Small-scale variations of base metal contents in black shale-hosted “Kupferschiefer” ore, Wettelrode Mine, Germany

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Abstract. The “Mansfeld-Sangerhausen” Mining District is well known for the mining history of base metal enriched black shale of the Kupferschiefer sequence. The mineralized black shale at the Röhrig Shaft, Wettelrode, shows a horizontal base metal variation, which is the subject of the present paper. Based on fifteen horizontal boreholes, parallel to the dip direction of the black shale, the profile was sampled and in-hole and laboratory geophysics were carried out.
Preliminary results by hand-held XRF show the base metal contents in distribution maps with different enriched zones. The mineralization occurs in different forms. Part of the mineralization is associated with small barite veins. Other ore minerals are finely disseminated within the black shale matrix. The main mineralization consists of chalcopyrite, pyrite, bornite and galena. The veins are also filled with calcite, dolomite and/or gypsum.

Keywords. Kupferschiefer, black shale, base metal mineralization, sediment-hosted copper, small-scale variation.

1 Introduction

The subject of this investigation is the small-scale base metal variation in black shale-hosted ore. Densely spaced horizontal boreholes, parallel to the dip direction of the mineralized Kupferschiefer strata, were drilled in an underground adit at Wettelrode Mine, Germany. Fifteen meters of drill cores, each approximately one meter long, have been recovered. The metal contents of the drill cores were screened by a hand-held XRF (NITON) and subsequently selectively sampled. Some of the boreholes will be tested by borehole geophysics for comparison, to localize the base metal mineralization by in situ Neutron Activation Spectroscopy (NAS) and X-ray fluorescence analysis (XRF). The distribution of base metals such as copper, lead, and zinc are in the focus of this investigation. The statistical nearest neighbour interpolation shows a horizontal variation of the base metal contents. To verify and explain this small-scale variation the distribution of the ore minerals has been investigated. This abstract gives an overview of the methods applied and of our preliminary results. The

