of streaks of pyrite and chalcopyrite and of minor ferroan dolomite, at the contact between quartz-veined light grey siliceous sandstone and a dark grey shale-sandstone bed, the latter constituting the stratigraphic hanging wall (Kraume 1960; Plate 72, Fig. 8). Rammelsberg shaft 12 level, cross cut at 1600 m grid east, 333 m into the cross cut. The matchstick is 4 cm long. A similar 25 cm-thick manto, exposed in the Hängebankstollen adit, contained 6% Cu, 2% Zn, trace Pb, 20% Fe, and 0.6 g/t Au (Kraume et al. 1955; p 240).

(C): Fine-grained siliceous sandstone containing disseminated aggregates of light brown, iron-poor sphalerite. Rammelsberg shaft 12 level, cross cut at 1600 m grid east, 448 m into the cross cut. The pen is 14 cm long. A 6 m-thick zone of similar mineralization, intersected by drill hole 26a/1950 on 9 level, cross cut 2025 m E, contained 0.1% Cu, 1.1% Zn, and 2.2% Pb (Kraume et al. 1955; p 241).

2.16 *Rammelsberg: Ore in black shale*

The Wissenbach black shale of the Middle Devonian Eifelian stage is subdivided into a lower sand-banded unit, and into an upper carbonate-bearing unit hosting the stratiform sulfide-barite ore.

(A): Lower sand-banded Wissenbach black shale, no mine location. The beds of fine-grained grey sandstone pinch and swell, and contain numerous ladder veins of white quartz indicating tectonic strain. The matchstick is 4 cm long.

(B): Diagenetic nodule (46 cm long) of carbonaceous ferroan dolomite, enclosing thin sulfide beds at the top and disseminated pyrite aggregates. The shrinkage cracks in the core and at the rim are filled with white calcite and minor pyrite (Kraume et al. 1955; plate 22). Rammelsberg shaft 8 level, shale-banded sulfide ore constituting the normal limb of the syncline below the overturned Neues Lager massive ore.

(C): Banded shale-sulfide-dolomite ore. Note the central bed of dark grey ferroan dolomite (slow reaction 5% HCl), in contact with nodular pyrite ± calcite. The large pyrite nodule is of diagenetic origin and indicates stratigraphic way-up to the left. Smaller pyrite nodules occur at the base of sulfide beds and in intercalated black shale. The sulfide beds consist of sphalerite, galena, minor ferroan dolomite, and accessory chalcopyrite. Locally, sulfides are mobilized into cleavage planes discordant to bedding, and the competent dolomite-pyrite bed is displaced at two planes. Rammelsberg shaft 8-10 level, shale-banded sulfide ore collected from the normal limb of the syncline below the overturned Neues Lager massive ore.

(D): Wissenbach shale enclosing a lens of massive pyrite-bearing sphalerite-galena ore. The black shale contains numerous diagenetic pyrite nodules, the larger ones aligned parallel to the cleavage like the massive ore. Rammelsberg shaft level 3 at 1200 m grid east. The matchstick is 4 cm long. Pyrite and dolomite nodules are abundant in a 30 cm thick zone in the stratigraphic footwall of the Neues Lager. Most consist of arsenical pyrite, and display a concentric or radial internal structure. Base metal sulfides are absent. Pyrite also forms thin layers in some dolomite nodules. Many nodules are fractured, quartz filling the fractures and forming aggregates in pressure shadows (Kraume et al. 1955; p 85). The nodules are absent where the Kniest alteration zone is in contact with massive ore.

2.17 *Rammelsberg: Shape of orebodies*

The generalized level plan on the left (modified from Gunzert 1979) illustrates the structural relationships on level 3 of the Rammelsberg shaft, 187 m above mean sea level. The lower sand-banded Wissenbach black shale (grey) encloses the upper carbonate-bearing black shale (no color) defining the isoclinal Rammelsberg syncline. The Altes Lager (AL) and Neues Lager (NL) massive sulfide lenses (black) grade into shale-banded sulfide ore (red) to the northeast and southwest. The sulfide ore is part of the overturned hanging-wall limb of the syncline, overridden along a thrust fault by the Kniest alteration zone (green) of hard silicified shale. The lens of barite (blue) and the dolomite-rich "ore horizon" (heavy dashed line), the lateral equivalent of the sulfide ore, mark the upright lower limb of the syncline. Both fold and thrust are offset by the Western and Eastern Mine Faults, part of the

Permo-Carboniferous strike-slip system. The Western Mine Fault (WMF) strikes N90°E, dips 60°S, and records dextral oblique-slip HW-block-down (lineation 40-50°W). The Eastern Mine Fault (EMF) is identical in strike and dip but mainly strike-slip (Kraume et al. 1955; p 126). The faulted off extension of the Altes Lager (Altes Lager West) was mined, but the smaller northeastern extension of the Neues Lager was not.

The longitudinal section on the right (modified from Kraume et al. 1955) shows the Altes Lager (AL) and Neues Lager (NL) massive sulfide lenses (black), the barite orebody (blue), and the projected position of manto and disseminated sulfides in Lower Devonian sandstone (orange) on the 9 and 12 levels (from Sperling 1986). The composite level plans below illustrate the irregular deformation of the Neues Lager massive sulfide on the upper levels of the mine, and the thick closure of the ore syncline on the lowermost levels.

The Rammelsberg (RB), Richtschacht (RS) and other mine shafts are outlined in green together with selected mine levels. The Rammelsberg shaft levels, shown also on subsequent slides, are listed relative to the mean sea level: TFS = Tagesföderstrecke ore-haulage adit (+329 m MSL), TJFS = Tiefer Julius Fortunatus Stollen drainage tunnel (+255 m), 1 level (+223 m), 3 level (+187 m), 5 level (+157 m), 7 level (+115 m), 8 level (+74 m), 9 level (+35 m), 10 level (-5 m), 11 level (-45 m), and 12 level (-85 m MSL). The mine grid easting is perpendicular to the local N60°E strike.

2.18 *Kniest footwall alteration zone*

Kniest is the mine term for a hard siliceous rock lacking the slaty cleavage of the surrounding black shale, which occurs in the structural hanging wall but stratigraphic footwall of the orebodies. Transitions into shale and whole-rock analyses indicate that the Kniest represents altered shale, strongly enriched in silica (67 wt.% versus 49%) and in iron (9.7% versus 5.6%; Kraume et al. 1955). The principal alteration minerals are quartz, minor sericite, iron-rich chlorite, ferroan dolomite, manganoan ankerite, and manganoan siderite. Disseminated aggregates of accessory pyrite, arsenopyrite, and sphalerite are common (Sperling and Walcher 1990; Muchez and Strassen 2006). The carbonates occur mainly at the margins, in stratabound zones marked by numerous strained nodules with radial or concentric internal texture. The carbonate nodules (1-3 mm) occur in a quartz-chlorite-sericite matrix, some enclosing pyrite or sphalerite grains. While Kniest marks the inner footwall alteration zone, disseminated Fe-Mn chlorite (47 wt.% FeO, <0.1% MgO, 1.3% MnO) marks the outer one, extending about 1 km laterally in the Wissenbach shale and 200 m into the Lower Devonian sandstone (Renner and Brockamp 1985), its occurrence coinciding locally with the sulfide mantos and spotted zones described previously (Slide 15). The metamorphic chlorites in distal shale are more magnesian (29% FeO, 12% MgO).

The composite level plans on the left (modified from Kraume et al. 1955) show the Kniest (green) in relation to the massive sulfides (black). Note the position of the hanging-wall spur of the Altes Lager (AL) on the upper two levels (TFS = Tagesföderstrecke, TJFS = Tiefer Julius Fortunatus Stollen). The bounding dextral strike-slip faults (Western and Eastern Mine Faults) are traced as red lines. The heavy dots mark where Kniest was brecciated and contained sulfide-dolomite±calcite veins along its contact with the Altes Lager. These veins constituted a low-grade stockwork orebody of 2.5 million metric tons, partly mined, at grades of 1.3% Cu, 3.0% Zn, 1.4% Pb, 28 g/t Ag, and 0.2 g/t Au (Kraume et al. 1955; p 229).

The photograph shows sulfide-veined Kniest from the Tagesförderstrecke level, 1550 m east, cross cut north at 75 m. The siliceous Kniest is transected by veins and fractures filled with pyrite, chalcopyrite, ferroan dolomite, and calcite. The grey vein selvages consist of disseminated carbonate. The pen is 14 cm long.

2.19 *Structure of Altes Lager and Kniest*

The series of NW-SE cross sections (modified from Kraume et al. 1955), stepping northeast at 50 m intervals, shows the location of the hanging-wall spur (Hangendes Trum) in the Altes Lager (AL) massive sulfide (black) relative to the position of the Kniest (green), the footwall alteration zone of silicified shale now located in the structural hanging wall. The Kniest is sulfide-veined close to the contact with the Altes Lager (heavy dot), and comprises four major lenses perhaps separated by thrust faults. The barite orebody (blue) and the Neues Lager (NL) massive sulfide first appear in the section at 1400 m grid east. Lenses of shale-banded sulfide ore are shown in red. Abbreviations: TFS = Tagesföderstrecke, TJFS = Tiefer Julius Fortunatus Stollen.

The Kniest contains two sets of veins (Kraume et al. 1955; p 233): (1) barren veinlets filled with quartz, minor chlorite, and rare albite which occur throughout the silica zone, and (2) sulfide-bearing veins filled with quartz, Fe-dolomite, calcite, minor barite, and rare chlorite and albite which constitute the stockwork ore. Some veins are deformed, and the sulfide assemblage changes according to that in the adjacent massive ore. The two principal strike directions of the veins are N50-60°E and N110-120°E, dips are steeply south. In the Neues Lager massive sulfide, joints oriented N45-55°E/65°SE and N110-125°E/70-90°SW occur, surveyed systematically on level 9. They are accompanied by tensional veins and rare normal faults oriented N135-150°E/±90° (Kraume et al. 1955, p 119). All of these structures are related to compression during isoclinal folding and to shear during subsequent thrust faulting, but are unrelated to the N90°E striking Western and Eastern Mine Faults.

(A): Reverse fault in shale-banded sulfide ore, Altes Lager West, Rammelsberg shaft level 7, looking northeast (after Kraume et al. 1955; p 129).

(B): Sulfide-veined Kniest, Tagesförderstrecke level, exploration drive east of the Bergeschacht internal shaft, looking northeast (after Kraume et al. 1955; p 233). Quartz-filled tension-gash veins (white) between sulfide-filled shear veins (light grey), probably generated during thrust faulting. Some sulfide veins are drag-folded, consistent with reverse shear.

2.20 *Structure of Neues Lager and Kniest*

The series of NW-SE cross sections (modified from Kraume et al. 1955), stepping northeast at 50 m intervals, shows the location of the Neues Lager (NL) massive sulfide (black) and shale-banded sulfide ore (red) relative to the position of the Kniest (green). The Altes Lager (AL) wedges out east of section 1550mE. The thinned uppermost part of the Neues Lager is in contact with Kniest but the central and lower parts are separated from Kniest by shale. Above level 7, the Neues Lager massive sulfide displays prominent drag folds consistent with a reverse sense of movement, particularly in section 1650 m east. Below level 9, the overturned massive sulfide thickens in the closure of the ore syncline, and shale-banded sulfide ore constitutes most of the upright limb. The fold closure was recognized and mapped by Hannak (Unpublished report 1956) and by Abt (1958). Abbreviations: TFS = Tagesföderstrecke, TJFS = Tiefer Julius Fortunatus Stollen.

BOTTOM LEFT: Series of NW-SE sections through the Neues Lager massive sulfide between levels 7 and 8, stepping northeast at 10 m intervals. Note the highly irregular nature of the drag folding (modified from Kraume et al. 1955). The folds indicate reverse movement.

2.21 *Deformation during reverse faulting*

The sulfide ore and Kniest in the overturned limb of the Rammelsberg syncline, oriented sub-parallel to the Hessenkopf thrust (Slides 13 and 14), were deformed during regional reverse faulting.

(A): The generalized cross section on the left (modified from Gunzert 1979) summarizes the structural elements of the Rammelsberg deposit. Lower Devonian sandstone (yellow) and Calceola shale (blue-grey) occur in the structural hanging wall of the overturned syncline, composed of Middle Devonian sand-banded (grey) and calcareous (no color) black shale of the Wissenbach facies. The Altes Lager (AL) and Neues Lager (NL) massive sulfides are mainly confined to the overturned limb, while shale-banded sulfide ore (red) and the dolomite-rich ore marker horizon (dashed red line) are located in the upright limb of the syncline. The small barite orebodies (bright blue) in the Schiefermühle quarry (G2) and underground (G1) are interpreted as part of the upright limb, stratigraphically above the ore horizon. The Kniest silica zone was folded into an anticlinal structure, silicified sandstone beds indicating a short overturned and a long upright limb (Abt 1958), and rotated into a position sub-parallel to the ore syncline. The Kniest mass was subsequently thrust over the Neues Lager into the Altes Lager wedging off the hanging-wall spur (Berg 1933).

(B): Photograph (after Wolff 1913) of the contact between the Neues Lager massive sulfide (light grey), forming a drag-fold bulge, and quartz-veined black shale capped by the plane of a reverse fault in the hanging wall (upper right corner). The lead-zinc-barite ore is finely banded. The banding is secondary and follows the sulfide-shale tectonic contact. Rammelsberg shaft level 7.

(C): NE-SW longitudinal section of the Rammelsberg deposit, looking northwest (modified from Gunzert 1969). The shale-banded sulfide ore (orange) at the northeastern and southwestern margins of the deposit is in conformable stratigraphic contact with massive sulfide (red), both are located in the overturned fold limb above the NE-plunging axis of the ore syncline (dark violet line). The contacts of the Altes (AL) and Neues Lager (NL) massive sulfide lenses beneath the Kniest (green) are shown as a red line where considered tectonic. The barite orebody is outlined in blue. The lower edge of the hanging-wall spur (lobed black line) in the Altes Lager is largely coincident with the upper edge of the Kniest, shown in dark green where in contact with ore and in light green where separated from the ore by black shale. The Kniest alteration zone spans the entire width of the deposit. Reverse faulting subsequent to folding moved the competent Kniest up, wedging off the hanging-wall spur in the Altes Lager (Abt 1958) and separating the originally continuous massive sulfide into two lenses (Gunzert 1969; 1979). The Western (WMF) and Eastern Mine Faults (EMF) displace the orebodies, and record post-folding oblique- and strike-slip, respectively. The Rammelsberg (RB) and Richtschacht (RS) shafts are projected.

2.22 *Brittle-ductile sulfide deformation*

Most macroscopic textures in Rammelsberg sulfide ore are the product of brittle-ductile deformation during folding and reverse faulting (e.g. Ramdohr 1953).

(A): Mylonitic texture in complex Cu-Zn-Pb ore (Melierterz), Neues Lager, Rammelsberg shaft level 10. Monomineralic streaks of yellow chalcopyrite, and disrupted pinch-and-swell bands of dark grey dolomite define the tectonic fabric in finely laminated sphalerite-galena ore. The gangue contains wisps of black bitumen and fractured, weakly rotated pyrite nodules. In contrast, pyrite grains disseminated in the sphalerite-galena matrix are not fractured. The matchstick is 4 cm long.

(B): Durchbewegungs texture in lead-zinc ore, Neues Lager, Rammelsberg shaft level 11-12 (+1700 m E, -56 m MSL). Rounded fragments of fine-grained pyrite, up to 3 cm long, and streaks of yellow chalcopyrite in a speckled matrix composed of interlocked aggregates of brown sphalerite, dark grey dolomite (slow reaction 5% HCl), and white-grey barite. Fragments and streaks are aligned parallel to the massive sphalerite band at the right, which encloses irregularly folded laminae of galena and pyrite. The matchstick is 4 cm long.

(C): Folded sedimentary bedding in shale-banded sulfide ore from the closure of the Neues Lager syncline, Rammelsberg shaft level 11, 1620 m east. Black shale beds alternate with sphalerite-galena-dolomite beds. The knife is 8.5 cm long.

2.23 *Rammelsberg: Sulfide textures*

Microscopic textures show that galena and chalcopyrite deformed by ductile recrystallization. Sphalerite, dolomite, and barite recrystallized but locally reacted in a brittle manner. Pyrite is commonly fractured but also forms subhedral porphyroblasts (Ramdohr 1953). The photomicrographs are in plane-polarized reflected light in air.

(A): Syn-kinematic recrystallization textures in complex Cu-Zn-Pb ore (Melierterz), Neues Lager, level 10-12, sample RAM-1c (19/70). Aligned sericite and chlorite plates (black) in brown-grey sphalerite (sp) are deflected at a dolomite aggregate (black). Hook-shaped chalcopyrite (yellow) and galena grains (light grey) are enclosed in hetero-granular sphalerite. Note the wavy gangue-chalcopyrite (ccp) band.

Sericite and chlorite are mostly aligned parallel to the tectonic banding in massive sulfide ore. Grains of native gold (3 μm; 6-10 wt.% Ag), native bismuth, and bismuthinite are concentrated in some chalcopyrite bands, so that parts of the Melierterz average 6-10 g/t gold. Rare electrum ($Au_{45}Ag_{55}$) is also present (Ramdohr 1953; Sperling 1986).

(B): Fractured pyrite in Zn-Pb ore (Braunerz), Neues Lager, level 10-12, sample

RAM-2e (16/64). Porphyroblastic pyrite (py), fractured after recrystallization, is in contact with brown pyrrhotite (po). The matrix consists of sphalerite (dark grey), galena (light blue-grey), and minor barite and dolomite (black). The fractures in the pyrite are filled with galena.

(C): Cataclastic and recrystallization textures in pyritic Zn-Pb ore (Braunerz), Neues Lager, level 10-12, sample RAM-2c (2.5/68). Band of medium-grey sphalerite (left) enclosing aligned plates of pyrrhotite (brown, anisotropic) and one grain of pyrite (py). This recrystallized band is in contact with a cataclastic one (right), where light blue-grey galena encloses fragments of sphalerite as well as post-kinematic porphyroblasts of carbonate (black), probably ferroan dolomite. One grain of magnetite (mag) partly replaces the smaller carbonate grain. Sparse plates of pyrrhotite (po) occur in the galena.

Syn-kinematic pyrrhotite plates in granular sphalerite are particularly common in pyritic Zn-Pb ore (Braunerz), and are generally well aligned parallel to the tectonic sulfide banding. In the pressure shadows of pulled-apart pyrite bands, the plates are randomly oriented, indicating crystallization after the main phase of strain. Post-kinematic accessory magnetite is widespread in the Neues Lager, sparse in the Altes Lager, and absent in shale-banded sulfide and in barite ore (Ramdohr 1953). It probably formed due to the oxidation of ferroan dolomite or ankerite to magnetite + calcite. Pyrrhotite is locally replaced by the more oxidized assemblage magnetite + pyrite (Sperling 1986; p 83).

(D): Recrystallization textures in sulfide-bearing barite ore (Grauerz), barite orebody, level 3, sample RAM-3b (6/60). Aggregate composed of sphalerite (sp), pyrite (py), galena (gn, scratched), and tetrahedrite (tth, isotropic). The gangue is barite (black). Tetrahedrite is the main silver mineral in the deposit, the silver content varying from a minimum of 0.5 wt.% and median values of 10-13% up to a maximum of 22% (Sperling 1986).

2.24 *Rammelsberg: Sulfide textures*

Remnant primary (sedimentary, diagenetic) and tectonic recrystallization textures occur side-by-side in both massive sulfide and shale-banded sulfide ore but are better preserved in the latter. The color photomicrographs are in plane-polarized reflected light in air.

