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Jérôme Gouin, Thierry Augé, Laurent Bailly, Patrick d'Hugues, Jean-Robert Disnar, et al.. Organic and mineral characteristics of Kupferschiefer ore from Lubin mine (Poland): implications for bioleaching of the ore.. Mineral Exploration and Research: Digging Deeper, 2007, Dublin, Germany. 4 p. insu-00154955

HAL Id: insu-00154955

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Submitted on 15 Jun 2007

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Organic and mineral characteristics of Kupferschiefer ore from Lubin mine (Poland): implications for bioleaching of the ore.

J. Gouin^{1,2}, T. Augé, L. Bailly, P. D'Hugues

¹ ISTO-CNRS-University of Orleans, UMR 6113, BP 6759, 45067 Orleans cedex 2, France

² BRGM, BP 6009, 45060 Orléans cedex 2, France.

J.R. Disnar, D. Keravis

ISTO-CNRS-University of Orleans, UMR 6113, BP 6759, 45067 Orleans cedex 2, France.

ABSTRACT: The ore mineral and organic matter content of the Lubin black shale (LBS) are compared with copper concentrate (LC) obtained by flotation. Study of a mineralized profile shows a good correlation between the S, TOC and Cu, Co and Ag content, suggesting syngenetic bacterial sulfate reduction (BSR) accumulation. The presence of disseminated and fracture filling rather than framboidal Cu-minerals, suggests formation via diagenetic processes. Compared to the black shale, the LC shows a lower HI and a higher OI, and a much more diverse ore mineral content. The black shale ore is composed of 15 vol. % sulfide, this proportion reaches 27 % in the LC whereas the TOC is similar in the LC and LBS. The ore mineral diversity in the LC is due to the contribution of mineralized sandstone and dolomite adjacent the black shale ore.

KEYWORDS: mineralization, organic matter, black shale deposit, copper concentrate

1 INTRODUCTION AND GEOLOGICAL SETTING

The Lubin mine belongs to the Kupferschiefer organic and copper-rich black shale deposit, which covers about 54.5% of Poland (Piestrzyński and Sawłowicz 1999). This deposit is located in southwestern part of Poland (Fig. 1). It is the largest copper deposit in Europe and one the largest in the world as regard to the copper reserves.

In the framework of the European BioShale project (<http://bioshale.brgm.fr>), aiming at evaluating biotechnology for beneficiation of black shale ore, we had the opportunity to study the Lubin black shale and various samples in order to characterize the product before and after the bioleaching treatment.

The Lubin ore deposit is of the stratabound polymetallic type, with a size of about 550km². The Kupferschiefer mineralization occurs between the uppermost Lower Permian Rotliegendes terrestrial redbeds and the Upper Permian Zechstein marine sequence (Oszczepalski 1999), in the southwestern part of Poland, within the North Sudetic basin and the

Foresudetic Monocline. These polymetallic ore-bearing sediments are developed in two distinct facies, a reduced one which consists of an organic-rich black shale containing base metal sulfides and an oxidized one (Rote Fäule) which consists of red-coloured organic-deficient shale containing most of the precious metals (Oszczepalski 1999 ; Piestrzyński *et al.* 2002).

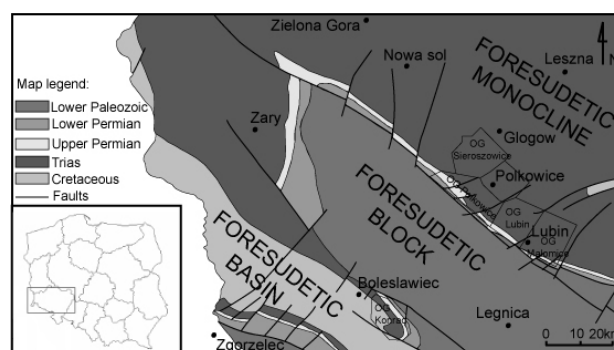


Figure 1. Geological map of Southwestern Poland, location of the Lubin deposit.

