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SULPHUR ISOTOPIC STUDY OF DÚBRAVA ANTIMONY DEPOSIT, NÍZKE TATRY MTS., CZECHOSLOVAKIA

(4 Figs., 2 Tabs.)

Abstract: Sulphur isotope investigation on sulphides and sulphates from various mineralization stages was applied to reveal the genetical aspects of ore formation of Dúbrava antimony deposit, hosted by granodiorites of Hercynian age. δ^{34}S values for pyrite increase from first stage to the third period of second ore stage from 0.6 to 6.3 ‰ per mil indicating dilution of the ore fluids due to crustal contamination in the later stage of mineral deposition. The whole range of δ^{34}S values determined for all sulphide studied (stibnite, sphalerite, pyrite) is a little wider from −1.7 to +6.3 ‰ per mil and may suggest derivation of ore fluid from granitic magma. The barite which was deposited in the last two mineralization period of second ore stage shows δ^{34}S range from 18 to 30,8 ‰ per mil. These values may be explained by dual source of sulphate sulphur – one was from oxidizing sulphidic ore fluid and second was probably derived from the leaching of evaporitic sequences or from hypersaline water of marine origin.

Key words: sulphur isotopes, sulphides, sulphates, Dúbrava antimony deposit.

Introduction

The isotopic ratio of sulphur in sulphides and sulphates are used for the interpretation of the genesis of any ore deposit. Application of the stable isotope geochemistry to the ore deposit research has been based on the understanding of the mechanism and magnitude of the isotope fractionation that accompany various geological processes. The interpretation of the sulphur isotope data is have been changed from time to time.

The Dúbrava antimony deposit is located on the northern slopes of Nízke Tatry Mts. in S-W direction a few km away from Liptovský Mikuláš town in Central Slovakia (Czechoslovakia). This deposit is of vein type which is hosted by granodioritic rocks of Hercynian age. This deposit is petrographically devided into two main ore stages. These stages, especially second ore stage is divided into four mineralization periods (Chovan, 1989). The first ore stage is composed of scheelite-molybdenite-pyrite mineralization. The first mineralization period of second ore stage is consisted of arsenopyrite-pyrite, second period is by sphalerite-stibnite-zinkenite-pyrite, third period is represented by tetrahedrite-pyrite-barite? and last period is by barite.

On the basis of main sulphide minerals (pyrite, stibnite, sphalerite) and sulphate (barite) occurrences and their sulphur isotopic composition authors discussed the origin of the ore fluids in Dúbrava antimony deposit.

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Analytical procedure

Pure sulphides and sulphate concentrate are separated by first of all from bromoform and afterwards by handpicking under the binocular microscope. The purity of sulphides and sulphates minerals are around 99.5 %. For the sulphur isotope analysis of sulphides, the sulphides were oxidized with cuprous oxide, by which sulphur dioxide obtained for analysis, which are enclosed in the sealed capsules.

For barite, first of all the samples of barite are mixed with 50 ml of acidic mixture of H_3PO_4, HI and concentrated HCl kept in the small phlask and heated up to 48 hours. One small phlask, which is attached with back cooling system (with pure nitrogen) from which H_2S passed to one cylinder which contain $Zn(CH_3COO)_2$, where H_2S converted into ZnS. This ZnS is later on burned with cuprous oxide to produce SO_2 which is later on analysed for sulphur isotope.

All the sulphur isotope data are reported in the usual per mil (‰) deviation from the Canon diablo troilite(CDT) standard. All the sulphur isotope analysis were performed on Finnigar-Mat-250 mass-spectrometer in the isotope laboratory of Dionýz Štur's Institute of Geology, Bratislava.

Results and discussion

The sulphur isotope analysis of various sulphides and sulphates, mainly stibnite, sphalerite, pyrite and barite are listed in Tab. 1 and Tab. 2. The total isotopic compositional variation in the Dúbrava antimony deposit is shown in the Fig. 1. The average compositional variation of sulphur isotope in sulphides and sulphates is very wide from −1.7 to +30.8 ‰ per mil. The lightest isotopic composition is recorded from sphalerite is −1.7 ‰ and the heaviest isotopic composition from barite is +30.8 ‰ per mil.

The isotopic composition of pyrite, according to petrographical observations in various mineralization period from two stages in the deposit, is showing increasing trends in $\delta^{34}S$ values from +0.6 to 6.3 ‰ per mil up to third period of mineralization of second ore stage. The $\delta^{34}S$ value of +0.6 ‰ is observed in the first ore stage, where the pyrite is associated with scheelite mineralization while +6.3 ‰ is observed in the third period of mineralization period of second ore stage ,where pyrite is associated with tetrahedrite mineralization. The variation in isotopic values of sulphur in pyrite can be seen from Fig. 2.

