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PRESENTATION NOTES

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

Slide presentation and explanatory notes
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The slide presentation in 4:3 tablet format is designed as an introduction to a vent-proximal Cu-Zn-Pb SEDEX deposit, the notes explaining each slide step-by-step. This version replaces Version 1 of the same title published in 2008. The author's images are initialed AGM and dated. A sister presentation of the vent-distal Meggen SEDEX Zn-Pb-Ba deposit in Germany is also available in the Mineral Deposit Archive (Mueller 2019).

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SUMMARY

The Rammelsberg Cu-Zn-Pb sulfide-barite deposit in the Harz mountains, northern Germany, was mined continuously for more than 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 copper-gold content (1% Cu, 0.5-1 g/t Au) of its 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 folded Kniest wedge spans the entire width of the deposit. Pyrite, arsenopyrite and sphalerite disseminations in the Kniest, and sulfide mantos and spotted replacement 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 shale-banded ore (2 Mt at 6.5% Zn, 3.5% Pb) and is compositionally zoned. Stratigraphically higher sulfide-gangue lenses extend 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. The lateral stratigraphic equivalent of the sulfide ore is 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 prior to erosion (9-10 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 succession (>1000 m) of Lower Devonian shelf sandstones and from paragneiss 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 indicating a genetic link between VMS and SEDEX, the two main classes of syn-sedimentary Cu-Zn-Pb sulfide deposits.

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 downloads from the SGA website. They are designed as teaching tools for digital projection and for the study on-screen in 4:3 tablet format. This text explains each slide step-by-step. 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). References quoted on the slides are listed below.

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) recognized that the ore differed from epigenetic Zn-Pb-Ag veins. As geology developed into an independent natural science, increasingly detailed studies led Schuster (1867), Wimmer (1877), Köhler (1882) and Klockmann (1893) to propose 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 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 (e.g. 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 *Slide 1. SGA disclaimer.*

2.2 *Slide 2. Title of Version 2.*

2.3 *Slide 3. Preface*

2.4 *Slide 4. Past production and grade*

The first written document of mining at the Rammelsberg dates from 968 AD. Operations ceased in 1988 after the total removal of the ore in place.

Massive sulfide: The massive sulfide ore, 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)

2.5 *Slide 5. 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). The Tornquist-Tessyre tectonic zone (TTZ) marks the craton boundary to the central European terranes. In Germany and elsewhere in 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 more than 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 sedimentary rocks (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 in Slide 6 is outlined in white.

2.6 *Slide 6. Variscan tectonic zones in 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-sulfide-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 and strike northeast. Most have vertical to overturned northwest limbs.

The slate-belt succession is 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 orthogneiss occurs 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 Saxothuringikum and Moldanubikum.

The Saxothuringian (grey) and Moldanubian Zones (pink) consist of para- and ortho-gneiss, 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) are erosional remnants of regional metamorphic nappes. Reviews of the regional geology are in Franke (2000) and Linnemann et al. (2003).

2.7 *Slide 7. Harz mountains: 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 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 periphery 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), perhaps uplifted Cadomian basement (Walter et al. 1995). The U-Pb zircon ages of the Brocken granite (283±2 Ma; Zech et al. 2010) and of Permo-Carboniferous felsic volcanic rocks east and north of the Harz (307±3 to 294±3 Ma; Breitkreutz and Kennedy 1999) indicate a 30 Ma-period of magmatic activity.

2.8 *Slide 8. 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 iron 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 sodic 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 (red) contains disseminated, stockwork, and breccia pyrite mineralization. The U-Pb age brackets of the International Commission on Stratigraphy (2018) are as follows: Middle Devonian Eifelian (393-388 Ma) and Givetian stages (388-383 Ma), Upper Devonian Frasnian (383-372 Ma) and Famennian stages (372-359 Ma).

Upper Devonian and Lower Carboniferous shales 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. They are absent in the centre of the Elbingerode complex where the limestone reef was emergent (Mucke 1973). The reef was covered by Lower Carboniferous greywacke (dot pattern) and by flysch of the Hüttenrode olistostrome (brown).

2.9 *Slide 9. Elbingerode volcanogenic hematite 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 measured plus 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. 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). Disseminated magnetite (9-16 vol%) is probably related to contact metamorphism in the aureole of the Brocken granite. Pyrite (<1%) occurs in cross cutting veins 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): Givetian thick-bedded basaltic 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. Königshütte, northwest end of the village, the outcrop is 25 m high.

