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TEMPERATURE DEPENDENCES OF SULFUR ISOTOPE FRACTIONATION FACTORS BETWEEN SULFIDES (EXPERIMENT AND IMPLICATIONS)

(*Tabs. 4*)

Abstract Elementar synthesis of pairs of molybdenum, lead, zinc, antimony, tungsten sulfides as well as of the galenite-herzenbergite pair have been carried out under controlled conditions. The temperature dependences were established for heavy sulfur isotope refractionation between the above sulfides and applied to the Losen ore field, Eastern Rhodopes, Bulgaria.

The sulfur isotope composition of sulfides from the productive galenite-sphalerite-chalcopyrite mineral assemblage from the Losen deposit was determined. The temperature of deposition of major metallic sulfides at the metal deposition stage were estimated. A decrease in the sulfur isotope content from + 7 to + 3 ‰ is related to the temperature drop from 350 to 250 °C in the course of evolution of the hydrothermal system.

Резюме: В контролируемых условиях были синтезированы из элементов попарно сульфиды молибдена с сульфидами свинца, цинка, сурмы, вольфрама, а так же пара галенит-герценберит. Получены температурные зависимости перераспределения тяжелого изотопа серы между указанными сульфидами, которые использованы на примере Лозенского рудного поля в Восточных Родопах (Болгария). Определен изотопный состав серы сульфидов продуктивной галенит-сфалерит-халькопиритовой минеральной ассоциации месторождения Лозен. Оценены температуры отложения основных металлических сульфидов на полиметаллической стадии. Понижение изотопного содержания серы от + 7 до+ 3 ‰ отражает понижение температуры от 350 до 250 °C в ходе эволюции гидротермальной системы.

Beginning with the classic paper of Jury (1947) in which he calculated stable isotope fractionation factors between species of geochemical interest, there has been an increasing use of stable isotope variation in natural materials for studies in the Earth and cosmic sciences. Equilibrium fractionation factors that measure the distribution of a rare stable isotope between two species have been determined directly by laboratory experiments and also by calculation using the methods of statistical thermodynamics. These fractionation factors have been used in geochemistry to quantify the conditions under which mineral phases undergo crystallization.

The present paper is concerned with the use of the heavy-to-light sulfur isotope ratios for deriving geological thermometers. The sulfur isotopic compositions of coexisting sulfides have been shown in a number of theoretical (Sakai, 1968, Bachinski, 1969) and experimental (Kajiwara et al., 1969, Kajiwara—Krouse, 1971) studies to be useful for determinations of the formation temperatures of these minerals.

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The proposed method is based on the fact that during the high-temperature formation or recrystallisation of sulfides, the sulfur isotopic content varies with the temperature.

However little was known on the sulfur isotope ratios in minerals synthetized under controlled conditions. Therefore a systematic experimental study has been designed to study isotope equilibria in the sulfides of molybdenum, zinc, lead, tin, antimony and tungsten with the aim of deriving isotopic geothermometers. The time and temperature dependences of the S^{34} fractionation factor (α) were determined for the above sulfides synthetized under equilibrium conditions.

According to the common practice, the S^{34}/S^{32} ratios are expressed as δ values which are defined as $\delta = (\alpha - 1) . 1000$, where

$$\alpha = \frac{(S^{34}/S^{32})\ \text{sample}}{(S^{34}/S^{32})\ \text{standard}}$$

Troilite from the Sikhote-Alyin meteorite was used as the standard ($\delta\ S^{34} = 0.0$ ‰) for reporting sulfur compositions. The measurements were performed by the compensation method on the MI 1309 mass spectrometer with a 90°-two beam analyzer. The run samples were prepared on a conventional apparatus for sulfide oxidation using copper oxide (Устинов—Гриненко, 1965). Reproductibility of results was within ± 0.4 ‰.