From Fig. 2. it can be observed that the variation in the first ore stage is very narrow (+0.6 to +1.9 ‰), average spread is only of 1.3 ‰ per mil. In the Dúbrava deposit second ore stage is devided into four mineralization periods. Among them, the first mineralization period has $\delta^{34}S$ value of +4.9 ‰, which is associated with arsenopyrite-pyrite mineralization. The second mineralization period is of economic importance in which stibnite, sphalerite and other sulphosalts are formed besides pyrite deposition have shown also narrow spread (+2.8 to 6.1) average spread about 3.3 ‰ per mil. The third period of mineralization shows also very narrow spread (+4.1 to 6.3 ‰). The fourth period of mineralization is associated with barite. In this period generally there is pausity of pyrite, if pyrite is present then in very minute amount so it is not possible to extract pure pyrite for sulphur isotope analysis. However, average all spread in isotopic values is very narrow about 3.6 ‰ per mil in all over the deposit from first ore stage up to third mineralization period of second ore stage.

Sphalerite, which was analysed from all over the length of the deposit, shows range of $\delta^{34}S$

Table 1

Sulphur isotopic composition of sulphides and sulphates from the Dúbrava deposit

S. No.	Location	δ^{34} S ‰ per mil		
		Stibnite	Sphalerite	Barite
1	Flotačná adit		+3.5	
2	Rakytova adit		+2.5	
3	Dogmár vein		+3.7	
4	Svätopluk adit		−0.3	
5	Predpekelná adit		−1.7	
6	Dogmár vein	+4.6		
7	Dogmár vein	+3.2		
8	Dogmár vein	+2.7		
9	Dogmár vein	+5.1		
10	Dogmár vein	+3.7		
11	Dogmár vein	+3.1		
12	Dogmár vein	+2.2		
13	Dogmár vein	+2.2		
14	Dogmár vein	+3.9		
15	Predpekelná adit	+3.1		
16	Predpekelná adit	+3.7		
17	Predpekelná adit	+1.7		
18	Predpekelná adit	+3.1		
19	Flotačná adit	+3.1		
20	Rakytova adit			+26.9
21	Dogmár vein			+26.5
22	Dogmár vein			+25.3
23	Dogmár vein			+30.8

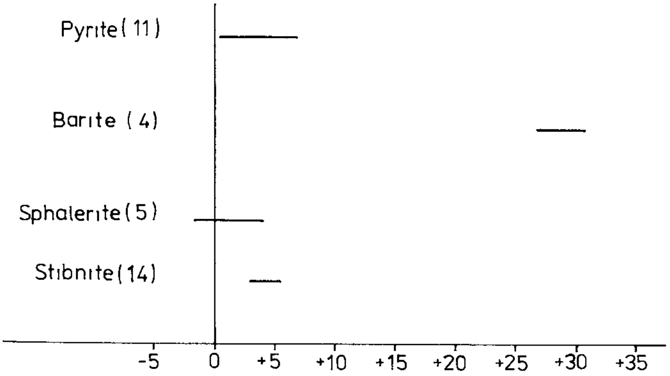

Fig. 1. Average spreading of δ^{34}S values in sulphides and sulphates from the Dúbrava deposit.

Table 2

Sulphur isotopic composition of barite, according to ore formation stage and mineralization periods from the Dúbrava deposit

S. No.	Location and sample description	δ^{34} S ‰ per mil			
		First ore stage	Second ore stage		
			Istperiod	IIndperiod	IIIrdperiod
1	Rakytova adit, associated with scheelite-molybdenite mineralization	+1.6			
2	Rakytova adit, associated with scheelite-molybdenite mineralization	+1.9			
3	Rakytova adit, associated with scheelite-molybdenite mineralization	+0 8			
4	Rakytova adit, associated with scheelite-molybdenite mineralization	+0.6			
5	Dogmár vein, associated with arsenopyrite mineralization		+4.9		
6	Dogmár vein, associated with sphalerite-zinkenite-stibnite mineralization			+5.5	
7	Ľubelská, associated with sphalerite zinkenite-stibnite mineralization			+6.1	
8	Svàtopluk adit, associated with sphalerite-zinkenite-stibnite mineralization			+5.4	
9	Flotačná adit, associated with sphalerite-zinkenite-stibnite mineralization			+2.8	
10	Ignác adit, associated with tetrahedrite mineralization				+4.1
11	Flotačná adit, associated with tetrahedrite mineralization				+6.3

values from −1.7 to 3.7 ‰ per mil. The average spread is about 4 ‰ per mil. Stibnite, which has close association with sphalerite shows δ^{34}S values spread over +1.7 to 5.1 ‰ per mil with an average spread of 3.4 ‰ per mil values. In stibnite, only one sample from Dogmar vein shows the maximum value and the lowest value of sulphur isotope is recorded from Predpekelná adit of Dúbrava deposit.