(B): TOP: Fine-grained hematite ore containing 5-7% calcite, 1% black bitumen, and 1% microfossils. Pillar at the bottom of the Gräfenhagensberg glory hole at the Herrmann shaft. The matchstick is 3 cm long. BOTTOM: Basaltic spilite lapilli tuff from 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. Büchenberg iron ore mine, level 1 (-55 m), stope close to the Herrmann shaft.

2.10 *Slide 10. 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) and titanium (200-600 ppm), the latter probably in rutile inclusions. Blebs of chalcopyrite and sphalerite are enclosed locally (Lange 1957; Mucke 1973).

The sulfur isotope values (per mil $\delta^{34}S$, ± 2σ) 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 in underground samples (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 from 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): Limonite-stained outcrops of quartz-sericite-pyrite altered keratophyre are 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 predates reef formation. Elbingerode, Kaltes Tal railway cut.

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

(C) Pyrite in silicified keratophyre: Light yellow-gray, fine-grained (0.1-0.5 mm), massive, crackle-brecciated quartz-pyrite rock: About 25-30 vol.% pyrite, very fine dark gray pyrite forms 2-5 mm aggregates and occurs disseminated in the groundmass. Brass-yellow pyrite fills a network of interconnected fractures. The groundmass consists of light grey chalcedonic quartz (hard > steel, conchoidal fracture) containing white pseudomorphs (0.5 vol%) after rectangular feldspar (2 mm). Spots of yellow tint may indicate sericite, and dark silica micro-fragments are cemented by light grey silica. No reaction with 3% HCl, non-magnetic, no Cu-Zn sulfides. Einheit mine, level 7 (257 m above mean sea level), stope 32, the matchstick is 3 cm long.

(D): 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. Some chert is recrystallized to white quartz. Both chert and quartz are cut by veinlets filled with coarser (0.5 mm) pyrite. Einheit mine level 13 (+102 m MSL, 380 m below surface), sample donated by Jens Kruse. The matchstick is 4 cm long.

2.11 *Slide 11. Goslar: Imperial town in 968 AD*

The Rammelsberg mine is located at the southern margin of the town of Goslar, where massive Cu-Zn-Pb sulfide ore of the Altes Lager outcropped on the steep slope of a valley in the Harz mountains. The lead isotope composition of Bronze Age items suggests that mining began as early as 1200 BC. In the southern Harz foreland near Osterode, archaeological excavations confirmed that Rammelsberg copper ore was smelted during Roman time in the 3rd century AD (Klappauf and Malek 2017). Goslar became a fortified 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 elevated gold and bismuth contents. Goslar was not destroyed during World War II. Medieval buildings remain prominent in the town centre.

The Rammelsberg mine closed in 1988 after more than 1000 years of continuous operation (production data from Walther 1986; Museum Rammelsberg, personal communication 2008). Mining activity was low during the period 1181-1209, when duke Heinrich the Lion destroyed the smelters at Goslar, and again from 1360 to 1460, when the bubonic plague killed part 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 during the 19th and 20th centuries as the industrial revolution progressed.

2.12 *Slide 12. Rammelsberg mine: World heritage*

The historic town center of Goslar and the surface buildings and underground workings of the Rammelsberg mine museum became a UNESCO world cultural heritage site in 1992 (www.rammelsberg.de). In 2010, the water system composed of 149 artificial lakes and 500 km of interconnected channels, constructed to power Ag-Pb-Zn mines in the Upper Harz (see Mueller 2020), was added to the UNESCO heritage area. This system (Upper Harz Water Regale) operated under royal protection from the 16th to the 19th century (www.oberharz.de).

(A): Looking east at the Rammelsberg mountain, at the flotation plant for the massive 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 for the stopes underground. Roeder, mine director from 1763 to 1810, introduced backfill to avoid the collapse of open stopes and permit the recovery of ore pillars. The honeycomb workings in the Altes Lager were replaced by systematic drives and crosscuts 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 across the Schiefermühle backfill quarry in Middle Devonian black slate of the Wissenbach facies forming the structural footwall of the Rammelsberg orebodies. The mine dumps in the foreground mark the approximate outcrop of the Altes Lager (AL) massive sulfide. The forest-covered mountain in the background is underlain by folded Devonian rocks of the Harz range, uplifted at the Harz North Rim Fault marked by the escarpment. The town of Goslar on the far right is located on Mesozoic platform sedimentary rocks.

