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ISOTOPIC COMPOSITION OF SULPHUR, CARBON AND OXYGEN IN MINERALS OF THE RUDŇANY SIDERITE — BARITE POLYMETALLIC ORES

(Figs. 3, Tabs. 2)

A b s t r a c t: In the presented paper an information on isotopic composition of carbon, oxygen and sulphur in carbonates including siderite, in sulphides and barite from veiny siderite-barite deposits of hydrothermal genesis from the Rudňany ore field in Spišsko-gemerské rudohorie Mts. is given. On the basis of oxygen and carbon isotopes it has been verified that both elements are of deep origin in the above-mentioned minerals. Sulphur has plutonogenous character in individual minerals and exogenous or mixed character in the others, especially in sulphate ions. Zonality in distribution of $\delta\ ^{34}S$ with depth has been proved. Carbon isotopes in fine-grained siderites occurring near the veins have not confirmed a synsedimentary origin of these siderites, but a hydrothermal-metasomatic origin.

Р е з ю м е: В статье дается информация о изотопном составе углерода, кислорода и серы в карбонатах и сидерите включительно, в сульфидах и барите из жильных сидерит-баритовых месторождений гидротермального генезиса из рудного поля Рудняны в Спишско-гемерском рудогорье. На основании изотопов кислорода и углерода было подтверждено, что оба элемента в вышеприведенных минералах глубинного происхождения. Сера в отдельных минералах плутоногенного и в других экзогенного или смешанного характера, прежде всего в сульфатных ионах. Была подтверждена зональность в распределении $\delta\ ^{34}S$ с глубиной Изотопы углерода в мелкозернистых сидеритах, встречающихся близ жил, не подтвердили синседиментационное происхождение этих сидеритов, а происхождение гидротермально-метасоматическое.

Introduction

Isotopic studies for this work have been carried out in three institutions:

a) D. Štúr Geological Survey in Bratislava (team of workers led by Ing. Dr. J. K a n t o r, CSc.),

b) the Department of Geochemistry of Stable Isotopes, Institute of Geochemistry and Physic of Minerals in Kiev (IGFM - AN Ukr. SSR., under the guidance of F. Ž u k o v, DrSc.), and

c) the Laboratories of the Geological Survey, Prague (team leader Ing. V. Š m e j k a l, CSc.).

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The results of analyses are listed in Tables 1 and 2 and represented in graphs 1, 2 and 3.

As the results of isotopic analyses obtained in the two Czechoslovak research centres (in Bratislava and Prague) and in the IGFM (in Kiev) proved to be essentially consistent, they can be regarded as satisfactorily checked and verified.

One od the most important objectives of the isotopic studies of elements C, S and O was to elucidate the genesis of the siderite-barite and sulphide mineralizations in the Rudňany ore field.

Basically relevant for the genesis of siderites are carbon and oxygen isotopes of fine-grained siderite, which could be considered as lithological, primarily sedimentary syngenetic carbonate. However, it also may represent hydrothermally metasomatically sideritized wall rock in the proximity of siderite veins.

Carbon isotopes

It should be noted that unequivocal determination of the genesis and derivation of carbon in siderites is an intricate problem the interpretations of which may more or less differ. According to one theory, the carbonate with the mean value of $\delta^{13}C$ equal to -5.0 ‰ originated from carbon dioxide of deep origin (G a l i m o v, 1968; O h m o t o — R y e, 1979), but opinions also exist that the carbon of deep origin is isotopically lighter. A l l a r d (1982) regards as typical mantle carbon of rift zones such a carbon whose $\delta^{13}C$ value is -6.5 ± 0.5 ‰, and considers the $\delta^{13}C$ values between 0 and -5 ‰ to be "crustal", i.e. influenced by sedimentary carbon. Whereas Š u k o l j u k o v (1980) gives for average deep-seated carbon $\delta^{13}C = -7.0$ ‰ and P o l j a k o v — S e l e c k i j (1982) -7 to -8 ‰, D e i n e s — G o l d (1973) report a relatively broad spread of -3 to -7 ‰. If we accept e.g. a $\delta^{13}C$ Value of -6.5 ‰ for the deep-seated carbon, the mean $\delta^{13}C$ of the Rudňany siderite equal to -4.2 ‰ could be interpreted in terms of a mixture of ca. 2/3 deep carbon with $\delta^{13}C = -6.5$‰ and ca 1/3 sedimentary carbon with $\delta^{13}C = +1$ to 0 ‰. In this case a deep-seated source could be assumed for the carbon in question, partly affected by carbon of sedimentary origin. Whatever interpretation is applied, the scatter of $\delta^{13}C$ values in the Rudňany siderites is very small. The opinion on a high degree of homogeneity of CO_2 and its deep origin is therefore correct, although the influence of several sources, not always of deep origin, is to be admitted. They must show themselves in particular during metasomatic alterations of wall rocks by hydrothermal solutions.

Isotopic composition of carbon in siderite veins of the Rudňany ore district invariably exhibits a small spread of $\delta^{13}C$ values -3.6 to -5.0 ‰), which is a sign of a relatively homogeneous source of CO_2 and virtually excludes any effect of organic matter.

The small range of changes in $\delta^{13}C$ of carbonates from siderites provides evidence for stable physico-chemical parameters during the genesis of ores. The stable values of pH and Eh in solutions were also maintained by the carbon in which the Devonian, Carboniferous and Permian sedimentary complexes are enriched.

In connection with the data given above we present here information on

palaeothermometric measurements conducted during the study of minerals of the Rudňany ore veins.

Palaeothermometric studies on these veins have been made only to a limited extent. On the basis of homogenization of gas-liquid inclusions, V a r č e k (1968) gives a temperature interval of 140—170°C (locally 200°C) for the genesis of barite, 140—165°C for siderite and 155—200°C for quartz, which indicates a relatively low-temperature character of mineralization. Temperatures of decrepitation (E l i á š — V a r č e k in V a r č e k, 1973) vary within intervals of 170—230°C for barite, of 240—280°C for siderite, and of 155—300°C for quartz. Decrepitation temperature of siderite increases with depth and thus the geothermal gradient of 1°C/10—13 m could be deduced for the hydrothermal solution.

