

A multistage origin for Kupferschiefer mineralization

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Abstract

New Re-Os age determinations on mineralized material from the Polish Kupferschiefer elucidate the timing of mineralization and thus the likely mechanisms of ore deposition. Three mineralization parageneses were analysed: (a) chalcocite as pore space filling in sandstone, (b) disseminated Cu-Mo mineralization in shale, and (c) massive, bedded copper sulphides. The resulting ages fall into two ranges: 245.2 (± 1.6) – 264.7 (± 1.8) Ma and 162.3 (± 0.8) – 184.3 (2.2) Ma. These results substantiate previous age determinations, although no Upper Triassic ages were found in this study. Some of the younger ages for the mineralization could represent alteration and recrystallization of existing sulphides. The results confirm that mineralization took place in several stages, from soon after Kupferschiefer sediment deposition in the Upper Permian and for at least 100my after, until at least the Cretaceous. The genesis of the mineralization can be explained by the episodic release of hydrothermal fluids from the subsiding adjacent Southern Permian sedimentary basin, although the relative importance of each successive mineralizing ‘event’ for introducing additional metals is as yet unknown.

Keywords: Kupferschiefer, Red Bed copper, Re-Os dating, Poland, Southern Permian Basin

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1. Introduction

The world-class Kupferschiefer mineralization of northern Europe has been the focus of many detailed geological, mineralogical, and geochemical studies, yet some aspects of the mineralization remain poorly understood. This is particularly true of the timing of the mineralization, which is a key component of any theory seeking to explain the deposit genesis. During the last two decades, there have been several attempts, using a variety of methods, to determine the age of Kupferschiefer mineralization. However, the results of these studies differ significantly and are somewhat contradictory (see Table 1). In this paper, we present the results of new Re-Os age determinations on mineralized material from the Polish Kupferschiefer, and combine these results with existing age information in order to elucidate the timing of mineralization, and thus the likely mechanisms of ore deposition.

2. Kupferschiefer mineralization

The Kupferschiefer mineralization continues to be an important global producer of copper and silver. Although the stratigraphic units which host this mineralization extend for large distances over much of northern Europe (>600,000 km² in areal extent ; 1500 km from western Russia in the east to Northern Ireland in the west), the historically economic portions are restricted to the southern margins of the Permian Basin, in southwest Poland and central Germany (Figure 1). The deposits in Germany have been subjected to a long history of mining (ca. 800 years), but these deposits are presently uneconomic and current production is restricted to southwest Poland (Lower Silesia-Dolny Slask). However, a recent probabilistic statistical analysis (Zientek et al., 2015) suggests that undiscovered resources of >100 Mt of Cu metal could be present in Germany and Poland. Active exploration has continued in regions of both former and current mining operations, and in completely new areas (e.g. the Spremberg region of eastern Germany).

In southwest Poland the horizons mined for copper extend laterally for ca. 600 km² and vary in thickness from 0.4 to several tens of metres. During the last 25

years, annual production of ore has amounted to about 30 Mt, from three principal mines: Rudna, Polkowice-Sieroszowice, and Lubin (USGS, 2015). Copper production has been steadily rising during this time period with resources currently estimated at about 1700 Mt of ore containing 3.3 Mt of copper and 102,000 t of Ag. Ore grades typically average ca. 2% Cu and 50 ppm Ag. There are, in addition, important byproducts, including Pb, Zn, Au, Ni, Pt-Pd, Re, and Se.

3. Geological overview

The geological and mineralogical characteristics of the Kupferschiefer have been extensively studied and thorough descriptions of the geology are to be found in Vaughan et al. (1989), Oszczepalski (1989,1999), Kucha (2003), Borg et al. (2012), and Zientek et al. (2015).

The Kupferschiefer mineralization in Poland is located in the southwestern margin of the Polish Basin which constitutes part of the larger Central European (Southern Permian) Basin. This basin formed after the Variscan orogeny by crustal thinning, extension, basin fill, and magmatism. Mining has taken place on either side of the Fore-Sudetic Block - the eastern North Sudetic trough to the south and the Fore-Sudetic monocline to the north (Figure 1), although production is now restricted to an area located 75 km NW of Wroclaw in the Fore-Sudetic monocline.

The Kupferschiefer (ss) is a ca. 0.5m- thick unit consisting of pyrite-, and carbonate-bearing, organic-rich shale. It occurs at the contact between uppermost Lower Permian (Rotliegend and Weissliegend) strata composed of terrestrial, fluvial-lacustrine red bed sediments and bimodal volcanic rocks, and unconformably overlying Upper Permian (Zechstein) transgressive continental and shallow-marine sediments (evaporites, carbonates, shales, and siliciclastics). The Cu-Ag mineralization transgresses these lithological boundaries and occurs in units both above and below the Kupferschiefer shale (Figure 2). Notably, current production in Poland includes only 12% derived from the Kupferschiefer (ss), with the majority mined from the Rotliegend, and lesser amounts from the Zechstein (Zientek et al.,

2015; KGHM, 2016). An oxidized, red-brown, ferruginous, sulphide-deficient zone known as the Rote Fäule is an important component of the mineralization, as a distinct vertical and lateral metal and mineral zonation exists adjacent to this secondary, redox front (Figure 2). The highest ore grades tend to occur adjacent to the Rote Fäule, with Cu (and Ag) being proximal and Pb ± Zn distal; locally, these zones overlap (Piestrzyński et al., 2015). The mineralogical zoning continues laterally into a barren, pyrite-rich facies, containing early framboidal and diagenetic pyrite. A significant precious metal (Au-PGE)-rich zone occurs locally in a transition zone adjacent to the Rote Fäule (e.g., Kucha, 1990; Kucha and Przybyłowicz, 1999; Piestrzyński and Sawłowicz, 1999).

The main ore minerals are chalcocite, covellite, digenite, chalcopyrite, and bornite, together with minor galena and sphalerite. More than 70 other metallic minerals have been identified, including Co-, Ni-, U- and noble metal-rich species. The ore minerals are typically fine grained and form disseminations, cement to clastic grains, veinlets, and replacements, both in stratiform and stratabound zones (e.g., Figure 3). Paragenetic schemes envisage the progressive development and expansion of the mineral and metal zonation outwards from the Rote Fäule on a regional scale. On a more local scale, the paragenesis in the copper zone is quite variable and Oszczepalski (1999) has asserted that “ a simple mineral succession is hard to construct”. However, it appears that the general succession is that of chalcopyrite followed by bornite which in turn is followed by chalcocite (e.g. Oszczepalski, 1999; Kucha and Pawlikowski, 1986).

Some distinctly later, vein-type mineralization is also present. These veins are not generally of economic importance except in parts of Germany where they contain relatively high contents of Co, As, and Ni (e.g. Wagner and Lorenz, 2002).

Unpublished studies by one of us (HK) have elucidated the distribution of the elements Mo and Re in the mineralization. The average contents of Re and Mo in the Polish Kupferschiefer ore are 0.6 and 39 ppm respectively, with the highest concentrations in bituminous shale (on average 10 ppm Re and 271 ppm Mo, but Mo concentrations can reach % levels). Castaingite (Cu,Fe)Mo₂S₅ accounts for about

75% of the Mo content of this mineralization and is the main host for biproduct Re and Mo. The Re content of castaingite has a broad range (<1 to 1,030 ppm Re) with an average Mo/Re ratio of 70:1. Molybdenite makes up about 10-15% of the total Mo budget and has a Mo/Re ratio of approximately 50:1. It is found in two distinct parageneses: primary and associated with the main Cu sulphide mineralization, and secondary, from the breakdown of castaingite (Figure 3c). There are in addition a large number of other Mo-bearing phases that have been identified, including complex chevrel phases (sulphides containing Mo plus various base metals, Fe or K).