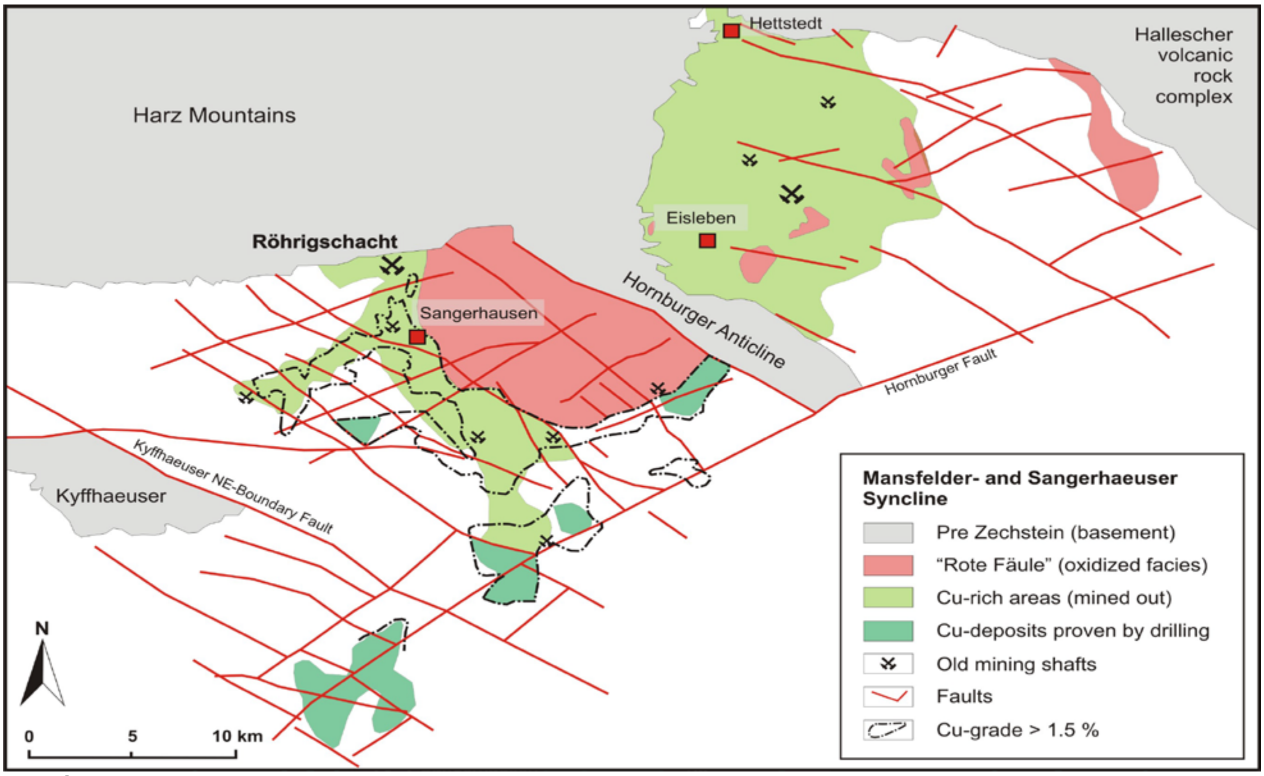

Figure 1. Simplified map of the “Mansfeld- and Sangerhausen” Mining District, with the oxidized facies (“Rote Fäule”) and the old Kupferschiefer mine shafts (modified after Stedingk et al. 2002 and Stedingk & Rappsilber 2000).

sample location is situated in the central part of Germany, the "Mansfeld-Sangerhausen" Mining District, south and east of the Harz Mountains (Fig. 1). The Röhrig Shaft of Wettelrode Mine was closed in the nineteen eighties and is now accessible as a mining museum. The adit with the sample locality is at a depth of approximately 283 m below surface.

2 Wettelrode - Kupferschiefer

The Southern Permian Basin is situated above basement rocks of magmatic arc origin, the Mid-European Crystalline High (Borg et al. 2012) and filled at the base with continental Variscan sediments (Ehling et al. 2008). During Permian times, the area was controlled by volcanism and a reactivation of NE-SW and NNE-SSW faults (Rentzsch and Franzke 1997). Felsic and mafic volcanic rocks occur in the Rotliegend sediments.

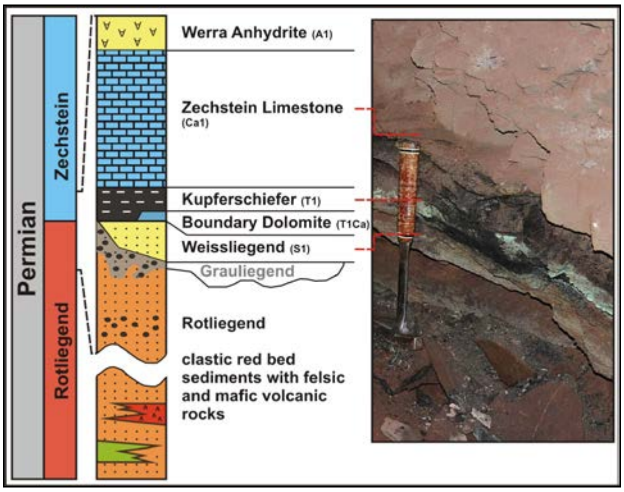

Figure 2. Stratigraphic column from Wettelrode (modified after Borg et al. 2012).

At the beginning of the Zechstein period, the level of the basin was approximately 200-300 m below sea level. Through continental rifting the basin was flooded from the Paleo North Sea and changed the climate from continental arid to stagnant shallow marine conditions (Paul 2006, Rentzsch and Franzke 1997). In the shallow sea a chemocline developed and the oxygen-rich surface water was separated from the oxygen-poor and sulphur-enriched deeper water (Radzinski 2008). Under these anoxic conditions, a black laminated clay-, marl- and limestone unit, with a high organic carbon content, was deposited (Paul 2006). An absolute age of 255 Ma is generally accepted (Borg et al. 2012). The Kupferschiefer is the base of the Zechstein sequence (Fig. 2) and overlain by carbonates and evaporites of seven evaporation cycles (Radzinski 2008).

The regional mineralization of the Kupferschiefer sequence is located at the southern edge of the Permian Basin and spatially related to southwest-northeast trending faults (Borg 1991). For the Sangerhausen Mining District late epigenetic mineralization ages of 149 and 53 Ma were reported (Borg et al. 2012). The Mining District shares a major secondary redox front, the so-called "Rote Fäule", which is associated to a metal bearing zone (Fig. 1).

3 Core screening and data interpolation

The boreholes were emplaced by a wet drilling process with a diameter of ten centimetres following the dip direction of the Kupferschiefer stratum and locally entered the top part of the footwall sandstone. Due to the softness of the rocks and of clastic layering of the black shale the drill cores were extremely fragile and commonly consist of broken pieces.

