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## Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

# Quantitative mineralogical analysis of European Kupferschiefer ore



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#### ARTICLE INFO

Keywords: Kupferschiefer Black shale XRD MLA Analysis Copper sulphides Rietveld refinement

## ABSTRACT

Kupferschiefer samples from five distinct deposits in Germany and Poland were studied with the aim to quantitatively determine their mineralogical composition using complementary approaches. Their inherently extremely fine-grained matrix, sheet silicate-dominated mineralogy, and highly variable copper sulphide content in the presence of organic components, render quantitative mineralogical analysis difficult. In an attempt to develop a comprehensive yet feasible analytical routine for Kupferschiefer black shale and associated sandstoneand carbonate-hosted ores, analytical techniques were tested and adapted to suit this purpose. This study focuses on a combination of mineralogical approaches using quantitative X-ray diffraction (XRD) and image-based automatic mineral liberation analysis (MLA). Quantitative bulk-powder XRD was achieved by Rietveld refinement, based on phase identification and selection of suitable structural models. The identified minerals were verified with scanning electron microscopic measurements coupled with energy dispersive X-ray spectroscopy (EDX) and optical microscopy. Results of QXRD and MLA were compared to chemical assay data. It is concluded that MLA and QXRD deliver satisfactory results for this complex raw material, but only when used in combination. When used independently, XRD and MLA are susceptible to significant errors related especially to sample preparation, mineral misidentification and quantification. To assure a successful quantitative mineralogical description of complex raw materials or processing products it is thus strongly recommended to verify all mineralogical information by independent analytical techniques - and to validate quantitative mineralogical information with quantitative chemical data.

### 1. Introduction

Polymetallic sulphide ores of the Central European Kupferschiefer ore deposits (Borg et al., 2012), are currently exploited for Cu, Ag, Mo, Co, Ni, and Re in Poland, with ongoing exploration in Poland and Germany. More than 37.4 Mt of Cu and 111 kt of Ag resources have been identified in Polish Kupferschiefer deposits (KGHM Polska Miedź, 2015). During recent and ongoing large-scale research into the hydrometallurgical and microbiological beneficiation of Kupferschiefer (Bioshale Project, 2007; Kutschke et al., 2015) the lack of reliable quantitative data for the mineralogical composition and microfabric for both ore, as well as processed samples, has been identified as a major obstacle for any effort to monitor and optimize recoveries and energy efficiency (Van den Boogart et al., 2011). Similar approaches are well established for beneficiation of other Cu ores (Vorster et al., 2001; Arslan and Arslan, 2002; Kodali et al., 2011).

In order to optimize resource and energy efficiency, there is an increasing need for detailed resource characterisation that goes beyond

quantitative mineralogy, and includes metal deportment, mineral association, grain and particle sizes as well as liberation (Lund and Lamberg, 2014). However, a satisfactory quantification of mineralogical and textural parameters has not been achieved for Kupferschiefer ores, mainly due to the inherently complex composition of the material. This is despite the fact that Kupferschiefer ores have been the subject of many mineralogical studies. Previous studies have typically focused on particular parameters, such as sulphide mineralogy (Kucha, 1982, 1993; Large et al., 1995; Kucha and Pryblowicz, 1999; Piestrzynski and Pieczonka, 2012), sheet silicate mineralogy (Vaughan et al., 1989; Bechtel et al., 1999, 2000), or the presence and abundance of organic carbon (Püttmann et al., 1991). Despite this abundance of detailed investigations there is an obvious lack of an holistic view of the mineralogy of Kupferschiefer-type ores.

Kupferschiefer *sensu stricto* refers to a carbonaceous black shale unit with a thickness of a few centimetres up to a meter that was deposited in response to rapid marine transgression into an intracontinental sedimentary basin during the Permian age (Wedepohl, 1964; Vaughan

http://dx.doi.org/10.1016/j.mineng.2017.10.007 Received 30 May 2017; Received in revised form 20 September 2017; Accepted 7 October 2017

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Abbreviations: XRD, X-ray powder diffraction; QXRD, Quantitative X-ray powder diffraction; MLA, Mineral liberation analysis; EDX, Energy-dispersive X-ray spectroscopy; SEM, Scanning electron microscopy; ICP-OES, Inductively coupled plasma – optical emission spectroscopy

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Fig. 1. A – XPL photomicrograph of Kupferschiefer s.s. sample P-KS-02 (left) illustrating the fine-grained texture of the sheet silicate and carbonate-rich matrix (M) with irregular lenses and layers of organic matter (C<sub>org</sub>). B – Photomicrograph in reflected light of sample P-KS-03 showing dissemination of copper sulphides (S, black arrows).