R o j k o v i č (1977) inferred from the results of measurements made by the homogenization method the following temperatures for the genesis of quartz: 125°C — Droždiak vein, horizon XIII; 149 and 156°C — Droždiak vein, horizon XIX; 204°C — Zlatník vein, horizon X.

Sulphur isotopes

The ratio of isotopes of sulphur from the Rudňany deposits varies greatly in individual types of sulphides and in different generations of pyrite as well. The values of $\delta^{34}S$ range within the interval of +7.4 to −9.40 ‰ (Tab. 1). Analyses of pyrites (Fig. 1) show that $\delta^{34}S$ values fluctuate about the meteoritic standard, i.e. from +2.5 to −2.0 ‰. A few samples have the value of +4.6 ‰, one +7.4 ‰, and to two others +9 ‰ and 12 ‰, respectively. The last value belongs to pyrite from younger carbonates. The low $\delta^{34}S$ values of pyrites suggest that fluids of deep origin could also have been a source of ore-forming solutions, which possibility is also indicated by the $\delta^{13}C$ values of siderite. Isotopic composition of sulphur in pyrites shows sporadically an increased amount of heavy isotope $\delta^{34}S$ (+4.5; +7.4; +9; +12 ‰). This increase might be due to the filtration of hydrothermal solutions through sulphate-bearing, especially Palaeozoic strata. Isotopic composition of sulphur in barite from the Rudňany district yields $\delta^{34}S$ values of +9 to +18 ‰. Such values are broadly characteristic of sulphur from the Devonian to Carboniferous and Permian evaporites.

Investigations have shown that the different isotopic composition of pyrite and sulphides of non-ferrous metals is common. Pyrites behave rather "conservatively", not adapting readily to the new chemical and isotopic equilibrium; frequently they belong to another (earlier) minerogenetic phase. Also other, e.g. kinetic, causes resulting from a lower mobility of pyrite (FeS_2) might be taken into consideration.

Ultrabasic rocks usually contain pyrites or pyrrhotites whose isotopic composition approaches the meteoritic standard. The action of solutions rich in CO_2 caused decomposition of pyrites under simultaneous liberation of hydrogen sulphide, which became a source of sulphur for sulphides having $\delta^{34}S$ equal or near to 0 ‰.

Measurements of $\delta^{34}S$ in barites provided values from +9 to +18.2 ‰, i.e. values characteristic of marine sedimentary evaporites. Solutions with a high

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Table 1

Isotopic composition of minerals of the Rudňany deposit

No.	Identification of the sample	Locality	Main minerals of the sample	Barite		Siderite (Carbonate)		Sulphide	Author
				δ^{34}S	δ^{18}O	δ^{13}C	δ^{18}O	δ^{34}S	
1	2	3	4	5	6	7	8	9	10

Rudňany, Droždiak vein, overlying stratum

No.	Ident.	Locality	Main minerals	δ^{34}S	δ^{18}O	δ^{13}C	δ^{18}O	δ^{34}S	Author
1	R-66	I/S	Sd, Tt, By	—	—	−4.5	−10.9	—	(3)
2	R-74	II/S	By, Sp, A, Su	+18.1	+13.9	—	—	+2.5	(2)
3	R-13a	II/V	Ch, By, Ko	—	—	—	—	−1.3	(3)
4	R-14	II/V	Sd, By, o. h.	+15.3	—	—	—	—	(2)
5	R-14a	II/V	Sd, By, o. h.	+15.7	+14.6	−4.0	−10.3	—	(4)
6	R-70	II/V	Sd, By	+15.9	+13.9	−4.2	−10.0	—	(3)
7	R-1	III/V	Sd, By	+13.3	—	—	—	—	(3)
8	R-4	III/V	Sd, Q, Su	—	—	−5.0	—	—	(4)
9	R-5	III/V	Sd, Q, Su	—	—	−4.5	—	+0.2	(2)
10	R-8	III/V	Sd, By, Tt	+18.0	+14.1	−4.6	−11.0	—	(2)
11	R-12	III/V	Sd, Q, Su	—	—	−4.5	—	—	(3)
12	R-99	IV/S	Sd, By	+16.4	+15.3	—	—	—	(2)
13	R-119a	IV/S	By, Sd	—	—	−3.6	—	—	(3)
14	R-121	IV/S	Sd, He, Su	—	—	−0.5	—	—	(2)
15	R-96b	VIII/S	Sd, Tt	—	—	−4.5	− 9.6	—	(2)
16	R-95	X/V	Py, Sp, Sd, A	—	—	−4.3	−12.5	+0.2	(3)
17	R-75	X/S	By, Sd, Ch	+18.2	—	−5.0	—	—	(2)
18	R-75a	X/S	By, Sd	+14.1	+13.9	—	—	—	(2)
19	R-93	X/V	Ch, Sd, Py	—	—	—	—	+0.0	(3)
20	R-76	X/S	Sd, Tt, Ch	—	—	—	—	−6.4Ch −8.0Tt	(2) (4)
21	KR-51	X/V-Bl.	Sd, By	+14.5	+14.8	−4.0	− 9.4	—	(2)
22	KR-55	X/V-Bl.	Sd, By, Su	+14.3	+14.2	−4.3	−14.7	—	(3)
23	KR-59	X/V-Bl.	Sd, By	—	—	−4.1	−10.2	—	(3)
24	KR-46	X/V-Bl.	Sd, By	+14.4	+14.1	—	—	−4.5TtCh	(3)
25	24/75/I/	X	—	—	—	—	—	−4.4Tt	(1)
26	R-31	XIII/Z	Sd, Q, Su, Ch, Tt	—	—	−4.7	—	−4.3	(2)
27	R-28	XIII/Z	Sd, Su	—	—	−4.7	—	−8.2ChtT −7.3	(4)
28	R-26	XIII/Z	Sd, By, Su	—	—	−4.0	—	—	(2)
29	R-84	XIII/Z	Sd, R, Py, By	—	—	—	—	+0.4	(2)
30	R-45	XIII/Z	Tt, Sd	—	—	—	—	−4.4	(4)
31	R-209	XIII/Z	Q-Fu rock with Py	—	—	—	—	+0.4	(4)
32	R-378	XIII/S	Ch	—	—	—	—	−0.7	(2)
33	R-58	XIII/S	Ch, Sd	—	—	4.3	—	+0.0	(2)
34	R-112	XIII/S	Sd	—	—	−3.9	−11.8	—	(3)
35	R-326	XIII/S	Fu-Q-K rock	—	—	−4.9	−11.1	—	(3)
36	FR-73	XIII/S	Se-Q-K rock	—	—	—	−12.1	—	(3)
37	R-90	XIII/V	Sp, Ch, Sd, A Py	—	—	—	—	+0.0	(2)
38	R-92	XIII/V	Ch, Sp, A, Sd, Py	—	—	—	—	+2.4	(2)
39	26/75/2/	XIII	Tt	—	—	—	—	−2.6	(1)

