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DIVERSITY OF THE SULFUR ISOTOPIC COMPOSITION IN THE INDIVIDUAL SULFIDE MINERALS FROM THE COPPER LUBIN MINE, SW POLAND

INTRODUCTION

In this area ore minerals usually create dispersed deposits, veins and caverns. Sulfide minerals often associate with other minerals like: tennantie, tetraedrite; sulfates: gypsum, barite, anhydrite; and carbonates: calcite and dolomite. Sulfur isotopic composition of these sulfides has been investigated already (Jowett (1991); Sawłowicz (1989), etc), nevertheless, the next research may provide a potential source of information necessary to explain some aspects of the genesis of copper deposits.

MATERIAL AND METHODS

A hundred and four samples of sulfide minerals collected in the area of the Lubin mine were used for the isotopic studies. The ore minerals samples were purified of possible carbonates, sulfates and organic matter by the hydrochloric acid and magnetic separation method. Sulfides were subsequently transformed into SO_2 with the use of Cu_2S. Sulfur isotopic ratios were determined on modified MI-1305 mass spectrometer at Institute of Physics at Marie Curie - Sklodowska University in Lublin. Accuracy of the measurement was higher than 0,1‰. Isotopic ratios were presented with $\delta^{34}S$ in relation to the CDT standard.

RESULTS

The analyzed samples of the sulfides were collected from the Boundary Dolomite, located directly under the Kupferschiefer; from Kupferschiefer and the first 8 meters of Zechstein Limestone, located directly above the Kupferschiefer. The ore concentration in the higher parts of Zechstein Limestone are very poor or none. With growing distance from the Kupferschiefer up and down the profile, the content of sulfides in the ore body decreases. At the Lubin copper mine the Kupferschiefer and the Zechstein Limestone are the main sources of the ore-deposits. The minerals which have been separated:

- **Pyrite Fe_2S** – The samples were collected from the roof part of the Kupferschiefer and the sill part of the Zechstein Limestone. They were mostly represented by dis-

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persed forms. The values of $\delta^{34}S$ range from -44,91 to -42,01‰ (average -42,73‰ for 9 samples).

- **Chalcocite Cu_2S** – The samples were collected from the Boundary Dolomite, the Kupferschiefer, and the Zechstein Limestone. They were represented by dispersed and vein forms. The values of $\delta^{34}S$ range from -39,90 to -22,70‰ (average -33,01‰ for 13 samples).

- **Chalkopyrite $CuFeS_2$ and Bornite Cu_5FeS_4** – The samples were collected from the Kupferschiefer and the Zechstein Limestone. They were mostly represented by vein forms. Their sulfur isotopic composition is very diverse. The values $\delta^{34}S$ for Chalkopyrite range from -35,00 to -24,80‰ (average -28,89‰ for 17 samples), and for bornite from -37,20 to -23,30‰ (average -31,66‰ for 16 samples).

- **Covelline CuS** – The samples were collected from the Zechstein Limestone. They were represented by vein forms. The value $\delta^{34}S$ range from –25,10 to –23,90‰ (average –24,27‰ for 3 samples).

- **Digenite Cu_9S_5** – The samples were collected from the Kupferschiefer. They were represented by dispersed forms. The values $\delta^{34}S$ range from–38,80 to –33,36‰ (average –35,86‰ for 13 samples).

- **Galena PbS and Sfalerite ZnS** – The samples were collected from the Kupferschiefer and the Zechstein Limestone. They were mostly represented by fine-crystaline galena, and disperse sfalerite. The value $\delta^{34}S$ for galena range from –29,80 to 23,69‰(average 25,37‰ for 15 samples), for sfalerite from –31,50 to –23,55‰ (average 27,13‰ for 11 samples).

- **Tennantite $Cu_{12}Sb_4S_{13}$ and Tetraedrite $Cu_{12}As_4S_{13}$ (series)** - The samples were collected from Boundary Dolomite. They were mostly represented by vein forms. They are isotoply the heaviest among all the found minerals. The values $\delta^{34}S$ range from –10,23 to –7,68‰ (average –11,79‰ for 7 samples).

CONCLUSION

Diversity of the sulfur isotopic composition in individual minerals is very large. All the values are negative. The negative values, and such a big diversity of $\delta^{34}S$ could result from: differences in crystallochemical structure of the individual minerals (sulfides), conditions of pH – pOH, and value of $\delta^{34}S$ in H_2S. The source of sulfur in the particular sulfides was H_2S, produced probably as a result of a bacterial reduction of sulfates (Michalik, Sawłowicz 2000). It is possible that these sulfides were created in a progressively closing system (Nielsen 1985). The lightest sulfides like pyrite ($\delta^{34}S$ value are very close Jowett (1991b), Sawłowicz (1989)), were formed at the beginning when the access to sulfates was practically unlimited. Progressively when the system was closing, the access to sulfates was more and more limited; isotoply heavier H_2S was being formed and heavier sulfides followed. And so we can advance a hypothesis that pyrite was a mineral formed in the early stage of the producing of the polymetallic ore deposits, while the mineral series tennantite-tetraedrite is the one that was formed at the last one. We should notice that there is a big diversity of the sulfur isotopic composition within the same mineral e.g. chalcocite or bornite. It may prove that the process of formation the ore mineralization was prolonged, multi-staged and multi-phased (Michalik, Sawłowicz 2000).

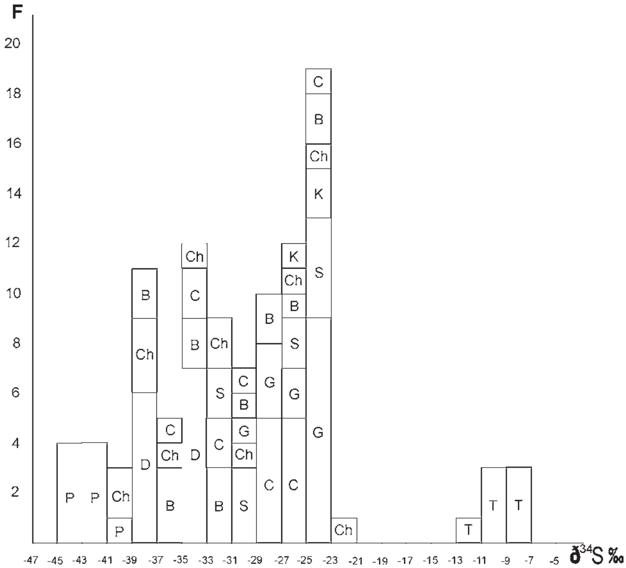

Fig. 1 Histogram of sulfur isotope composition of sulfide minerals, Lubin copper mine. *P-pyrite; Ch- chalcocite; D-digenite; B-bornite; C-chalkopyrite; S-sfalerite; G-galena; K- covelline; T-tennantite-tetraedrite*

Zechstein evaporates could be the second source of sulfur in the later stage of composing the sulfide mineralization, which explains the improvement of younger minerals in a heavier isotope (for Permian evaporates $\delta^{34}S$=10‰). The isotope research proved that the process of forming the polymetallic ore deposits on the Sudetic Monocline was very long and very complicated.

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