Experimental part

Equilibrium sulfides in the systems sphalerite-molybdenite, galenite-molybdenite, galenite-herzenbergite, tungstenite-molybdenite and antimonite-molybdenite were synthetized in quartz capsules with 50 % excess sulfur of super purity grade. Pure (99.5 %) metallic zinc, lead, tin, antimony and tungsten were crushed to grains of up to 30 μm. Powdered molybdenum (grains not larger than 10 μm) obtained by reducing molybdenum oxide was 99.9 % pure. The reagents charged into capsules were separated from one another with quartz wood or sand that while not interfering with the flow of gaseous sulfur kept the metals apart. At the same time, both metals reacted with the mobile sulfur. As a result, the gas phase promoted the isotope exchange between the sulfides and excess sulfur by the reactions

$$AS^{32} + S^{34} = AS^{34} + S^{32} \tag{1}$$
$$BS^{32} + S^{34} = BS^{34} + S^{32} \tag{2}$$

and after summation, the isotope exchange between the sulfide proceeds as:

$$AS^{32} + BS^{34} = AS^{34} + BS^{32} \tag{3}$$

The capsules were evacuated to $1 \div 3 . 10^{-6}$ mm mercury column, welded in the oxygen forch and held in furnacles at every given temperature for various periods of time. All runs were conducted in sillite KO-14 furnaces with automatic temperature control. The temperature was measured by a platinum--rhodium thermocouple; the temperature regulation was accurate to ± 5 °C. Run durations were based on preliminary kinetic experiments. The run pro-

Table 1

Equilibrium constants for isotope exchange of reaction (7)—(11)

t, °C	$1000 \ln \alpha \frac{A}{B}$, ‰				
	$\frac{\text{sphalerite}}{\text{molybdenite}}$	$\frac{\text{galenite}}{\text{molybdenite}}$	$\frac{\text{galenite}}{\text{herzenbergite}}$	$\frac{\text{tungstenite}}{\text{molybdenite}}$	$\frac{\text{antimonite}}{\text{molybdenite}}$
300±5	2.9±0.4	1.4±0.4	3.5±0.4	3.2±0.3	2.6±0.3
400±5	2.1±0.1	1.0±0.4	2.2±0.3	1.9±0.2	1.7±0.2
500±5	1.6±0.1	0.7±0.1	1.4±0.2	1.3±0.1	1.1±0.1
600±5			0.8±0.1	0.5±0.1	1.6±0.1

ducts were quickly in cold water to prevent any isotopic exchange taking place during cooling. The capsules were opened and owing to the cotton wool position the sulfides produced in the runes were easily separated from one another.

The sulfides were ground in an agate mortar, washed with carbon tetrachloride to remove sulfur and identified by X-raying on a DROH-1,5 diffractometer.

The kinetic analysis has shown that the Δ values which are normally defined

$$\Delta\ \delta\ S^{34}{}_{A-B} = \delta\ S^{34}{}_{A} - \delta\ S^{34}{}_{B} = 1000 \ln \alpha_{A-B} \tag{4}$$

as attain finally a constant value to indicate that the equilibrium isotope exchange had been achieved.

According to Bigeleisen—Mayer (1947), the constant for isotopic exchange relates to the temperature in the following way:

$$\ln \alpha = AT^{-2} + B \tag{5}$$

where A and B are experimentaly derived constnats, T is the absolute temperature. Hence,

$$100 \ln \alpha_{A-B} = \Delta\ S^{34}{}_{A-B} = AT^{-2} + B \tag{6}$$

Table 2

Times of equilibration

sulfide pair	run duration, days			
	300 °C	400 °C	500 °C	600 °C
$ZnS—MoS_2$	210	100	60	—
$PbS—MoS_2$	70	50	20	—
$PbS—SnS$	70	20	10	10
$WS_2—MoS_2$	140	80	60	30
$Sb_2S_3—MoS_2$	120	70	40	30

Table 3

Sulfur isotope compositions of sulfides from the Losen ore field

N	Sample No.	substance	δS^{34}, ‰	number of determinations
1	L-129	ZnS 1	7.0 ± 0.1	3
2	L-129	$CuFeS_2$ 1	6.0 ± 0.2	3
3	L-129	PbS 1	4.8 ± 0.3	2
4	L-122	ZnS 1	6.9 ± 0.1	3
5	L-97	ZnS 1	7.5 ± 0.1	2
6	716/450	FeS_2	10.0 ± 0.1	3
7	719/410	FeS_2	7.7 ± 0.1	3
8	722/573	FeS_2	7.9 ± 0.4	3
9	726/502	FeS_2	7.7 ± 0.2	3
10	L-82	PbS	4.8 ± 0.3	3
11	L-55	PbS	5.0 ± 0.1	3
12	L-88	PbS	4.8 ± 0.3	3
13	L-81	PbS	5.0 ± 0.1	3
14	L-116	PbS	4.8 ± 0.2	3
15	L-116(kp)	PbS	4.5 ± 0.2	8