Although many early studies advocated a syngenetic origin for the mineralization, current opinion supports a post-depositional (diagenetic or epigenetic) origin for the majority of the sulphide mineralization (e.g., Jowett, 1986; Jowett et al., 1987b; Kucha and Pawlikowski, 1986; Cathles et al., 1993; Wodzicki and Piestrzynski, 1994; Blundell et al., 2003; Brown, 2014). Cited evidence includes: (1) textures that show sulphides replacing quartz grains, calcite cement, and pyrite framboids; (2) metal zonation that is locally discordant to the stratigraphy; and (3) the presence of mineralized veinlets. Although slight variants to the models for the mineralization process have been proposed, most favour the expulsion of saline brines from adjacent, subsiding, sedimentary basins, leaching of metals from Rotliegend red beds and associated volcanic rocks, migration of fluids towards basement highs, and subsequent metal precipitation where these oxidized fluids came into contact with sulphide- and organic-rich sediments of the Kupferschiefer shale and/or with other, more reduced fluids (see also confirmation of this model by Sverjensky, 1987). Precipitation of metals was probably accomplished by bacterial, and at higher temperatures possibly thermochemical, sulphate reduction by organic material, which generated sulphides (initially framboidal pyrite, later replaced by Cu sulphides). Temperatures of mineralization up to 120-150°C have been suggested using illite stable isotope geothermometry, hydrocarbon thermal maturation parameters, vitrinite reflectance and fluid inclusion data (e.g. Bechtel and Hoernes, 1993).

4. Pre-existing geochronology

The depositional age of the Kupferschiefer stratigraphic unit at the Rotliegend – Zechstein boundary is generally accepted to be within the range 258 to 260.4 Ma (Menning et al., 2006; Slowakiewicz et al., 2009). This age range is based on stratigraphic, palaeomagnetic, micropalaeontological and C-isotopic correlations and compares favourably with the Re-Os isochron age of 257 ± 1.6 Ma derived by Brauns et al. (2003). However, these authors combined and plotted data from different lithologies (shale, sulphides, conglomerates) and so this isochron may represent a mixing of components and thus not signify a robust age. In addition, they analyzed several suites of samples, but only found that one suite (from Sangerhausen) had not been reset/disturbed. The use of Re-Os methods to date organic-rich sedimentary rocks requires careful sampling and analysis, in order to ensure that detrital material is not incorporated (Selby and Creaser, 2003). This sampling constraint could explain some of the variability of Re-Os ages obtained from previous studies of Kupferschiefer strata rich in organic matter; these ages scatter and have large uncertainties (e.g. Pasava et al., 2010), or are too old relative to the known biostratigraphic age of the formation (e.g. Pasava et al., 2007b).

The age for the Kupferschiefer stratigraphic unit reported by Brauns et al. (2003) also agrees, albeit to a lesser extent, with the less-precise Re-Os isochron age of 247 ± 20 Ma of Pasava et al. (2010) for unmineralized Kupferschiefer shale at Zdrada (northern Poland). Also broadly coeval are the (indirect/extrapolated) K-Ar ages of 249-267 Ma for authigenic ('neofomed') illite from unmineralized Kupferschiefer shale in northwest Poland reported by Bechtel et al. (1999). However, these ages also have relatively large uncertainties, possibly as high as ± 20 m.y. Notwithstanding these results, a more precise age for the Kupferschiefer deposition is needed, and indeed Slowakiewicz et al. (2009) have stressed that the age of the Polish Kupferschiefer should be considered approximate and uncertain until more precise dating is available

Because the Cu-Ag mineralization is now widely accepted as being post-depositional in nature, its time of formation must therefore post-date that of the Middle Permian sedimentary units. Some Early Cretaceous dykes and faults cut the ore, seemingly with little sulphide remobilisation, but it is unclear whether this upper age limit can be applied to all of the mineralized zones.

Previous age determinations of the Kupferschiefer mineralization have been based either on indirect methods (e.g. palaeomagnetism of the Rote Fäule, K-Ar dating of illite) or direct methods utilising sulphide material (e.g. Re-Os or U-Pb, palaeomagnetism of sulphide-rich ore). Most dating studies of mineralized material have been focused in two areas: southwest Poland and the Mansfeld/Sangerhausen region of Germany (Figure 1). A compilation of recent age estimations for the Kupferschiefer mineralization is presented in Table 1 and suggests three distinct age ranges, as discussed below.

4.1 Middle Permian Mineralization

One of the first determinations of the age of Kupferschiefer mineralization resulted from a palaeomagnetic study in mines in the North Sudetic trough of SW Poland (Jowett et al., 1987a). Jowett et al. (1987a) were not able to measure primary magnetization in sulphide material but they did find that the Rote Fäule hematite had a chemical remnant magnetisation which they thought had been acquired during the mineralization process. Using the accepted European polar wandering curves, their results favoured an age of hematite formation (and thus Cu sulphide mineralization also) at ca. 240 (220-250) Ma. Subsequently, Nawrocki (1997, 2000) reconstructed the apparent polar wander path for northern Europe and, on the basis of this revision, proposed that the mineralization age reported by Jowett et al. (1987a) was too young, and that a modified age of 245-255 Ma for the Rote Fäule is preferred. The newer polar wandering paths of Torsvig et al. (2001) suggest that a more precise mineralization age based on the Jowett et al. (1987a) data is 250-255 Ma.

Pasava et al. (2007a) undertook a Re-Os isotopic study of sulphide-rich Kupferschiefer calcareous black shale and limestone from the Lubin deposit in southwest Poland and obtained an isochron age of 240 ± 3.8 Ma.

4.2 Triassic mineralization

Bechtel et al. (1999) carried out a detailed study of illite from the Kupferschiefer and discovered that H and O isotopic compositions, crystal type, and crystallinity changed in relation to the extent of Cu-Ag mineralization. On this basis, these authors proposed the presence of different proportions of detrital and diagenetic (epigenetic) illite populations; the formation of the epigenetic illite appeared to be coeval with the sulphide mineralization. By combining K-Ar age data on bulk illite samples with the relative proportions of the different illite types, Bechtel et al. (1999) obtained age estimates for the various generations. By subtracting the detrital components, they derived an age for the illite of 190-216 Ma that equates to formation during the sulphide mineralization process. The difference between this age range and that of Jowett et al. (1987a) for the Rote Fäule hematite has generated some debate (e.g., Nawrocki, 2000). However, as a consequence, revised interpretations suggested either that mineralization was 'polycyclic' or that the Rote Fäule hematite formed relatively quickly, whereas illite formation took longer and extended over tens of millions of years (Bechtel et al., 2000). Subsequently, it has been discovered that there are several generations of Rote Fäule formation (see below).

Patzold et al. (2002) sampled a small section of core from the Kupferschiefer in the Mansfeld district of Germany and analysed conglomerate, marl, and two associated sulphide samples for Re and Os geochronology. They derived a Re-Os isochron that suggests an age for mineralization of $204.3 \text{ Ma} \pm 0.5$; this age is similar to the range of K-Ar illite ages. They further suggested that Re was remobilised from the Re-rich Kupferschiefer black shale and that the entire sequence was reset by hydrothermal fluids at this time. Mikulski and Stein (2012) also used Re-Os methods and reported an isochron age of 212 ± 7 Ma for sulphides from bornite/chalcopyrite veinlets in ore from the Lubin and Polkowice mines in Poland. It is worth pointing

out that among the published Re-Os studies theirs is the only one that restricted analysis to sulphide material rather than also including host lithologies.

