

EFFECT OF ORGANIC MATTER ON THE COLOR OF SPHALERITE FROM THE SILESIA-CRACOW LEAD-ZINC DEPOSITS, POLAND

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Abstract. Using gas chromatography-mass spectrometry (GC-MS) sphalerite samples from lead and zinc mines of the Silesian-Cracow region were studied in terms of the effect of organic matter on their coloration. The results indicate no correlation between the abundance and chemical composition of organic matter and sphalerite coloration. TOC values for investigated samples are in the range of 0.5-1.28%. A basic feature characterizing all samples is very similar distribution of *n*-alkanes, with a predominance of short-chain *n*-alkanes (from *n*-C₁₃ to *n*-C₂₁) over long-chain *n*-alkanes (from *n*-C₂₅ to *n*-C₃₅). Among the isoprenoids pristane dominates over phytane (Pr/Ph ratio in one sample is even 8.95), which does not correspond to previous studies (Karwowski et al. 2001) and may be due to the multi-source nature of organic matter present in sphalerite inclusions from the Silesian-Cracow Zn-Pb deposits. The occurrence of hopanes with 17 β ,21 β (H) stereochemistry indicates a low maturity of test samples.

Keywords: organic matter, color of the sphalerite, Silesia-Cracow Zn-Pb deposits, GC-MS methods

Introduction

Silesian-Cracovian Zn-Pb ore deposits are commonly classified as Mississippi Valley-type (MVT) deposits (Anderson & MacQueen 1982; Sass-Gustkiewicz et al. 1982; Wodzicki 1987; Leach & Sangster 1993; Lewczuk & Symons 1995; Leach et al. 2001, 2010; Bradley & Leach 2003). These deposits are divided into four districts: Bytom, Zawiercie, Olkusz and Chrzanów (Fig. 1) and occurring mainly within the so-called ore-bearing dolomites of the Middle Triassic (Muschelkalk), while in the Zawiercie area also among carbonate rocks of the Devonian age (Cabała 2002). Coaly accumulations within the Zn-Pb deposits of the Silesian-Cracow region are well known (Althans 1891; Stappenbeck 1928; Lipiarski 1971; Krajewski et al. 1971; Kołcon & Wagner 1983; Sass-Gustkiewicz & Kwiecińska 1994, 1999; Kwiecińska et al. 1997). Additionally, the organic matter liquid inclusions in sphalerite were described by Karwowski et al. (1979) and Kozłowski (1995), however only Karwowski et al. (2001) undertook preliminary molecular geochemical studies of biomarkers from such inclusions.

Sphalerite, the cubic polymorph of ZnS, exhibits a wide range of compositional variations in natural specimens (Patrick et al. 1993; Axelsson and Rodushkin 2001; Di Benedetto et al. 2005) where other metal cations can replace Zn in the tetrahedral site. One consequence is that sphalerite is the major source not only of Zn, but also of Cd, In, Ge, and Ga. These cations may affect the color zoning in sphalerite, known from many MVT deposits.

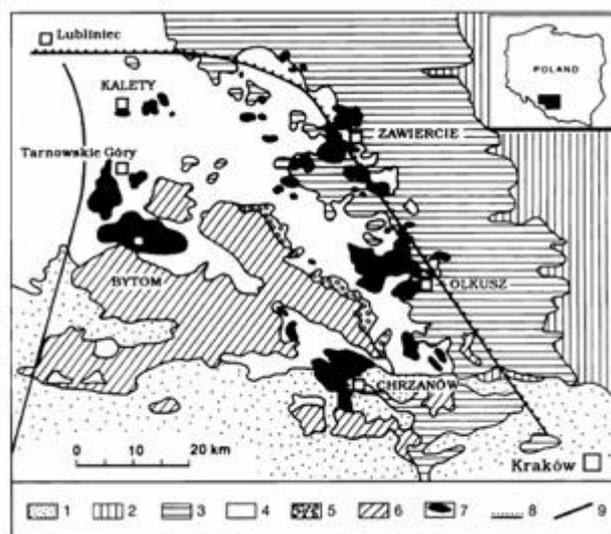


Fig.1. Geological map of Silesia-Cracow Zn-Pb ore district (after Sass-Gustkiewicz & Kwiecińska, 1999). 1 - Tertiary, 2 - Cretaceous, 3 - Jurassic, 4 - Triassic, 5 - Permian, 6 - Carboniferous, 7 - Zn-Pb ore deposits, 8 - Cracow-Lubliniec fracture zone, 9 - deep fracture.