Barite is the only sulphate mineral found in the deposit area, which represented the last stage of mineral paragenesis. Barite shows heavy enrichment in δ^{34}S values, which ranges from +25.3 to 30.8 ‰ per mil. The barite also shows narrow spread of 5.5 ‰ per mil. All over the deposit the average spreading in sulphides of sulphur isotopic composition of only 3.2 ‰ per mil.

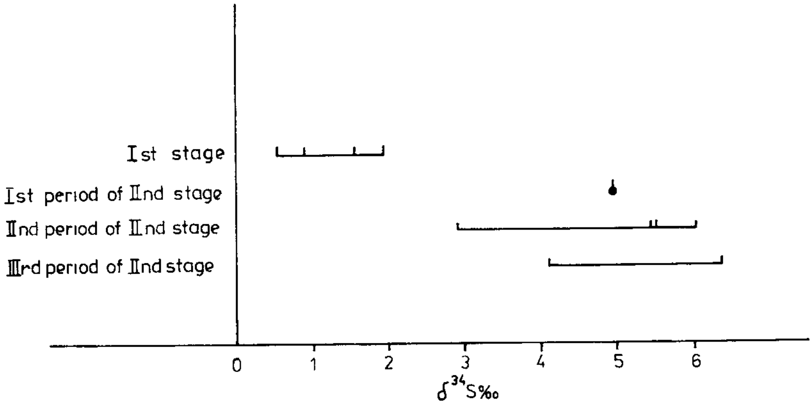

Fig. 2. Variation in $\delta^{34}S$ values in different generations of pyrites from the Dúbrava deposit.

Chemical environment of deposition

The temperature of mineral deposition were probably in the range of 250 ± 50 °C and may have decreased with time. Such a temperature range is consistent with a measured filling temperature of fluid inclusions in the quartz gangue mineral associated with sulphide or sulphate mineral deposition.

In the Fig. 3, the stability field of minerals at the time of deposition is shown. The $\delta^{34}S$ contours are drawn for $\delta^{34}S_{\Sigma S}$ ‰ per mil and indicating the isotopic composition of barite, pyrite and sphalerite. The stability fields for pyrite, pyrrhotite, magnetite and hematite at $\Sigma S = 0.01$ m are also shown. The cross-hatched area in the figure indicate the probable environment of deposition of Dúbrava deposit. The associated gangue mineral assemblage at the deposit is quartz-sericite-chlorite-carbonate. The appearance of carbonate mineral suggest formation under higher pH condition (Fig. 3).

None of the above mentioned facts take into account of dropping temperature during sulphide or sulphate deposition and changes in f_{O2} due to mixing of ore fluids with seawater (e. g. Sata, 1973). Large (1977) observed that the mixing of ore fluids with seawater results in an increase in pH, f_{O2} and ΣS, together with fall in the temperature and leads to the mineral precipitation of pyrite-sphalerite ± galena assemblage around the hydrothermal vent on the sea floor. Such a theory may be applicable for Dúbrava deposit but in the deposit area no occurrence of galena is observed by authors.

Source of sulphur

The stibnite composition ranges from +1.7 to 5.1 ‰ per mil of sulphur isotope with an average spread of 3.4 ‰ per mil. Most of the values of $\delta^{34}S$ in stibnite is concentrated around. 2.9 ‰ per mil. As Coleman (1977) and Robinson–Farrand (1982) pointed out that the igneous type of samples of granite have $\delta^{34}S$ values in the range of −3.6 to +5 ‰ per mil.