4.3 Jurassic/Cretaceous mineralization

Through improvements in palaeomagnetic instrumentation, Symons et al. (2011) were able to study the palaeomagnetism of Kupferschiefer ore material (containing magnetite and pyrrhotite) at Sangerhausen. Their results indicated an age of 149 ± 3 Ma, i.e. Late Jurassic and thus much younger than previous estimates for the age of mineralization. They concluded that the older palaeomagnetic dates obtained by Jowett et al. (1987a) indicate that the Rote Fäule is either a primary feature or due to Late Permian diagenesis, and hence that the Kupferschiefer ore and the Rote Fäule did not form contemporaneously. Symons et al. (2011) further concluded that mineralization models invoking early diagenesis are unlikely to be valid, rather that sulphide formation occurred by more recent alteration and/or recrystallization events.

Other Jurassic ages for the mineralization are supported by the results of Kucha and Przybylowicz (1999) who obtained an age range of 175-180 Ma using U/Pb analyses of thucholite (Th- and U-bearing pyrobitumen) from Lubin. This thucholite is associated with noble metals and a discrete (third) hematite stage, but is paragenetically separate from the main copper minerals. More recently, Kucha (unpublished study) has identified various U- and Th- rich phases (huttonite, monazite and coffinite) associated with castaingite in quartz from the Lubin mine and used the U/Pb ratios (determined by microprobe) to derive a preliminary age of 130 Ma.

Michalik (1997) obtained K-Ar ages of 83-186 Ma for illite directly associated with mineralized sandstones in the mines of southwest Poland. Because this illite appears to be replaced by sulphides, it was concluded that the sulphide mineralization occurred later than formation of this illite. Maliszewska and Kuberska (2009) also obtained K-Ar ages of illites occurring as cements in Rotliegend sandstones from western Poland. Their ages range from 114 to 187 Ma and are important because,

although the sandstones are unmineralized, they demonstrate that crystallization (and thus hydrothermal fluid activity) continued into the Cretaceous.

The palaeomagnetic studies of Jowett et al. (1987a) and Symons et al. (2011) also introduced the possibility of components of a Tertiary mineralizing event. Improved palaeomagnetic procedures allowed Symons et al. (2011) cast doubt on the ages of Jowett et al. (1987a), but stated that their proposed 53 ± 3 Ma age was feasible.

In summary, it is therefore apparent that a wide range of ages has been reported for Kupferschiefer mineralization, albeit from locations far apart in Germany and Poland, and based on different methods and materials. Unfortunately, many of these studies are only available in abstract form and often do not give much detail, so it is difficult to evaluate the results fully. Furthermore, the use of phases associated with the mineralization (e.g. palaeomagnetism, illite) must be considered ambiguous unless a clear genetic relationship to the mineralization can be demonstrated. Clearly, direct dating of Cu-mineralized material is to be preferred, yet even here the published isotopic dating has indicated more than one mineralization age. There is, therefore, a need to generate more geochronological data to better evaluate these diverse age ranges. Our new Re-Os study, undertaken on sulphide minerals, is a response to that need.

5. Samples and Methods

Sulphide-rich samples used in the current study were collected from ore-bearing units in the Fore-Sudetic monocline of SW Poland (Rudna (51.502N;16.107E), Polkowice (51.486N;16.062E), Lubin, (51.446N;16.123E)) and include material that could be enriched in Mo (and thus Re) (Table 2). Sulphide samples were readily separated under a microscope, except for two samples (LZ, LZ5) in which the mineralized material is fine grained and admixed with host shale.

The samples used in this study come from 3 different associations:

1) Mineralized uppermost Weissliegend sandstone (Figure 3a) which is representative of the dominant Cu-ore material. In these samples, chalcocite has infilled pore spaces

and partially replaced matrix silicates. Sample P1/2 from Polkowice East contains quartz and chalcocite, whilst sample KP3 from Rudna contains chalcocite in a matrix of quartz, with minor illite, kaolinite and dolomite. The chalcocite in this latter sample is also associated with minor djurleite.

2) Concentrically banded, massive Cu ore from the Lubin mine, exhibiting colloform textures (sample KP4, Figure 3b). Bornite, pyrite and chalcopyrite-rich zones have been separated and analysed.

3) Bituminous and gypsiferous Kupferschiefer shale containing molybdenite, covellite, castaingite and other chevrel phases as described above (Figure 3c) and therefore representative of Mo (Re)-rich material (samples LZ and LZ5, both from the base of the shale unit in Lubin West).

Re-Os analysis was performed in the Laboratory for Sulfide and Shale Geochronology and Geochemistry in the Durham Geochemistry Centre at the University of Durham. The methodology essentially followed that of Selby et al. (2009). Approximately 20-40 mg of each sulphide separate and a known amount of tracer solution were digested together in a carius tube for 48 hrs at a temperature of 220°C in 3 ml of 11 N HCl and 15.5N HNO₃. The extracted sample-tracer mix was isolated and purified via solvent extraction (using CHCl₃), micro distillation, anion column, and single-bead chromatography. The purified Re and Os were loaded onto Ni (for Re) and Pt (for Os) filaments and measured by negative thermal ionisation mass spectrometry. Isotopic compositions were determined with a Thermo Electron Triton mass spectrometer via ion counting in a secondary electron multiplier, in peak-hopping mode for Os and static Faraday collection mode for Re.

In common with much of the Kupferschiefer mineralization, there is a distinct enrichment in Re in the sulphide samples (0.7 to 8.8 ppm). Initially a traditional analytical method was adopted that used a mixed ¹⁹⁰Os and ¹⁸⁵Re tracer spike solution. However, the samples did not appear to contain any non-radiogenically derived (common) Os (cf. Mikulski and Stein, 2012). This result meant that the ¹⁹⁰Os/¹⁸⁸Os values for the spiked samples were very close to that of the spike value, making it nearly impossible to resolve any common Os and thus yield a true isotopic

composition. All of the measured $^{187}\text{Os}/^{188}\text{Os}$ values were very high (>100 , some >400) and it is assumed that all of the ^{187}Os within these samples is radiogenic in origin.

To overcome this issue, the samples were spiked as if being molybdenite, using ^{185}Re and normal Os or a double-Os spike of $^{190}\text{Os} + ^{188}\text{Os}$. Both approaches allowed the determination of model ages, with the double spike method permitting the quantification of any common Os component. Some samples were re-analysed using this molybdenite procedure and the results again suggest that different ages are present, but again that common Os is very low (low parts per trillion, ppt).

The samples were further analysed using a triple spike (mixed $^{185}\text{Re} + ^{190}\text{Os} + ^{188}\text{Os}$) that allowed monitoring of common Os and confirmed a difference in ages within the sample suite.

The analytical blank for the analysis was 2.4 pg for Re and 0.5 pg for Os, with a $^{187}\text{Os}/^{188}\text{Os}$ value of 0.25 ± 0.15 .