(A): Diagenetic pyrite in recrystallized sphalerite, pyritic Zn-Pb ore (Braunerz), Neues Lager, level 10-12, sample RAM-2b (0/71). An unstrained aggregate of framboidal pyrite (py), probably formed during diagenesis by bacterial sulfate reduction, occurs next to a secondary pyrrhotite aggregate (po) intergrown with chalcopyrite (ccp) and gangue. The matrix consists of sphalerite (medium grey) enclosing blue-grey galena and moderately aligned plates and blebs of brown pyrrhotite.

Most of the pyrrhotite formed during dynamo-thermal metamorphic recrystallization, probably by exsolution from more Fe-rich primary sphalerite. The average sphalerite composition, given by the analysis of a purified concentrate, is 94% ZnS, 5% FeS, 0.8% MnS, 0.24% CdS, 150 g/t mercury, and 65-75 g/t indium (Kraume et al. 1955; p 262). Electron microprobe analyses indicate that the iron in sphalerite varies from 1.0 to 6.7 wt.% Fe (Sperling 1986; p 102).

(B): Diagenetic and colloform pyrite in shale-banded sulfide ore (Banderz), Neues Lager, level 8-10, sample RAM-4a (6/66.5). Diagenetic pyrite framboids (py) are rimmed by chalcopyrite (ccp) and sphalerite (sp) in a dolomite gangue (black). Colloform pyrite (pale yellow) is preserved in the larger chalcopyrite aggregate (dark yellow, locally tarnished pink).

(C): Microfossils in shale-banded sulfide ore (Banderz), Neues Lager, level 8-10, sample RAM-4b (19/61). Pyritized sporangium (spore capsule), rimmed by blue-grey galena (gn) and medium grey sphalerite (sp), and filled mainly with dolomite. Diagenetic pyrite framboids occur in the adjacent bituminous shale. The rare fossils preserved in the ore represent a transported fauna (gastropods, ostracods, goniatites) and transported plant remains (spores). None are considered indicative of water depth (Sperling 1986).

(D): Primary sphalerite grain (medium grey) enclosing zones of chalcopyrite (white-grey), the innermost one consisting of 50% chalcopyrite. The grain is partly overprinted by a recrystallized band (right) of the same sulfides (modified from Ramdohr 1953; Fig. 96). This zoned texture may have formed during the diagenetic recrystallization of layered chalcopyrite-sphalerite gels (Fig. D1). Alternatively, direct crystallization from a colloidal solution may create ordered sphalerite and chalcopyrite growth zones (Fig. D2), perhaps encrusted by sulfide gel (from Ramdohr 1953; Fig. 100).

2.25 *Altes Lager: Zoned massive sulfide*

The Altes Lager massive sulfide lens contained 7.3±0.3 million metric tons, including the faulted off Altes Lager West, and an additional 0.5 million tons in the Hangendes Trum hanging-wall spur (Sperling and Walcher 1990; p 29 and 48). Remnant ore on level 7 of the Rammelsberg shaft, left after the discovery of the Neues Lager, was systematically analyzed in the 1940s and provided grades of 1.3% Cu, 21.7% Zn, 7.9% Pb, 12.8% Fe, and 1.8% barite. Based on assay records from the higher levels, Kraume et al. (1955; p 151-158, 382-384) estimate the average grade of the Altes Lager at 2% Cu, 18% Zn, 10% Pb, and 14% Fe. Gold varied from 0.1 to 1.4 g/t and silver from 50 to 720 g/t. Prior to flotation in 1936, the ore was hand-sorted according to the dominant sulfide and sent to the smelter.

Gangue: The gangue minerals in both the Altes and Neues Lager massive sulfides are carbonate, barite, minor quartz, Fe-chlorite, sericite, and accessory albite and bitumen. The carbonate assemblage comprises primary ferroan dolomite (Mg:Fe = 2:1), marked by an elevated strontium content of 1500 ppm (Renner 1986), minor ankerite, and minor secondary calcite of metamorphic origin. Some of the carbonate is zoned from ankerite cores to dolomite rims (Ramdohr 1953). The barite contains more strontium (1.1-2.2 wt.% $SrSO_4$) where primary textures are preserved and less (0.3-1.1%) where it is recrystallized (Sperling 1986; p 102). The chlorite is iron-rich (36-45 wt.% FeO, 2-9% MgO), and the sericite is ordered 2M illite (cations: 1.5-1.7 K, 0.6-0.8 Fe+Mg; Renner 1986). Like in the Kniest, high manganese contents are attributed to substitution in carbonate and in chlorite. Pseudomorphs of pyrite and marcasite after diagenetic (?) gypsum crystals are widespread, suggesting that the sulfate was a minor component of the primary gangue (Ramdohr 1953).

The longitudinal section of the Altes Lager on the left shows the distribution of the main ore types looking northwest. The orebody was zoned in sulfide and gangue content, ferroan dolomite giving way to upper barite, and pyrite + chalcopyrite giving way to upper sphalerite + galena. Kraume et al. (1955) distinguish four ore lenses stacked from the stratigraphic footwall to the hanging wall:

Sulfur ore (Schwefelerz): The lowermost lens (yellow) consisted of massive pyrite and about 20% carbonate, and minor chalcopyrite (1% Cu), sphalerite (4% Zn), galena (2% Pb), and barite (1%). Silver (50 g/t) and gold grades (0.1-0.3 g/t) were low. Hydrothermal quartz constituted a major part of the gangue locally (Kraume et al. 1955; p 250).

Pyritic ore (Kiesiges Erz): The lens above (red) still contained abundant pyrite and carbonate, but more sphalerite (8-12% Zn), galena (5% Pb), and chalcopyrite, the latter concentrated in thick layers (up to 18% Cu). Manganese was strongly enriched (3-5% Mn). Silver (up to 150 g/t) and gold (0.1-0.4 g/t) were variable.

Brown ore (Braunerz): The next lens (grey) consisted mainly of sphalerite (32% Zn) and galena (20% Pb), minor chalcopyrite (1% Cu), variable amounts of carbonate, and up to 4% barite. Much of the ore was low in gangue (<5 vol.%). The gold grade (1 g/t) was high, while the silver grade (about 100 g/t) remained below that of the upper lead-zinc ore. The brown ore extended not as far to the east (dotted line) as the lower lenses.

Lead-zinc ore (Bleizinkerz): The uppermost lens (black) contained abundant sphalerite (20-24% Zn) and galena (10-12% Pb), minor pyrite, and little chalcopyrite (0.4-0.8% Cu). Barite (average 20%) was the predominant gangue, and increased towards the hanging wall and to the northeast, where barite beds (80% sulfate) up to 1 m thick substituted for the sulfide ore (area outlined in blue). The eastern edge of the lens (heavy black and blue lines) did not extend as far to the east as the brown ore below. The average silver and gold grades are estimated at 150 g/t and 0.5 g/t, respectively. However, precious metal grades were lower (70-80 g/t Ag, 0.1 g/t Au) in barite-rich parts. Beds of sphalerite ore at the hanging wall contact contained up to 194 g/t mercury (Kraume et al. 1955; p 256).

(A): Grey barite bed in pyrite-bearing sphalerite-galena ore, the left contact (footwall) of the barite is marked by a movement plane. Upper part of the Neues Lager massive sulfide, 6 m below the Bergesfahrt level (+308 m MSL), 1543 m east.

(B): On the left "brown ore", fine-grained sphalerite containing 20% galena in streaks, and laminae and sparse nodules of white barite (no mine location). On the right "copper ore", chalcopyrite banded by thin dolomite-rich layers and streaks of sphalerite. Altes Lager, Rammelsberg shaft level 1 (1. Firste). The red pen is 14 cm long.

2.26 *Neues Lager: Zoned massive sulfide*

The Neues Lager massive sulfide lens contained 19.3±0.7 million metric tons of ore (Sperling 1986; p 108). The orebody was systematically analyzed on levels 3 and 5, and on levels 7 to 12 where it attains greatest thickness. Based on these data, the average grade is estimated at 2% Cu, 21% Zn, 12 % Pb, 10% Fe, and 26 % barite (Kraume et al. 1955; p 172). The longitudinal section shows the distribution of ore types looking northwest. From the stratigraphic footwall to the hanging wall:

Pyritic ore (Kiesiges Erz): Pyrite-carbonate ore (red), enriched in copper and zinc by layers of chalcopyrite (18% Cu) and sphalerite (30-40% Zn), formed several major lenses about 2 m thick, which were loosely connected by thinner (0.2 m) ones between (not shown). The carbonate and related manganese content (1-2 wt.%) was lower than in the Altes Lager, and barite was absent. Average silver and gold grades were 120 g/t and 0.8 g/t, respectively.

Complex Cu-Zn-Pb ore (Melierterz): Complex Cu-Zn-Pb ore (grey), characterized by discontinuous yellow and brown sulfide bands, formed a single large lens about 6 m thick containing 4% Cu, 22% Zn, 8% Pb and 12% Fe (Kraume et al. 1955; p 141). Barite (14%) was more abundant than carbonate (3%). High silver (230 g/t) and gold (3 g/t) grades made the "Melierterz" the most valuable ore in the mine.

Lead-zinc ore (Bleizinkerz): Lead-zinc-barite ore (black) formed the uppermost lens, about 2 m thick where overlying Melierterz, and 6 m thick at the margins. The ore contained 0.4-0.8% Cu, 20% Zn, 10% Pb, and 8% Fe. The barite content averaged 30%, and both barite and lead increased towards the hanging wall and towards the margin of the lens, where intercalated beds of massive barite occurred (not shown). Average silver and gold grades were 170 g/t and 0.7 g/t, respectively. The mercury content (70 g/t) was about twice the deposit average (Kraume et al. 1955; p 256). Note that the upright limb of the syncline is not represented on the longitudinal section. Folding down this limb results in the lead-zinc ore extending below level 12, beyond the other lenses (Sperling 1986).

(A): Lead-zinc ore from the upper part of the Neues Lager, brown sphalerite-galena bands alternate with grey barite bands. Rammelsberg shaft level 10 at 1411 m east (10. Firste = 10 m above level). The red pen is 14 cm long.

(B): Complex Cu-Zn-Pb ore (Melierterz) from the central part of the Neues Lager, characterized by prominent streaks of dark yellow chalcopyrite in brown sphalerite, wrapping around grey carbonate-barite boudins. Minor pyrite. The sulfide banding is parallel to the slaty cleavage in the Wissenbach shale. Rammelsberg shaft level 10 at 1585 m grid east.

2.27 *Tuffs, ore marker horizon, and barite beds*

The three NW-SE sections show the position of the barite beds (blue) in relation to the ore marker horizon (OH), the lateral stratigraphic equivalent of the sulfide orebodies (modified from Gunzert 1979). The ore horizon in these exposures is about 10 m thick, and comprises black shale marked by numerous thin beds of ferroan dolomite (brown). Chlorite (26-36 wt.% FeO, 9-16% MgO; Renner 1986) and chalcedony are major components, and arsenical pyrite, sphalerite, and galena (>2300 ppm Zn+Pb) minor or accessory ones (Sperling and Walcher 1990).

Tuffs: The Calceola and Wissenbach shales contain at least 22 beds of altered tuff 2-20 cm thick. Two prominent marker beds of tuff (red), 100-300 cm thick, are associated with the ore horizon and, together with others, support stratigraphic correlation and structural interpretation in the mine (Abt 1958). The tuffs consist essentially of quartz, illite and lesser chlorite, contain minor igneous quartz and biotite, and accessory zircon, tourmaline, and apatite (Kraume et al. 1955). They are are high in potassium (5.3-8.7 wt.% K_2O) and low in titanium content (0.13-0.44 % TiO_2; Abt 1958), indicating a felsic composition prior to alteration by seawater. Most are probably alkali rhyolite air-fall tuffs.

Schiefermühle slate quarry: The Wissenbach slate northeast of the Rammelsberg shaft was quarried as backfill for the underground stopes. On benches 3 and 4, barite beds (G2) are exposed over a strike length of 60-70 m, and are subdivided into a lower and upper unit, 2-3 m and 4-5 m thick, separated by black shale. Small barite nodules (2-3 mm) with radial internal texture are abundant (e.g. Ramdohr 1953). The base-metal content is low (500-2000 ppm Cu+Zn+Pb; Sperling and Walcher 1990). The barite beds occur in the core of the Rammelsberg syncline and form part of the northwestern upright limb. Stratigraphically, they are about 30 m above the ore horizon and thus younger than the massive sulfide orebodies. The Altes Lager is part of the southeastern overturned limb and is in faulted contact with the barite beds, the intercalated black shale being attenuated and sheared (Gunzert 1979).

Level 3: The barite ore (G1, Grauerz) exposed in the Rammelsberg shaft level 3 crosscut is in an equivalent stratigraphic position above the ore horizon, and is also interpreted to form part of the upright limb of the Rammelsberg syncline. The overturned limb is completely sheared out at the major thrust marking the footwall of the Kniest silica zone. The barite orebody is up to 120 m long and 12 m thick, and consists of 80% barite and minor sulfide layers. Quartz, albite, calcite, and illite + chlorite occur in variable amounts (Ramdohr 1953). The measured reserves of the G1 orebody amounted to 0.2 million metric tons at 0.1% Cu, 3.8% Zn, 2.8% Pb, 1.8% Fe, 140 g/t Ag, and 33 g/t Hg (Kraume et al. 1955; p 256, 332). About half of this tonnage has been mined. The photograph shows strained sulfide-free barite from the Grauerz orebody on level 3 of the Rammelsberg shaft, 1450 m east.

Level 1: The third cross section on the Rammelsberg shaft level 1, in the cross cut south at 1510 m grid east, shows a barite bed in the stratigraphic hanging wall of the Neues Lager massive sulfide, here located in the overturned limb of the Rammelsberg syncline. This exposure supports the interpretation that the sulfide-poor barite beds, which may represent separate bodies, are younger than the main sulfide ore (Gunzert 1979).

2.28 *Rammelsberg: Sulfur isotopes*

Sulfur isotope studies on Rammelsberg ore include those of Anger et al. (1966) and Nielsen (1985) by conventional methods, and that of Eldridge et al. (1988) by SHRIMP ion microprobe. These data are discussed first in the context of depositional constraints, followed by an evaluation of dynamo-metamorphic and post-tectonic granite-related overprinting. The published lead and osmium isotope data are reviewed last.

Sulfur isotopes: The diagram on the left, modified from Nielsen (1985), shows the $\delta^{34}S$ values of base-metal sulfides (black), pyrite (red), and barite (blue) according to stratigraphic position in the mine succession. Background values are provided for the Calceola and Wissenbach shales, followed by those from sulfide-barite veins in the footwall silica alteration zone (Kniest), and from a pyrite-chalcopyrite lens at the base of the Neues Lager. The values from the Neues Lager massive sulfide are sorted according to stratigraphic height, and those from barite ore represent the younger G1 body 30 m above the main ones (Gunzert 1979).

Nielsen (1985) and Eldridge et al. (1988) argue that the mineralizing fluid was reduced and carried sufficient H_2S in solution to precipitate the bulk of the sulfides after discharge at the sea floor. The $\delta^{34}S$ values of base-metal sulfides in the Calceola shale, the Cu-Fe ore, and the late barite ore are remarkably similar indicating a constant isotope composition in the fluid (5-10‰) inconsistent with a magmatic source (0±5‰). Middle Devonian marine anhydrite in Belgium has a mean $\delta^{34}S$ value of 22.3±0.8‰ (Nielsen 1985), considered to represent Devonian seawater, as there is no isotope fractionation between dissolved and crystalline sulfate. Nielsen (1985) suggests that such marine sulfate, trapped in the Devonian sediments below the Rammelsberg deposit, was leached and reduced at high temperatures (>440°C) deep in the hydrothermal system providing H_2S to the ore fluid. The sulfide isotope values are within the equilibrium fractionation (-15‰) of this process. In contrast, the barite in the orebodies precipitated when ocean water mixed with the brine and dissolved marine sulfate reacted with barium discharged into the Rammelsberg basin (Anger et al. 1966).

The ore fluid probably discharged at about 300°C into a stratified brine pool, as indicated by the sulfur-isotope fractionation temperatures (range: 150-450°C, mean: 300°C) of galena-sphalerite (n=8) and pyrite-barite pairs (n=9). The minerals analyzed recrystallized during deformation and their co-precipitation is in question (Nielsen 1985). However, Eldridge et al. (1988) demonstrate that primary isotope compositions are preserved at the micrometer scale. The range of temperatures is much narrower than those of other SEDEX and VMS deposits (Eldridge et al. 1983), where unreasonably high values (>500°C) and the extreme range are attributed to disequilibrium.

The isotope signatures of sulfides and barite were influenced by bacterial sulfate reduction (Nielsen 1985; Eldridge et al. 1988), which took place during early diagenesis when the mud cooled to less than 120°C (Southam and Saunders 2005). Pyrite, in particular, shows variable and in part distinctly negative values, indicating that some (in framboids and nodules?) crystallized from biogenic H_2S. The $\delta^{34}S$ values of the base-metal sulfides in the Neues Lager increase systematically with stratigraphic height from the minimum source value (5-10‰). Assuming partly closed system conditions for the total hydrogen sulfide in the pool, the removal of light sulfur in biogenic pyrite gradually increased the $\delta^{34}S$ of the other sulfides with time (Nielsen 1985).

Dynamo-thermal metamorphism: The mineral assemblage 2M illite + Fe-Mg chlorite + quartz ± albite (Renner 1986), and the absence of chloritoid and biotite in the Wissenbach shale at the mine indicate peak temperatures of less than 300°C, and most likely less than 260°C (Bucher and Frey 2002; p 230). Quartz veins oriented parallel to the slaty cleavage in black shale of the Schiefermühle quarry contain CO_2-bearing aqueous inclusions of low salinity (0.4-5.0 wt.% NaCl eq.), which homogenize at 160-200°C (Muchez and Stassen 2006). In the absence of a pressure correction, 200°C is taken as the metamorphic minimum. The fluid was probably reduced given equilibrium with its black shale host.

Kniest veins: Most Kniest veins are interpreted to result from shear during post-folding reverse faulting (Kraume et al. 1955). Strained calcite and dolomite from sulfide-bearing veins contain two generations of inclusions (some stretched?): (1) moderate salinity aqueous ones (4.9-10.3 wt.% NaCl eq.) homogenizing at 130-160°C, and (2) low salinity (1.0-2.3 wt% NaCl eq.) aqueous ones homogenizing at 225-260°C (Muchez and Stassen 2006).

Oker granite: Post-kinematic magnetite + calcite after ankerite and magnetite + pyrite after pyrrhotite in the Neues Lager indicate moderately oxidized fluids, perhaps related to the emplacement of the Oker granite. Buried cupolas of this pluton are indicated by magnetic anomalies south of Goslar (Paul 1975). The isotopically light sulfur of barite in the Kniest veins indicates formation by oxidation and dissolution of sulfide sulfur (Nielsen 1985). Some Kniest veins contain aqueous inclusions in unstrained late-stage calcite and quartz, which are saline (17.3-20.2 wt.% NaCl eq.), contain significant calcium chloride, and homogenize at 108-155°C (Muchez and Stassen 2006). In any case, the veins are secondary and do not provide information about the P-T-X conditions during massive-sulfide deposition.

Metal content: The average Rammelsberg ore mined during 1950-54 contained 1% Cu, 19% Zn, 9% Pb, 1.2 ppm Au, 160 ppm Ag, 500 ppm As, 800 ppm Sb, 70 ppm Bi, 50 ppm Sn, 40 ppm Hg, 20 ppm In, 10 ppm Tl, 0.04 ppm Pt, and 0.02 ppm Pd (Kraume et al. 1955; p 245). In modern sea-floor VMS deposits, such a high Cu-Au-Bi signature is considered indicative of fluid input from oxidized I-type magmas, while a high As-Sb-Sn-Hg content characterizes the more reduced deposits in sediment-filled basins where the fluids interacted with bituminous terrigenous material (Hannington et al. 2005). The lead and osmium isotope compositions of massive sulfide from the Neues Lager (Meier 1974; Lévêque and Haack 1993; Tischendorf et al. 1993) indicate a large component of radiogenic lead and osmium, probably leached from detritus in the Lower Devonian sandstones and from paragneiss (?) in the basement below the deposit.