1	2	3	4	5	6	7	8	9	10
40	29/75/6/	XIII	Tt	—	—	—	—	−0.7	(1)
41	R-372	XIII/S	Se-Q-K	—	—	−3.6	−12.5	—	(3)
42	R-47	XVI/Z	Sd, Sp	—	—	−4.7	—	—	(2)
43	R-48	XVI/Z	Sd, Py	—	—	−3.8	—	−1.7	(2)
44	R-105	XVI/S	Sd, Ch	—	—	−3.8	—	+4.6	(2)
45	R-85	XVI/S	A, Sd, Py	—	—	—	—	+0.0	(2)
46	R-61	XVI/S	Tt, Sd	—	—	—	—	−3.3	(4)
47	R-228a	XVI/S	Fu-Q-K rock	—	—	−3.4	−11.9	—	(3)
48	27/75/4/	XVI	—	—	—	—	—	−3.6	(1)
49	R-342	XIX	Chl-Q-K rock	—	—	−4.5	−14.9	—	(3)
50	FR-225	XIX	Fu-Q-K(Do) rock	—	—	−4.3	−12.4	—	(3)
51	R-336	XIX	Fu-G rock with Py	—	—	—	—	−0.8	(3)
52	R-341	XIX	Fu-Q-K rock	—	—	−3.9	−11.6	—	(3)

Rudňany, Zlatník vein

53	Zl-3	Zlatník gallery	Tt, Sd, By	—	—	—	—	−9.1	(4)
54	Zl-9/1	—||—	Tt, Sd	—	—	—	—	−9.4	(4)
55	161	—||—	Sd, By	+15.0	—	—	—.	—	(4)
56	163	—||—	Sd, By	+14.6	—	—	—	—	(4)
57	164	—||—	Sd, By	+ 9.8	—	—	—	—	(4)
58	166	Zlatník gallery	Sd, By	+13.1	—	—	—	—	(4)
59	Zl-19	VII	Q, Sp, Py	—	—	—	—	+12.2	(4)
60	Zl-4	XVI	A, Sd, Py He, Ch,	—	—	—	—	+7.4	(2)
61	FR-263	XVI	Sediment Do	—	—	−0.8	−11.2	—	(3)
62	R-59a	XIII	Sd, Su	—	—	−3.7	−11.1	—	(3)
63	R-59c	XIII	Sd, Tt	—	—	—	—	−2.12	(4)
64	25/75 2/	XVI	Tt	—	—	—	—	−2.7	(1)
65	28/75 5/	XVI	Tt	—	—	—	—	−3.2	(1)
66	—	XVI	Tt	—	—	—	—	−7.5	(1)
67	60	XVI	R	—	—	—	—	+3.7	(1)
68	61	XVI	R	—	—	—	—	+3.5	(1)
69	58	XVI	By	+14.9	—	—	—	—	(1)
70	59	XVI	By	+14.0	—	—	—	—	(3)

Rudňany bore-hole

71	FR-22	Chl-Ma rock	Do	—	—	−6.9	−12.5	—	(3)
72	FR-5	A-Ma rock	K	—	—	−1.3	−16.9	—	(3)
73	FR-17	Ma-K rock	K	—	—	−9.6	−11.9	—	(3)

Rožňava, Mária vein

74	21/75 1/	VI	By	+ 6.5	—	—	—	—	(1)
75	22/75 2/	VIII	By	+. 4.2	—	—	—	—	(1)
76	23/75 3/	IX	Tt	+ 4.1	—	—	—	—	(1)

Dobšiná, Steinseifen

77	FD-74	Georgi pit heap	Fu-Q-K rock	—	—	−2.8	−17.1	—	(3)

Continuation of Tab. 1

	2	3	4		6	7	8	9	10
Košické Hámre, Teplý potok									
78	FHK-60	—	Fu-Q-K rock		—	—	−4.5	−10.5	—	(3)
Ostrý Harbek at Veľký Folknár									
79	FHK-15	—	Chl-Q-K		—	—	−5.3	−11.4	—	(3)
Muránska Dlhá Lúka									
80	FMDL-8	—	Fu-Q-K rock		—	—	−4.8	−14.0	—	(3)
Bôrka N border of the village									
81	FBO-1	—	Fu-Q-K rock		—	—	−6.0	−11.9	—	(3)

Explanations: I/S — first horizon, centre (horizons denoted by Roman numerals, S — centre, Z — West, V-bl. — E block), Sd — siderite, Tt — tetrahedrite, By — barite, Sp — specularite, A — ankerite, Su — sulphides, Ch — chalcopyrite, Ko — covellite, o.h. — wall rock, Q — quartz, K — carbonate, Chl — chlorite, R — cinnabar, Br — breunnerite, Ma — talc, A — antigorite. 1. — N. A. O z e r o v a in 1977, 2. — F. I. Ž u k o v, L. T. S a v č e n k o, 3. — V. Š m e j k a l, 4. — J. K a n t o r, 1977. Documentation of analysed samples from the Rudňany ore field compared with those from other localities of the Spišsko-gemerské rudohorie (the latter are not contained in the catalogue of chemical and spectral analyses of vein minerals).