Final uncertainties were calculated by full error propagation of uncertainties in the Re and Os measurements, blank values, isotopic compositions, spike calibrations, and reproducibility of the standard Re and Os values. Model Re-Os ages were calculated using the equation, $\ln(^{187}\text{Os}/^{187}\text{Re} + 1)/\lambda$, including the decay constant (λ) of $1.666\text{e}^{-11}\text{a}^{-1}$ (Smoliar et al., 1996).

6. Results

Results of the Re-Os sulphide analyses (abundances), together with calculated model ages based on decay of ^{187}Re to ^{187}Os (Smoliar et al., 1996), are presented in Table 2.

The sulphide samples are all enriched in Re at the parts per million level (~ 1.1 - 8.9 ppm) (demonstrating that it is not just the Mo-bearing phases that host this element). The bulk of the osmium abundance ($>99\%$) is radiogenic ^{187}Os derived from the radioactive decay of ^{187}Re .

The calculated ages clearly differ, even for samples collected from the same mine. The oldest apparent ages of ca. 262.7 (± 1.3) and 264.7 (± 1.8) Ma are obtained for chalcocite in sandstone from the Polkowice deposit. Even with the calculated uncertainties, these ages are slightly older than the accepted age of the Kupferschiefer unit at (c.260 Ma). To date, pre-Kupferschiefer mineralization has not been described in the Rotliegend sandstones so this date could certainly be incorrect. However, because of uncertainties regarding the previously published Re-Os dating studies, as noted above, the accepted depositional age for the Kupferschiefer needs confirmation and so this calculated age must await further verification.

The colloform, banded sulphides from Lubin produce Re-Os ages in the range of 242.0-252.5 Ma. These ages compare favourably with the (recalculated) palaeomagnetic (hematite) ages of Jowett et al. (1987a) (250-255Ma) and the Re-Os age of Pasava et al. (2007a) (240Ma), the latter for samples of mineralized shale and limestone.

Sulphide-rich shale samples from Lubin yield model ages within the range 162.3-184.3 Ma (with the triple spike determinations indicating the slightly older part of this range, 177.4-184.3 Ma). The chalcocite (plus minor djurleite) in sandstone from Rudna gives a rather similar age of 173.3 (± 1.1) Ma.

These ages are consistent with the U/Pb thucholite age of 175-180 Ma reported by Kucha and Przybylowicz (1999), as well as the illite ages mentioned above. Interestingly, no Triassic ages comparable to those found by Mikulski and Stein (2012), for material from the same mines as used in this study, have been obtained.

7. Discussion

Previous age determinations of the Kupferschiefer mineralization have tended to produce one limited age range and postulate one phase of mineralization for each sample suite and it is only recently that models for Kupferschiefer mineralization have incorporated the full spectrum of published ages (e.g., Zientek et al., 2015). The current study is realistically the first to generate a range of ages using one technique

and for material collected in close proximity. Overall, the total age range obtained on our samples is 162.3 (± 0.8) Ma to 264.7 (± 1.8) Ma (Table 2). Therefore these results extend the range of Re-Os ages for Kupferschiefer mineralization significantly, but also appear to confirm other published (direct and indirect) age data.

Our range in Re-Os ages is hardly surprising considering that numerous mineralogical and paragenetic studies (cited above) have demonstrated convincingly that mineralization did not occur in one stage. Several paragenetic stages are commonly described for the whole region, each related to distinct and separate phases of mineralization (e.g., Michalik and Sawlowicz, 2001); this paragenesis also includes several stages of hematite formation in the Rote Fäule (Jung and Knitzschke, 1976; Kucha, 2003). Many of the models for Kupferschiefer mineralization stress a progressive development of the mineralizing system, from synsedimentary processes to early and then late diagenesis, to later replacement (e.g., Vaughan et al., 1989; Sun and Puttmann, 1997). Additionally, dilatant, crosscutting sulphide bearing veins exist (e.g., Salski 1977; Jowett, 1987) but although definitely later, their significance in terms of the overall mineralization process is unclear. Thus, proposed models for the mineralization have included descriptive terms such as ‘polycyclic’ (Nawrocki, 2000), ‘episodic’, a ‘continuum’ (Vaughan et al., 1989), ‘multistage and long term’ (Michalik and Sawlowicz, 2001), and ‘extended over tens of millions of years’ (Bechtel et al., 2000).

The key finding of our study is that the range of Re-Os ages reported previously for Kupferschiefer mineralization appears to be correct. There must have been several phases of ‘mineralization’ (*sensu lato*) that extended over a much longer period of time than most previous workers have proposed (e.g., the 5-10 m.y. of Jowett, 1986, or the 20 m.y. of Vaughan et al., 1989). Any theory on ore genesis for the Kupferschiefer must take this extended age range into account, but also must accommodate the entire range of potential processes from diagenesis to epigenesis.

Our study supports the concept of an important mineralizing stage in the late Permian-early Triassic, relatively soon after Kupferschiefer deposition. This stage formed the chalcocite infilling of sandstone and the massive chalcopyrite-bornite ore.

In addition, the ages for separate minerals in these samples do not correlate with the simple Cu sulphide paragenetic scheme mentioned above.

The younger ages found in our and previous studies point to subsequent mineralization processes in the late Triassic and Jurassic; however, it is not immediately clear how important these younger mineralization 'events' are. The Upper Triassic (212 Ma) date obtained by Mikulski and Stein (2012) for sulphide veinlets, indicates the presence of a subsequent, crosscutting phase of mineralization that is possibly an overprint on the earlier phase of Permian mineralization (240-255 Ma).

In our samples, the even younger (Jurassic) ages could also represent, in part, the subsequent alteration and replacement of earlier mineralization via metal remobilisation (e.g., djurleite replacing chalcocite, breakdown of chevrel phases). However, these age data do not easily support the proposal that this Jurassic event was the major ore-forming process (as inferred from the palaeomagnetic study of Symons et al., 2011).

It would be valuable to know to what extent the younger Re-Os ages reflect post-depositional processes. Weathering has the potential to disturb the Re-Os system in organic-rich rocks (e.g., Jaffe et al., 2002). These samples (and those from the other studies described above) were collected from underground mines at depths of between 500-1000m but the likelihood of such secondary effects remains unclear. More important to consider is post-depositional mobilization of Re and Os from organic-rich rocks due to later hydrothermal activity (e.g., Kendall et al. 2009), but its significance for these samples is likewise difficult to evaluate.

The proposed successive periods of mineralization are consistent with continued and progressive burial of sediments, compaction of (especially) clay-rich lithologies, expulsion of increasingly saline pore waters, migration of these waters along permeable pathways, and associated episodic fluid release, from ca. 260 to 150 Ma. The petrographic and age dating studies of Maliszewska and Kuberska (2009) and Schoner et al. (2008) show that several diagenetic stages of mineral growth and pore space cementation occurred after sediment burial, and hence that multiple events

of fluid migration took place from early diagenesis in the Late Permian through the successive stages of basin development and sediment burial during the Mesozoic.

Basin modelling by Karnkowski (1999) and Pletsch et al. (2010) has demonstrated that deposition and subsidence of sediments continued at various rates at different locations in the Polish Basin, leading to accumulation of up to 10 km of sediment and temperatures at depth in excess of 120°C. The maximum rates of subsidence were achieved during late Rotliegend and Zechstein times (ca. 260-230 Ma), but subsequently continued at lower rates until the Late Cretaceous when basin inversion occurred. Subsidence rates were not constant and periods when subsidence and heat flow increased could have led to specific episodes of increased fluid release and mineralization. Zientek et al. (2015) illustrated the association between basin development and periods of mineralization, and this approach has been adopted and extended here, with the addition of further age determinations and taking into account revised stratigraphic boundary ages (Figure 4).