2.29 *SEDEX brine pool versus Kuroko mound*

The volcanogenic Kuroko deposits in the Miocene Green Tuff Belt of Japan (Ishihara 1974) are among the few sulfide-sulfate deposits containing massive stratiform "black ore" similar in base and precious metals grade to the Rammelsberg. An example is the Tsunokakezawa-1 orebody in the Fukuzawa mine: 3 Mt at 1.13% Cu, 15.4% Zn, 3.3% Pb, 93 g/t Ag, 0.6 g/t Au (Tanimura et al. 1983). The characteristics of a typical Kuroko VMS are compared to the model developed for the Rammelsberg discussing genetic implications.

Kuroko VMS: The deposits occur in the bimodal volcanic succession of a marine back-arc rift basin separating the Asian continent and the Japanese islands. Most are underlain by dacite/rhyolite and overlain by felsic tuff, mudstone or younger submarine flows including basalt. The schematic section through a Kuroko VMS is modified from Eldridge et al. (1983).

The mound of massive sulfides above the paleo-sea floor is capped by a thin and laterally extensive hematite-bearing chert (not shown). Upper barite ore (blue, barite > sulfide) is underlain by massive black sphalerite ore (black, sp + brt > py + gn > tth), which grades downward into chalcopyrite-bearing black ore (grey, sp + brt > py > ccp + qtz). The inner part consists of massive yellow chalcopyrite-pyrite ore (red, ccp + py > qtz) displaying cross cutting replacement contacts to the upper black ore. All these ore types are commonly eroded and deposited down slope in clastic graded sulfide beds (brown, heavy dot). Stratiform gypsum-anhydrite bodies (not shown) occur at the periphery of the sulfide mound, which grades down- and inward into massive pyrite (yellow, py + qtz >> ccp) located above a funnel-shaped epigenetic stockwork (green). The stockwork ore is zoned from outer silica-sphalerite (black dots, qtz > sp > py) to inner silica-chalcopyrite (red dots, qtz > py > ccp), part of a wider quartz-chlorite-sericite alteration pipe grading outward into montmorillonite- and zeolite-bearing zones.

Fluid inclusions from the stockworks of five Kuroko deposits document a intensifying hydrothermal system in the feeder zone and in the mound, beginning with the deposition of minor pyrite + quartz at 200±50°C, followed by the main-stage Zn-Pb black ore at 290±50°C, then chalcopyrite-rich yellow ore at the thermal peak of 330±50°C (overprinting black ore), and finally minor sphalerite mineralization at 280±20°C (Pisutha-Arnaud and Ohmoto 1983). Absence of fluid boiling indicates a minimum water depth of 1800 m. Fluid salinities of 3.5-5.5 wt.% NaCl equivalent (rarely 7%) and cation ratios suggest that the discharge fluid consisted of evolved seawater. As the lead isotopes of the sulfide deposits are more radiogenic than those of the Miocene volcanic rocks, Fehn et al. (1983) conclude that the hydrothermal cells extended more than 1 km below the deposits into Oligocene conglomerates and Paleozoic basement phyllites. Shallow circulation at the discharge site entrained cold seawater causing the precipitation of anhydrite, gypsum and barite (Farrell and Holland 1983). The Kuroko model has been refined by the study of active volcanogenic sulfide mounds on the present ocean floor (e.g. Petersen et al. 2000).

Rammelsberg SEDEX: The mine succession is dominated by black shale and siltstone, and volcanic rocks are absent except for thin beds of rhyolitic air-fall tuff (diagram modified from Gunzert 1969). The Rammelsberg is a vent-proximal SEDEX deposit, unlike most in this class (80%; Leach et al. 2005). The Kniest feeder zone (green) is a broad linear structure spanning the entire width of the sulfide ore, and may represent an altered fault. In contrast to the Kuroko feeder pipes, the Kniest does not constitute primary ore as the stockwork veins mined are secondary. The main alteration assemblage (quartz + chlorite + sericite) is similar but more reduced: the chlorite is Fe-rich and Mn-siderite and ankerite are abundant at the Kniest margins. The massive sulfides, virtually undiluted by detritus above the vent, were not deposited as a solid mound but as a layered mud in an euxinic basin. At the margin of this basin (brown), the gel-textured and crystalline sulfide mud became interbedded with bituminous shale on a mm- to cm-scale. Remarkably similar to Kuroko are the vertical sulfide-sulfate zones: barite ore (blue) at the top, sphalerite-barite ore below (black), underlain by chalcopyrite-rich sphalerite-barite ore (grey), the famous gold- and silver-rich Melierterz. The principal gangue then changes to ferroan dolomite in the underlying pyrite-chalcopyrite ore (red), which still extends as a thin blanket across three quarters of the deposit. Massive pyrite (yellow) forms the lowermost but much smaller lens, probably centered on the Kniest vent before deformation. While Kuroko-style zone refining, the high-temperature chalcopyrite replacement of main-stage sphalerite, cannot be proven due to the strong recrystallization of the Rammelsberg ore, it is reasonable to assume similar overall mineralization temperatures of 250-350°C for the discharge fluid, an assumption consistent with the average sulfur-isotope fractionation temperature of 300°C.

These temperature estimates agree with those determined for sulfide muds and veins in the Atlantis II Deep of the Red Sea, the only modern brine-pool basin. The Atlantis II Deep is filled with 5 km^3 of brine, stratified into a lower euxinic layer of 61.5°C and into an upper layer of 50°C, partially oxygenated. The basin mud contains two sulfide-rich zones, and a dry salt-free resource of 92 Mt at 0.46 wt.% Cu, 2.06% Zn, 41 g/t Ag, and 0.51 g/t Au (Bäcker and Richter 1973; Pottorf and Barnes 1983; Hannington et al. 2005). The discharge fluid (>335°C, H_2S>SO_4) deposited sphalerite (17 mol% FeS) + cubanite + chalcopyrite + pyrite/pyrrhotite in veins beneath the sea floor, and the same assemblage with lower iron sphalerite (3.5-4.5% FeS) in mud layers at 200-250°C. Mixing with a shallow fluid (<250°C, SO_4>H_2S) is indicated by the presence of anhydrite (Pottorf and Barnes 1983).

A similar scenario may apply to the Rammelsberg hydrothermal system given the sulfur isotope signature of the stratiform barite, the presence of sparse but widespread gypsum pseudomorphs, and an average FeS content of 5% in sphalerite. Kuroko-style peak fluid temperatures of 300-350°C and mud-deposition temperatures of about 250°C set the vent-proximal Rammelsberg apart from vent-distal SEDEX deposits (e.g. McArthur River), where these temperatures are estimated at 250°C and 150°C, respectively (Large et al. 2005).

2.30 *Total Zn-Pb content of ore horizon*

Spillage from the Rammelsberg brine-pool basin caused a km-scale, stratigraphically controlled base-metal anomaly confirming beyond doubt that the deposit is "sedimentary-exhalative" as proposed by Ramdohr (1928, 1953). The equivalent of the Rammelsberg deposit, the "ore horizon", has been traced in drill holes for a distance of 3 km to the northwest where it attains up to 28 m thickness. The horizon is bedded on a 10 mm scale by alternating grey carbonate and bituminous black shale. In the Schiefermühle quarry at the mine, the carbonate beds consist of 32-58% $CaCO_3$, 12-25% $MgCO_3$, 6-15% $FeCO_3$, 0.1-1.2% $MnCO_3$ and 11-20% shale, indicating ferroan dolomite as the main constituent. The intercalated shale beds consist of 42-65% Fe-rich chlorite (30-36 wt.% FeO; Renner 1986), 6-12% illite, 1-15% chalcedony and quartz, 4-11% albite, and 2-8% dolomite. They are enriched in chlorite relative to average Wissenbach shale. Calcite forms the shells of microfossils (ostracods, styliolinae). Pyrite occurs disseminated, in nodules (<0.5 cm), and in layers up to 2 mm thick, and contains up to 1.2% arsenic. Sphalerite and galena are accessories (Walcher 1986; Sperling and Walcher 1990).

The regional distribution of lead and zinc in the marker horizon, based on more than 1000 analyses of 0.5 m core sections, is shown in the "unfolded" paleo-geographic map modified from Sperling and Walcher (1990) who interpret the deposit as three separate sulfide lenses. In an area up to 500 m distant, all the base metals are highly anomalous (>2300 ppm Zn+Pb), zinc is more abundant than lead (Zn/Pb = 2:1), and As, Sb, and Hg are enriched. At a distance of 500-3000 m, the average contents are 620 ppm Pb, 300 ppm Zn, and 42 ppm Cu in the ore horizon, compared to background values of 48 ppm Pb, 105 ppm Zn, and 37 ppm Cu in the Wissenbach shale. The anomaly thus extends at least 3 km from the ore deposit, lead being more abundant than zinc (Walcher 1986).

The regional database of lead-zinc analyses indicates that the total metal content of the ore horizon, in a circular area of 3 km radius, is 9 million metric tons of lead and 4 million tons of zinc (Sperling and Walcher 1990). If 50% of the Altes Lager massive sulfide were eroded, the total high-grade ore would amount to 35 million metric tons. This estimate increases to 40 million tons, provided the Altes Lager was about the same size as the Neues Lager. At 25% combined zinc plus lead, the amount of base metals trapped as ore is 9-10 million tons, less than half the total produced (>22 million tons Zn+Pb).

2.31 *Harz: Middle Devonian Goslar basin*

The Middle Devonian topography and sedimentary environment of the western Harz are introduced in three steps: (A) review of present outcrops, (B) a cross section through the autochthonous units, (C) paleo-geographic maps based on outcrops and drill holes.

(A): Geologic map of the western Harz mountains, part of the 1:100,000 sheet compiled by Hinze et al. (1998), showing the Variscan basement uplifted at the Harz North Rim Fault (black dashed line). The Rammelsberg deposit (RB) is located south of Goslar (GS) in an anticlinorium composed of Lower Devonian sandstones (brown), Middle Devonian black shales (olive-green) with intercalated diabase sills (dark green), and Upper Devonian calcareous shales (yellow). The Devonian rocks, bounded by faults sub-parallel to the HNRF, occur within a wider area of Lower Carboniferous greywacke (grey). Note the Iberg limestone reef (IB, light blue) west of the town of Clausthal-Zellerfeld (CLZ). The post-folding Oker pluton (OP, pink) east of the Rammelsberg may have caused the crystallization of magnetite in the sulfide ore. Buried granite cupolas are indicated by magnetic anomalies south of Goslar (Paul 1975).

(B): Schematic NW-SE section through the western Harz (modified from Engel et al. 1983) illustrating the Middle to Upper Devonian basin-and-ridge topography and its burial under Carboniferous flysch. Carboniferous sedimentation begins with black shale and chert (black) overlain by greywacke (light grey), which thickens and becomes younger to the northwest (goniatites zones). The Acker tectonic unit of quartzites (dark grey, dotted) may be allochthonous. The Devonian rocks are structured by syn-sedimentary faults into the West Harz paleo-high (brown) and the Goslar paleo-basin (GSB). Marine facies such as the Iberg reef (IB), probably built on basaltic spilites (green), condensed limestones (blue), and thin calcareous shales (yellow) are located on the paleo-high.

(C): The paleo-geographic maps (modified from Brinckmann et al. 1986) show the locations of the Rammelsberg (RB), of Goslar (GS), and of deep drill holes (red dots) used to reconstruct the topography during the Middle Devonian Eifelian and Givetian stages. In the Goslar basin (GSB, medium grey), the Wissenbach black shale is more than 800 m thick while it is less than 100 m on the West Harz High (WHH, yellow). The Eifelian Rammelsberg deposit formed where the slope between basin and ridge was steep (short fat arrows) and probably faulted. The Goslar basin persisted during the Givetian when the Iberg reef (IB, blue) west of Clausthal-Zellerfeld (CLZ) began to form.

2.32 *Europe: Devonian back-arc basin*

The Middle Devonian paleo-geography of central Europe (Ziegler 1990; modified from Map Supplement 12), illustrates the location of the Meggen (M) and Rammelsberg (R) SEDEX deposits in the sediment-filled basin at the southern margin of the Old Red Continent (medium grey = moderate topographic relief; light grey = low relief). The continent, also termed Laurussia, comprised the Laurentian and Baltic Precambrian cratons, joined by the Caledonian fold belt (520-420 Ma), and exotic Gondwana-derived continental blocks.

During the Middle Devonian, lacustrine and fluviatile sediments (orange) accumulated in basins on the continent and along the shoreline of the marine rift to the south, grading into deltaic and coastal sandstones (yellow). Shallow-marine mudstone (dark olive-green), carbonate (blue) and anhydrite (pink) were deposited on the outer shelf. The SEDEX sulfide-barite deposits formed near the shelf edge in a rifted deep-water basin characterized by pelagic shales (light gray-green), sand-silt turbidites (brown), and alkaline bimodal volcanic rocks (black stars). The rift basin was subdivided by the Mid German High into the northern Rhenish and the southern Saxothuringian sub-basins, and developed on a basement of Gondwana-derived continental crust. Rifting probably progressed to the formation of oceanic crust in local spreading centers (Franke 2000). The continental-margin rift basin, active during the entire Devonian over a period of about 50 Ma, was located in a back-arc position relative to the Ligerian-Vosgian Cordillera, a fold belt of high topographic relief (dark gray) and calc-alkaline magmatism (plutons = black crosses).

2.33 *Devonian plate-tectonic setting*

Reconstructions of the plate-tectonic setting of the Rammelsberg and Meggen SEDEX deposits differ with regard to the accretion of Gondwana-derived micro-continents to the Laurussian mega-continent. These exotic blocks are characterized by crust consolidated during the peri-Gondwana Cadomian orogeny (650-550 Ma). They include Avalonia (London-Brabant massif, Rhenohercynian terrane), Amorica (Brittany, Normandy, Massif Central), Bohemia (Saxothuringian and Moldanubian terranes), and Iberia. There is consensus that Avalonia, which lacks Upper Ordovician glacio-marine sediments, separated from Gondwana during the Middle Ordovician, drifted north, and docked with Laurussia during the Lower Silurian (Ziegler 1990). Avalonia now underlies southern England, Belgium, and most of northern Germany, including the Variscan slate belt (Rhenohercynikum).

(A): Reconstruction by Ziegler (1990): The assembled northern mega-continent Laurussia during the Middle Devonian (Givetian; 392-385 Ma), separated from the southern mega-continent Gondwana (GW) by a deep ocean. Continental areas elevated above sea level are in yellow, and large faults are traced in pink. The present-day coasts of northwestern Canada, Greenland, and northern Europe are outlined in red for geographic orientation. Shallow marine basins on the continental shelf are light grey, deep continental basins medium grey, and basins floored by oceanic crust dark grey.

Avalonia, Amorica, and Bohemia, all accreted during the Caledonian orogenic cycle, are part of the southern continental margin of Laurussia since the Silurian. The Rhenish-Saxothuringian rift basin, marked by the approximate location of the Rammelsberg and Meggen SEDEX deposits (red dot), is in a back-arc position relative to the active fold belt of the Ligerian-Vosgian Cordillera, part of the larger Variscan orogen (black) suturing Laurussia. A calc-alkaline magmatic arc developed in the combined Americian and Bohemian micro-continents above a north-dipping subduction zone (thick blue saw-tooth line) consuming the oceanic crust between Gondwana and Laurussia. During the Middle Devonian, Iberia (outlined in red) was accreted as part of two Gondwana-derived blocks, which collided with the Appalachian-Ligerian-Vosgian subduction system (Ziegler 1990). The collision of Laurussia and Gondwana during the Carboniferous led to the closure of the Rhenish-Saxothuringian basin and to the creation of the Permo-Triassic super-continent Pangea.

(B): Reconstruction by Linnemann et al. (2003): Laurussia (ORSC = Old Red Sandstone Continent) and Gondwana about 400 Ma ago, shortly before the Middle Devonian (398-385 Ma). Avalonia has been accreted to the southern margin of Laurussia, and is located behind an arc-trench system (black saw-tooth line) consuming crust of the Rheic ocean. The Rhenish basin containing the SEDEX deposits (now the Rhenohercynikum in Slide 5) formed by rifting in Avalonian crust when compressive stress from the arc-trench system eased, perhaps due to a change in subduction direction caused by the Acadian collision (Laurentia/Amazonia). Remnants of the Late Silurian-Early Devonian magmatic arc are preserved as greenschists and orthogneisses (440-400 Ma zircon U-Pb) in the Northern Phyllite Zone and in the Mid-German Crystalline Rise (see Slide 5), both marking the southern suture of Avalonia (Franke 2000). The other micro-continents, Iberia (I), Amorica (A), Saxothuringia (SX), Barrandia (B, also named Moldanubia), the Proto-Alps (PA), the Turkish Plate (TP), and Iran (IR) remained at the rifted margin of Gondwana at high southern latitudes. In the case of Saxothuringia, this paleo-geographic position is indicated by the provenance of detrital zircons, the occurrence of Upper Ordovician glacio-marine sediments, and consistent Sm-Nd model ages in the sedimentary succession from the Cambrian to the lowermost Carboniferous (Linnemann et al. 2003). Apart from Avalonia, all micro-continents were accreted during the Variscan orogeny when Gondwana collided with Laurussia.

(C): Present-day northwest Pacific (modified from Shupe 1992): The plate tectonic setting is perhaps comparable to the Middle Devonian one outlined above. Oceanic crust of the Pacific is subducted at the Bonin-Japan-Kuril (BJK) arc-trench system (thick red saw-tooth line): beneath island arcs of the Asian continent in the Japan-Kuril segment, and beneath oceanic crust of the Phillippines plate along the Izu-Bonin ridge (IBR). The Phillipines plate, in turn, is subducted at the Ryukyu arc-trench system (RA). Back-arc rift basins in continental crust, similar to the Rhenish one, are represented by the Okinawa Trough (OT) and by the Sea of Japan basin (JB). The Sea of Japan opened about 65 Ma ago, when back-arc spreading caused Japan to drift away from the continent. Renewed spreading at 25-5 Ma in the

Yamato subbasin caused rifting, bimodal volcanism, and deposition of the submarine Green Tuff succession on the continental crust of Honshu and Hokkaido. Pliocene compression and uplift of the GreenTuff Belt (dark orange area) led to the exposure of Kuroko VMS deposits on the Japanese islands (Ohmoto 1983). The Okinawa Trough, a 1000-2300 m deep marine rift located behind the Ryukyu Arc, is characterized by a high heat flow, by bimodal basalt-rhyolite volcanism, and by a thick sediment cover rich in terrigenous material and organic matter. Active hydrothermal vents discharge at temperatures of up to 320°C, and deposit barite and sulfides rich in Pb, As, Sb, Hg, Ag, and Au (e.g. Hannington et al. 2005).

2.34 *Rammelsberg: Key genetic features*

If condensed to key genetic features, distinct similarities emerge between the Rammelsberg SEDEX and the Kuroko VMS deposits.

<u>Plate-tectonic setting:</u> Back-arc rifts comparable to the Rammelsberg setting are developed at the Pacific margin of the Asian continent. A seawater-recharged hydrothermal system extending deep into continental crust and/or thick terrigenous sediments is probably essential to generate particularly high-grade Zn-Pb-Ag-Ba massive sulfides such as the Kuroko and Rammelsberg “black ores”. In the case of the Rammelsberg, the succession underlying the deposit comprises Lower Devonian shelf sandstones (>1000 m thick) and Cadomian paragneisses of the Avalonian basement (represented by the raft of Ecker gneiss in the Brocken pluton).