Also organic matter (OM) occurrence within sphalerite inclusions from MVT deposits has been taken into account by some authors as a coloration trigger (Campbell 1967; Roedder 1967, Roedder & Dwornik 1968) but detailed studies has not been undertaken. This study aims

to clarify the effect of the organic matter on sphalerite color from three districts (Bytom, Olkusz and Chrzanów) of Silesian-Cracovian Zn-Pb deposits, and can provide an important data in relation to the other MVT deposits.

Material and methods

Organic matter studies have been undertaken on five samples of layered (“dark” and “light” layers) sphalerite (Fig. 2) from various localities – Pomorzany Mine (Olkusz area), Trzebionka Mine (Chrzanów area) and Orzeł Biały Mine (Bytom area). In another 6 samples of sphalerite from Pomorzany Mine and Orzeł Biały Mine, “dark” and “light” layers were separated by steel chisel and later in the study were analyzed separately.



Fig. 2. “Dark” and “light” layers in sphalerite from Pomorzany Mine. The layers were separated alongside drawn curve.

Total organic carbon and total sulfur

The total organic carbon (TOC) and total sulfur (TS) contents were determined using an Eltra CS-500 IR-analyser with a TIC module. The calcium carbonate content was calculated as $\text{CaCO}_3 = 8.333 \times \text{TIC}$, assuming that all carbonate occurs as calcite. The total carbon (TC) and total iron current (TIC) contents were measured using an infrared cell detector of CO_2 gas, which was evolved by combustion under the oxygen atmosphere for TC, and was obtained from reaction with 50% phosphoric acid for TIC. Calibration was made by means of Eltra standards. TOC content was calculated as TC minus TIC. Analyses were performed at the Faculty of Earth Sciences, University of Silesia in Sosnowiec.

Extraction and separation

The bituminous fraction of organic matter from investigated samples was extracted with dichloromethane (DCM) using an ultrasonic washer. All extracts were collected, evaporated, weighed and stored in amber glass and under freezing conditions. At the next stage, the extracts were separated into main compound groups such as aliphatic hydrocarbons, aromatic- and polar compounds. Using a standard column, the saturated fraction was eluted under gravity with *n*-pentane (1.8 ml) using small aliquots at first ($3 \times 100 \mu\text{l}$), allowing each of the aliquots of

solvent to drain down to the silica gel. After elution of saturated fraction, using a standard column, the aromatic fraction was collected by eluting with *n*-pentane/dichloromethane (7:3 v/v, 1.8 ml) using small aliquots at first ($3 \times 100 \mu\text{l}$), allowing each of the aliquots of solvent to drain down to the silica gel. After elution of the aromatic fraction, using a standard column, the polar fraction was collected by elution with methanol/dichloromethane (1:1 v/v, 1.8 ml) using small aliquots at first ($3 \times 100 \mu\text{l}$), allowing each of the aliquots of solvent to drain down to the silica gel. More details on the separation method have been published by Bastow et al. (2007).

Gas chromatography–mass spectrometry (GC–MS)

The GC–MS analyses were undertaken by an Agilent 6890 Series Gas Chromatograph interfaced to an Agilent 5973 Network Mass Selective Detector and Agilent 7683 Series Injector (Agilent Technologies, Palo Alto, CA). A $0.5 \mu\text{L}$ sample was introduced into the cool on-column injector under electronic pressure control, with helium (6.0 Grade) being utilised as the carrier gas at a constant flow rate of 2.6 mL/min. The GC separation was on either of two fused-silica capillary columns:

- (1) J&W HP5-MS (60 m \times 0.32 mm i.d., 0.25 μm film thickness) coated with a chemically bonded phase (95% polydimethylsiloxane and 5% diphenylsiloxane). The GC oven temperature was programmed from 40°C (isothermal for 1 min) to 120°C at a rate of 20°C/min, then to 300°C at a rate of 3°C/min, the final temperature being held for 35 min.
- (2) J&W DB35-MS (60 m \times 0.32 mm i.d., 0.25 μm film thickness) coated with a chemically bonded phase (65% polydimethylsiloxane and 35% diphenylsiloxane). The GC oven temperature was programmed from 50°C (isothermal for 1 min) to 120°C at a rate of 20°C/min, then to 300°C at a rate of 3°C/min, with the final temperature being held for 45 min.

The GC column outlet was connected directly to the ion source of the mass spectrometer and the GC–MS interface was kept at 280°C, whilst the ion source and the quadrupole analyser were at 230°C and 150°C, respectively. Mass spectra were recorded from m/z 45–550 (0 to 40 min) and m/z 50–700 (above 40 min), with the mass spectrometer being operated in the electron impact mode (ionization energy 70 eV).

An Agilent Technologies Enhanced ChemStation (G1701CA ver. C.00.00) and the Wiley Registry of Mass Spectral Data (8th Ed.) software were used for data collection and mass spectra processing. Analyses were performed at the Faculty of Earth Sciences, University of Silesia in Sosnowiec.

Results

The analyzed samples contains a similar amount of TOC (Table 1, Fig. 3) in the range of 0.05% to 0.18% (although in one sample from Trzebionka Mine TOC =

1.28%). There are no significant differences in TOC values between “dark” (from 0.08% to 0.1%) and “light” (from 0.05% to 0.1%) sphalerites. Total sulfur (TS) values, entirely represented by sulfide sulfur, is similar in all samples ranging from 28.5% to 32.3% (Table 1).

Table 1. The total organic carbon (TOC) and total sulfur (TS) values in examined samples.

Sample	TOC [%]	TS [%]
SFPM1	0.11	31.47
SFPS1	0.12	31.23
SFPS5	0.18	31.39
SFTR1	0.12	29.73
SFTR3	1.28	28.58
CSFPM1	0.08	31.64
CSFPM2	0.08	31.61
CSFPM3	0.08	31.94
CSFPS1	0.09	30.89
CSFPS2	0.08	31.36
CSFPS3	0.1	31.79
JSFPM1	0.05	32.21
JSFPM2	0.06	31.72
JSFPM3	0.1	31.69
JSFPS1	0.1	30.77
JSFPS2	0.09	31.65
JSFPS3	0.08	31.54

SFPM1 – sphalerite from “Pomorzany Mine”; SFPS1, SFPS5 – sphalerites from “Orzeł Biały Mine”; SFTR1, SFTR3 – sphalerites from “Trzebionka Mine”; CSFPM1-CSFPM3 – “dark” sphalerites from “Pomorzany Mine”; CSFPS1-CSFPS3 – “dark” sphalerites from “Orzeł Biały Mine”; JSFPM1-JSFPM3 – “light” sphalerites from “Pomorzany Mine”; JSFPS1-JSFPS3 – “light” sphalerites from “Orzeł Biały Mine”.

The study of organic matter extracts from the “Pomorzany Mine”, “Orzeł Biały” and “Trzebionka Mine” performed by using gas chromatography-mass spectrometry (GC-MS) revealed its immature nature.

The basic feature characterizing the investigated samples is the very similar distribution of *n*-alkanes (Fig. 4) irrespective of the sphalerite color, with a maximum at *n*-C₁₆ and definite preponderance of short-chain *n*-alkanes (from *n*-C₁₃ to *n*-C₂₁) over long-chain *n*-alkanes (from *n*-C₂₅ to *n*-C₃₅).