R-228A — Rudňany, Mier, hor. XVI, crosscut 02, drift entry E, crosscut in S, ca. 40 m E of meas. point 79,6 m from opening, E face, fuchsite-quartz-carbonate (dolomitic) rock; R-326 — Rudňany, Mier, hor. XIII, drift to the E from crosscut 04 to crosscut 06, opposite m. point 180, S face, fuchsite-quartz-carbonate (siderite) rock; FR-263 — Rudňany, Zlatník vein, hor. XVI, gallery to the E, 17 m W of m. point 67, S face, sedimentary dolomites, ca. 0.5 m bed in chlorite slates; FR-73 — Rudňany, Mier, hor. XIII, crosscut 02 to the N, 39 m N of m. p. 145, E face, sericite-quartz-carbonate (sideritic) rock (fine-grained sedimentogenic siderite in the sense of J. T u r a n); FR-249A — Rudňany, Mier. hor. XVI, crosscut 02Z in N, 24,5 m N of m. point 287, E face, sericite-quartz-carbonate rock formed at the expense of conglomerate. Carbonate consists of siderite; FR-5 — Rudňany, Zlatník vein, drill hole Ry-II-Z, 430.7—431 m, antigorite-talc-carbonate rock; FR-22 — Rudňany, drill hole Ry-58/R101, 40.0—40.2 m. chlorite-talc-carbonate rock; R-342 — Rudňany, hor. XIX, gallery to the W, crosscut in N, at meas. p. 41.2 m from facing, E face chlorite-quartz-carbonate rock; FD-74 — Dobšiná, Steinseifen, pit heap of Georgi gallery, fuchsite-quartz-carbonate (dolomitic) rock; FKH-15— Ostrý harbek near Veľký Folknár chlorite-quartz-carbonate (breunneritic) rock; FMDL-8 — Muránska Dlhá Lúka, ca. 2 km from the village, fuchsite-quartz-carbonate (breunneritic) rock; FR-225 — Rudňany, hor. XIX, gallery S-XIX-V, crosscut in N, at meas. p. 182, 21.5 m W, 4 m from the opening, E face, fuchsite-quartz-carbonate (dolomitic) rock; R-372 — Rudňany, Mier, hor. XIII, gallery, crosscut 02, drift entry to E, ca. 70 m from the opening, N face, (chlorite) — sericite-quartz-carbonate (sideritic) rock; R-341 — Rudňany, hor. XIX, gallery in W, crosscut in N at meas. p. 41.2 m from the facing, E well, fuchsite-quartz-carbonate (sideritic) rock; FBO-1 — Bôrka, N outskirts of the village, fuchsite-quartz-carbonate (dolomitic) rock; FR-17 — Rudňany, drill hole Ry- -76 R-282. 83.70 m, talc-carbonate rock; FKH-60 — Košické Hámre, Teplý potok, fuchsite-quartz-carbonate (dolomitic) rock.
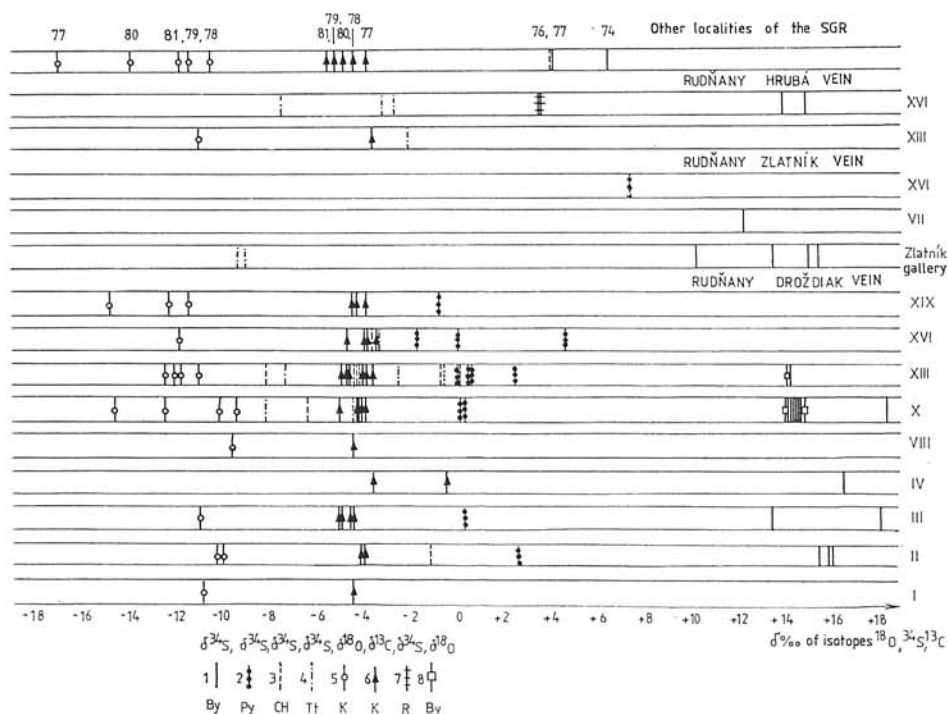
Fig. 1. Isotopic composition of Rudňany minerals.

Explanations: The value $\delta^{34}S$, $\delta^{18}O$ and $\delta^{13}C$ in ‰ are plotted on the x axis, the depth data on the y axis. 1 — $\delta^{34}S$ in barite (By), 2 — $\delta^{34}S$ in pyrite (Py), 3 — $\delta^{34}S$ in chalcopyrite (Ch), 4 — $\delta^{34}S$ in tetrahedrite (Tt), 5 — $\delta^{18}O$ in carbonates (K), 6 — $\delta^{13}C$ in carbonates, 7 — $\delta^{34}S$ in cinnabar (R), 8 — $\delta^{18}O$ in barite (By), numbers above the δ values above the upper line are ordinal numbers of analysed samples collected at different places of Spišsko-gemerské rudohorie (see expl. of Tab. 1).