<u>Submarine bimodal volcanism:</u> Submarine ridges of vesicular basalt and minor trachyte and alkali rhyolite characterize the Rhenish rift basin, which is mainly filled with clastic sediments derived from the continental shelf. The volcanic rocks indicate a fertile, high heat-flow environment. District-scale spilitization indicates extensive seawater circulation.

<u>Submarine ore deposits:</u> In the Rhenish basin, the volcanogenic deposits located on volcanic ridges are oxidized and include hematite ore, sub-economic at present, and barren pyrite (+ sulfate?) mineralization, the latter associated with spilitized trachyte/rhyolite. The Rammelsberg SEDEX deposit is distal to volcanic ridges, and is hosted by bituminous shales/siltstones in the rift-faulted transition zone between paleo-basin and paleo-high, the high marked by limestone reefs and a condensed stratigraphy. The faults probably facilitated the emplacement of a large sill or pluton to drive the hydrothermal system (e.g. Kraume et al. 1955), enabled the deep circulation of seawater, and generated the sub-basin to trap the discharged fluid in a brine pool on the sea floor. Spillage from the brine pool generated a kilometer-scale Zn-Pb anomaly.

<u>Cu-Zn-Pb massive sulfides:</u> Particularly Cu-Au rich and high-grade SEDEX deposits like the Rammelsberg require vent-proximal sulfide deposition, high fluid discharge temperatures of 300-350°C, and a sheltered basin to prevent dilution by clastic material. The Rammelsberg discharge fluid was reduced, relatively alkaline, and carried H_2S. Silica, Fe-chlorite, sericite, Mn-siderite and ankerite replaced black shale and siltstone in the feeder zone. Ankerite and ferroan dolomite were also the main gangue in the lower part of the massive sulfide giving way to seawater-precipitated barite in the upper part.

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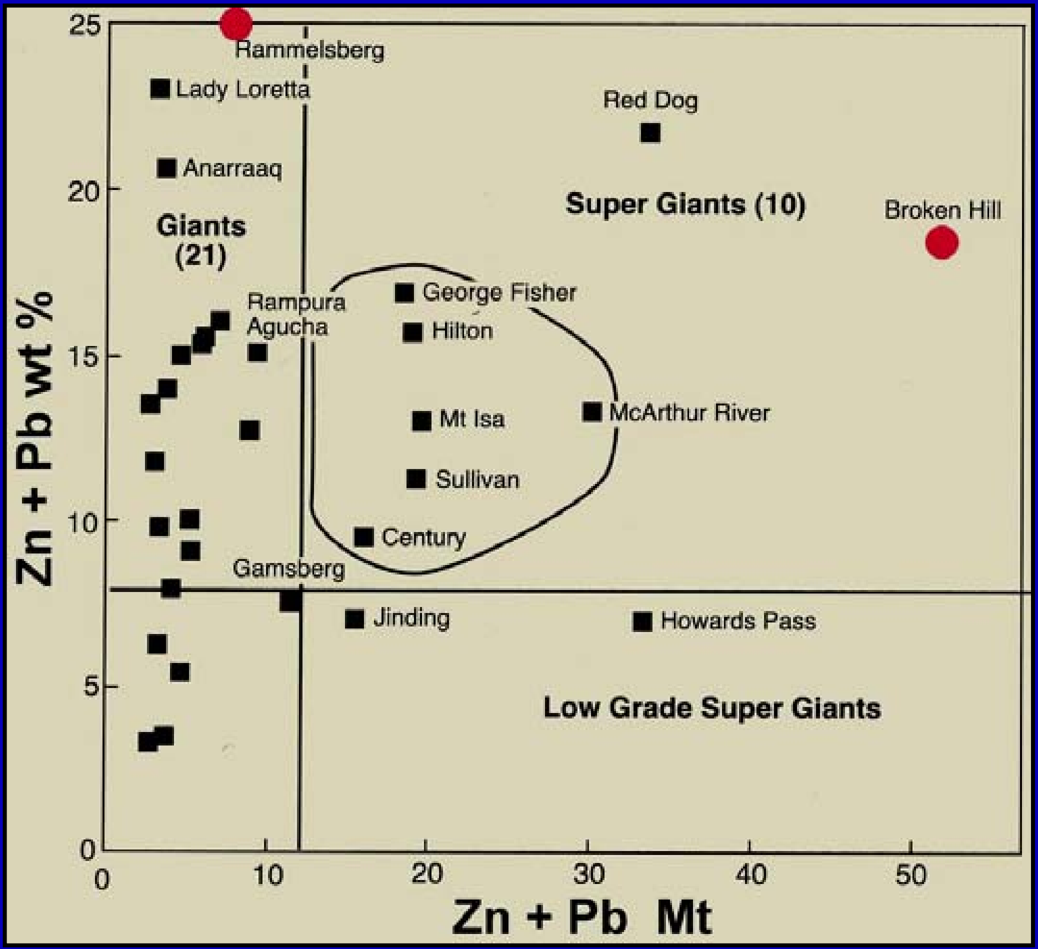
The Rammelsberg shale-hosted Cu-Zn-Pb sulfide-barite deposit, Germany: Linking SEDEX and Kuroko-type massive sulfides

by Andreas G. Mueller
andreas@conceptual.net.au

Rammelsberg: Past production + grade

Kraume et al. (1955), diagram modified from Large et al. (2005)

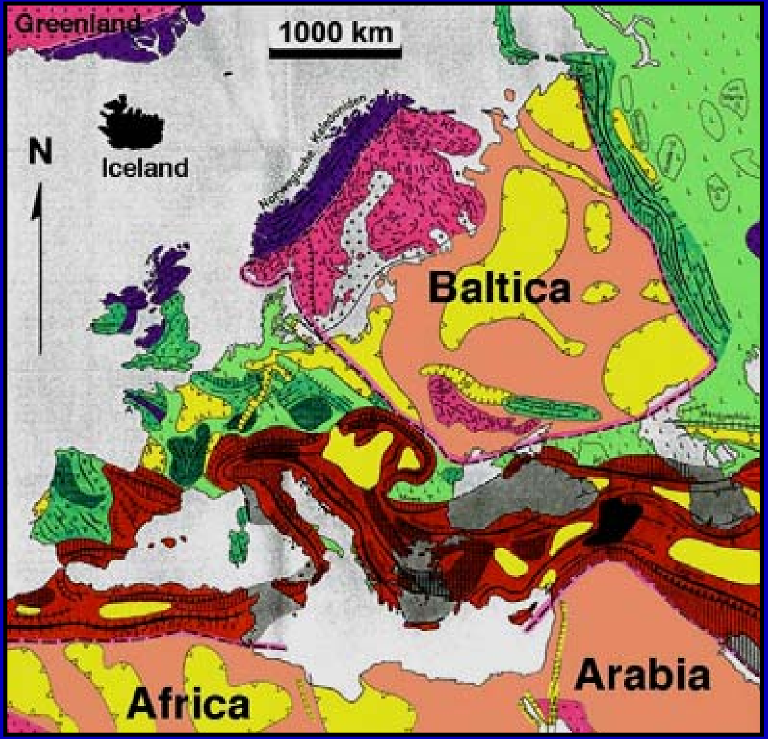


Massive sulfide ore: 27 Mt at 1% Cu + 19% Zn + 9% Pb + 160 g/t Ag + 0.5-1 g/t Au

Shale-banded sulfide ore: 2 Mt at 0.6 % Cu + 6.5% Zn + 3.5% Pb + 60 g/t Ag

Base metal: 7-8 Mt

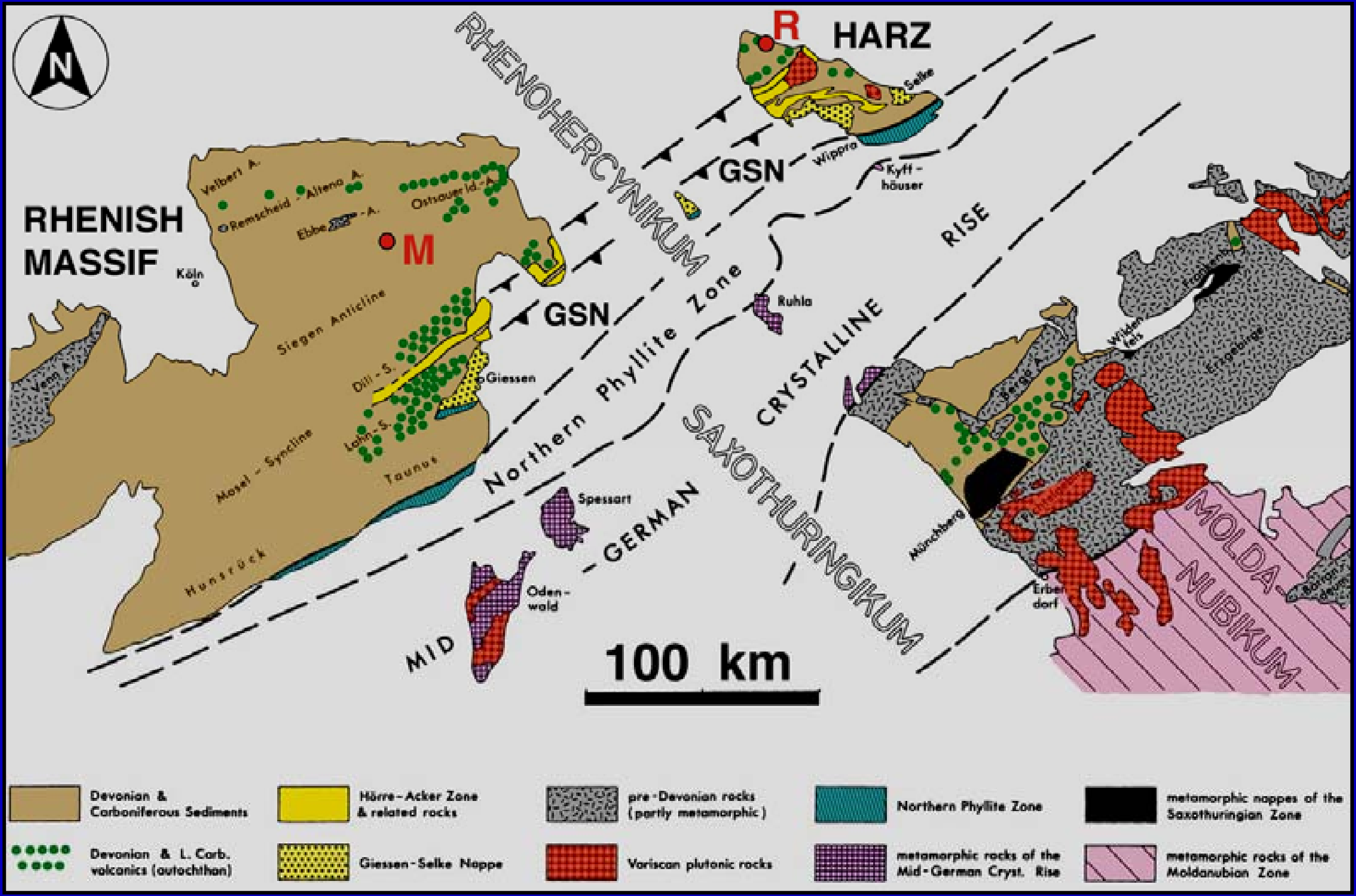
Variscan orogen and Alpine foreland tectonics in Europe



Europe, geology, modified from Meinhold (1971)
Germany, landscapes, modified from Schulze (1976)

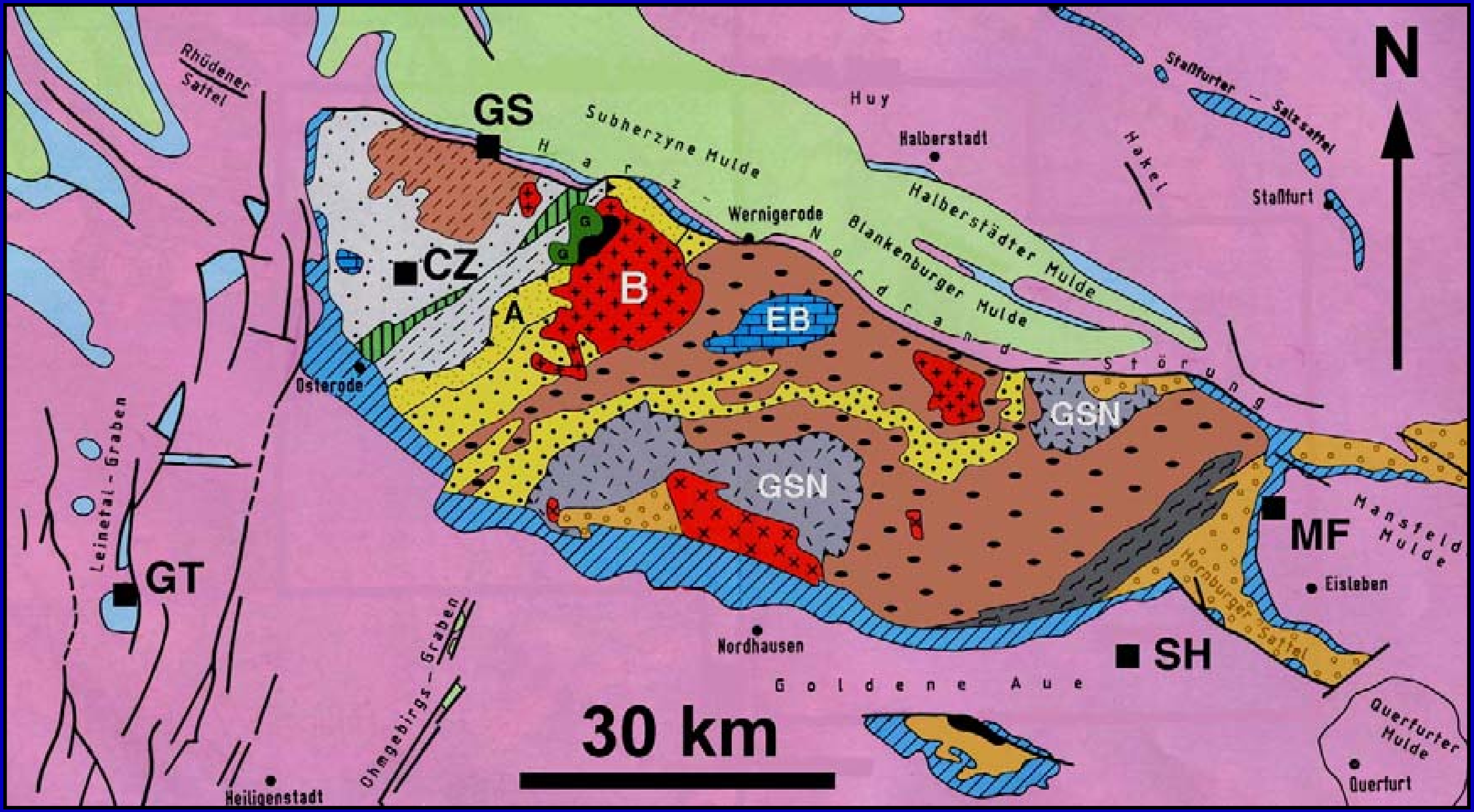
Variscan tectonic zones, Germany

Modified from Engel et al. (1983)



Harz mountain range: Geologic map

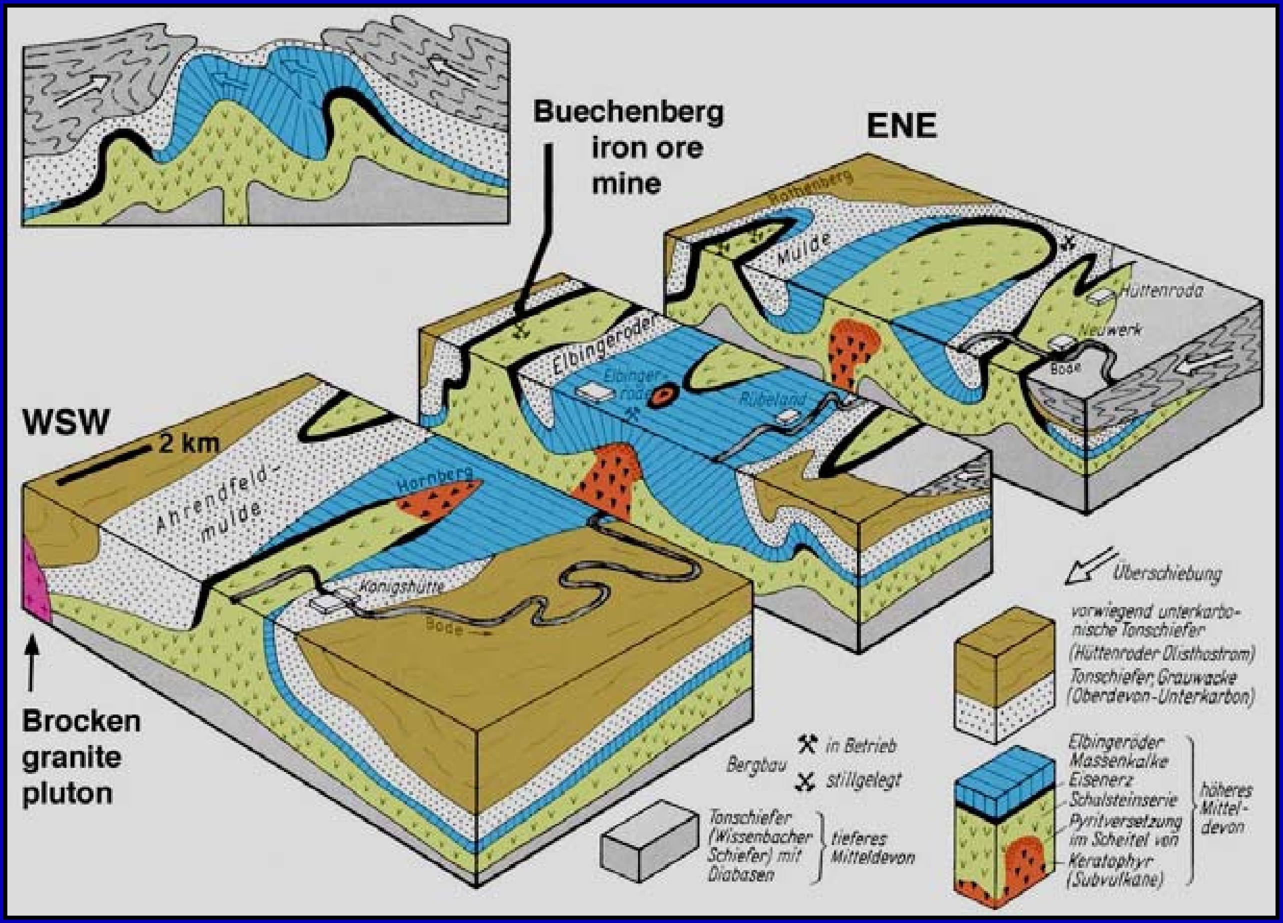
Modified from Hinze et al. (1998)



Devonian Elbingerode volcanic complex

Block diagram modified from Wagenbreth and Steiner (1990)