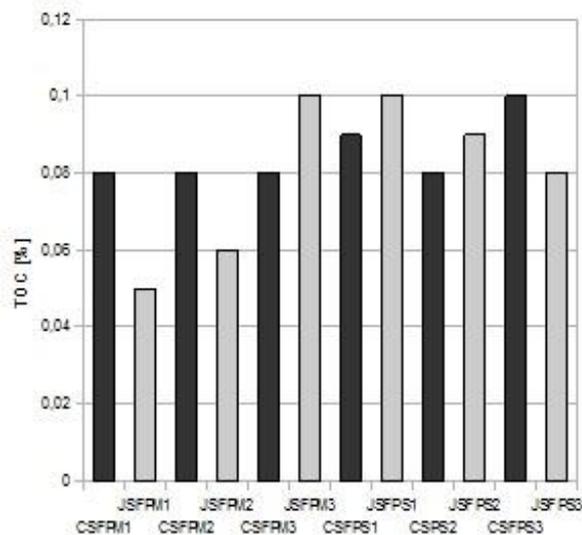


Fig. 3. The total organic carbon (TOC) values in “dark” (dark grey column) and “light” (light grey column) sphalerite samples.

Odd-to-even predominance (OEP) values (see Peters et al. 2005 and references therein) are above 1.0, however samples from “Orzeł Biały Mine” shows higher OEP values than sphalerites from “Pomorzany Mine” (Table 2). The high concentration of pristane and its domination over *n*-alkanes (see Pr/*n*C₁₇, Table 2) suggests a low degree of thermal maturity of all investigated samples. Pristane to phytane (Pr/Ph) ratios are relatively high and in the most samples are above 5 (only in one sample Pr/Ph ratio is lower but still over 1.0).

Table 2. Basic molecular parameters for “dark” and “light” sphalerites.

Sample	OEP	Pr/Ph	Pr/ <i>n</i> C ₁₇	Ph/ <i>n</i> C ₁₈
CSFPM1	1,1	5,28	6,99	1,64
CSFPS1	1,7	1,98	6,28	5,38
JSFPM1	1,09	6,36	6,94	1,32
JSFPS1	1,63	8,95	7,2	1,25

$$\text{OEP} = (\text{C}_{21} + 6\text{C}_{23} + \text{C}_{25}) / (4\text{C}_{22} + 4\text{C}_{24})$$

Pr/Ph – Pristane to phytane ratio

Pr/*n*C₁₇ – Pristane to *n*-heptadecane ratio

Ph/*n*C₁₈ – Phytane to *n*-octadecane ratio

The hopanoides distribution is very similar in all samples. Among this group, the predominant component is C₂₉ hop-(17)21-ene. Hopanes are represented mainly by 17 α ,21 β (H) and 17 β ,21 α (H) stereoisomers among which 22R epimers prevail over 22S epimers. C₃₀ 17 β ,21 β (H) is also present.