CO_2 content are capable of leaching iron, barium and a whole series of other metals which gave rise to minerals of the Rudňany veins.

It can be assumed that barite had formed through mixing of thermal Fe and Ba^{2+}-bearing carbon-dioxide waters with waters of aquifers, enriched in sulphate solutions. It is to be noted that the Permian complexes lying above the Rudňany veins contain several layers of anhydrite and gypsum of evaporitic origin, and even syngenetic evaporite barite has been found there (F o r g á č, in print).

As the solubility of barite increases with rising temperature, the amount of barite is minimum in the zones where the temperature of hydrothermal solutions attained 200°C. The amount of barite increases abruptly towards the ground surface because the decline in temperature causes its precipitation. This is also supported by changes in the redox potential of solution.

A comparison of the results of isotopic, chemical and thermobarometric studies permits to assume that the siderite-barite-sulphide veins were forming

at temperatures of 140—280°C under the predominance of fluids and solutions in which carbon and sulphur occurred in a homogenized, more or less equilibrium state. These fluids had a high partial pressure of CO_2 and a low concentration of sulphur ($<10^{-6}$ — 10^{-4} mol/l). Thermodynamic computations (Š č e r b a ň — D r o z d o v s k a j a, 1981) have shown that siderite may originate within a narrow pH interval (6—7), at a temperature below 200°C and concentration of sulphur of up to 10^{-5} mol/l. At higher sulphur concentrations and higher pH and Eh, the siderites are replaced by sulphides and hematite.

On the basis of the research results two sources may be postulated for the sulphur of siderite-sulphide-barite veins: a deep source or a source related to basic and ultrabasic rock environment, and an exogenous source represented by sediments containing evaporites or biogenic pyrite in Devonian, Carboniferous and Permian complexes. Carbon dioxide derives predominantly from a deep, fairly stabilized source, which was not influenced in a high degree by secondary sources producing CO_2.

Oxygen isotopes

The isotopic composition of oxygen in minerals of the Rudňany deposit can be assessed only from a small number of analyses. We may thus far assume that the variability of the $\delta^{18}O$ value of carbonates was caused by changes in the $\delta^{18}O$ values of hydrothermal solutions or in temperature durring the crystallization of carbonates.

The average isotopic composition of oxygen of water of the hydrothermal solution can be calculated from the mean value of $\delta^{18}O$ of siderites (i.e. —11.7 ‰ PDB) and the temperature of crystallization, which was obtained by studying the homogenization of gas-fluid inclusions. Since there are several temperature data available, two $\delta^{18}O$ values of water can be calculated, corresponding to the lower and upper limits of the most probable range of crystallization temperature, i.e. 150 to 200°C. At 150°C the average siderite (with $\delta^{18}O = -11.7$ ‰ PDB) is in equilibrium with water[1] having the $\delta^{18}O$ equal to +6.1 ‰ SMOW, and at 200°C with water whose $\delta^{18}O$ is +9.3 ‰ SMOW[2]. The mean of the two values is +7.7 ‰ SMOW, i.e. close to that of magmatic water (+7.0 % SMOW).

The data on the isotopic composition of oxygen in siderites thus support the derivation of water from deep sources; the influence of meteoric water can be practically ruled out.

In contrast, carbonates from the listwänites (samples FR-5 and FD-74) contain lighter oxygen than the average Rudňany carbonates, which provides evidence for different conditions of their origin. As long as low-temperature carbonates are concerned, meteoric water might have participated in their forma-

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[1] As the precise fractionation factor of oxygen in the siderite-water system is unknown, the equation for the calcite-water system was applied (O ' N e i l — C l a y-t o n — M a y e d a, 1969).

[2] Isotopic analyses of C and O given in the Tables are related to the PDB standard, viz. to the marine Cretaceous belemnite from the Peedee Formation, S. Carolina, but most recently the SMOW standard (Standard Mean Ocean Water) is universally used. Eq. for conversion: $\delta^{18}O_{SMOW} = 1.03086 \times \delta^{18}O_{PDB} + 30.86$.

tion, but if magmatic water is considered, the computed temperature of carbonate crystallization results at about 300°C.

Additional analyses of oxygen isotopes in barites provided a certain possibility of studying the relationship between siderite and barite.

Isotopic composition of oxygen in barites shows a minimum variability (mean $\delta^{18}O$ in barite is $+14.3 \pm 0.4\ ^0/_{00}$ SMOW), which suggests that the isotopic composition of oxygen of the ore fluid did not change during the crystallization of barite.
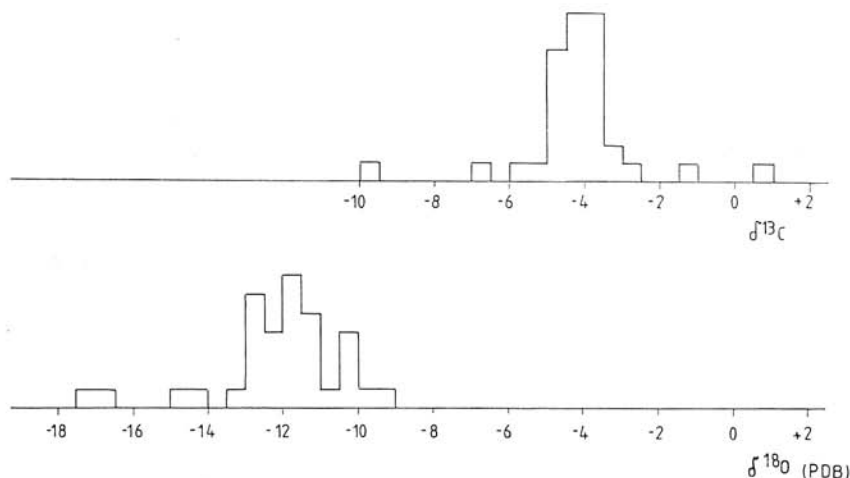
Fig. 2. Histogram of $\delta^{13}C$ and $\delta^{18}O$ values from the Rudňany ore field.