Givetian limestone reef (500 m thick): 100 Mt quarried to 2003

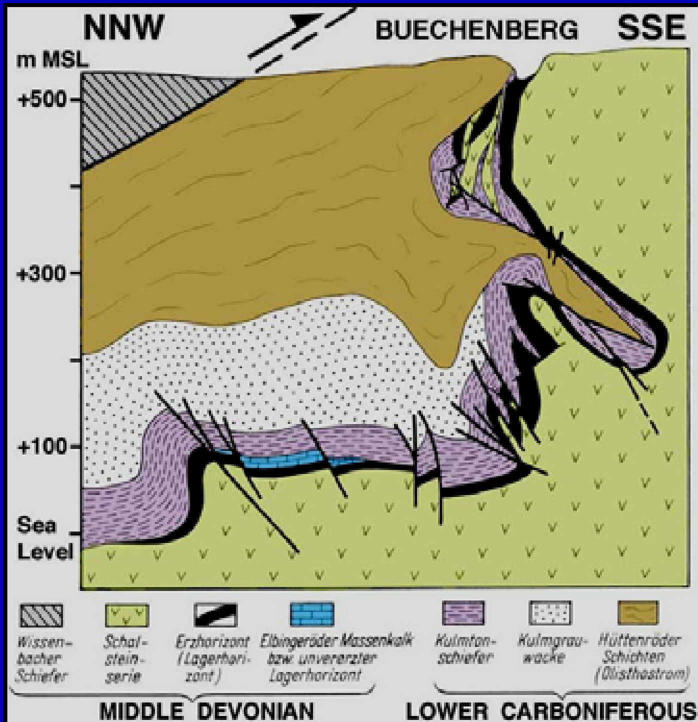


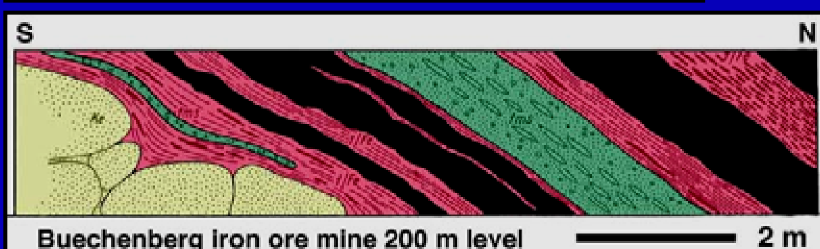
Givetian bimodal basalt - trachyte complex >700 m thick altered by seawater to spilite + kerato-phyre

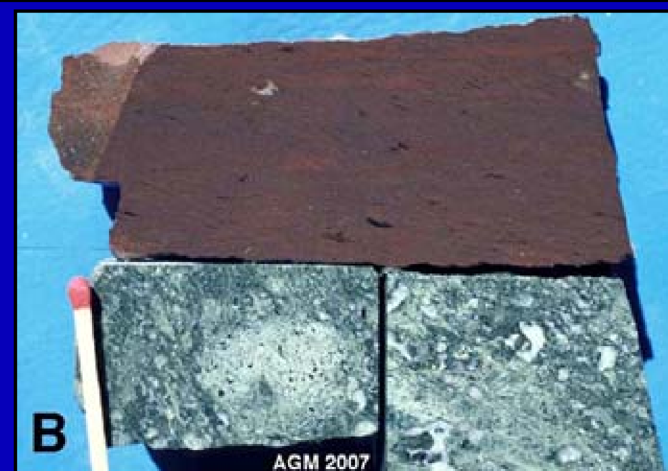
Elbingerode volcanogenic iron ore

Production: 25 Mt at 25% Fe to 1970, reserves: 51 Mt at 23% Fe

Stedingk et al. (2002), sections modified from Reichstein (1959), Wagenbreth & Steiner (1990)



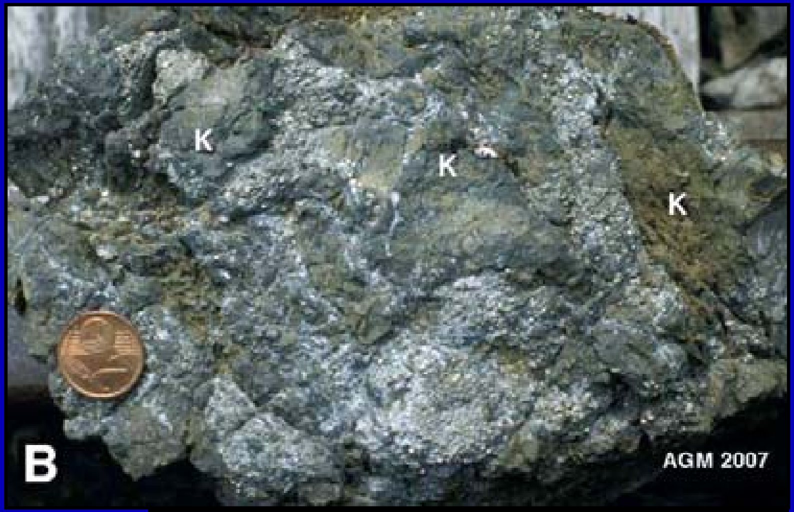


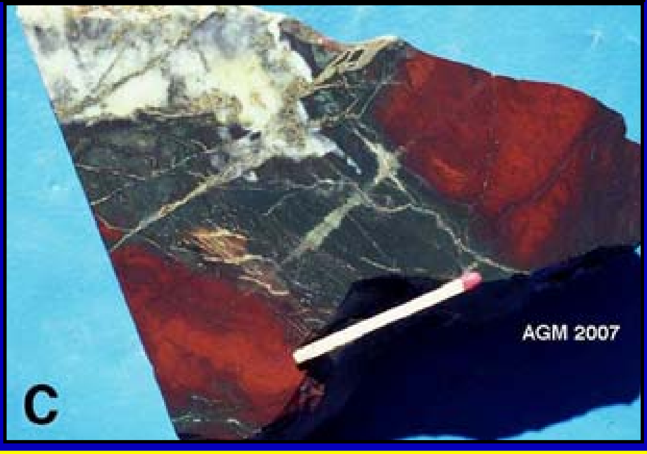


Elbingerode volcanogenic pyrite

Production: 13 Mt keratophyre at 25% pyrite (Stedingk et al. 2002)

δ^{34}S pyrite: -6.6 ± 1.2 ‰, Cu-Zn-Pb <500 ppm (Scheffler 1975)





Goslar: Imperial town in 968 AD

Otto the Great (936-973) establishes imperial residence, local silver coins abundant after 968 AD.

Rammelsberg cumulative production

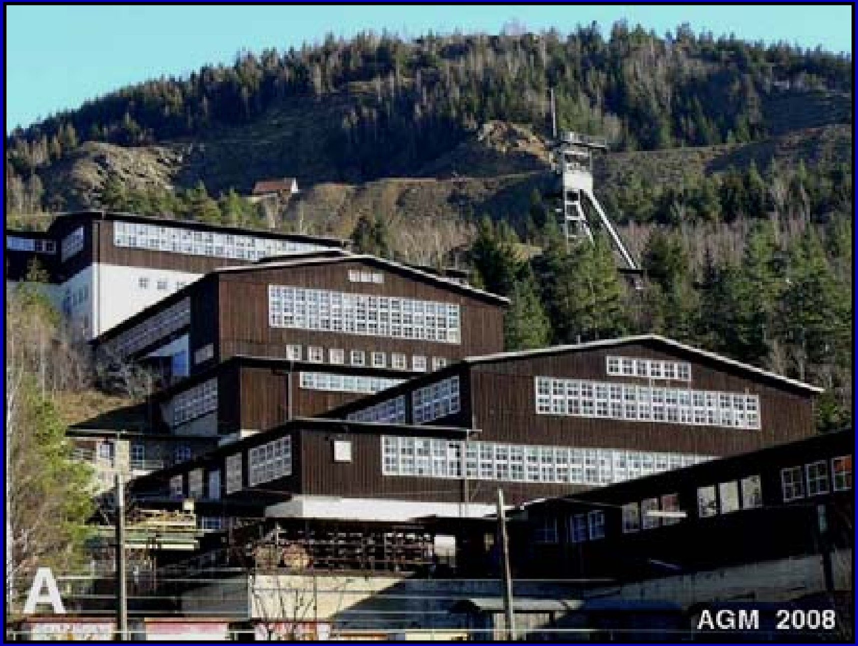
968-1360 AD:	2.8 million tons
1460-1648 AD:	6.2 million tons
1649-1866 AD:	8.8 million tons
1867-1988 AD:	26.3 million tons

Data: Walther (1986), Museum Rammelsberg (2008)

Otto-Adelheid Pfennig, silver coin ca. 985 AD

House of the baker's guild, 1507 AD

Rammelsberg mine: World heritage



Rammelsberg mine museum:
www.rammelsberg.de

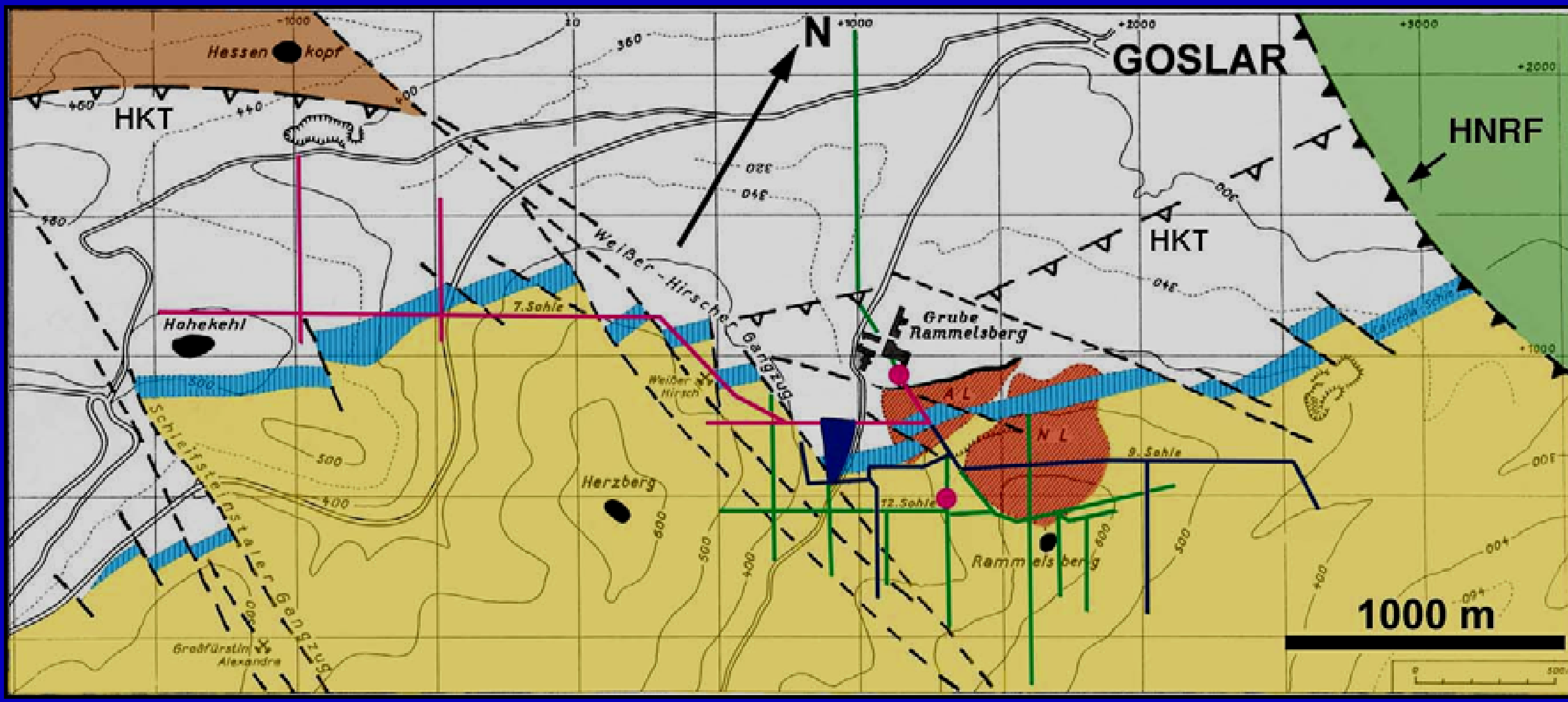
A. Shaft and flotation plant
B. Power plant
C. Harz rim, town of Goslar

Rammelsberg mine: Water system

Raths Tiefster drainage tunnel (1150 AD) and 18th century water-wheel pump

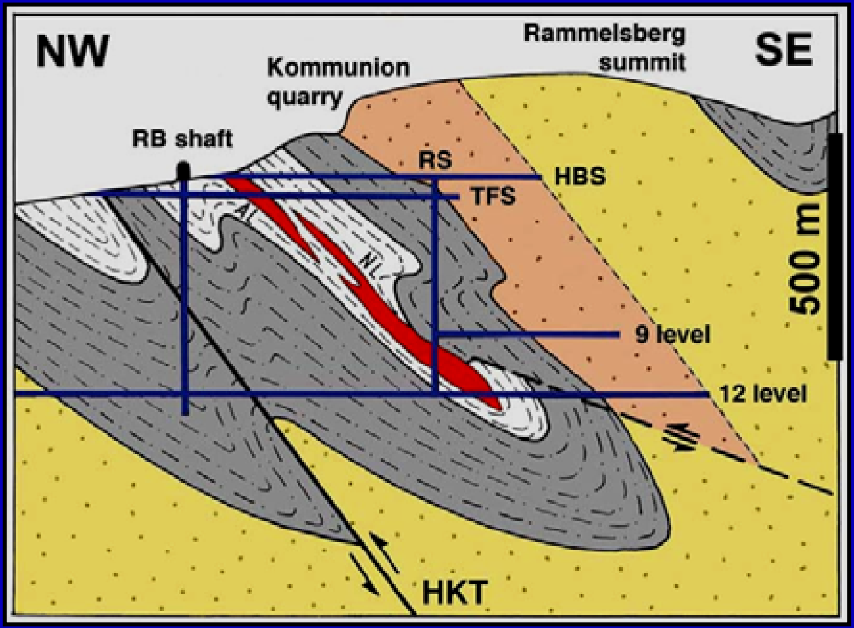
Rammelsberg district geology

Modified from Kraume (1960)



Rammelsberg: Structure in cross section

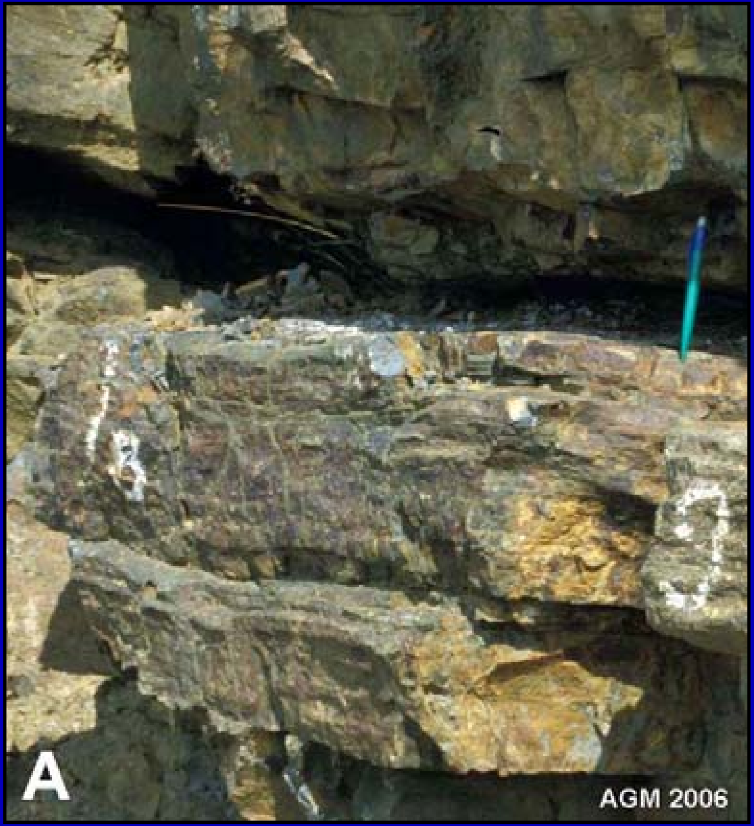
Cross section modified from Hinze et al. (1998)



A. Look east at Lower Devonian sandstone and Middle Devonian black shale

B. Look NE, slaty cleavage in Wissenbach black shale

Rammelsberg: Cu-Zn-Pb sulfides in sandstone

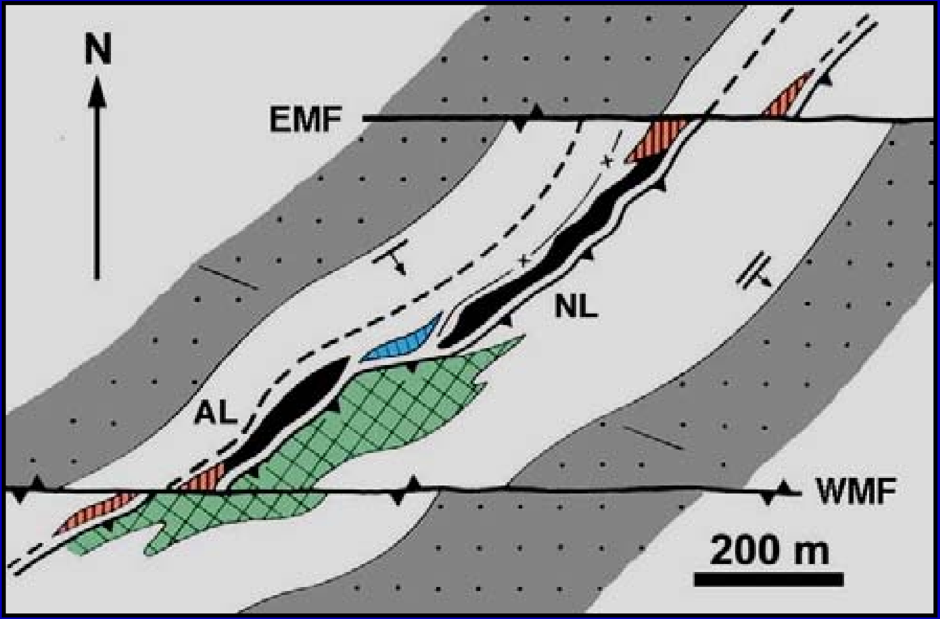


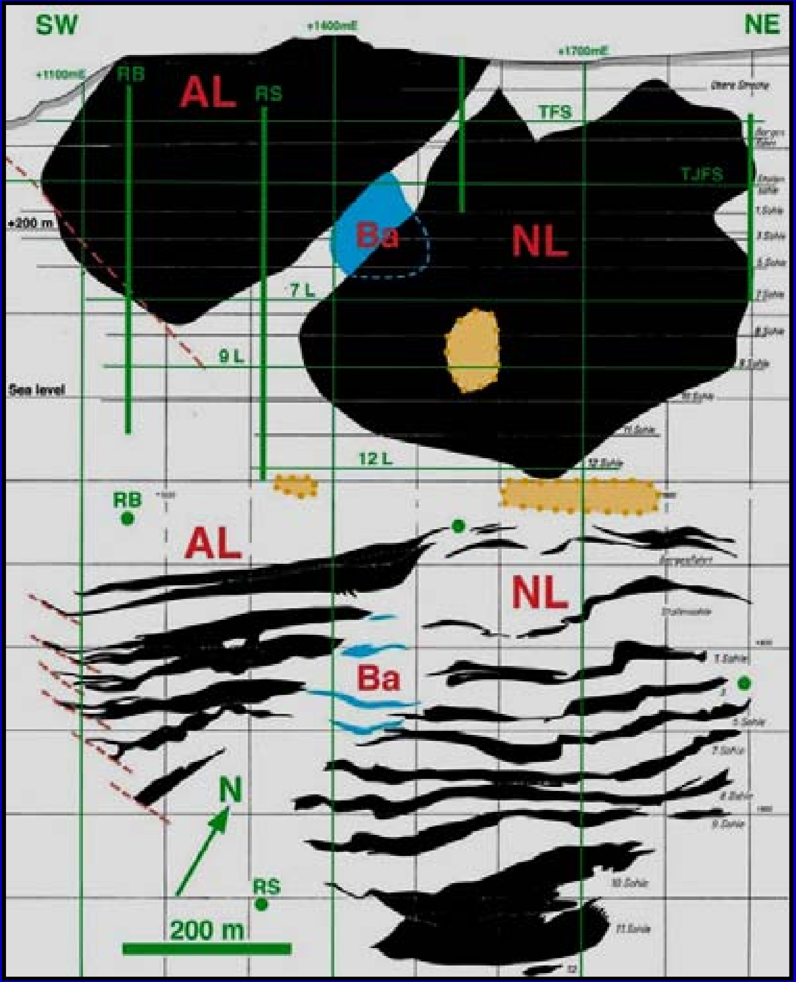
A. Thin manto in quarry
B. Pyrite-ccp manto
C. Sphalerite spots