So in the case of Dúbrava deposit sulphur for stibnite deposition was derived from igneous source, where all the mineral deposition is hosted by granodioritic rocks. As Kantor (1974) pointed that the Pezinok antimony deposit is the combination of epigenetic and synsedimentary processes, but in the Dúbrava deposit the source of sulphur for sulphide deposition is

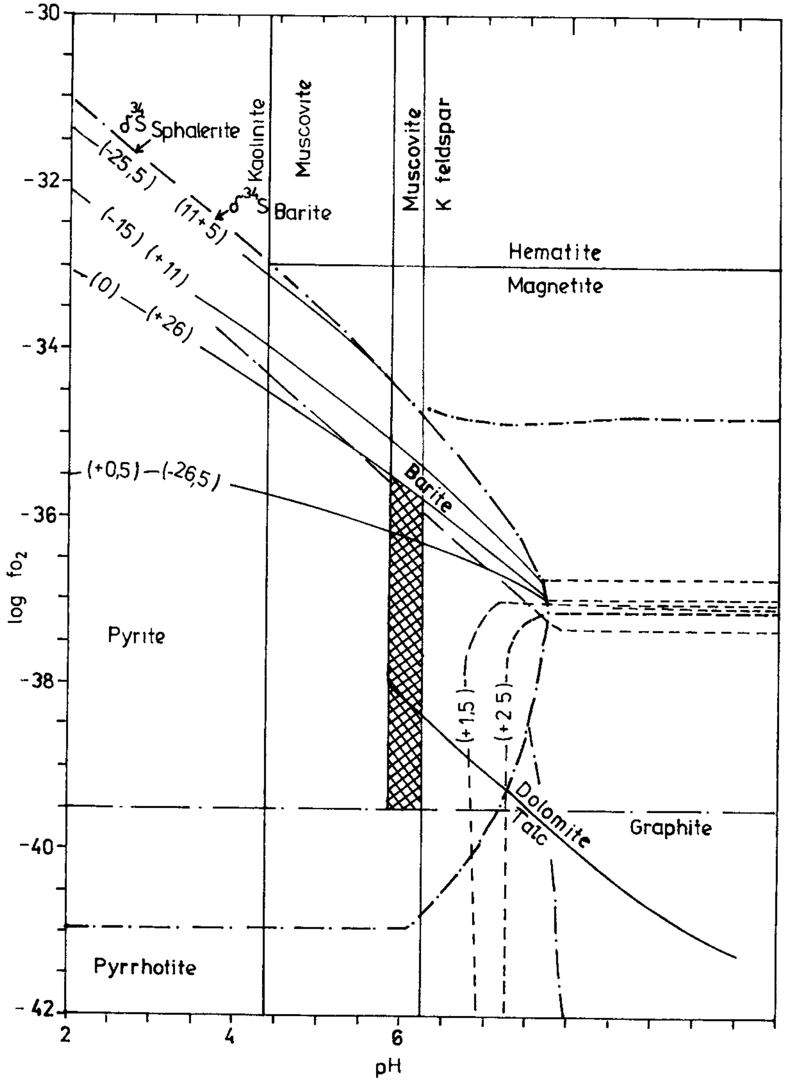

Fig. 3. A log f_{O_2} pH diagram for the Dúbrava ore deposit.
Sulphur isotope contours (fine solid lines and dashed extensions) are drawn for $\delta^{34}S_{\Sigma S} = 0$ ‰ per mil, T = 250 °C, ionic strength = 1, and $m_{K^+} = 0.1$ m, $Ba^{2+} = 10^{-3}$ m (after Rye– Ohmoto, 1974). The talc-dolomite boundary for $H_4SiO_4 = 10^{-2}$ m, $Ca^{2+} = 10^{-2}$ m and $C = 10^{-1}$ (after Large, 1975). Cross-hatched area is showing depositional environment for the Dúbrava deposit.

probably mantle derived, because all the values have concentrated around 0 ‰ per mil with an average value of 3.2 ‰ per mil. As the pyrite from the first ore stages shows distinctly average value of 1.2 ‰ per mil, which indicate that the sulphur derived form homogeneous mantle magma source, which is having probably granitic composition.

The later on enrichment of sulphur in $\delta^{34}S$ values in the younger generation of pyrite indicating the mixing of marine water or crustal sulphur. The sphalerite, which also shows narrower spread in ^{34}S values indicating igneous derivation of sulphide sulphur.

As in the whole figure of isotopic composition of sulphides show narrow spread (Tabs. 1 and 2). By utilization of sulphur isotope data and fluid inclusion temperatures, the range of $\delta^{34}S_{H_2S}$ value for the deposit is calculated to be −1.7 to 5.1 ‰ per mil, but the sulphur isotopic composition of total sulphur in the solution ($\delta^{34}S_{\Sigma S}$) in the Dúbrava deposit may differ form $\delta^{34}S_{H_2S}$ value as also observed by So et al., (1983) and by Shelton et al. (1980), too.