The values of isotopic fractionation of oxygen in the barite-water system have been defined with more precision only recently; according to K u s a k a-b e - R o b i n s o n (1977):

$$1000 \ln \text{(barite-water)} = 3.10 \times 10^6 \times T^{-2} - 7.3$$

The curve of this equation is very similar to the curve of oxygen isotopic fractionation in the calcite-water system, which is also used for the system siderite-water, whose curve has not yet been calibrated experimentally.

The application of the equations of O' N e i l — C l a y t o n — M a y e d a (1969) does not make it possible to determine from the ^{18}O values the temperature of barite origin with satisfactory accuracy and thus establish its co-genetic character with siderite.

Another problem to be solved relates to the difference between the conditions under which barite and siderite crystallized. R o j k o v i č (in this paper) and other authors believe the barite to be younger, representing a separate period of mineralization successive to the siderite mineralization. There are, however, parageneses, in deeper parts of the deposit in particular, in which barite is synchronous with or even older than siderite.

In the upper parts of veins, barite as a later product of crystallization metasomatically replaces siderite.

The authors advance a preliminary opinion that the hydrothermal solutions obtained sulphate ions by leaching evaporites during their ascent. Their $\delta^{18}O$ (SO_4) values were changing only slightly by equilibration with the water of hydrothermal solution, because the oxygen (and sulphur as well) of sulphates is isotopically similar to that of evaporitic sulphates. Only in Permian evaporites oxygen and sulphur are isotopically lighter. The effects of subsurface factors on barite crystallization are also indicated by a slightly less positive $\delta^{18}O$ value of "equilibrium water", and by the fact that barite, in contrast to siderite, occurs mainly in the surface parts of the deposit.

Fig. 3. Graph showing isotopic composition of oxygen and carbon in carbonates of the Rudňany ore field. (Numerals are numbers of samples listed in Tab. 1).

Isotopes in individual minerals

The general considerations and information, on which interpretation of concrete isotopic values ($\delta^{34}S$, $\delta^{13}C$, $\delta^{18}O$) in the minerals of Rudňany ores can be based, are here complemented by a detailed analysis of the data obtained. These are listed in Tab. 1, compiled from the results of analyses performed by authors whose names are given in the first paragraph of this paper (they are denoted in the Table by numerals 1—4). The ‰ values are arranged according to individual minerals, and their paragenesis is determined on the basis of veins, horizons and some other features. Supplementary data are presented in the catalogue of the chemical properties of minerals.

Pyrites

Most of the pyrite samples show $\delta^{34}S$ values from −2 to +2.5 ‰, and only a small part of analyses gave heavier sulphur with $\delta^{34}S$ values of +4.5 to +12 ‰. The last sample, however, represents pyrite from an ankerite-sulphide carbonate vein, which belongs to a later, different type of mineralization. It appears that heavier sulphur is characteristic of pyrite from this mineralization type ($\delta^{34}S$ = 12.2, +7.4). K a n t o r (1977) recorded that also part of barites have such a $\delta^{34}S$ value (e.g. sample No. 164 gave +9.8 ‰). The $\delta^{34}S$ value in pyrites of the Droždiak vein (see graph 1) is broadly the same in all horizons, varying between −2 and +2.5 ‰. Similar values have been determined in pyrites from the fuchsite assemblage and in pyrite from listwänitic rocks, i. e. hydrothermally altered hyperbasites. The sulphur involved has $\delta^{34}S$ value near to the meteoritic standard.

Remarkably, cinnabar taken from the Hrubá vein also contains sulphur with $\delta^{34}S$ = +3.65 ‰, whereas sulphur from tetrahedrites shows negative $\delta^{34}S$ values.

This different distribution of sulphur isotopes in tetrahedrite and cinnabar may be interpreted as evidence for a separate cinnabar supply period or for the influence of a specific rock environment.

Chalcopyrites

According to analytical results, chalcopyrites are enriched in light sulphur although chalcopyrites with a $\delta^{32}S$ value of −1.3 to +0.0 ‰ also exist. These values have been obtained on three samples from the Droždiak vein, which were analysed in Kiev. The samples from the same vein, analysed by K a n t o r (1977), have a greater amount of light sulphur with $\delta^{34}S$ values between −2.12 and −8.16 (4 samples), which suggests an increase of the heavier sulphur isotope with depth. The analyses made in Kiev, however show that chalcopyrite may have the $\delta^{34}S$ value near the meteoritic standard even on horizon XIII of the Droždiak vein, where a value of −8.16 ‰ was also determined. From this it follows that the light sulphur diminution with depth is not systematic and that the isotopic composition of sulphur in chalcopyrite is highly variable.

Tetrahedrites

Tetrahedrite is the most interesting mineral of the Rudňany paragenesis and it has been studied in detail because it contains Hg, Ag, Cu and other elements. B e r n a r d (1958, 1961) and R o j k o v i č (1977, 1981) studied the chemistry of the Rudňany tetrahedrite and the relationship between the changes in microelement content and the depth of occurrence of this mineral and its lattice constant. Investigations have confirmed that the contents of Cu, Zn, As and Pb increase with depth (and the values of lattice constants decrease). On the other hand, tetrahedrite from higher horizons has higher Hg, Sb and Ag amounts. The study of sulphur isotopes thus proved to be a relevant item of exploration of the Rudňany ore deposit. K a n t o r (1977) stated (in Partial summary report on research problem No. 3/73-VČ) a remarkable zoning in the distribution of sulphur isotopes, which is roughly parallel to the changes in their chemistry. The author analysed tetrahedrite from the Zlatník vein (2 samples), the Hrubá vein (1 sample), the Stredná vein (1 sample) and the Droždiak vein (4 samples). These analyses are given in the catalogue, in Tab. 1 and Fig. 1; the additional samples taken and analysed by N. A. O z e r o v a come from the Hrubá vein (3 samples) and the Droždiak vein, horizon XIII (3 samples).