Although Late Cretaceous inversion seems to have marked the end of basin subsidence (Kley et al., 2008), the age estimates by Symons et al. (1995) for carbonate-hosted Pb-Zn mineralization in nearby Upper Silesia indicate that the generation and expulsion of mineralizing fluids from the basins could have continued into the Tertiary. Mississippi Valley type Pb-Zn mineralization in Europe is generally accepted as having formed by the expulsion of fluids from subsiding sedimentary basins, and it has been proposed that these fluids are stored in the deeper parts of basins for tens of millions of years prior to release (e.g., Muchez et al., 2005). The scenario for formation of the giant Kupferschiefer Cu-Ag deposits is envisaged here as being similar, albeit with different source rocks and different transport and precipitation mechanisms.

Previous attempts to quantify the volumes of fluid involved in the Kupferschiefer mineralization have advocated the presence of relatively high concentrations of copper in the hydrothermal fluids (e.g., 1000 ppm; Jowett, 1986; 127 ppm; Cathles et al., 1993; 60 ppm; Blundell et al., 2003), values not readily found elsewhere in fluids from similar, low-temperature sedimentary basin environments (e.g. Sverjensky,

1987). If these younger ages do in fact mark the introduction of significant amounts of additional metals, then the extension of the mineralizing process into at least the Jurassic would allow the involvement of a greater volume of fluid, additional to that derived from the compaction of Permian and Triassic sediments. This could therefore lower the required copper concentrations closer to levels observed in other basinal brines.

However, key questions remain. In particular, what is the proportion of sulphide mineralization generated during each stage of mineralization and how much of each successive phase is new (externally derived metals) and how much records the remobilization of existing material? More geochronological (and other isotopic) studies, in combination with detailed petrographic studies, will be necessary to answer these important questions on the origin and timing of Europe's largest known copper resource.

8. Conclusions

1) New Re-Os age determinations on mineralized material from the Polish Kupferschiefer deposit have generated two age ranges: 242-265 Ma (Upper Permian – Middle Triassic) and 162-184 Ma (Lower – Middle Jurassic).

2) These results substantiate previously published age determinations and argue for a mineralization process that took place over a period of at least 100my, but in at least three main stages (240-255, 200-215 and 160-185 Ma).

3) These ages support a mineralization model that invokes the movement of hydrothermal fluids from the adjacent, subsidising, Polish Basin. Subsidence of this basin continued until at least the Cretaceous and it is proposed that mineralization was generated by episodic fluid release.

4) Some of the younger 'events' could represent alteration and recrystallization of existing sulphides; this certainly seems to be the case for the younger, Mo-rich, copper mineralization.

5) The relative importance of reworking existing material versus introduction of additional metals is as yet unknown.

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Age (Ma)	Method	Phase/Unit	Location	Source
250-255	Palaeomagnetism	Rote Fäule (hematite)	North Sudetic Trough mines	Jowett et al. 1987a; Nawrocki 1997, 2000; Torsvig et al. 2001
240 (3.8)	Re-Os	Sulphide-rich shales	Lubin	Pasava et al. 2007a
212 (7)	Re-Os	Bornite and chalcopyrite veinlets	Lubin and Polkowice	Mikulski and Stein 2012
204.3 (0.5)	Re-Os	Sediments and sulphides	Mansfeld	Patzold et al. 2002
190-216	K-Ar	Illite	SW Poland	Bechtel et al. 1999
175-180	U-Pb	Thucholite	Lubin district	Kucha and Przybylowicz 1999
149 (3)	Palaeomagnetism	Kupferschiefer (sulphide-rich)	Sangerhausen	Symons et al. 2011
114-187	K-Ar	Illite in Rotliegendes sandstone	Western Poland	Maliszewska and Kuberska 2009
130	U-Pb	Huttonite - monazite	Lubin	Kucha (unpublished)
83-96	K-Ar	Illite in mineralized Weissliegendes sandstone	North Sudetic Trough	Michalik 1997
159-186			Fore Sudetic monocline	
?53 (3)	Palaeomagnetism	Kupferschiefer (sulphide-rich)	Sangerhausen	Symons et al. 2011

Table 1: Published age determinations for Kupferschiefer mineralization and associated recrystallization events. Ages in brackets are the age uncertainty.

Sample	Material	Location	Method	Re(ppm)	±	187Re(ppm)	±	187Os(ppb)	±	Os(c) (ppt)	Age	±
P1/2	Chalcocite in sandstone	Polkowice East	normal Os addition	4.88	0.02	3.07	0.01	13.47	0.05		262.7	1.3
P1/2			triple spike	4.36	0.02	2.74	0.02	12.10	0.05	1.50	264.7	1.8
KP4	Massive, colloform sulphides	Lubin	normal Os addition	8.69	0.04	5.46	0.02	22.36	0.08		245.3	1.2
KP4			triple spike	8.90	0.04	5.59	0.02	22.98	0.03	4.00	246.2	1.1
KP4a	Chalcopyrite*	Lubin	triple spike	4.85	0.03	3.05	0.02	12.47	0.06	18.53	245.2	1.6
KP4b	Bornite*		triple spike	1.23	0.01	0.77	0.00	3.25	0.01	0.32	252.5	1.7
KP4c	Pyrite*		triple spike	4.68	0.03	2.94	0.02	11.89	0.05	20.26	242.0	1.6
LZ	Mixed sulphides in shale **	Lubin West	normal Os addition	7.66	0.03	4.82	0.02	13.04	0.05		162.3	0.8
LZ			¹⁹⁰ Os/ ¹⁸⁵ Re	6.45	0.02	4.05	0.02	12.35	0.08	99.40	182.6	1.4
LZ			triple spike	4.78	0.02	3.01	0.01	8.90	0.01	4.5	177.4	0.8
LZ5	Mixed sulphides in shale **	Lubin West	triple spike	8.47	0.07	5.32	0.05	16.37	0.13	226	184.3	2.2
KP3	Chalcocite in sandstone	Rudna	triple spike	1.06	0.01	0.67	0.00	1.92	0.01	4.5	173.3	1.1

* Separates from bulk sample KP4

** Includes Cu, Pb, Fe and K bearing Mo-sulphides

Os(c) = common osmium

Ages calculated using a decay constant of Re to Os of $1.666 \times 10^{-11} \text{ yr}^{-1}$

Table 2: Re-Os isotopic data and derived ages (Ma) for mineralized samples from the North Sudetic monocline