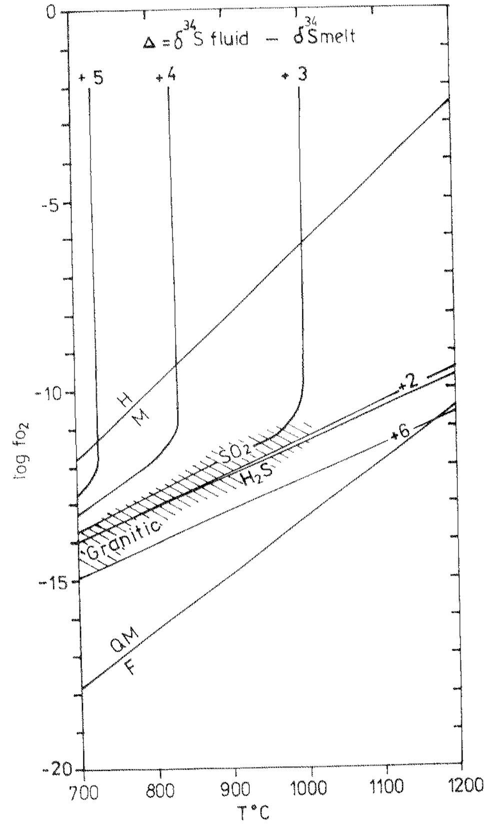

Fig. 4. A log f_{O_2} versus temperature diagram showing sulphur isotope fractionation between magmatic fluids and hydrothermal granitic melts at P_{H_2O} = 1 Kb (after Ohmoto–Rye, 1979). SO_2/H_2S line is an equal activity boundary. F = fayalite, H = hematite, M = magnetite, Q = quartz.

Ohmoto–Rye (1979) have shown that the isotopic composition of sulphur in a magmatic fluid with a hydrous melt of granitic composition (log f_{O_2} = 12.1000 bars, 800 °C and an initial melt value of $\delta^{34}S$ near to 0 ‰ per mil) will have $\delta^{34}S$ fluid value near to 3 ‰ per mil. As the total average value of sulphide minerals are 3.2 ‰ per mil from Dúbrava deposit. It is therefore tempting to interpret the source of sulphur is an igneous source, probably from associated granodioritic intrusion. The small variation in the f_{O_2} of the melts could result in a marked difference of $\delta^{34}S$ values of sulphur in a magmatic fluid in equilibrium with the melts (Fig. 4).

For the consideration of the source of sulphate sulphur, which caused the barite deposition in the deposit area at the last stage of depositional process. The barite shows heavy enrichment in $\delta^{34}S$ values, which are considerably different from sulphidic sulphur isotopic composition. The earlier values for barite from Dúbrava deposit were reported by Kantor–Ďurkovičová (1977) ranges from +18.3 to 33.3 ‰ per mil. As in this study, the $\delta^{34}S$ values show quite heavy enrichment of sulphur upto 30.8 ‰ per mil. If authors take earlier reported values into consideration in explaining the source of sulphur for barite deposition. The possible explanation of the barite $\delta^{34}S$ values involves a dual sulphate source. The light sulphate probably was derived from the oxidation of the aqueous sulphide in the sulphidic ore fluid. Some occurrences of sulphide mineral in the proximity of barite indicate local presence of H_2S there during mineralization process. Variable incorporation of H_2S derived sulphate at a $\delta^{34}S$ value around 16 ‰ per mil with heavier sulphate ($\delta^{34}S$ values at least between 30–34 ‰ per mil) (Kaiser et al., 1987). The same case is observed in $\delta^{34}S$ values of barite from Dúbrava deposit, which can account for the observed range of barite $\delta^{34}S$ values.

The isotopically heavy sulphate was present at the depositional site, which was the product of an oxidizing subsurface fluid, which derived from equally heavy sulphate containg sea water or may be from evaporitic rocks and may be deposition of such heavier sulphatic barite caused by barite-precipitation-dissolution process that cycles barium between oxygenated and reduced zones in either redox-stratified wet sediment or sea water (Cecile et al., 1983) which may be one explanation for the heavy isotopic values of sulphate sulphur observed in the deposit. The same type of view regarding the occurrence of heavy and light isotopic sulphate were expressed by Shanks et al. (1987)

Conclusion

The sulphur isotopic study in the Dúbrava antimony deposit of various sulphide minerals revealed that the source of sulphur was igneous derived from mantle probably the granitic magma having homogeneous composition, but later on enrichment in $\delta^{34}S$ values of sulphide minerals indicating some crustal contamination.

The sulphate mineral barite, which was deposited from the mixing of two sulphate sources as evidenced given by sulphur isotopic values in the barite samples.

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The first author is responsible for language correctness.