As the new data corroborated the zoning of sulphur isotopic composition, the exception to this rule are to be ascribed to tectonic processes, which explanation has been proposed by K a n t o r. B e r n a r d also regarded them as responsible for abrupt changes in the Hg content in tetrahedrite. The new eight analyses bear out the lowering of the negative $\delta^{34}S$ value with the increase in the depth of sampling. This corroboration of K a n t o r' s conclusion on the increase in heavier sulphur and in Cu, As and Zn contents with depth may imply that sulphur in tetrahedrite from deeper horizons shows a more primary character than sulphur of higher horizons. The latter is probably more contaminated with lighter sulphur from sedimentary wall rocks. The distribution of isotopes may have also been influenced by thermodynamic conditions of the hydrothermal process.

Barites

Isotopic studies of barite have shown that it contains heavy sulphur, which according to the $\delta^{34}S$ value corresponds to sulphur of the Devonian-Carboniferous up to Permian sedimentary evaporites. Most analyses have been made on barite samples from the Droždiak vein. The $\delta^{34}S$ values range from +11 to +18 ‰ and lower with depth. The $\delta^{34}S$ values from the Zlatník deposit are somewhat lower (from +10 to +15‰).[3]

Of interest are the analytical results obtained on the Mária vein in Rožňava, where the $\delta^{34}S$ values in barite vary between +4.2 and +6.54 ‰. The source area of sulphate ions was there obviously different, being less affected by younger sedimentary complexes than in the Rudňany ore district, where the Devonian, possibly up to Triassic, complexes and their evaporite sulphates may

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[3] Data taken from K a n t o r's report (K a n t o r, 1977).

have influenced the metallogenic process. However, the overall dispersion of $\delta^{34}S$ values in the barite of the Rudňany ores is not very great, ranging from $+9$ to $+18$ ‰.

The oxygen isotopes in barite are listed in Tab. 1. As mentioned above, the $\delta^{18}O$ values in barite and siderite do not permit to determine conclusively at what temperature the two minerals originated, and therefore we cannot decide whether or not the solutions from which $BaSO_4$ and $FeCO_3$ crystallized were co-genetic. Because of the differences between $\delta^{18}O$ of siderite and barite we incline to the opinion that the siderite and barite mineralizations showed different isotopic relations already during crystallization of these minerals. It is to say that the barite crystallized at a later date contains a slightly larger amount of lighter oxygen isotope, which can be attributed to the interaction of primary hydrothermal solutions with the water of meteoric origin. This evolution of solutions and formation of barium sulphate need not have character of abrupt changes; it can occur gradually and does not manifest itself before the later phases of ore formation following the main siderite period. The problem concerning the relationship between the siderite and barite crystallization periods requires further isotopic studies, mainly on samples chosen specially for this purpose. Isotopes of oxygen and sulphur in Rudňany barite are presented in Tab. 2.

Table 2

Isotopes of oxygen and sulphur in barite

Indication of the samples	$\delta^{18}O$ SMOW	$\delta^{34}S$ CDT
R — 99	+15.3	+15.7
R — 75a	+13.9	+14.1
R — 8	+14.1	+18.0
R — 74	+13.9	+18.1
R — 70	+13.9	+15.9
KR — 46	+14.1	+14.4
R — 14a	+14.6	+15.7
KR — 51	+14.8	+14.5
KR — 55	+14.2	+14.3

For explanations see Tab. 1

Changes in the isotopic composition depending on the intensity of listwänitization and differences in lithology

Rock samples for isotopic analyses were selected by I v a n for the purpose of clarifying changes in the isotopic composition of carbon and oxygen in dependence on the intensity of hydrothermal-metasomatic alteration of rocks. Samples come from the Rudňany ore field and other parts of the Spišsko-gemerské rudohorie. The group of samples of carbonate-bearing rocks can be divided into the following sets:

A) Sedimentary dolomite $\delta^{13}C$ +0.8
   (Rakovec Group) $\delta^{18}O$ −11.2
B) Apo-ultrabasite[4] metasomatites
   (listwänites)

    1. Apo-ultrabasite listwänites with dolomite, arranged according to the increasing grade of alteration[5]

		$\delta^{13}C$	$\delta^{18}O$
FR—5	(Ant+T+K) (first grade of alteration)	−1.3	−16.9
FR—17		−9.6	−11.9
	(T+K)		
FR—22		−6.9	−12.5
R—342	(Ch+Q+K)	−4.5	−14.9
R—228A		−3.4	−11.9
	(F+Q+K)		
FR—225		−4.3	−12.4

    The samples were taken from different parts of the Droždiak vein. Sample FR-5 (Zlatník vein) represents the first grade of alteration - talcization and carbonatization of the breccia of antigorite serpentinite. This process need not be linked up with other alteration and ore-forming processes. Paragenesis is expressed in columns by the following symbols: Ant = antigorite; T = talc; K = carbonate; Ch = chlorite; Q = quartz; F = fuchsite; si = siderite; d = dolomite.