Results are presented for a 110cm thick profile through the reduced zone in the Lubin mine (LUP2-1 lowermost sample: boundary dolo-

mite, LUP2-2 to 9: black shales, LUP2-10 to 12 uppermost sample: dolomites), analyzed to study sulfide distribution and relationships between metal enrichments and organic matter. An "average black shale sample" (LBS) and the Lubin copper concentrate (LC) were also analyzed to compare the black shale ore and the industrial metal-enriched material for copper recovery. The Lubin copper concentrate (LC) is the final industrial product of the Lubin mine, obtained by flotation processes of a composite run of mine constituted by the three main formations of the Kupferschiefer: dolomite, black shale and sandstone.

2 MINERALIZATION

The most mineralized part of the orebody is the Kupferschiefer laminated black shale, with an average copper content of 7.1% (Piestrzyński and Sawłowicz 1999) on an average thickness of about 80cm. It shows a high organic content (TOC of 7-8% in average), clay minerals (illite), calcite/dolomite, detrital quartz and feldspars, and base metal sulfides. The organic matter is mainly represented by amorphous material of bituminite type, with vitrinite in various proportion and inertinite particles (Koch 1996). The main ore minerals are chalcocite, digenite, covellite, bornite, chalcopyrite, pyrite, tennantite, galena, sphalerite and silver minerals (Piestrzyński *et al.* 2002).

3 METHODS

Rock-Eval Pyrolysis assay performed with a "Turbo" model RE6 pyrolyzer. Sulfide minerals were analyzed using a Camebax SX50 electron probe microanalyzer (EPMA) in routine conditions. For LBS and LC samples, sulfides minerals were concentrated by bromoform densimetric separation. The heavy fraction was compacted with a hydraulic press to obtain a disk which was then polished and analyzed by counting point technique with EPMA with a step of 200 μ m in same conditions as described above in order to accurately determine the proportion of each mineral. Chemical analysis of the bulk samples was carried out by atomic absorption spectrophotometry and induced coupled plasma spectrophotometry. Loss of ignition was measured by heating the samples at 1000°C for 1h.

4 LUBIN PROFILE

4.1 Organic matter characterization

Two different types of organic matter (OM) can be distinguished in the profile of the reduced zone between black shale and dolomite samples. The black shale horizon is rich in OM, the TOC ranges from 5.27% to 13.7% (Fig. 2). This OM is typically of marine origin (type II kerogen) with high values of hydrogen index (HI up to 361 mg HC/g TOC) and low values of oxygen index (OI below 10 mg CO₂/g TOC) (Fig. 2). To the contrary, in all dolomite samples, the OM seems to be of terrigenous origin (type III kerogen). The TOC and HI are much lower (up to 1.11% and 93 mg HC/g TOC) and OI much higher (above 10 mg CO₂/g TOC). This is probably due to the low TOC contents with an artificial contamination of OI by carbonate material (Katz 1983).

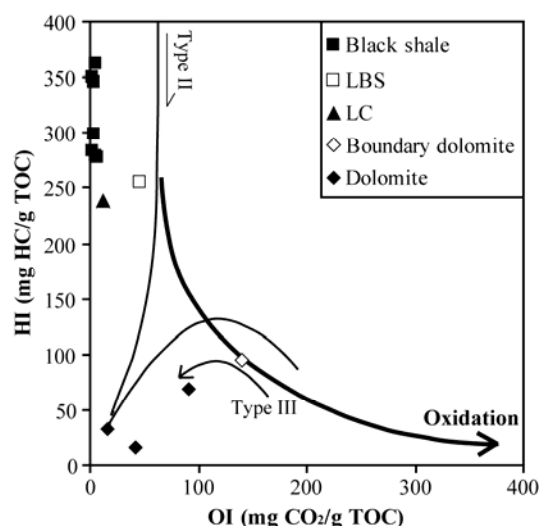


Figure 2. Hydrogen Index vs. Oxygen Index for recognition of genetic type of organic matter. Genetic paths after Espitalie *et al.* (1985).