2.13 *Slide 13. 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 of 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 the blessing in the form of hydropower. Channelled 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 designed a highly efficient underground water-wheel system, which remained in operation until 1909 (Dettmer 2005).

2.14 *Slide 14. 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 (RB), the Richtschacht internal shaft (RS; red dots), and the exploration drives and cross cuts on level 7 (red lines), level 9 (dark blue lines), and level 12 (green lines) are shown. The indigo blue wedge represents the Herzberg water reservoir. The mountain summits are traced in black.

The fossil-rich Calceola shale (light blue), about 60-70 m thick, separates Lower Devonian sandstone (yellow) from the Middle Devonian (Eifelian) black shale of the Wissenbach facies (white). 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. The folded lithologic units and the thrust are offset at WNW-trending strike-slip faults, part of the Permo-Carboniferous system including the Western and Eastern Mine Faults (WMF, EMF), and the Harz North Rim Fault (HNRF). The HNRF juxtaposes Mesozoic platform sediments (green) and the Variscan basement. Reactivation during Alpine foreland compression caused periodic uplift of the Harz block from the Late Cretaceous to the Pliocene.

2.15 *Slide 15. Rammelsberg: Structural cross section, tuff marker beds*

Northwest-southeast cross section through the Rammelsberg and Richtschacht shafts (modified from Abt 1958), both connected by two adits (HBS = Hängebankstollen, TFS = Tagesförderstrecke), the Tiefer Julius Fortunatus Stollen (TJFS) drainage tunnel, and by deeper levels. The section shows the overturned succession of Lower Devonian sandstone (yellow) and Middle Devonian Calceola shale (light blue) in the structural hanging wall of the Altes Lager (AL) massive sulfide lens deformed during reverse faulting. The Wissenbach black shale, sub-divided into a lower sand-banded (grey) and upper calcareous facies (white) contains the "Kniest" quartz-chlorite-ankerite alteration zone (green) in the stratigraphic footwall and infolded barite beds (at surface) in the stratigraphic hanging wall of the Altes Lager. The overturned "mine syncline" (white) and associated thrust faults are offset at the Permo-Carboniferous Western Mine Fault (WMF).

A thin bed of basaltic tuff (1.0-2.4 wt. % TiO_2) marks the basal contact of the Calceola shale, which also contains nine beds of felsic tuff (0.14-0.25 % TiO_2) 1-20 cm thick. The Wissembach black shale contains at least another 14 felsic tuff beds (0.14-0.44 % TiO_2) 1-100 cm thick (Abt 1958). Correlated tuff (red) and associated sandstone marker beds (yellow) outline tight to isoclinal anticlines and synclines in the structural footwall of the overturned "mine syncline" (white). The felsic tuffs are characterized by high potassium (4.6-7.9 % K_2O) and low to moderate sodium contents (0.1-2.2 % Na_2O; Abt 1958). They consist mainly of quartz and illite, minor diagenetic carbonate, pyrite, muscovite and chlorite, and remnant igneous quartz, biotite, apatite and zircon (Kraume et al. 1955).

The Lower Devonian (Emsian) succession, 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 (Eifelian) units all 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 upper 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 an Eifelian sedimentary basin. The U-Pb age brackets of the International Commission on Stratigraphy (2018) are as follows: Emsian stage (408-393 Ma), Eifelian stage (393-388 Ma).

2.16 *Slide 16. Altes Lager orebody: Structural setting*

(A): Looking south in 2018 across the archaeological excavation site in the backfilled open cuts on the Altes Lager massive sulfide lens at the southwest rim of the Schiefermühle quarry. The hill of in-situ Wissenbach black slate in front of the Rammelsberg shaft headframe (RB) is in the structural footwall of the orebody. The depression marked by rocks in the left foreground is a medieval shaft not yet excavated. A tunnel with oak supports dating from the early 14th to the late 15th century has been re-filled for protection. Lakebed sediments in the open cuts contained hand-sorted massive pyrite, ropes, wool clothing, felt caps and carved wood preserved by the acid water. The oldest item found is a leather shoe sole dated at 1020 AD (Klappauf and Malek 2017).