For first information on the base metal contents, the drill cores were measured every 20 centimetres five times by hand-held XRF (NITON). Where the drill core was intact, the measurements were done on all sides of the drill core. Where the drill core was fragmented, the measurements were done on five pieces and/or on the fine material (Fig. 3). Where the drill core partly intersected the footwall sandstone, only the black shale was analysed for the correlations.

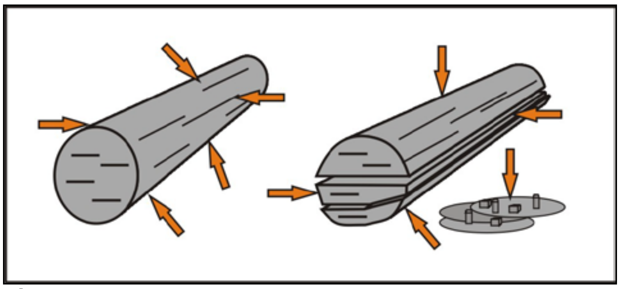

Figure 3. Illustration of five measurements on the drill core and on broken material by hand-held XRF.

Each of the drill cores can be defined by six or seven base metal average grades. The measurements were plotted and their spatial relation between distance and grade was illustrated. A nearest neighbour interpolation was used to calculate the data for copper, lead and zinc (Fig. 4).

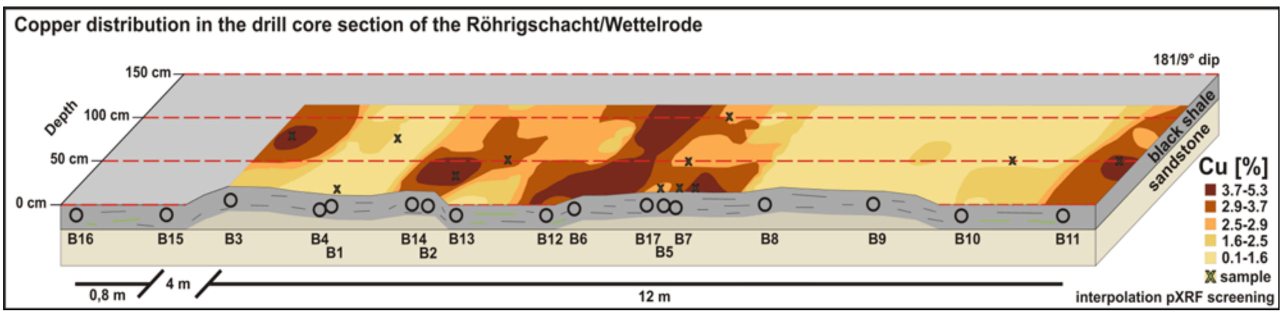

Figure 4. Copper distribution in narrowly spaced horizontal boreholes within the black shale stratum of the Kupferschiefer.

4 Wettelrode – base metal mineralization

The black shale (Kupferschiefer) is approximately 10-15 cm thick and dips 9° S. The unit comprises interlayered dark to black laminated mud-, marl- and limestone. The dark colour is an indication for a high bituminous content. Characteristic for the local black shale is also the visibility of small carbonate lenses and small veins, filled with gypsum, calcite, barite and ore minerals (Fig. 5).

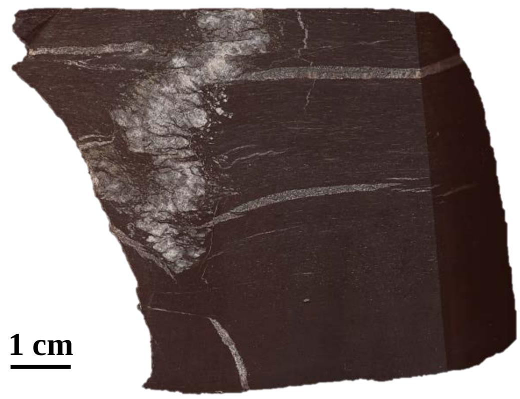

Figure 5. Dark black shale with horizontal barite veins and a vertical calcite and dolomite filled vein.