4.2 Metal distribution

The boundary dolomite (LUP2-1) and the upper dolomite (LUP2-10 to 12) are poor in organic matter, and show very low metal contents: less than 1 wt.% Cu, less than 2 wt.% S, and less than 100-200 ppm As, Co, Ni, Ag. Organic-rich black shales (LUP2-2 to 9) exhibit, to the contrary higher contents of S (up to 7.5 wt.%), Cu (up to 14.4 wt.%) and hundreds of ppm As, Co, Ni, Ag.

The highest TOC, and metal content is observed in sample 2, except for S, and, there is a global tendency of decrease in metal contents toward the top of the profile (Fig. 3). Some en-

richments in As, Co, Ni are observed in the middle of the profile corresponding to a higher content in cobaltite-gersdorffite group minerals. The top of the profile is marked by an enrichment in S, Cu, Ag.

The metal patterns are globally in agreement with the S and TOC content, indicating that these metals were accumulated by bacterial sulfate-reduction during shale ore formation (Sun and Püttmann 1997). This process would however result in the formation of framboidal texture for the Cu-minerals as described by Sawlowicz (1990). With the exception of framboidal pyrite occurrences in black shale (mostly in algal filaments), the mineralization occurs as fine-grained disseminations and as fracture fillings indicating a base metal enrichment of diagenetic origin (Sun and Püttmann 1997).

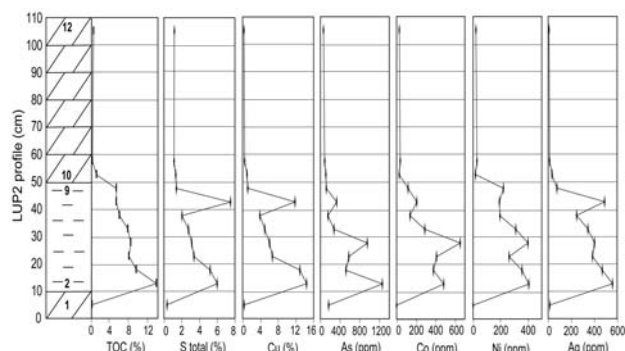


Figure 3. TOC and major elements distribution in LUP2.

5 COMPARISON OF LBS VS. LC

5.1 Geochemistry

LBS has a TOC value of 6.89%, lower than the mean value for the black shale ore of the profile (TOC = 7.98%), whereas TOC for LC is in the range with 7.63%. The OM, which composes LBS and LC is of marine origin as supported by the HI (254 and 237 mg HC/g TOC respectively) and OI (47 and mg CO₂/g TOC) (Fig. 2). Compared to the black shale of the profile, the two samples (LBS and LC) exhibit lower HI and higher OI (Fig. 2). LBS sample was probably collected in a more oxidized zone.

Table 1 shows that the Lubin black shale has a similar composition to the average black shale of the profile. Compared to black shale ore, LC is enriched in total S and base metals, and depleted in V. The highest metal content in LC, (As - Pb - Zn being more than 10-times higher

in the concentrate than in black shale ore), point to a probable input of metals from sandstones and/or dolomites, and the V depletion seems to be due to an effect of dilution (by the contribution of dolomite and sandstone in the concentrate) or a stronger affinity with gangue minerals.

Table 1. Geochemical data of average LUP2 black shales, LBS and LC.

	Avg. LUP2-BS	LBS	LC
TOC (%)	7.98	6.89	7.63
S _{tot.} (%)	3.9	2.56	12.5
Ag (ppm)	372.3	340	910
As (ppm)	522.6	206	4930
Co (ppm)	334.5	234	1384
Cu (%)	7.73	8.6	17.1
Ni (ppm)	292.6	304	534
Pb (ppm)	121.1	112	4.74 %
V (ppm)	1084.3	1530	854
Zn (ppm)	117.6	10	8330

5.2 Sulfide quantification

As mentioned previously, LC is enriched in metal compared to black shale ore. This is confirmed by the fraction of heavy minerals (mainly sulfides) extracted from each sample. LBS is composed of 15% of sulfides and 85% of gangue minerals (OM, quartz, clay minerals, carbonates), whereas LC contains 27% of sulfides and 73% of gangue minerals.