(B) Looking from the southwest rim of the Schiefermühle quarry northeast at the Wissenbach black slate in the structural footwall of the backfilled Altes Lager (AL) orebody, the benches are about 6 m high. The waste rock dumps (white arrow) belong to medieval shafts. A syncline (dashed white line) marked by barite beds intercalated with black shale, interpreted as the core of the sulfide-sulfate bearing "mine syncline" (Gunzert (1979), forms the stratigraphic hanging wall of the overturned Altes Lager. The contact is a narrow reverse (?) fault zone composed of friable black schist.

(C): Outcrop of Wissenbach black shale 70 m upslope from the Rammelsberg shaft in the structural hanging wall but stratigraphic footwall of the overturned Altes Lager. The slaty cleavage dips about 45° southeast. The lens cap (white arrow) is 5 cm across.

2.17 *Slide 17. Rammelsberg: Feeder zone Cu-Zn-Pb sulfides*

The simplified NW-SE section through the Rammelsberg (RB) and Richtschacht (RS) shafts, modified from Stedingk and Wrede (in Hinze et al. 1998), shows the Altes (AL) and Neues Lager (NL) massive sulfide orebodies (red) within the overturned "mine syncline" defined by calcareous upper Wissenbach (white) in sand-banded lower Wissenbach black shale (grey). The Calceola shale is not shown. The position of the Hessenkopf thrust (HKT) is approximate.

Subeconomic base-metal mineralization (orange) occurs in the Lower Devonian sandstones (yellow) forming the structural hanging wall but stratigraphic footwall of the Rammelsberg deposit. Sulfide mantos (5-25 cm thick) peneconcordant to bedding, and zones of disseminated sulfides (up to 6 m thick) are exposed in the Kommunion quarry, in the Hängebankstollen (HBS) 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 fractured.

(A): Replacement manto, composed of streaks of pyrite, chalcopyrite and 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).

(B): 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).

2.18 *Slide 18. Rammelsberg: Sulfide 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 concentrically zoned ferroan dolomite, which encloses disseminated pyrite aggregates and thin sulfide beds at the top. 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 in the normal limb of the syncline below the overturned Neues Lager massive sulfide 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 younging 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 from the normal limb of the syncline below the overturned Neues Lager massive sulfide 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 texture. 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.

2.19 *Slide 19. 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 (white) defining the isoclinal Rammelsberg "mine 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 stratigraphic 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 south-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 projection 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 thickening of the ore in the closure of the 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 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.

2.20 *Slide 20. 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 iron-rich chlorite, sericite, 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 siliceous Kniest marks the inner footwall alteration zone, disseminated Fe-Mn chlorite (47 wt.% FeO, <0.1% MgO, 1.3% MnO) marks the outer zone 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 17). 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 sulfide ore (black). Note the position of the hanging-wall spur of the Altes Lager (AL) on the upper adit levels (TFS = Tagesföderstrecke, TJFS = Tiefer Julius Fortunatus Stollen). The Kniest was brecciated and contained sulfide-dolomite ± calcite veins along its contact with the Altes Lager. These veins constituted a low-grade stockwork (heavy dot pattern) 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 bounding strike-slip faults (Western and Eastern Mine Faults) are traced in red.

(**A**) Sulfide-veined Kniest from the Tagesförderstrecke level, 1550 m grid 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.

(B) Looking NNW at a vertical, NW-striking barite ± sufide extension vein in siliceous Kniest stained with blue-green copper sulfate, Tagesförderstrecke level, Bergeschacht adit at 1658 m grid east, the hammer is 50 cm tall.

2.21 *Slide 21. Structure of the 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 pattern), 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 adit, TJFS = Tiefer Julius Fortunatus Stollen drainage tunnel.

The Kniest contains two sets of veins (Kraume et al. 1955; p 233): (1) barren veins 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 were 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.

2.22 *Slide 22. Structure of the 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) pinches 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 syncline (Abt 1958), and shale-banded sulfide ore constitutes most of the upright limb. Abbreviations: TFS = Tagesföder-strecke adit, TJFS = Tiefer Julius Fortunatus Stollen drainage tunnel.

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 folds (modified from Kraume et al. 1955), which indicate reverse movement.

2.23 *Slide 23. Deformation during reverse faulting*

The sulfide ore and Kniest in the overturned limb of the Rammelsberg syncline were deformed during reverse faulting.