Rammelsberg: Ore in black shale

Rammelsberg: Shape of orebodies

Modified from Kraume et al. (1955) and Gunzert (1979)



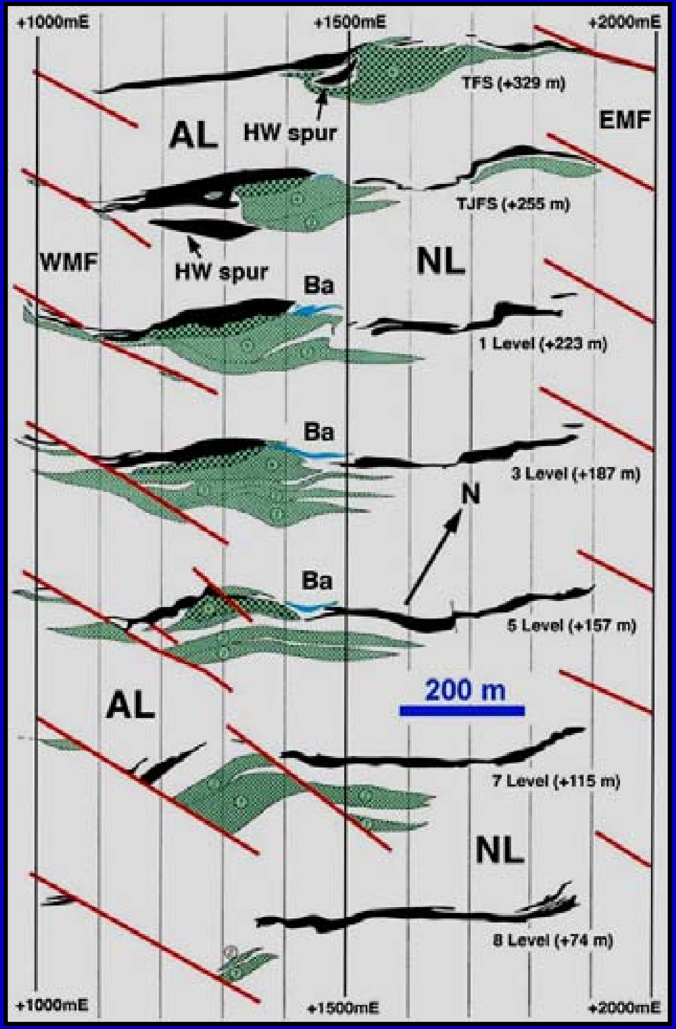


Left: Geologic map Level 3

Right: Longitudinal section + composite level plans

Kniest footwall alteration zone

Composite level plans modified from Kraume et al. (1955)

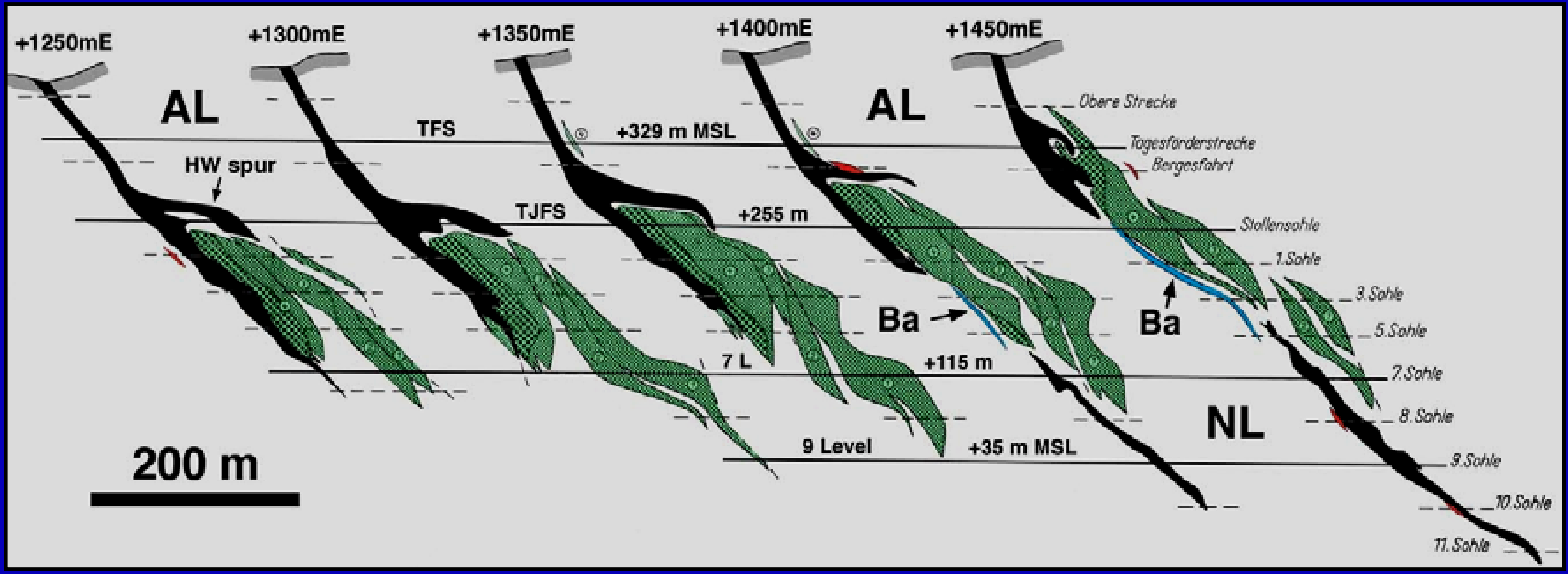


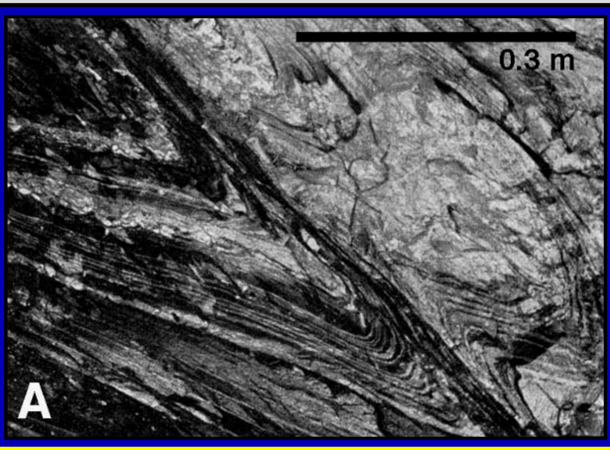
Kniest = Quartz ± chlorite ± ankerite replacement of shale

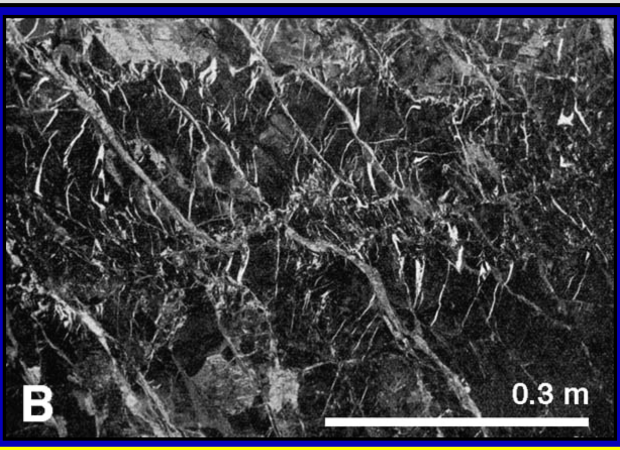
Sulfide-veined Kniest:
2.5 Mt at 1.3% Cu + 3.0% Zn + 1.4% Pb + 28 g/t Ag

Structure of Altes Lager and Kniest

Modified from Kraume et al. (1955)





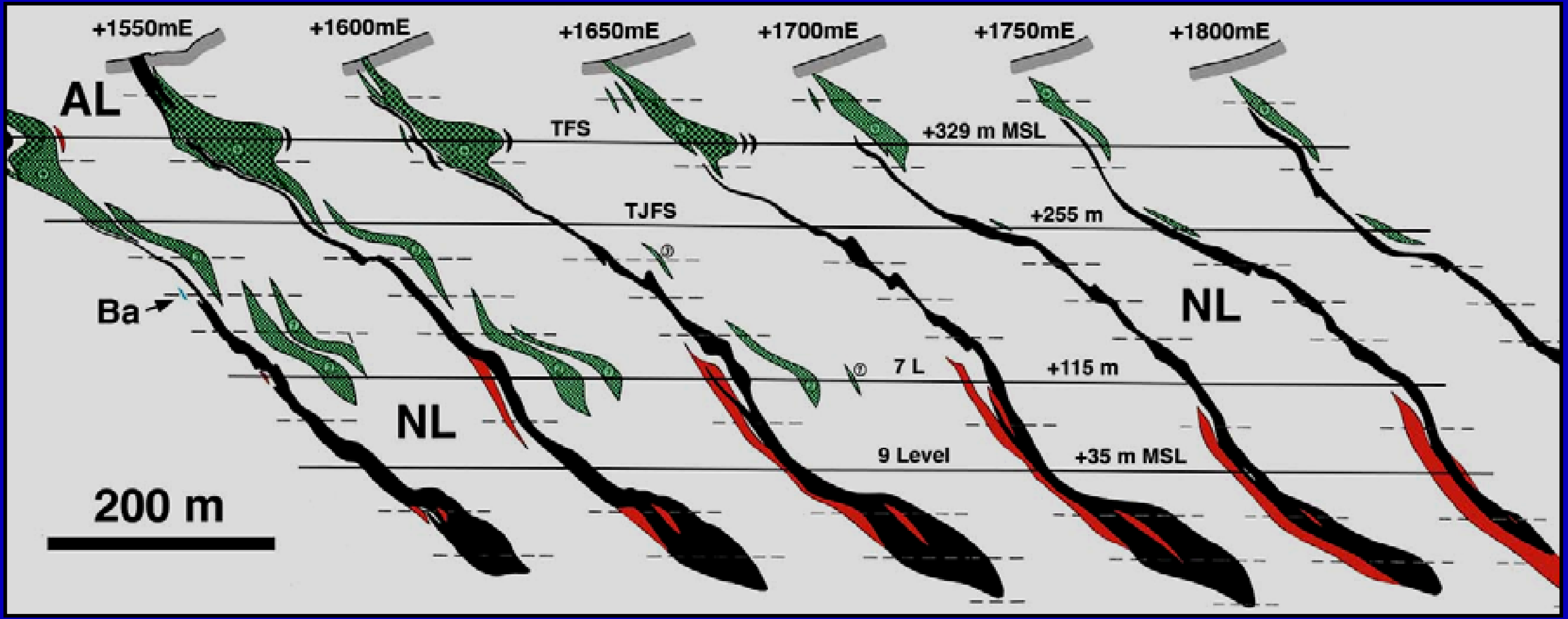


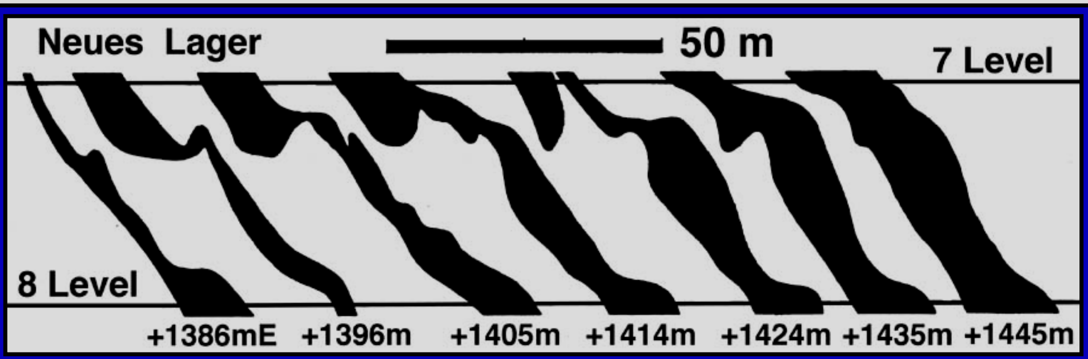
A.
AL ore

B.
Kniest

Structure of Neues Lager and Kniest

Modified from Kraume et al. (1955)

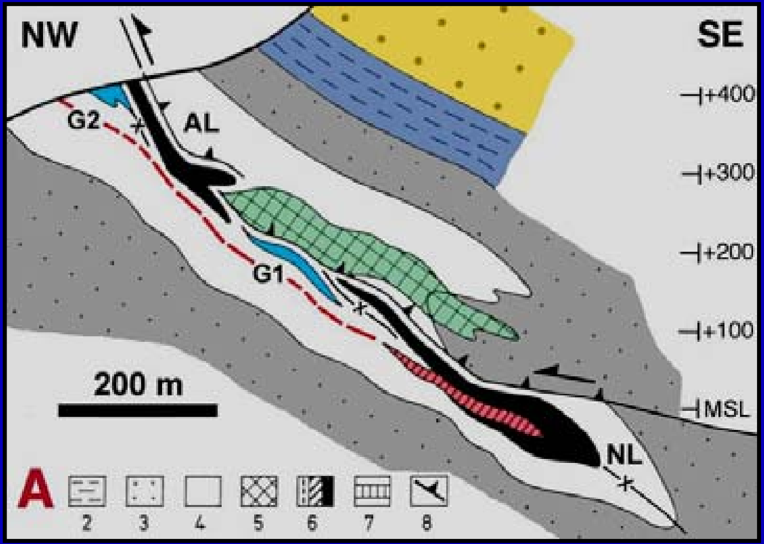


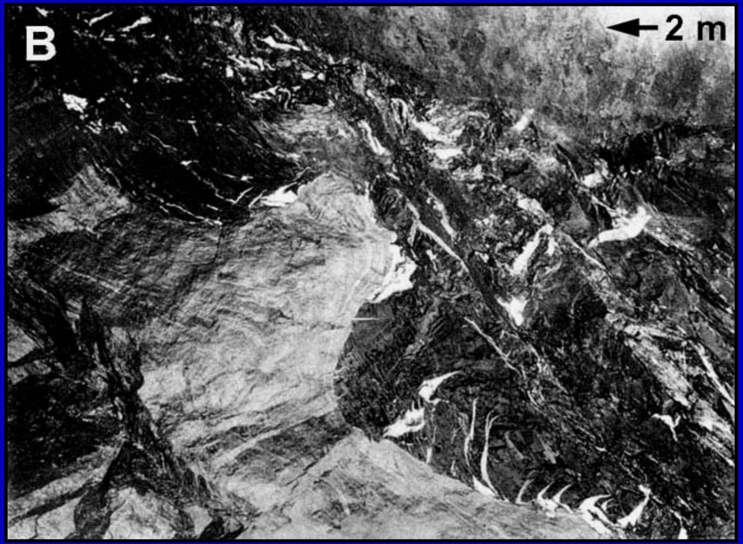


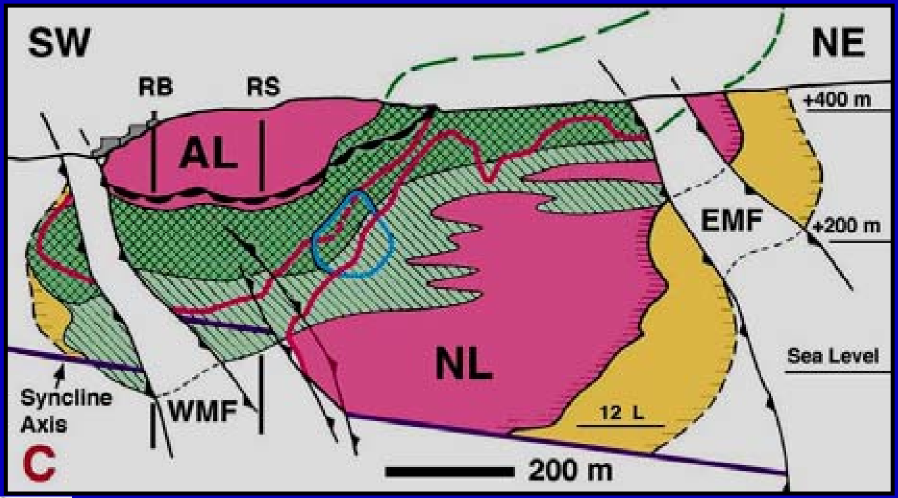
Left: Drag folds In NL massive sulfide, reverse movement

Deformation during reverse faulting

Modified from Wolff (1913), Gunzert (1969), Gunzert (1979)