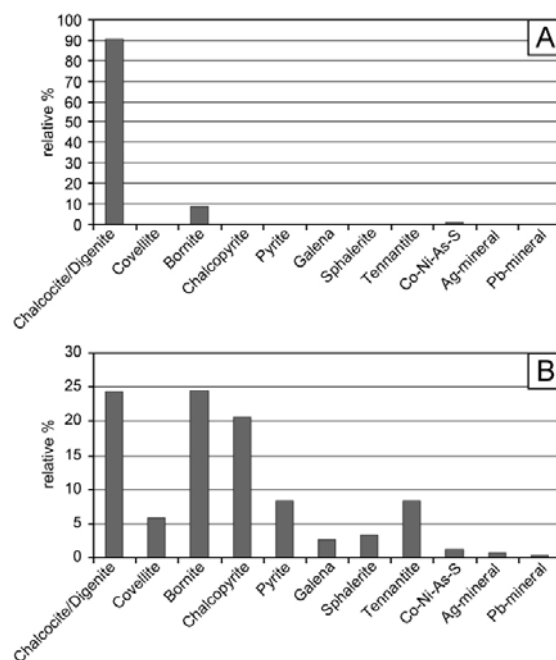


Figure 4. Relative proportion of each mineral phase in the heavy fraction in A) LBS and B) LC.

The differences observed in the chemical composition are reflected by the mineral composition. The sulfide fraction of LBS is mainly composed of 3 main minerals (Fig. 4): chalcocite/digenite (>90%) - the distinction between the two was not possible with the technique used - and bornite (9%), with traces of Co-Ni-sulfarsenides (0.6%).

On the contrary, the sulfide fraction of LC is composed of about 11 minerals (Fig. 4). The 4 most abundant minerals are chalcocite/digenite (24.4%), bornite (24.5%) and chalcopyrite (20.6%), representing roughly 70% of the sulfide fraction. Three other minerals representing more than 20% of the sulfide fraction are pyrite (8.3%), tennantite (8.3%), covellite (5.8%). Less common minerals include galena (2.7%), sphalerite (3.3%), Co-Ni-sulfarsenides (1.2%). Rare Ag- and Pb-bearing minerals represent less than 1% of the sulfide fraction, and are poorly characterized.

The LBS is composed of 85% gangue minerals, 13.6% chalcocite/digenite, 1.4% bornite and 0.1% Co-Ni-sulfarsenide. The LC is more complex. It contains 73% gangue minerals, 6.6% chalcocite/digenite and bornite, 5.6% chalcopyrite, 2.2% pyrite and tennantite, 1.6% covellite, and less than 1% of other minor minerals (Table 2).

Table 2. Mineral composition and relative proportions in LBS and LC.

	LBS	LC
Chalcocite/Digenite (%)	13.6	6.6
Covellite (%)		1.6
Bornite (%)	1.4	6.6
Chalcopyrite (%)		5.6
Pyrite (%)		2.2
Galena (%)		0.7
Sphalerite (%)		0.9
Tennantite (%)		2.2
Co-Ni-sulfarsenide (%)	0.1	0.3
Ag-mineral (%)		0.2
Pb-mineral (%)		0.1
Gangue (%)	85	73

6 CONCLUSIONS

The black shale from the reduced zone of Lubin mine is rich in OM (marine origin) and base metals. The element enrichment (Cu, S, Co, Ni, Ag, V) is correlated with the presence of OM. Some metals such as Pb, Zn, As are however preferentially concentrated in sandstone and/or dolomite.

The black shales and Cu-concentrate from Lubin have similar organic material, but are different with regard to their metal contents and mineralization.

Some Cu-bearing sulfides, such as chalcopyrite, are known to degrade poorly during industrial bioleaching processes. It is thus important to quantify the sulfide, content and composition, in the black shale ore and Cu-concentrate to evaluate bioleaching efficiency for metal recovery.

ACKNOWLEDGEMENTS

This work was financially supported by the European Commission in the frame of Bioshale European project (6th Framework program - NMP2-CT-2004-505710), in collaboration with CUPRUM (Poland).

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