(A): The generalized NW-SE cross section (modified from Gunzert 1979) summarizes the structural elements of the Rammelsberg deposit. Lower Devonian sandstone (yellow) and Calceola shale (blue) form the structural hanging wall of the overturned syncline composed of Middle Devonian sand-banded (grey) and calcareous (white) black shale of the Wissenbach facies. The Altes Lager (AL) and Neues Lager (NL) massive sulfide lenses are mainly confined to the overturned limb, while shale-banded sulfide ore (red) and the mineralized dolomite-chlorite "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 (green) was deformed into an anticlinal structure (Abt 1958), and rotated into a position sub-parallel to the ore syncline. The competent Kniest mass was subsequently thrust over the Neues Lager and 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 strained below the plane of a reverse fault. The lead-zinc-barite ore is finely banded. The banding is secondary and follows the sulfide-shale tectonic contact, Rammelsberg shaft level 7.

(C): SW-NE longitudinal projection of the Rammelsberg deposit and the Rammelsberg (RB) and Richtschacht (RS) shafts 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 ore (red), both located in the overturned fold limb above the NE-plunging synclinal axis (dark violet line) defined by the ore. The pinch-out contacts of the Altes (AL) and Neues Lager (NL) massive sulfide lenses beneath the Kniest (green) are interpreted as tectonic (thick red line). 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 sulfide 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.

2.24 *Slide 24. 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): Blasto-mylonitic texture in complex Cu-Zn-Pb ore (Melierterz), Neues Lager, Rammelsberg shaft level 10. Streaks of yellow chalcopyrite and disrupted pinch-and-swell bands of dark grey dolomite define the tectonic fabric in recrystallized, finely laminated sphalerite-galena ore. The gangue contains wisps of black bitumen and fractured, weakly rotated pyrite nodules. 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 matrix composed 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 on the right, which encloses 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 grid east. Black shale beds alternate with pyrite-sphalerite-galena and dolomite beds. The Swiss knife is 8.5 cm long.

2.25 *Slide 25. Rammelsberg: Sulfide textures*

Microscopic textures show that galena and chalcopyrite were 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, polished mount RAM-1c (19/70). Aligned sericite and chlorite plates (black) in brown-grey sphalerite (Sp) wrap the central 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 (6-10 wt.% Ag), native bismuth, and bismuthinite are concentrated in some chalcopyrite bands, so that parts of the Melierterz contain 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, mount 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, mount RAM-2c (2.5/68). The band of medium-grey sphalerite on the left encloses 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 mostly 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, mount RAM-3b (6/60). Aggregate composed of sphalerite (Sp), pyrite (Py), galena (Gal, scratched), and tetrahedrite (Tth, isotropic). The gangue is barite (black). Tetrahedrite is the main silver mineral in the deposit. The silver content varies from a minimum of 0.5 wt.% and median values of 10-13% up to a maximum of 22% (Sperling 1986).

2.26 *Slide 26. 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 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, mount 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 dynamothermal 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, mount 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 large chalcopyrite aggregate (dark yellow, locally tarnished pink).

(C): Microfossils in shale-banded sulfide ore (Banderz), Neues Lager, level 8-10, mount RAM-4b (19/61). A spore capsule is replaced by pyrite (Py), filled with dolomite, and rimmed by blue-grey galena (Gal) and medium grey sphalerite (Sp). 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). 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; Ramdohr 1953).

2.27 *Slide 27. 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 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 limited assay records from 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 projection 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, 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 did not extend as far to the northeast (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 were intercalated with the sulfide ore (area outlined in blue). The eastern edge of the lens (heavy black and black-blue lines) did not extend as far to the northeast 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 at the hanging wall contact contained up to 194 g/t Hg (Kraume et al. 1955; p 256).

(A): Massive pyrite (Schwefelerz), fine-grained (0.5-1 mm) granular texture, 70-80 vol.% pale yellow pyrite, non-magnetic, intergrown with 20% light grey chalcedonic quartz (hard), about 0.1% interstitial dark-yellow chalcopyrite and 0.5% dark brown sphalerite. Pores after leached carbonate occur in spots of white iron sulfate coating. Schiefermühle quarry, October 2018, hand-sorted waste-rock forming part of the back-fill in a medieval open cut (14th century AD) in the Altes Lager orebody. The Australian 2 Dollar coin is 20 mm across.