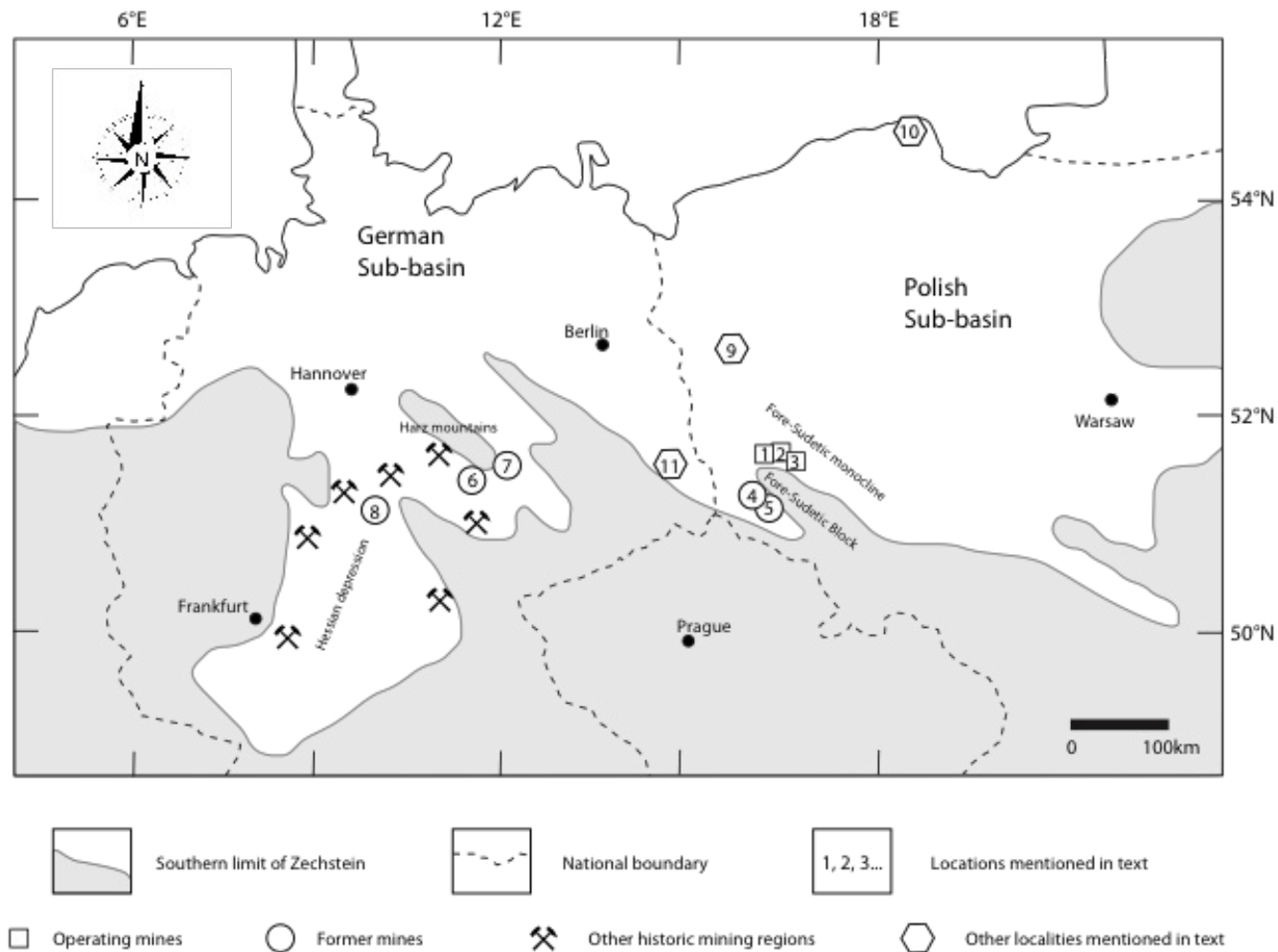


Figure 1. Locations of the Kupferschiefer mines and other studies mentioned in the text. After Borg et al. (2012), Oszczepalski (1989) and Zientek et al. (2015). Locations: 1: Polkowice; 2: Rudna; 3: Lubin; 4: Konrad; 5: Lena; 6: Sangerhausen; 7: Mansfeld; 8: Richelsdorf; 9: Miedzychod; 10: Zdrada; 11: Spremberg.

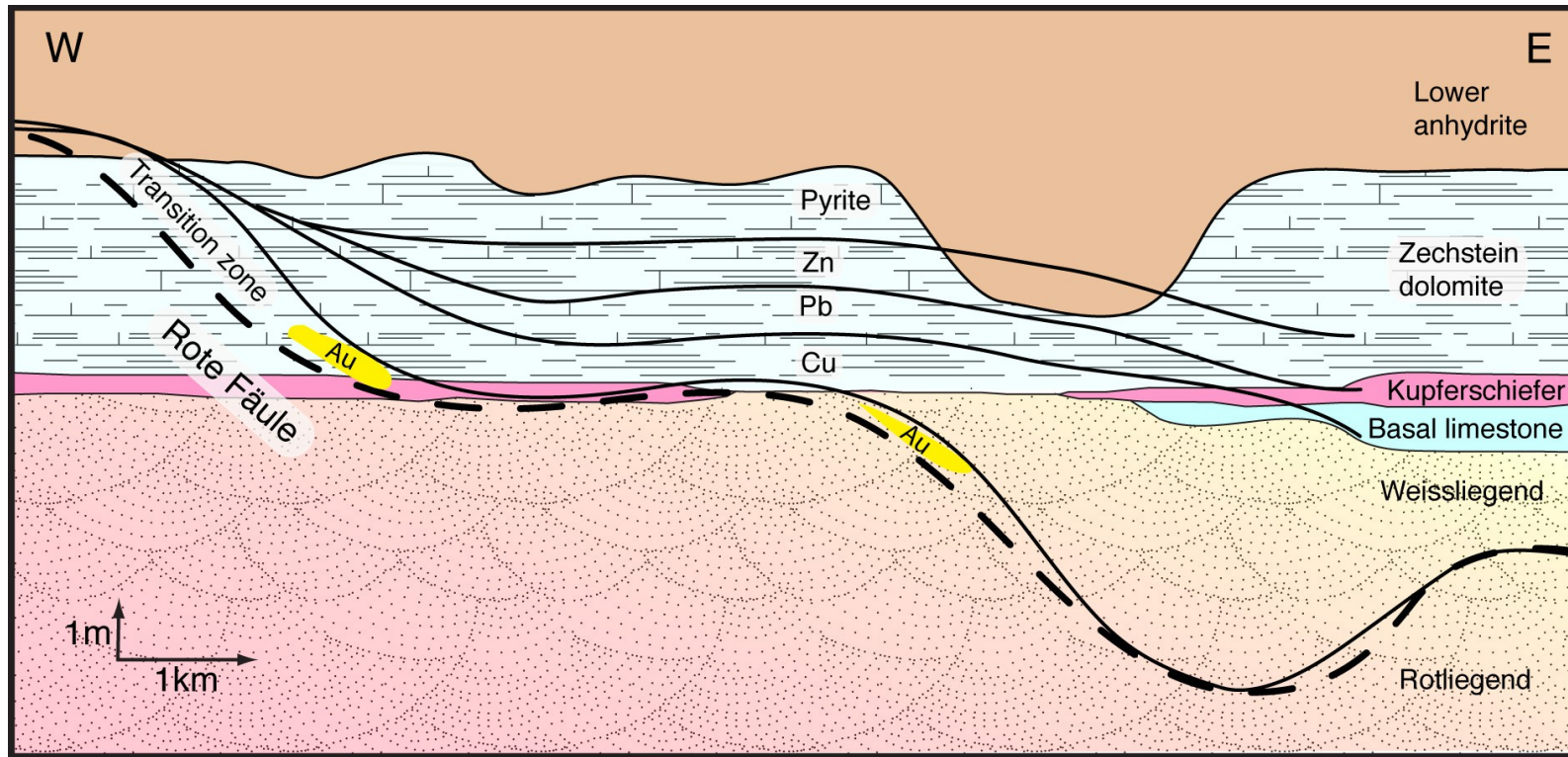


Figure 2. Diagrammatic composite cross-section of mineralization and stratigraphy in the North Sudetic monocline mining region (modified after Oszczepalski, 1999, and Kucha and Pawlikowski, 1986).