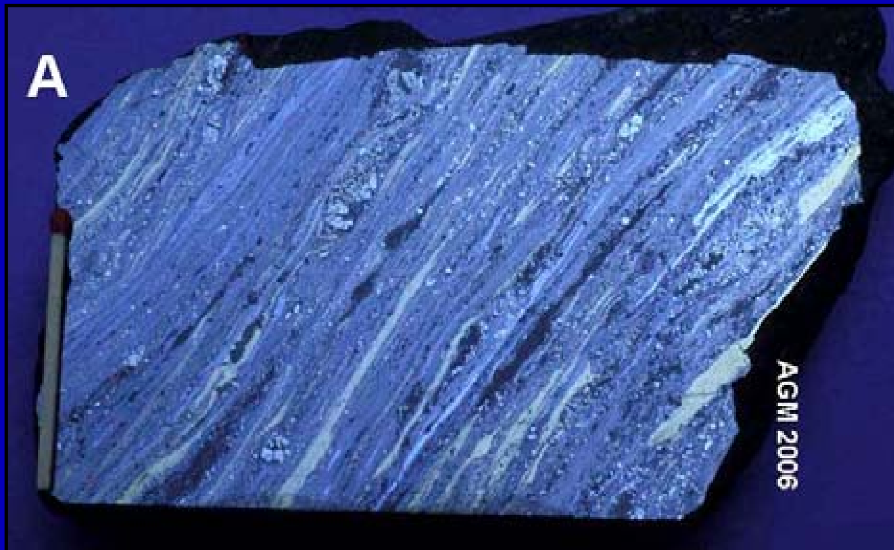


A. Cross section

B. Drag fold in Neues Lager massive sulfide

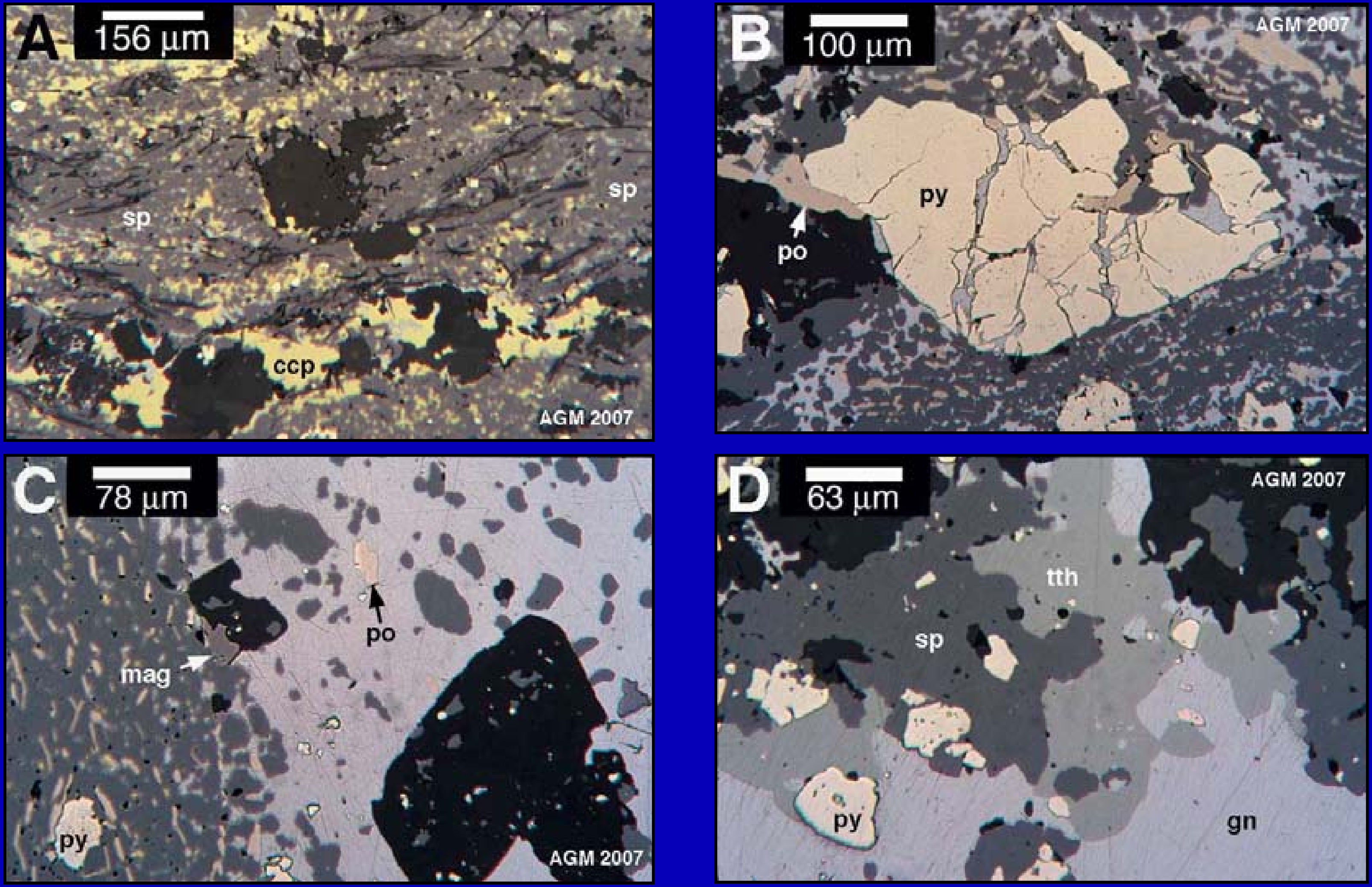
C. Longitudinal section

Brittle-ductile sulfide deformation

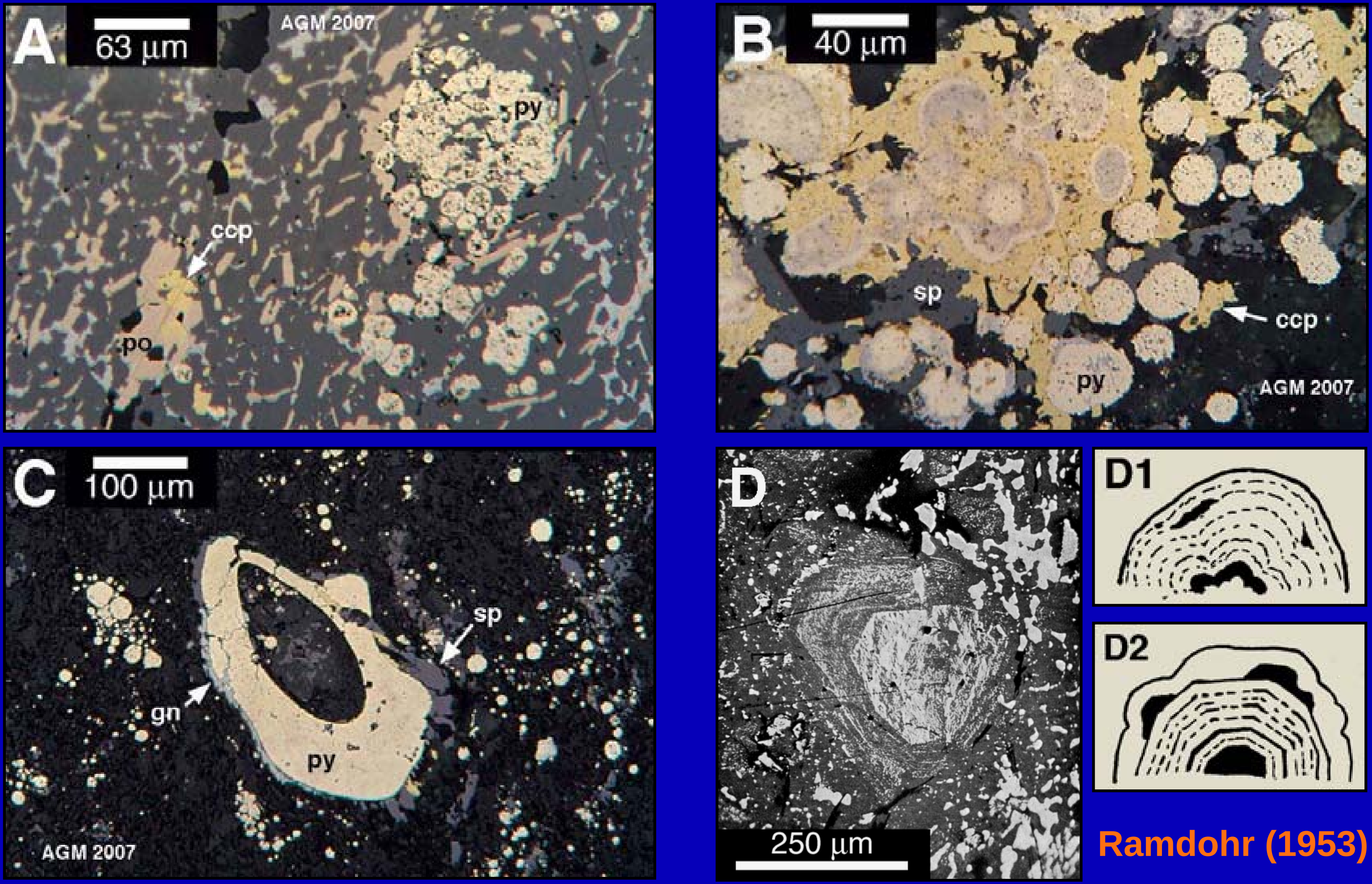


A. Mylonitic sulfide ore, rolled pyrite nodules
B. Breccia ore, pyrite fragments in sphalerite
C. Folds in shale-banded sulfide ore

Rammelsberg: Sulfide textures



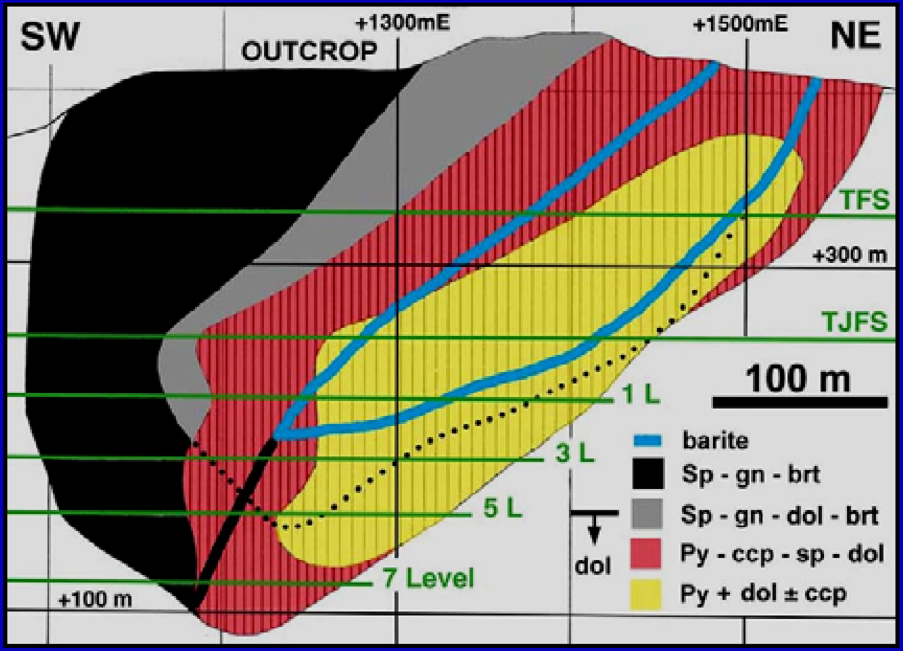
Rammelsberg: Sulfide textures



Ramdohr (1953)

Altes Lager: Zoned massive sulfide

Longitudinal section modified from Kraume et al. (1955)



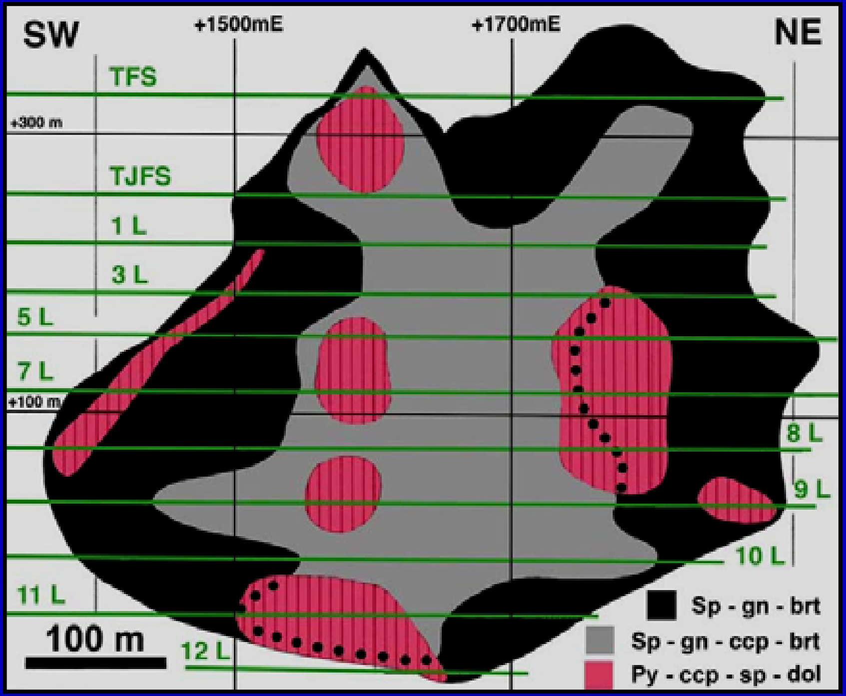
8 million tonnes

A. Barite bed in pyritic sphalerite + galena

B. Sphalerite ore and chalcopyrite ore

Neues Lager: Zoned massive sulfide

Longitudinal section modified from Kraume et al. (1955)



19 million tonnes

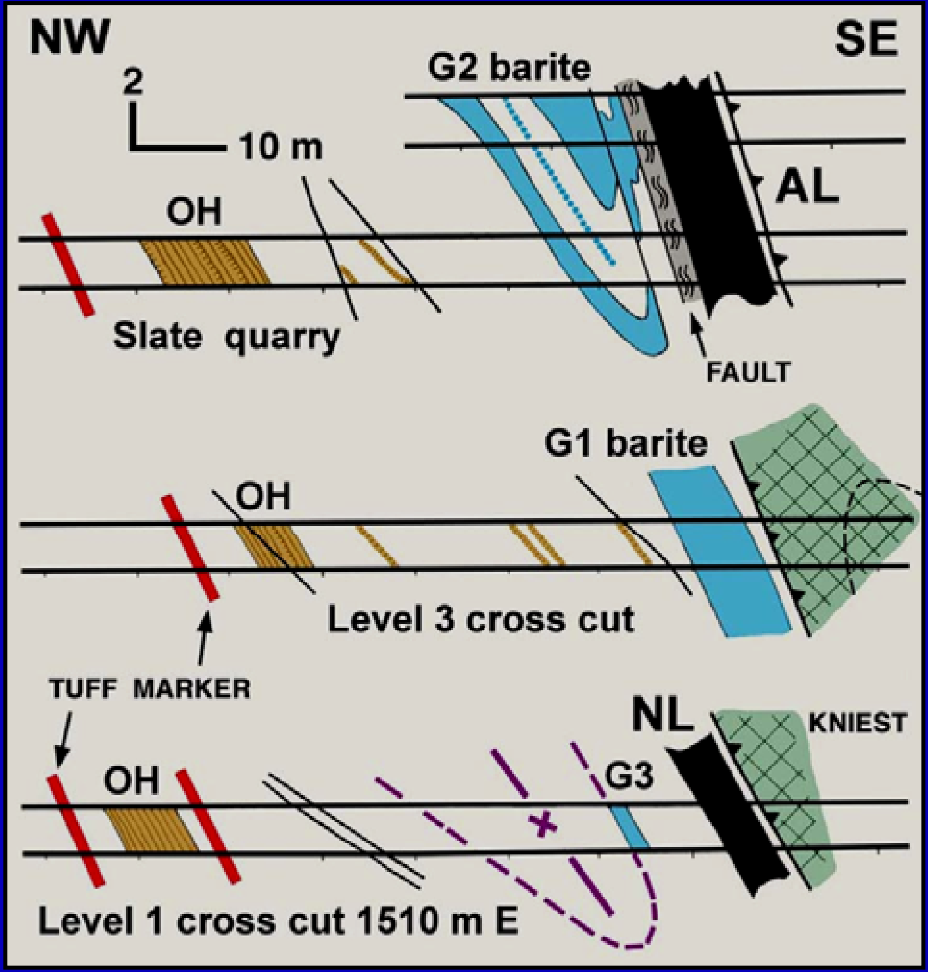
A. Banded sp-gn-barite

B. Banded ccp-sp-gn

3 g/t Au, 230 g/t Ag

Tuffs, ore marker horizon, and barite beds

Sections modified from Gunzert (1979)



Barite ore: 0.2 Mt, 80% brt, 3.8% Zn, 2.8% Pb, 140 g/t Ag
Ore horizon: Fe-dolomite, chlorite, pyrite
Felsic tuffs: qtz-illite schist, igneous qtz, biotite, zircon

Rammelsberg: Sulfur isotopes

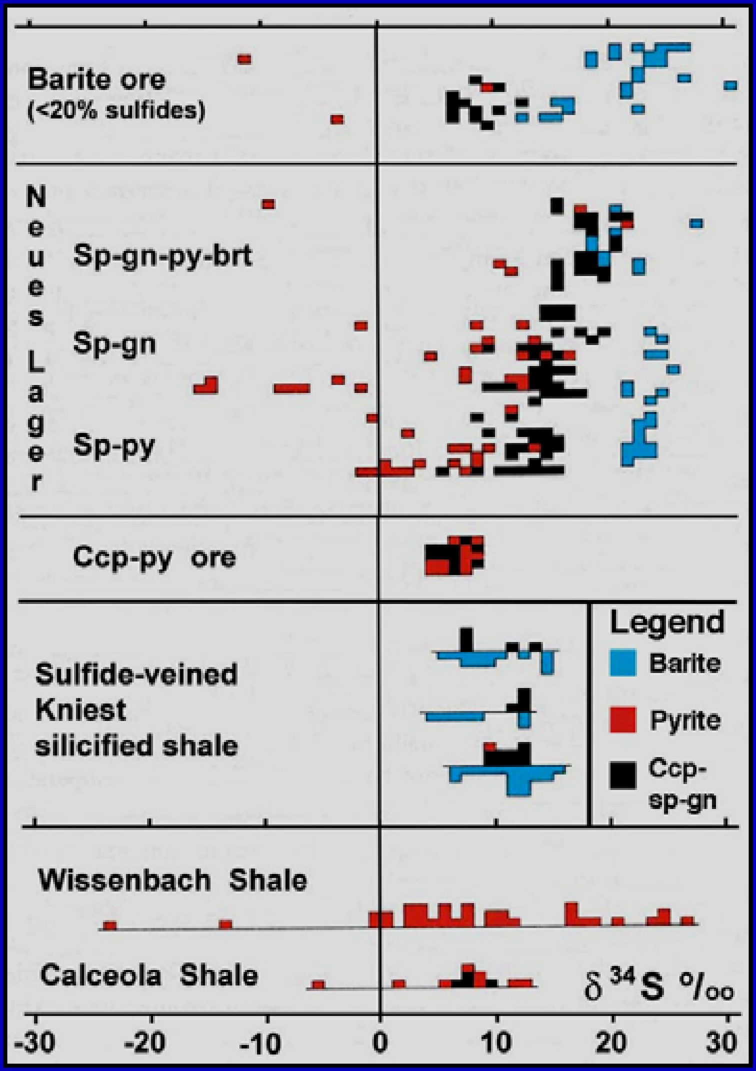


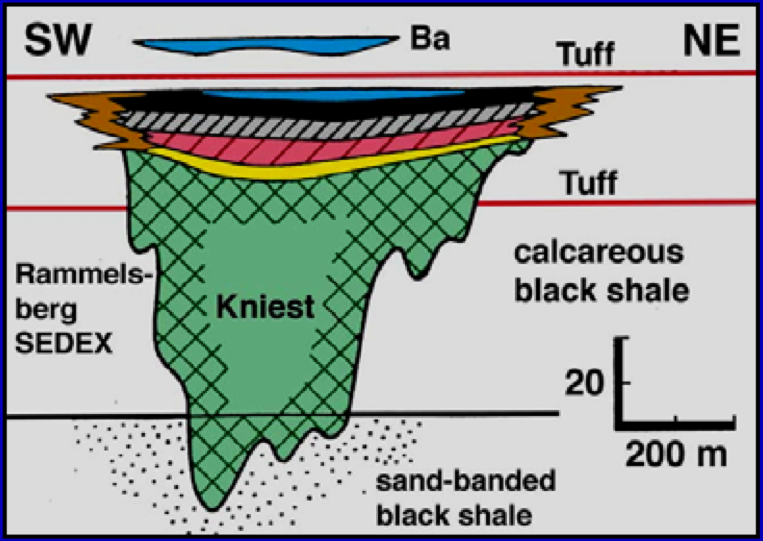
Diagram modified from Nielsen (1985)

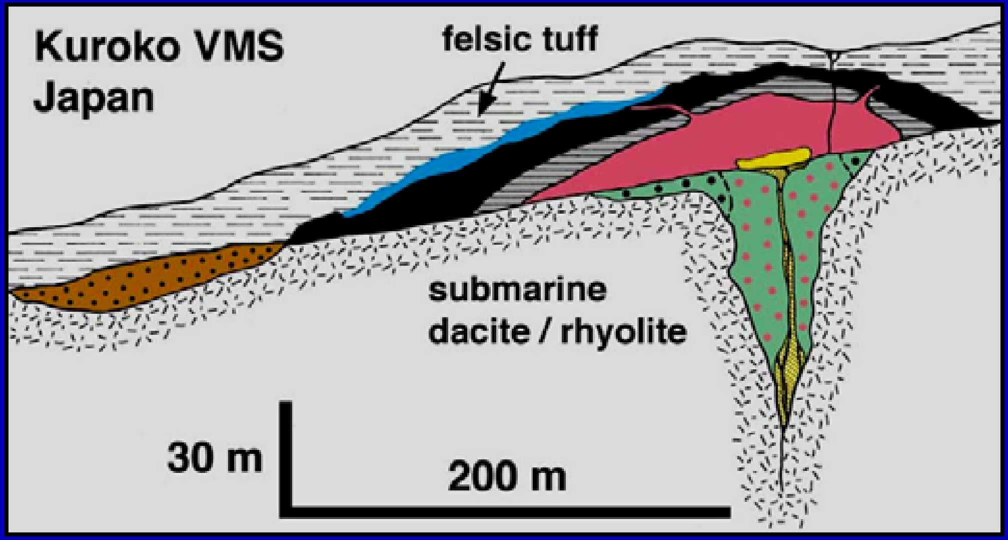
For sulfides, H_2S in fluid derived from marine sulfate in the sediments below by inorganic reduction. Seawater sulfate for barite. Isotope fractionation at 300±150°C. Diagenetic pyrite by bacterial sulfate reduction.