(B): On the left “brown ore”, fine-grained sphalerite containing minor galena 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 samples are representative of the high-grade ore hand-sorted prior to flotation in 1936. The red pen is 14 cm long.

2.28 *Slide 28. 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 projection shows the distribution of ore types looking northwest. From the stratigraphic footwall to the hanging wall:

Pyritic ore (Kiesiges Erz): Pyrite-carbonate ore (red) with layers of chalcopyrite (18% Cu) and sphalerite (30-40% Zn) formed several lenses about 2 m thick, which pinched laterally to less than 0.2 m but remained connected. The carbonate and related manganese content (1-2 wt.%) was lower than in the Altes Lager. 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 above the 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 margin of the lens, where beds of massive barite were intercalated (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 normal limb of the syncline is not shown on the longitudinal projection. 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 and blue-grey galena alternate with grey barite bands. Rammelsberg shaft level 10 at 1411 m grid 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 grey carbonate-barite nodules or 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.

2.29 *Slide 29. Ore marker horizon, tuffs 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 (brown) in these exposures is about 10 m thick, and comprises black shale marked by numerous thin beds of ferroan dolomite. Fe-chlorite and chalcedony are major components, and arsenical pyrite, sphalerite, and galena (>2300 ppm Zn+Pb) minor or accessory ones (Sperling and Walcher 1990).

Tuffs: Two prominent marker beds of felsic tuff (red), up to 100 cm thick, are associated with the ore horizon and support stratigraphic correlation. The tuffs consist essentially of quartz, illite and lesser chlorite. They contain minor igneous quartz and biotite, and accessory zircon, tourmaline and apatite (Kraume et al. 1955). High potassium (5.3-8.7 wt.% K_2O) and low titanium contents (0.13-0.44 % TiO_2; Abt 1958) indicate a felsic composition prior to alteration by seawater. Most probably represent alkali rhyolite air-fall tuffs.

G2 barite, 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 separated by black shale. The barite beds occur in the core of the "mine syncline" and form part of the northwestern upright or normal limb. Stratigraphically, they are 30 m above the ore horizon and thus younger than the massive sulfide orebodies. The Altes Lager, part of the southeastern overturned limb, is in faulted contact with the barite-shale succession (Gunzert 1979).

G1 barite, Level 3: The barite ore (G1, Grauerz) exposed in the Rammelsberg shaft level 3 cross-cut is also stratigraphically above the ore horizon, and is thus interpreted to form part of the upright limb of the "mine syncline". The overturned limb is completely sheared out at the thrust marking the footwall of the Kniest silica mass. 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, illite and chlorite are accessory (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 was mined. The photograph shows strained sulfide-free barite from the Grauerz orebody on level 3 of the Rammelsberg shaft, 1450 m grid east.

G3 barite, Level 1: The third cross section on the Rammelsberg shaft level 1, south cross cut at 1510 m grid east, shows a barite bed (G3) in the stratigraphic hanging wall of the Neues Lager massive sulfide, here located in the overturned limb of the "mine syncline". This exposure supports the interpretation that the sulfide-poor barite beds, which probably represent separate bodies (G1 to G3), are younger than the main sulfide ore (Gunzert 1979).

2.30 *Slide 30. G2 barite syncline in the Schiefermühle quarry*

(A): Stratigraphic section (modified from Hannak 1981): barite beds intercalated with black shale form a succession about 12 m thick. Two shale intervals (2.6 and 4.65 m; marked in red) are shown as breaks. Barite beds (blue) are up to 1 m thick. Some are finely crystalline, whereas others are composed of packed spheroids (dot pattern) 1-2 mm in diameter with radial internal texture. The beds consist of 80-95 wt.% $BaSO_4$, 0.25-0.60% $SrSO_4$, and minor calcite, sphalerite, galena and pyrite. The sulfate $\delta^{34}S$ values are mostly +27.8 to +31.4‰ but increase to +36.7‰ in the uppermost part of the section. The base-metal contents of barite-shale beds (45-80 wt.% $BaSO_4$) vary from 100-600 ppm Pb, 400-600 ppm Zn, and 200-600 ppm Cu (Sperling and Walcher 1990).

(B): Syncline in barite beds, Schiefermühle southeast wall, 2nd bench below the surface, the Estwing hammer is 32 cm long.