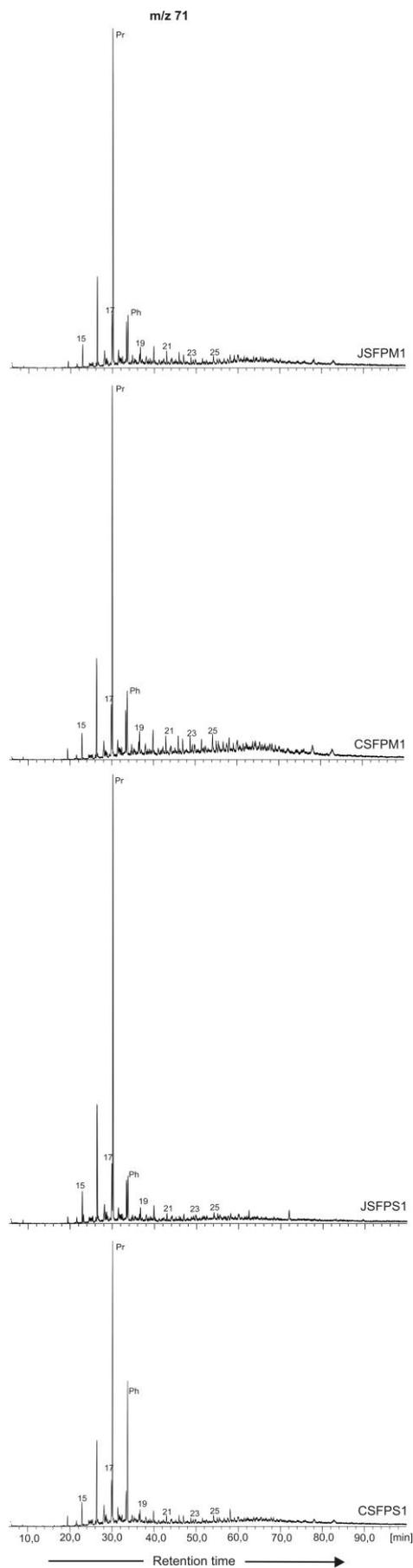


Fig. 4. *N*-alkanes distribution in test samples.

4. Discussion

The issue of coloration variability and compositional zoning in sphalerites from MVT deposits was studied by many authors (Roedder & Dwornik 1968; Hubicka-Ptasińska et al. 1983; Axelsson & Rodushkin 2001; Di Benedetto et al. 2005). Organic compounds in very low concentrations can cause intense colors, however, despite the common occurrence of the organic matter as inclusions in sphalerites from MVT deposits (e.g. Kozłowski 1995), in this study, no relationship between OM presence and sphalerite coloration has been observed. Moreover, sphalerites of different coloration from the same localities does not vary in OM abundance (see TOC values, Fig. 3) or hydrocarbon composition (Fig. 4).

Distribution of *n*-alkanes and hopanoids is similar to previous studies on organic matter in sulfides from Silesia-Cracow Zn-Pb deposits (see Karwowski et al. 2001). The presence of hopanes with 17 β ,21 β (H) stereochemistry and preponderance of R homophane epimers, confirms the low maturity of test samples and corresponds to a vitrinite reflectance equivalent to $R_0 < 0,4\%$ (Peters et al. 2005). Interestingly, isoprenoids distribution is completely different than in above mentioned study, with phytane predominance over pristan. In all investigated samples for the purpose of this study Pr/Ph ratio is relatively high (Table 2), which point to an oxic depositional environment. These significant differences may be due to a multi-sourced origin of the hydrocarbons trapped in zinc sulfide previously suggested by Karwowski et al. (2001).

Because of the lack of correlation of iron content with sphalerite coloration reported by Roedder & Dwornik (1968), the other cause of coloration can be deviation from stoichiometric ZnS composition suggested by Roedder & Dwornik (1968). Those investigators propose that intense color of sphalerite could be connected with deviations from stoichiometry and shows synthetic non-stoichiometric TiO₂ as an example.

5. Conclusions

This study excludes the possibility of the organic matter effect on the coloration of sphalerite from MVT deposits because of no correlation between OM occurrence and the color of banded sphalerite.

Therefore, the author points to the need for research into other causes of coloration, including sphalerite non-stoichiometry impact study on its color.

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Abstrakt

Przy zastosowaniu chromatografii gazowej sprzężonej ze spektrometrią mas (GC-MS) zbadano próbki sfalerytu z kopalni cynku i ołowiu regionu śląsko-krakowskiego pod kątem wpływu materii organicznej na ich barwę. Otrzymane wyniki wskazują na brak korelacji między ilością oraz składem chemicznym materii organicznej a barwą sfalerytu. Wartości TOC dla badanych próbek mieszczą się w przedziale 0.5–1.28%. Charakterystyczną cechą wszystkich próbek jest bardzo zbliżona dystrybucja *n*-alkanów, z wyraźną przewagą *n*-alkanów krótkołańcuchowych (od *n*-C₁₃ do *n*-C₂₁) nad długołańcuchowymi. Wśród izoprenoidów przistan dominuje nad fitanem (stosunek Pr/Ph w jednej próbce wynosi nawet 8.95), co nie odpowiada wynikom poprzednich badań (Karwowski et al. 2001) i może być spowodowane wielozródłowym charakterem inkluzji materii organicznej w sfalerytach ze śląsko-krakowskich złóż Zn-Pb. Obecność hopanów o strukturze 17β,21β(H) wskazuje na bardzo niską dojrzałość termiczną badanych próbek.