The mineralization is dominated by four minerals chalcopyrite, pyrite, bornite and galena. Smaller amounts of sphalerite and antimonite could be identified too.
Ore minerals up to one cm are especially associated with calcite, ankerite or dolomite vein mineralization and mainly consist of pyrite and chalcopyrite. Further smaller ore minerals like sphalerite, galena and bornite are associated to barite veins. Some zones of the black shale are barren, containing only diagenetic framboidal pyrite. However the main part of the black shale unit is mineralized by finely disseminated ore and the intergrowth of different ore minerals, as well as with barite and carbonate minerals is typical (Fig. 6). Recent literature (Borg et al. 2012) reports two major epigenetic pulses of metal introduction to the Kupferschiefer.

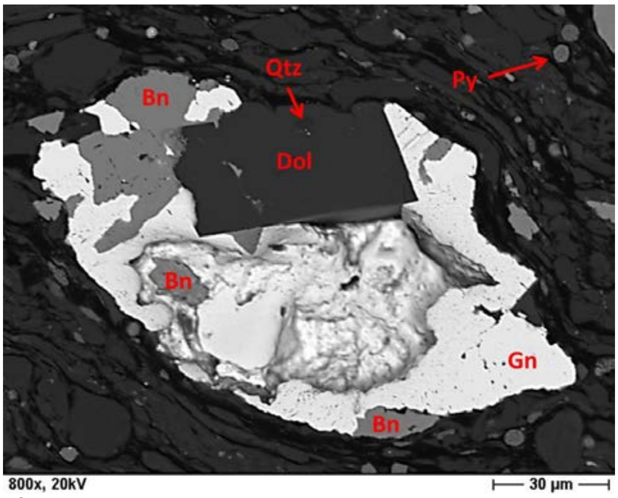

Figure 6. Galena (Gn) intergrowth with bornite (Bn) and dolomite (Dol). Framboidal pyrites (Py) close beside it (BSE).

4 Results

The black shale of the Kupferschiefer is base metals rich. The drill cores show, visible to an unaided eye, ore unmineralized and mineralized parts.
The base metals distribution maps, screened by hand-held XRF (NITON), identified copper, zinc and lead enriched areas. Using the example of copper in Figure 4, a copper rich zone (up to 5 %) is located in the middle of the interpolated distribution map. The nearby less copper mineralized areas are partly higher mineralized with zinc (up to 1.6 %) or lead (up to 2.8 %). Copper rich zones are low in zinc and lead.
A bulk sample analysis of the black shale unit yielded an average total organic carbon content (TOC) of 14.4 % and a total inorganic carbon content (TIC) of 0.1 %