(C): Finely crystalline grey barite with shale partings from the outcrop shown in (B), the Euro 5 cent coin is 21 mm across.

(D): Barite spheroids in black shale: Each spheroid is composed of radially oriented crystals grown on a central nucleus. Tiny albite crystals rim the spheroids. Photomicrograph in crossed polarized light of a barite bed in shale-banded sulfide ore from the Altes Lager West, Level 9, drill hole 34/51 at 36.5 m depth, +1100 m grid east (modified from Kraume et al. 1955).

Spheroid formation: The barite spheroids have been interpreted as diagenetic nodules, in analogy to the cm-sized, radially textured or concentrically zoned pyrite nodules common in black shale at the stratigraphic footwall of the sulfide ore. Rims of albite and tiny inclusions of shale and albite are considered evidence for growth below the seawater-sediment interface (Ramdohr in Kraume et al. 1955). The early diagenetic segregation of iron-silica gel into quartz rosettes and stilpnomelane in banded iron formation (Ewers and Morris 1981) may represent a similar process. However, diagenetic growth alone cannot explain the concentration of closely packed spheroids in individual barite beds and their absence in others, which are finely crystalline.

Alternatively, barite crystals and/or gel nucleated on particles suspended in dense brine forming spheroids, which settled when they reached a certain weight and size (1-2 mm). Similar depositional features have been described from the Meggen SEDEX deposit, where pyrite spheroids averaging 35 microns in diameter form packed layers in the sulfide orebody, and mm-sized barite spheroids form layers in the sulfate margins (Ehrenberg et al. 1954; Mueller 2019). Thus, the G2 barite spheroids may be interpreted as evidence for brine-pool sedimentation in the Rammelsberg deposit. This does not preclude radial crystal growth in the soft sediment during early diagenesis.

2.31 *Slide 31. Rammelsberg: Sulfur and radiogenic isotopes*

Sulfur isotope studies of 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 according to stratigraphic height. Those from barite ore represent the younger G1 body 30 m above the sulfide orebodies (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 on 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‰), which is 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 estimated is much narrower than that of other SEDEX and VMS deposits (Eldridge et al. 1983), where unreasonably high values (>500°C) and an 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). 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 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.

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).

Lead and osmium isotopes: While the sulfur isotope data provide constraints on the source of sulfur, lead and osmium isotopes provide some constraints on the source of the metals. The average lead isotope composition of galena-rich massive sulfide (n=8) from the Neues Lager is: 206/204 Pb = 18.246, 207/204 Pb = 15.619, 208/204 Pb = 38.188 (Wedepohl et al. 1978; Lévêque and Haack 1993; Tischendorf et al. 1993). The tightly clustered analyses plot between the Cumming & Richards Model 3 (1975) and the Doe & Zartman (1979) Orogene evolution curves in both the thorogenic and uranogenic Pb-Pb diagrams, well apart from the Upper Crust curve of Doe and Zartman (1979). The Cumming & Richards Model 3 uranogenic Pb-Pb age is 340 Ma, distinctly younger than the Eifelian stratigraphic age (393-388 Ma; International Commission on Stratigraphy 2018) of the host rock. A crustal lead component, leached from detritus in the Devonian sandstones and from basement paragneiss (?) below the deposit, is consistent with these data but an igneous component cannot be ruled out.

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 osmium (10-30 mg) recovered from 0.6 tonnes of Neues Lager sulfide consists of 83% radiogenic ^{187}Os (Meier 1974), derived from the Beta-decay of ^{187}Re, compared to 1.6% average natural abundance. The Rammelsberg sulfides thus qualify as low-level highly radiogenic (LLHR), characteristic of hydrothermal systems with a large crustal source component (Stein et al. 2000).

2.32 *Slide 32. 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 metal 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 island arc. Most are underlain by dacite/rhyolite lavas and overlain by felsic tuff, by mudstone or younger submarine flows including basalt. The schematic section through a Kuroko VMS is modified from Eldridge et al. (1983).

The solid 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: sphalerite + barite > pyrite + galena > tetrahedrite), 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: chalcopyrite + pyrite > quartz) 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: pyrite + quartz >> chalcopyrite) 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 hydrothermally 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 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 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 rift 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. Meggen, McArthur River), where fluid temperatures are estimated at 250°C to 150°C (Large et al. 2005).