et al., 1989; Paul, 2006) in Central Europe. Stratabound sulphide mineralization is widespread along the southern margin of the sedimentary basin (Borg et al., 2012). The Kupferschiefer s.s. is bounded by a lower sandstone and an upper carbonate unit, respectively. Sulphide mineralization occurs in all three lithotypes that together comprise the geological resource of the Kupferschiefer (Borg et al., 2012). Host rock, ore mineralogy, and grade vary greatly not only between the different lithotypes, but also along local and regional trends within the different lithotypes. Ore within the German Mansfeld district, for example, is essentially confined to the Kupferschiefer s.s., in comparison to the Sieroszowice ore in Poland, where a very significant proportion is contained in sandstone and carbonate lithotypes (Wedepohl, 1964; Paul, 2006; Borg et al., 2012). The origin of the polymetallic mineralization is not well constrained, but is likely related to multi-stage diato epigenetic hydrothermal fluid flow events (Michalik and Sawlowicz, 2001; Borg et al., 2012).

The ore mineralogy of the Kupferschiefer s.s. is exceptionally complex. Styles of mineralization range from finest dissemination (Fig. 1), coarser replacement and impregnation, to vein- and breccia-hosted sulphide mineralization. More than 80 ore minerals have been described in the Kupferschiefer ore (Piestrzynski and Pieczonka, 2012), with Cu contained mostly in chalcocite-group minerals, bornite, and chalcopyrite. Other important ore minerals include sphalerite, galena, enargite, cobaltite, and tennantite (Vaughan et al., 1989; Matlakowska et al., 2012). Noble metals (Au, Ag and PGMs) occur in sulphides and as discrete minerals (Vaughan et al., 1989; Piestrzynski and Sawlowicz, 1999; Piestrzynski and Pieczonka, 2012).

A further characteristic of Kupferschiefer s.s. is the very fine-grained matrix which is composed of sheet silicates, namely illite, kaolinite, and chlorite. These sheet silicates, commonly clay sized ( $< 2 \mu$ m), can account for more than 50 wt% of the Kupferschiefer s.s. The sheet silicates are very finely intergrown with variable amounts of carbonate minerals, namely calcite, dolomite, and ankerite (Wedepohl, 1964; Bechtel et al., 2000; Matlakowska et al., 2012). Finally, Kupferschiefer s.s. contains up to 30 wt% organic matter ( $C_{org}$ ), with an average of about 5 wt% (Speczik, 1995). The organic matter has been characterized as kerogen type II, primarily of marine origin, with the addition of minor amounts of type III (Sun and Püttmann, 2004). This organic carbon forms thin bedding parallel lenses and is finely disseminated between sheet silicates and carbonate minerals (Fig. 1).

Complex mineralogy, fine-grained texture, disorder and structural variability of the clay minerals, and amorphous nature of the organic component, all pose significant challenges for the comprehensive and quantitative mineralogical characterization of Kupferschiefer ore.

In this investigation, we employ a combination of quantitative X-ray diffraction (QXRD) and SEM-based image analysis (MLA) (Fig. 2) to



Fig. 2. Schema of method-specific characteristics and advantages.

investigate pitfalls and find possible solutions for the quantitative mineralogical characterization of the Kupferschiefer s.s. The analytical methods applied are largely complementary. Minerals are identified by the attributes of their crystal structure by X-ray powder diffractometry, whilst SEM-based image analysis relies on compositional contrast in mineral chemistry. Results of quantitative X-ray powder diffractometry (QXRD) by multiphase Rietveld refinement (Rietveld, 1967; Hill and Howard, 1987) can be highly accurate and allow the quantification of abundances of minerals present down to 0.5 wt% in representative powder samples (König and Spicer, 2007; Parian et al., 2015). However, an increase in the number and crystallographic complexity of the contained minerals (Omotoso et al., 2006; Parian et al., 2015), and the presence of amorphous materials, render reliable quantification by QXRD increasingly difficult.

SEM-based image analysis (Gu, 2003), in contrast, allows the reliable identification of even trace minerals and the reliable quantification of mineral abundances well below 1 wt% (Fig. 2). Furthermore, MLA provides numerical values for microfabric attributes such as grain size and shape, mineral associations and mineral liberation. However, SEM-based image analysis does not permit differentiation of polymorphs or minerals that have a very similar mineral chemistry (e.g., chalcocite and digenite; Kehrer, 2016). An even more profound limitation of SEM-based image analysis concerns the fact that analysis is always limited to a 2D surface, rather than a 3D volume, as well as the limit of lateral resolution that can be attained during EDX analysis using an electron beam. As a result of the extremely fine grain sizes, encountered in the Kupferschiefer s.s, EDX spot analyses report compositional information not only from the mineral grain in question, but also from surrounding grains. Such mixed spectra are difficult to assign to a single mineral

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