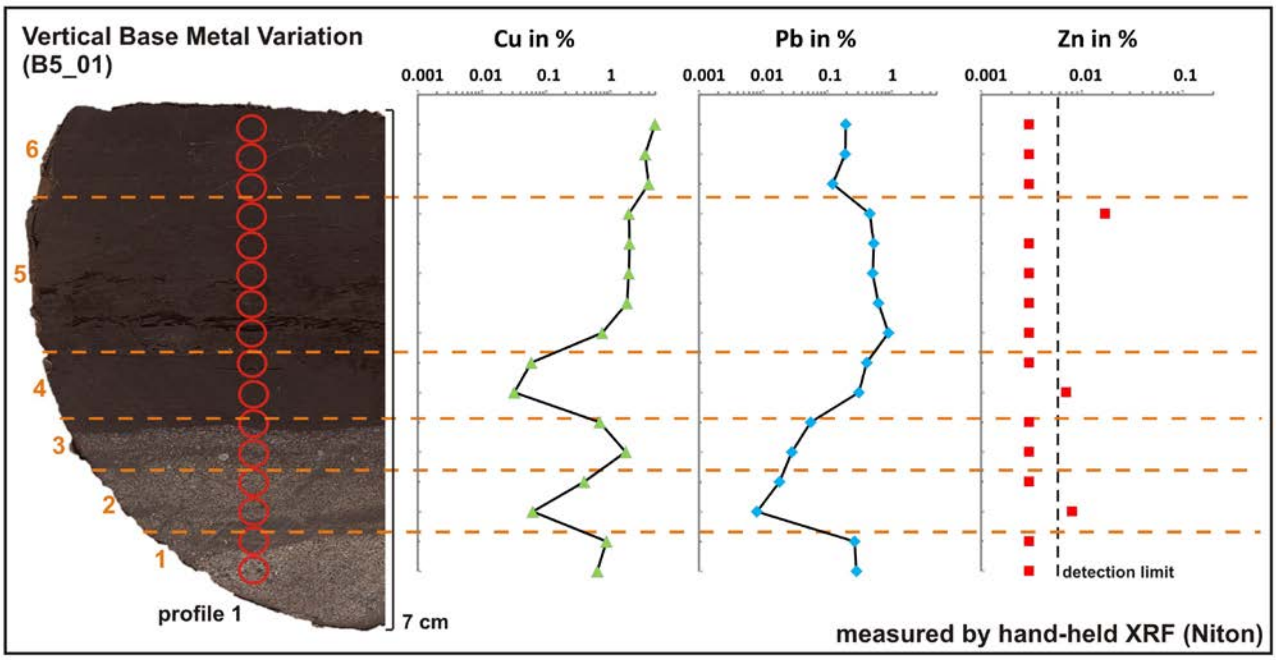

Figure 7. Vertical hand-held XRF (NITON) profile showing the variations in the metal concentrations.

(UVR-FIA GmbH 2015). The geochemical bulk sample analysis (ICP-MS) of the black shale unit (15 cm) amounted to 3.40 % copper, 1.04 % lead, 0.13 % zinc, 815 ppm cobalt, 157 ppm nickel and 79 ppm silver.

A profile (Fig. 7) showing the contact zone between the footwall sandstone (Weissliegend) and the lower black shale (Kupferschiefer) was measured by hand-held XRF (NITON). Using the copper values six different ore zones could be defined, three in each lithological unit. Zone two (Fig. 7) is characterized by a clay lens and a lower copper value. Zone three is directly related to the black shale unit and has the highest copper amount in the sandstone footwall. A higher amount of antimonite can be found in this zone. The lowest black shale zone (4) is nearly barren of copper. An increase of copper is measurable in zone five. The highest copper values can be found in zone six. Lead increases from zone two to zone five where the highest values are identified. The highest copper values in zone six are related to a decrease in lead. Zinc is close to the detection limit of the hand-held XRF, wherefore a trend could not be identified. The varying quantity of the ore minerals bornite, chalcopyrite, galena and antimonite is significant for the single zones.

Additionally a horizontal profile in zone six was measured but a lateral variation in base metal contents does not exist.

5 Geophysics

The geophysical measurments were done by a modular built logging tool (SNR-70) including the methods such as X-Ray fluorescence (XRF), Gamma-Ray Spectroscopy, and Neutron Activation Spectroscopy (NAS). Because of radiation protection aspects, only Gamma-Ray Spectroscopy has been used in-situ. Based on the base metal distribution, a selective number of points were analysed three times for 20 minutes each. With Gamma-Ray Spectroscopy, the presence of natural nuclides can be proven and provides the basis for the Neutron Activation Spectroscopy in the laboratory. NAS uses e.g. $^{252}{}_{98}Cf$ as a source of radiation to detect elements quantitatively and qualitatively. To classify the atomic nucleus of the sample, an interaction with the neutrons occurs and different products can originate. These activation products can be radioactive and decay with their typically half-life period. A characteristic radiation can be used for analyses during the activation process as well as the subsequent decay. Four phases are necessary for the measurements. The first is the irradiation phase. The second is the damping phase. The duration is important for selecting activation products with a short or long half-life period and to prevent spectral interferences. The third is the measuring period. With gamma spectrometry a spectrum is recorded. With the position of the peak-like signals the activation products can be identified and the height of the signals is proportional to the element content. The element content can be determined by comparison with an internal standard. A spectral analysis computer program is used to evaluate and convert the data into element contents and display these as graphs. A low number of elements (up to ten) must be defined for each analyse, depending on measurement time and radiation source.

6 Conclusion

The black shale unit is enriched in base metals. The geochemical bulk sample analysis (ICP-MS) shows an amount of 3.40 % copper, 1.04 % lead, 0.13 % zinc, 815 ppm cobalt, 157 ppm nickel and 79 ppm silver. The mineralization is dominated by pyrite, chalcopyrite, bornite, galena and sphalerite. Some parts of the profiles are characterized by parallel bedding and cross cutting veins (e.g. barite and calcite) and larger ore mineral aggregates (up to 2cm). Three base metal distribution maps (Cu, Pb & Zn) and vertical sample profiles (e.g. Fig. 7) based on hand-held XRF (NITON) measurements show a strong horizontal and vertical ore mineral zonation.

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