2.33 *Slide 33. Total Zn-Pb content of the ore horizon*

Spillage from the Rammelsberg brine-pool basin caused a km-scale, stratigraphically controlled base-metal anomaly confirming that the deposit is "sedimentary-exhalative" as proposed by Ramdohr (1928, 1953). The equivalent of the Rammelsberg sulfide 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 the 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 accessory (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 long 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 in the ore horizon are 620 ppm Pb, 300 ppm Zn, and 42 ppm Cu, compared to background values of 48 ppm Pb, 105 ppm Zn, and 37 ppm Cu in the Wissenbach black shale. The anomaly thus extends at least 3 km from the ore deposit. In the outer zone, lead is 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 was 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 estimated at 9-10 million tons, less than half the total produced (>22 million tons Zn+Pb).

2.34 *Slide 34. Harz: Middle Devonian Goslar basin*

The Middle Devonian topography and sedimentary environment of the western Harz are introduced in three steps: (A) 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 block of Devonian rocks, bounded by faults sub-parallel to the HNRF, occurs within Lower Carboniferous greywacke (grey). Note the Iberg limestone reef (IB, light blue) west of the town of Clausthal-Zellerfeld (CLZ). The post-folding Oker granite 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). 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 (393-388 Ma) and Givetian stages (388-383 Ma; ICS 2018). 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.

2.35 *Slide 35. Europe: Devonian back-arc rift 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 (393-383 Ma; ICS 2018), 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 grey-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 grey) and calc-alkaline magmatism (plutons = black crosses).

2.36 *Slide 36. 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: 388-383 Ma; ICS 2018) is separated from the southern mega-continent Gondwana 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 American 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 (393-383 Ma; ICS 2018). Avalonia has been accreted to the southern margin of Laurussia, and is located behind an arc-trench system (black saw-tooth line) consuming the crust of the Rheic ocean. The Rhenish basin containing the SEDEX deposits (now the Rhenohercynikum in Slide 6) 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. Remnants of the Late Silurian-Early Devonian magmatic arc are preserved as greenschists and orthogneiss (440-400 Ma zircon U-Pb) in the Northern Phyllite Zone and in the Mid-German Crystalline Rise (see Slide 6), both marking the southern suture of Avalonia (Franke 2000). The other micro-continents, Iberia (I), Amorica (A), Saxothuringia (SX), Barrandia (B, also named Moldanubikum), 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): This 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 (bright green area) led to the exposure of the 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 (Hannington et al. 2005).

2.37 *Slide 37. Rammelsberg: Key genetic features*

Plate-tectonic setting: Continental-margin, sediment-filled, rifted back-arc basin, a setting perhaps comparable to the present-day Pacific margin of the Asian continent. A seawater-recharged hydrothermal system extending deep into continental crust overlain by thick terrigenous sediments may be essential to generate high-grade Zn-Pb-Ag-Ba massive sulfides such as the Kuroko and Rammelsberg “black ores”.

Submarine bimodal volcanism: Submarine ridges of basalt and minor trachyte and alkali rhyolite characterize the Rhenish rift basin, which was mainly filled with clastic sediments derived from the continental shelf. The widespread spilitization of volcanic rocks indicates a fertile, high heat-flow environment marked by seawater circulation.

Submarine ore deposits: In the Rhenish basin, the volcanogenic deposits on basaltic ridges consist of hematite, and of barren pyrite (+ sulfate?) replacement associated with trachyte and rhyolite. In contrast, the Rammelsberg SEDEX deposit is associated with felsic air-fall tuffs distal to volcanic ridges. The sulfide-barite ore was deposited at the margin of a deep-water black shale basin structured by rift faults. The feeder fault is traced by reduced quartz-chlorite-ankerite replacement. Spillage from the discharge site generated a km-scale, stratiform Zn-Pb anomaly.

Cu-Zn-Pb massive sulfides: Cu-Au-rich SEDEX deposits like the Rammelsberg require the vent-proximal deposition of sulfide muds in a brine pool, trapped in a basin sheltered from the influx of clastic material. The Rammelsberg fluid was reduced, carried H_2S, and discharged onto the sea floor at 250-350°C. Ankerite and Fe-dolomite in the lower part of the massive sulfide give way to barite in the upper part precipitated by fluid mixing with seawater.

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