    2. Change in the isotopic composition during the secondary sideritization of apo-ultrabasite fuchsite-quartz-carbonate (dolomite) rocks (= F+Q+K(d)):

		$\delta^{13}C$	$\delta^{18}O$	
R—228		−3.4	−11.9	
	(F+Q+K(d))			
Fr—225		−4.1	−12.4	
R—326		−4.9	−11.7	sideriti-
	(F+Q+K(si))			zation
R—341		−3.9	−11.6	

The samples were taken in different parts of the Spišsko-gemerské rudohorie.
    3. Sideritization of apo-ultrabasite listwänites taken from (approximately one place), Mier vein, horizon XIX:

		$\delta^{13}C$	$\delta^{18}O$
R—342	(CH+Q+K(d)), ca.6 m from the siderite vein	−4.5	−14.9

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[4] Term taken from I v a n (in press)
[5] Accurate localization of samples given in explanations of Tab. 1

R—341   (F+Q+K(si)), nearer to the
          siderite vein   −3.9   −11.6

4. Apo-ultrabasite F+Q+K(d) rocks from different localities in the Spišsko-
-gemerské rudohorie:

Rudňany	R—228A	F+Q+K	−3.4	−11.9
	Fr—225		−4.3	−12.4
Dobšiná FD—74			−2.8	−17.1
Bôrka FBO—1			−6.0	−11.9
Košické Hámre FKH—60			−4.5	−10.5
Mur. Dl. Lúka	FMDL—8, breunnerite et al.		−4.8	−14.0
	FKH—60, F+Q+K(d)		−4.5	−10.5
loc. Košické Hámre FKH−15, CH+Q+K (breunn)			−5.3	−11.4

The two last samples represent the end members of the "dolomite" and
"breunnerite" branches of alteration.

C) The sericite-quartz-carbonate (siderite) apobasites (pelosiderites, or sedi-
mentogenic siderites in the sense of T u r a n)

FR—249A	−3.6	−12.9
FR—73	−4.3	−12.4
R—372	−3.6	−12.6

From the examination of changes in the isotopic composition caused by
alteration (listwänitization) of differing intensity and from the differences
in the lithology of altered and unaltered rocks the following results can be
inferred:

The sedimentary carbonate (dolomitic) rocks of the Rakovec Group show
a different $\delta^{13}C$ value (+0.8 ‰). The difference is evident, although it has
been obtained only by a single analysis.

The carbonates of talcized apo-ultrabasite metasomatites are $\delta^{13}C$-depleted
−6.9; −9.6 ‰) relative to the rocks showing the maximum grade of metasoma-
tic alteration, during which fuchsite originated. Isotopic composition of these
carbonates is very close to that of vein siderite ($\delta^{13}C$ −3.4 to −5 ‰). As the rock
was probably altered already before the origin of siderite (FR-5 — Zlatník
vein, antigorite serpentinite), the $\delta^{13}C$ value is then anomalous (−1.3 ‰) and
the $\delta^{18}O$ value as well; it shows the greates $\delta^{18}O$ depletion. −16.9 ‰. The
apo-ultrabasite (fuchsite) rocks from different localities of the Spišsko-gemer-
ské rudohorie have $\delta^{13}C$ from −3.4 to −4.9 ‰ and ^{18}O between +11 and
+12.5 ‰. These not greatly varying values, which for the most part belong
to samples taken from other than Rudňany deposits, can be accounted for
by the conditions of alterations and the character of the primary rocks. They
are near to the values of the Rudňany fuchsitic rocks.

Siderites from the sericite-quartz-carbonate rocks (pelosiderite or "sedimento-
genic" siderite in the sense of J. T u r a n) do not differ appreciably in the
$\delta^{13}C$ values from those of the vein siderite (−3.6 to −4.6 ‰). From the $\delta^{13}C$
values it can thus be inferred that these fine-grained siderites in the wall

rocks are of metasomatic origin. They show a strikingly smaller scatter of $\delta^{18}O$ values, compared with the highly variable $\delta^{18}O$ value of carbonates in the metasomatites (from -10 to -17 ‰). This points to the varying conditions and varying $\delta^{18}O$ values during hydrothermal alterations of metabasites and ultrabasites.

Conclusion

The studies of O, C and S isotopes have furnished fairly reliable information on the origin of siderite, barite and sulphides of the Rudňany deposits. It has been borne out that the sulphur in the minerals of the Rudňany ores shows a considerable scatter of $\delta^{34}S$ values (from -9 to $+18$ ‰) and is evidently of diverse origin. Relatively high positive $\delta^{34}S$ values in barite indicate the derivation of sulphate sulphur from the Devonian up to Permian evaporites. Pyrite sulphur has $\delta^{34}S$ values similar to those of meteoritic sulphur, but in some pyrites even heavier $\delta^{34}S$ values ($+1$ to $+12$ ‰) have been determined. Positive $\delta^{34}S$ values also occur in cinnabar, whereas chalcopyrite and tetrahedrite show negative $\delta^{34}S$ values. These differences in the isotopic composition of individual sulphides cannot be explained unequivocally: either sulphur of different sources participated in the formation of sulphides, or the isotopic equilibrium was affected by kinetic processes. The problem remains open. The isotopic composition of carbon is much simpler; it seems that a relatively uniform and considerably homogenized endogenous source was involved, but a small admixture of sedimentary carbon cannot be ruled out. Synsedimentary siderites, excluding dolomites and carbonates of the Rakovec Group, have not yet been evidenced isotopically. The oxygen isotopes indicate that the ore filling was forming under varying temperature or physicochemical conditions (varied composition of O isotopes in solutions). This caused fluctuation of $\delta^{18}O$ values in carbonates within a spread of -17 to -10 ‰. As is also confirmed by the $\delta^{13}C$ values, most of the Rudňany siderites crystallized from solutions corresponding in their $\delta^{18}O$ values to water from a deep source. Recent investigations have confirmed vertical zoning in the distribution of sulphur isotopes in tetrahedrite, as was determined before by K a n t o r (1977).

The oxygen isotopes in barite and siderite underwent evident changes, chiefly in the upper parts of the deposit; they were probably caused by changes in the $\delta^{18}O$ values and /or in the temperature of hydrothermal solutions. They were contaminated wirth the evaporite sulphates from the wall rocks, which controlled the distribution of $\delta^{18}O(SO_4)$ values during crystallization of barite from hydrothermal solutions. These surface effects of circulating waters were occasionally accompanied by tectonic events. The explanation of the relationship between barite and siderite from oxygen isotopes requires still special study and particular selection of rock samples.

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