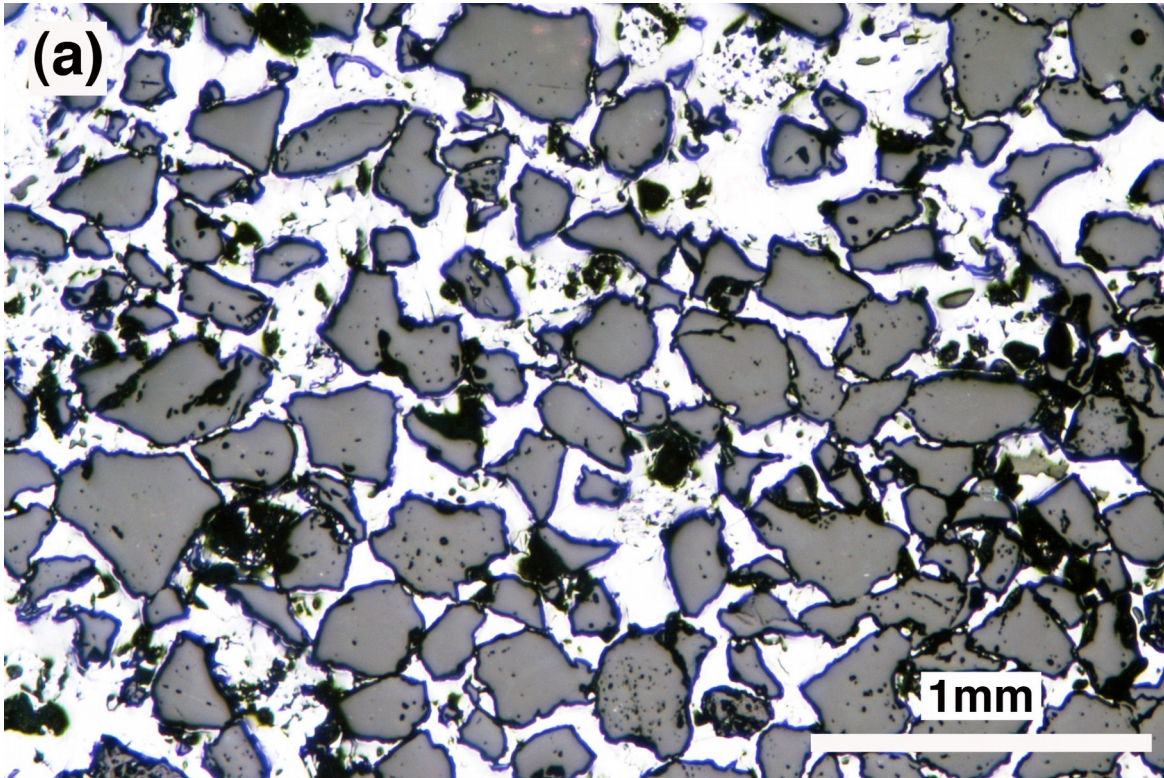


Figure 3a. Sandstone-hosted ore in sample KP3 from Rudna (reflected light; plane polarised). View shows pore space between quartz grains (grey) in sandstone infilled by chalcocite (white).

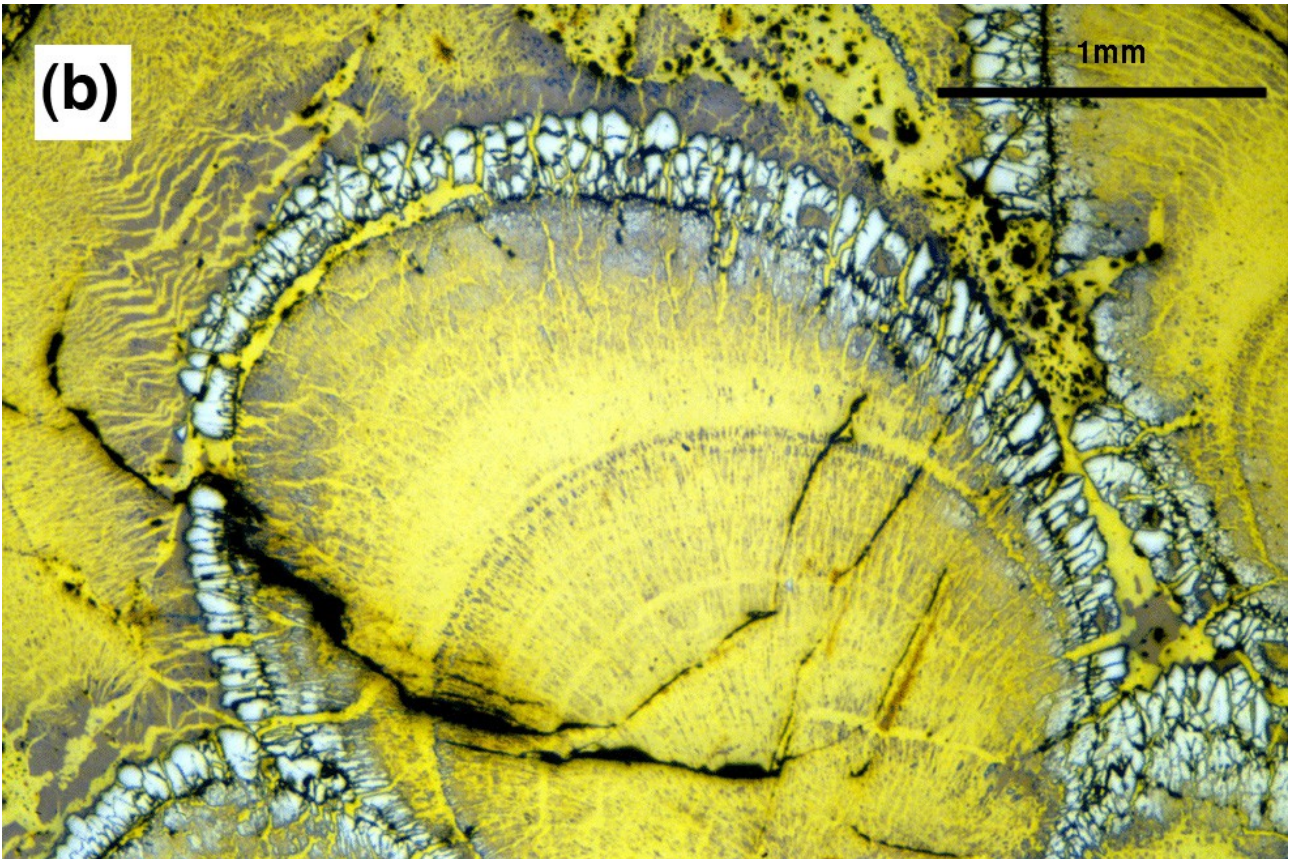


Figure 3b. Massive copper ore in sample KP4 showing concentrically banded/colloform chalcopyrite (yellow), pyrite (creamy white) and bornite (pink brown) (reflected light; plane polarised).