Metamorphism: Barite in Kniest veins formed by oxidation and dissolution of Lager sulfide. Magnetite + calcite in massive sulfide by oxidation of ankerite?

Sedex brine pool versus Kuroko mound

Modified from Gunzert (1969) and Eldridge et al. (1983)



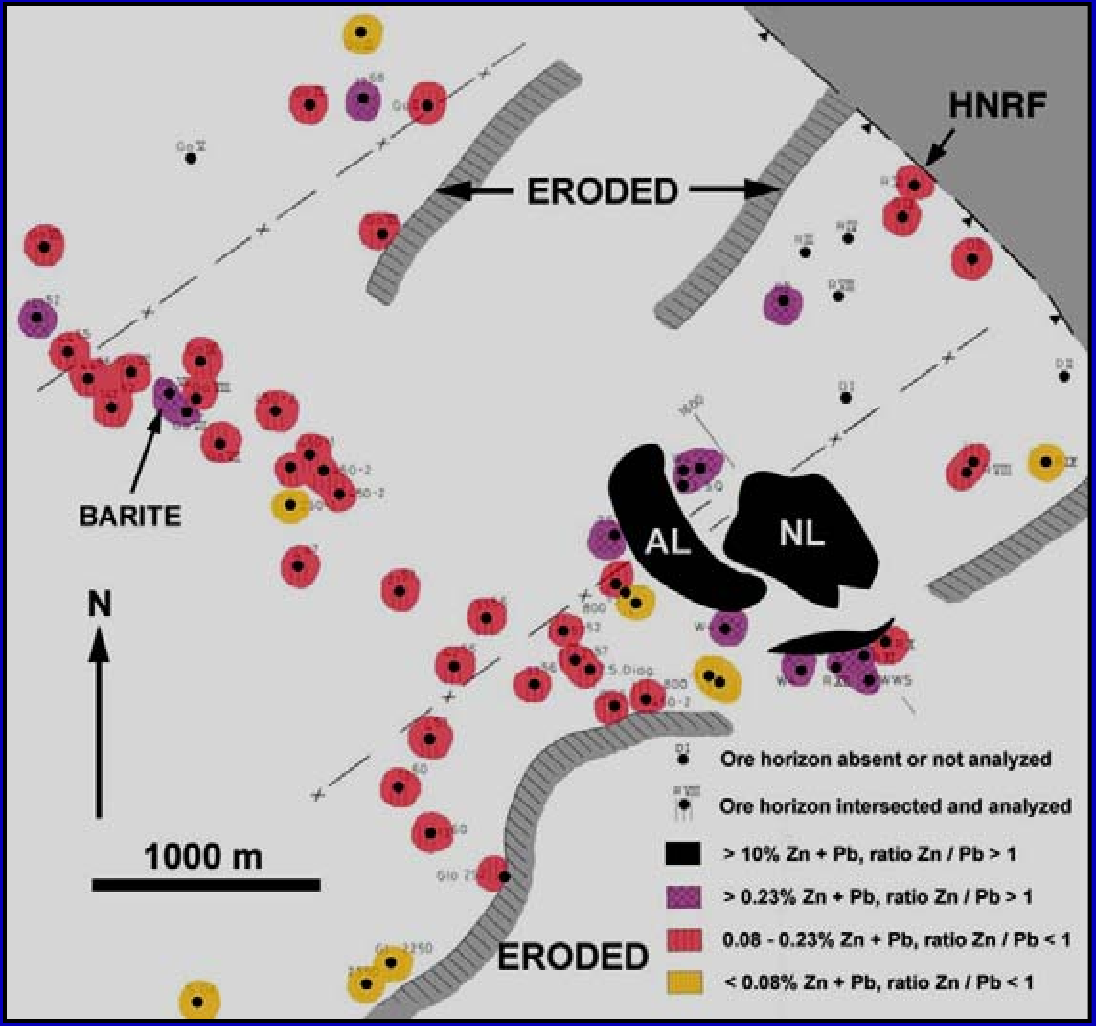


Rammelsberg: sulfide mud layers in brine pool, inter-bedded with black shale.
Discharge fluid: 300°C ?
Metamorphic fluid in Kniest veins (1-5 wt % NaCl$_{eq.}$) up to 250°C.

Kuroko: massive sulfide mound on volcanic surface, partly transported.
Exchanged sea ± magmatic hydro-thermal water (3.5-7 wt % NaCl$_{eq.}$)
Black Zn-Pb ore: 200-300°C
Yellow Cu ore: 300-350°C

Total Zn-Pb content of ore horizon

Modified from Sperling and Walcher (1990)



Ore deposit prior to erosion: 35-40 Mt at 25% Zn + Pb = 9-10 Mt base metal

Ore horizon (20 m thick) at 0.5-3km distance from deposit grades 620 ppm Pb + 300 ppm Zn

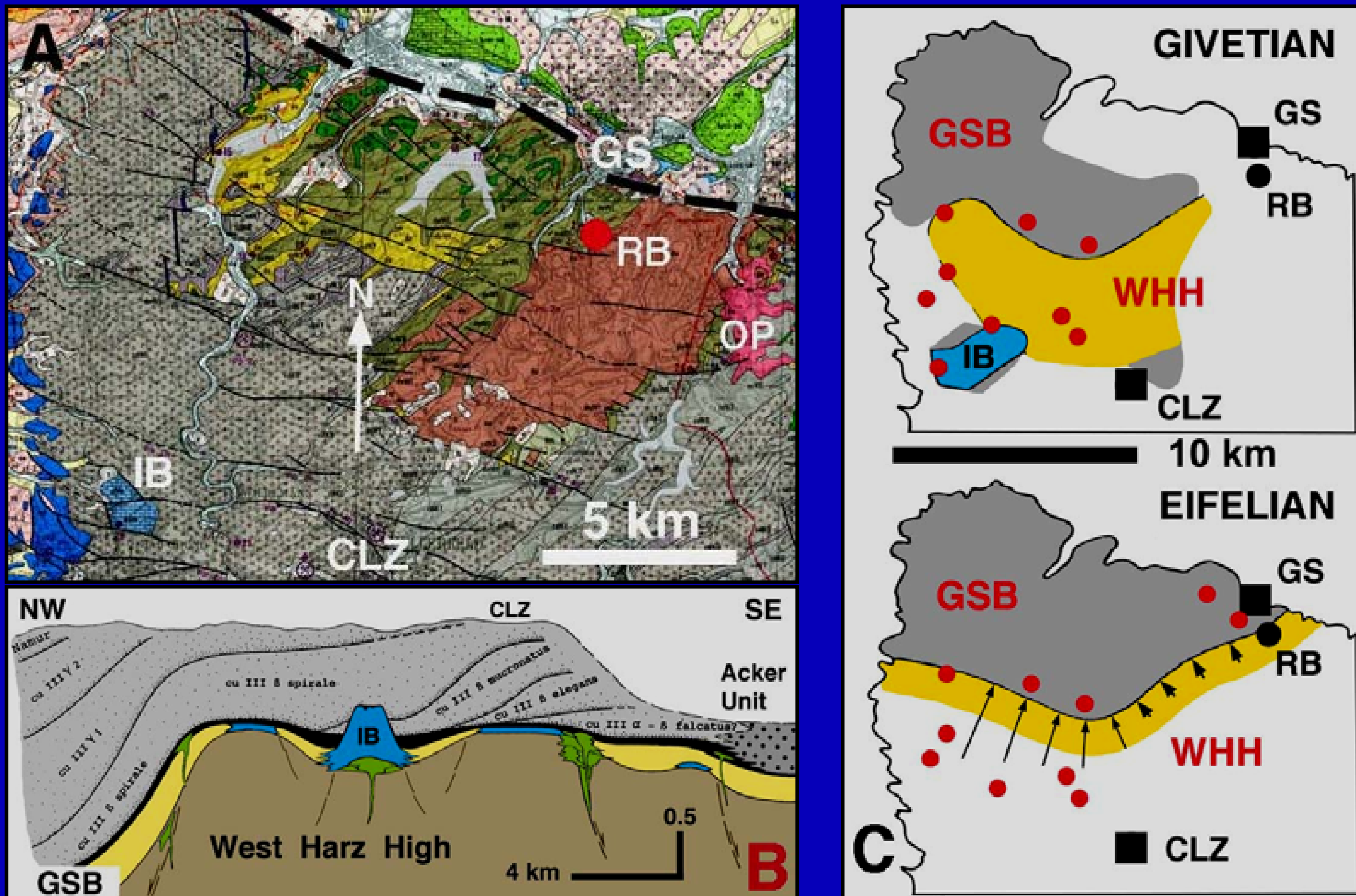
Local shale: 48 ppm Pb + 105 ppm Zn

Ore horizon in 3 km radius: 13 Mt metal

Total system: > 22 Mt Zn + Pb

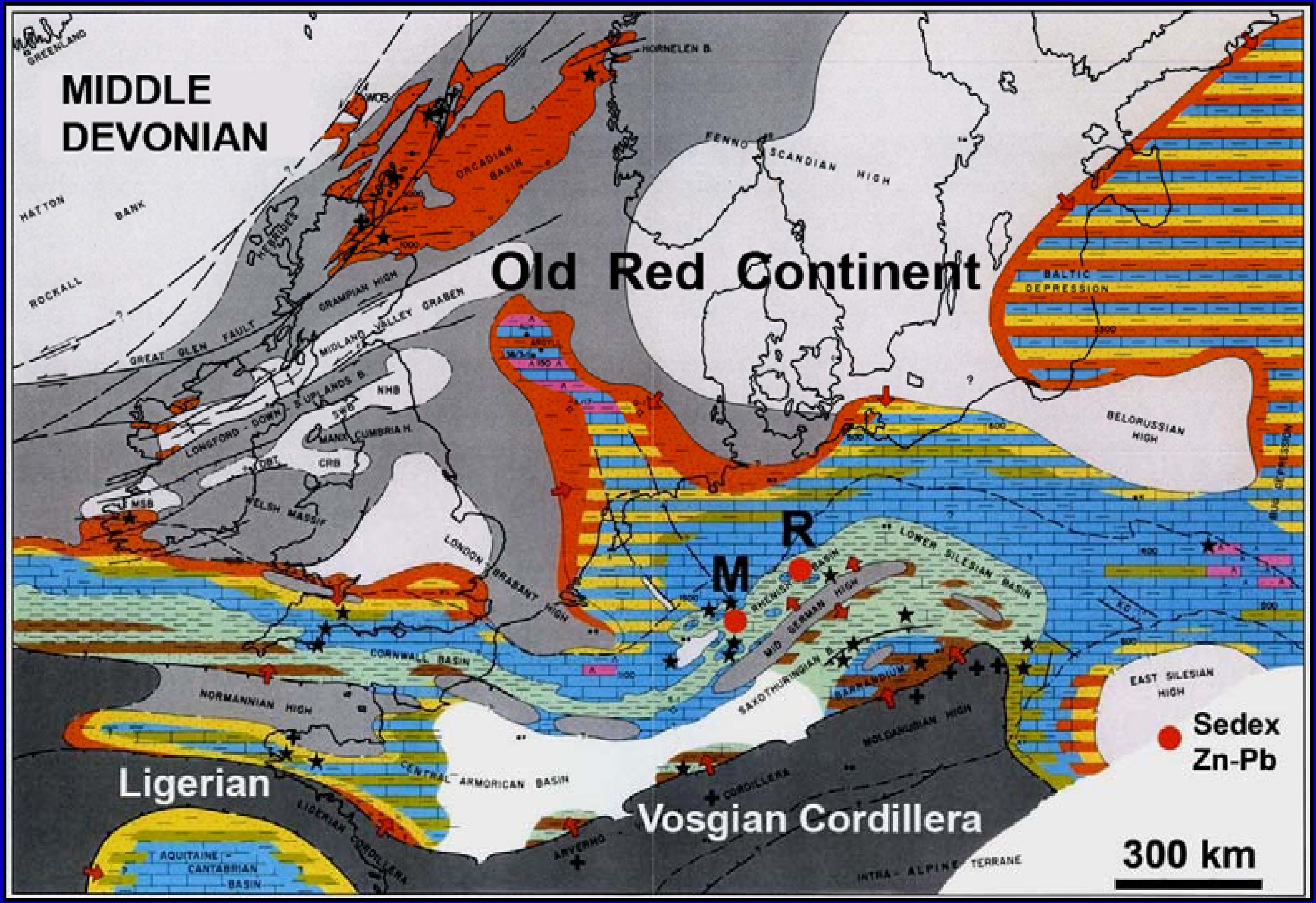
Harz: Middle Devonian Goslar basin

Modified from Engel et al. (1983), Brinckmann et al. (1986), Hinze et al. (1998)



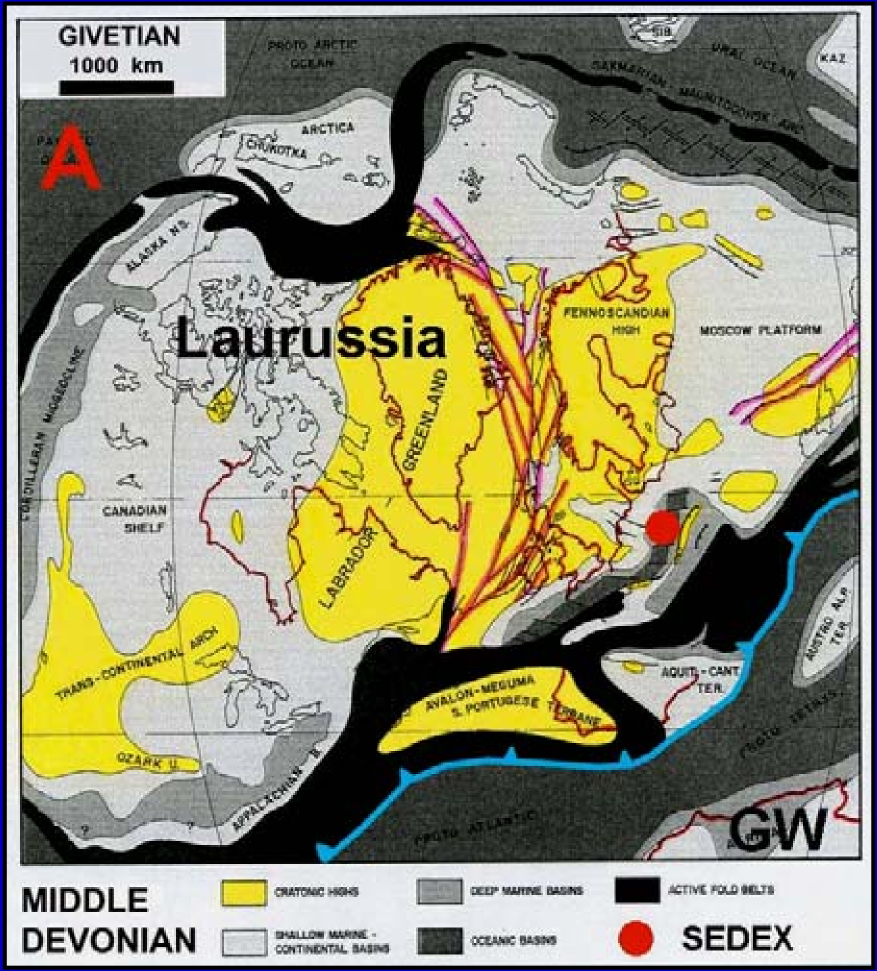
Europe: Devonian back-arc basin

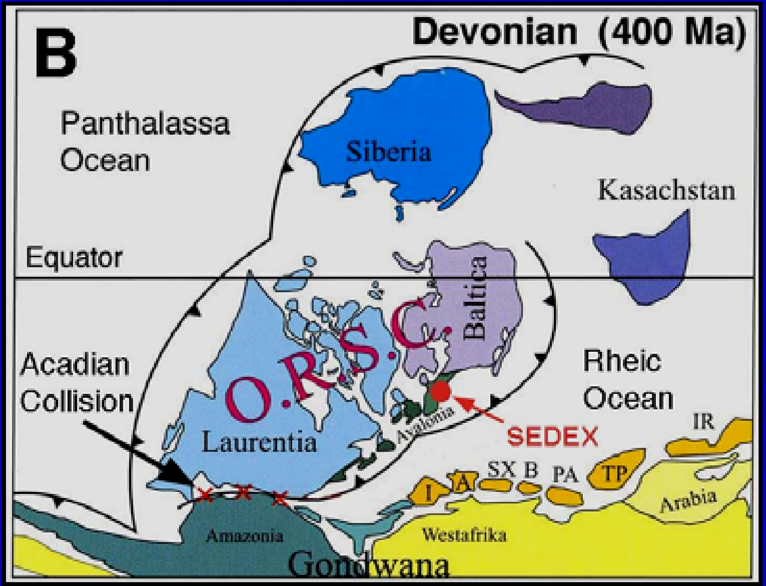
Modified from Ziegler (1990)

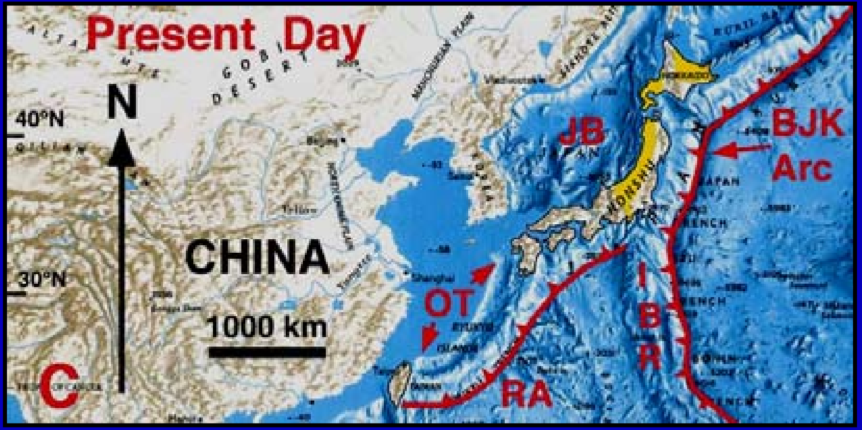


Devonian plate-tectonic setting

Modified from Ziegler (1990), Shupe (1992), Linnemann et al. (2003)







Rammelsberg: Key genetic features

Plate-tectonic setting: Continental-margin, sediment-filled, rifted back-arc basin

Submarine bimodal volcanism: Rift-related basalt and trachyte/alkali rhyolite lavas and tuffs, district-scale spilitization

Submarine ore deposits: Proximal hematite beds with basalt, pyrite mineralization with trachyte / rhyolite on volcanic ridges, distal SEDEX sulfide-barite ore in black shale basins

Rammelsberg deposit: Located at the margin of a deep-water black shale basin structured by rift faults. Feeder fault marked by reduced silica-chlorite-ankerite replacement

Cu-Zn-Pb massive sulfides: Vent-proximal, deposited as mud at 250-350°C, mixed with seawater barite in a brine pool