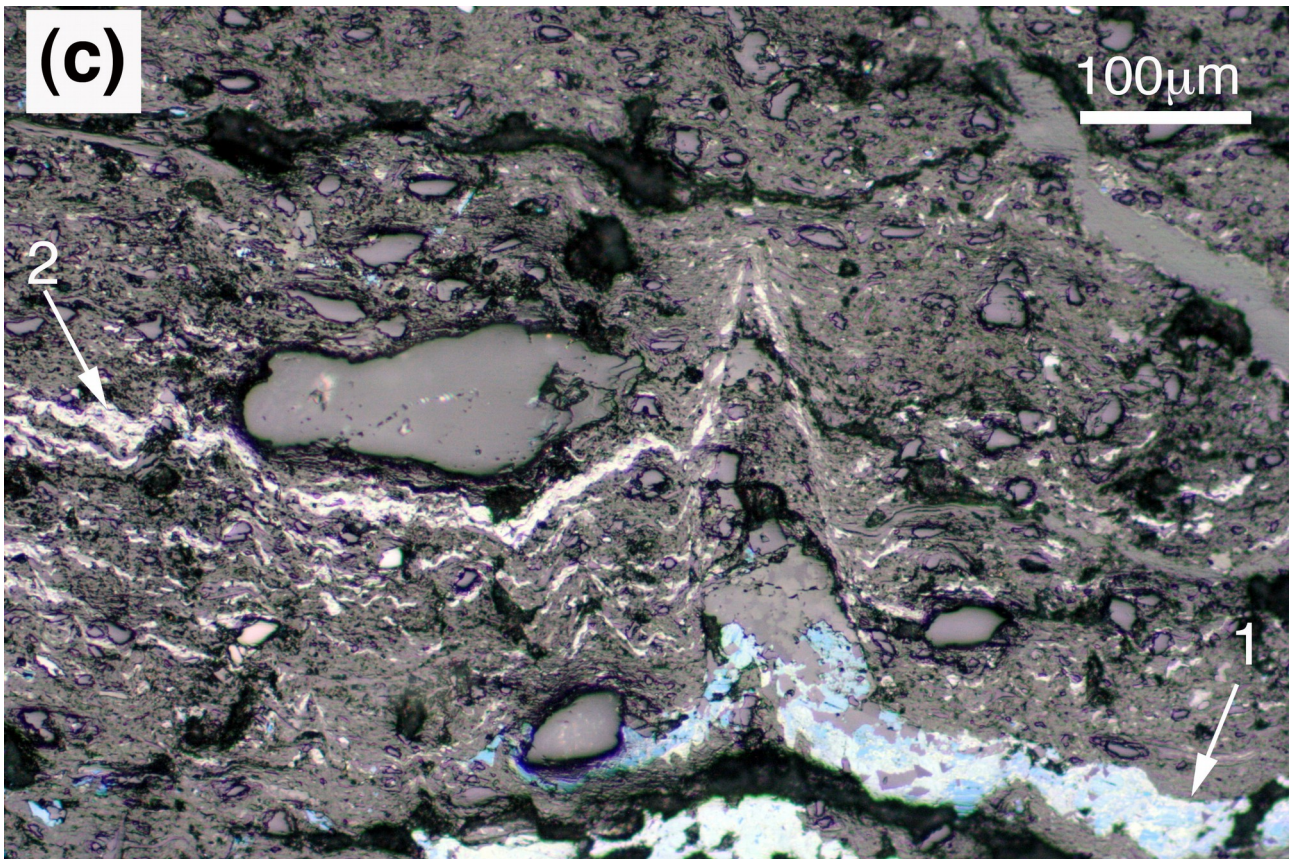


Figure 3c. Mo-rich shale sample from Polkowice East (reflected light; plane polarised). Sample shows a layer of castaingite, covellite and digenite (1) and molybdenite (2), in a folded matrix of quartz, clay and organics.

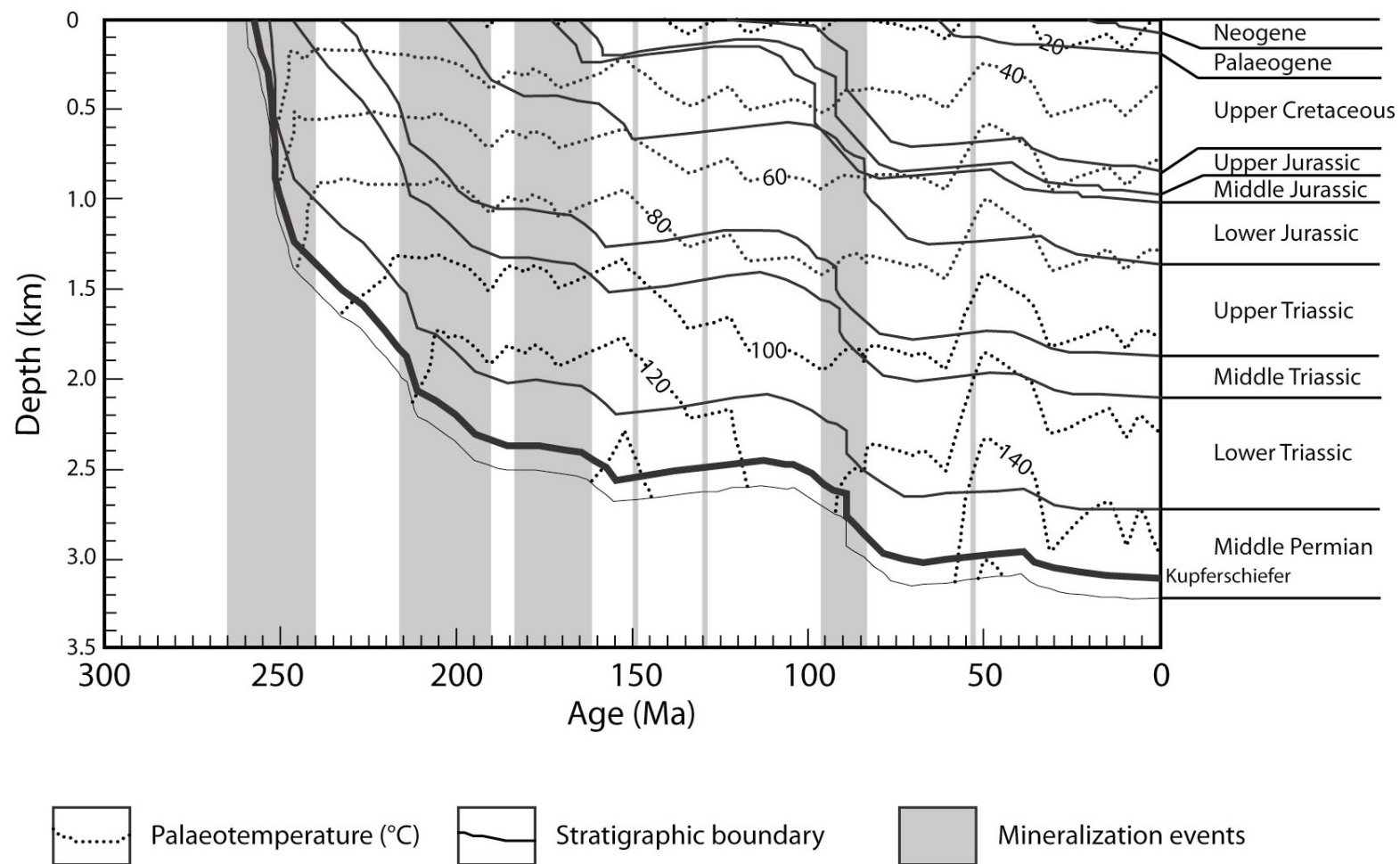


Figure 4. Illustration showing burial history of sediments in the Międzychód-4 borehole, Poland. Superimposed are proposed ages for Kupferschiefer mineralization. Burial history from Pletsch and others (2010) (but with revised stratigraphic boundary ages). Kupferschiefer mineralization age information from this study and references in Table 1.