The following isotope exchange reactions

$$ZnS^{32} + 1/2\ MoS_2{}^{34} = ZnS^{34} + 1/2\ MoS_2{}^{32} \tag{7}$$
$$PbS^{32} + 1/2\ MoS_2{}^{34} = PbS^{34} + 1/2\ MoS_2{}^{32} \tag{8}$$
$$PbS^{32} + SnS^{34} = PbS^{34} + SnS^{32} \tag{9}$$
$$1/3\ Sb_2\ S^{32}{}_3 + 1/2\ Mo\ S^{34}{}_2 = 1/3\ Sb_2\ S^{34}{}_3 + 1/2\ Mo\ S^{32}{}_2 \tag{10}$$
$$1/2\ W\ S^{32}{}_2 + 1/2\ Mo\ S^{34}{}_2 = 1/2\ W\ S^{34}{}_2 + 1/2\ Mo\ S^{32}{}_2, \tag{11}$$

were least-squared to give the following temperature dependences:

$$10^3 \ln \alpha \frac{ZnS}{MoS_2} = 9.6 \,.\, 10^5\, T^{-2} + 0.10 \tag{12}$$

$$10^3 \ln \alpha \frac{PbS}{MoS_2} = 4.7 \,.\, 10^5\, T^{-2} - 0.28 \tag{13}$$

$$10^3 \ln \alpha \frac{PbS}{SnS} = 9.4 \,.\, 10^5\, T^{-2} - 1.15 \tag{14}$$

$$10^3 \ln \alpha \frac{WS_2}{MoS_2} = 1.04 \,.\, 10^6\, T^{-2} - 0.79 \tag{15}.$$

$$10^3 \ln \alpha \frac{Sb_2S_3}{MoS_2} = 8.6 \,.\, 10^6\, T^{-2} - 0.34 \tag{16}$$

Table 4

Results of geothermometers sphalerite-chalcopyrite, sphalerite-galenite and chalcopyrite-galenite

Sample No.	pair	$\Delta_{A-B} = \delta_A - \delta_B$	T°, C
L-129	$ZnS - CuFeS_2$	0.4	290
L-129	$ZnS - PbS$	2.2	320
L-129	$CuFeS_2 - PbS$	1.8	270

the correlation factors being, respectively, 0.899; 0.826; 0.947; 0.799 and 0.839 (Bigeleisen—Mayer, 1947; Суворова—Тенишев, 1976). Tab. 1 gives the equilibrium constants for isotope exchange reactions (7)—(11). The equilibration time are found from Tab. 2.

The results from this study make it possible to estimate the formation temperatures of hydrothermal sulfide deposits of molybdenum, antimony, tungsten, tin, lead and zinc. The order of deposition as well as the coefficients of temperature dependence equations as calculated for the pair sphalerite-galenite from the present data agree closely with Kajiwara and Krouse's (Kajiwara et al., 1969; Kajiwara—Krouse, 1971) results. The equations derived were used to study the galenite-sphalerite-chalcopyrite assemblage from the Losen ore field, Eastern Rhodopes.

The Losen ore field is part of a multi-root, surface volcanic-intrusive ore field that has evolved through the prevolcanic, volcano-intrusive, ore-metasomatic and post-ore stages. The multistage hydrothermal process has resulted in the formation of 10 paragenetic mineral assemblages of which galenite-sphalerite-chalcopyrite is the only productive one (Богданов, 1983).

Lenticular or sheet-like galenite-sphalerite-chalcopyrite ore bodies occur in the near-surface zone extending along Palaeogene sediments, rhyolites and pyroclastic rocks (Янев и др., 1975). Galenite and galenite-chalcopyrite bodies, both vein and scattered, occur in the immediate vicinity of subvolcanic quartz-diorite-porphyrite bodies and metamorphic rocks forming the pre-Cambrian crystalline base.

Tab. 3 presents the sulfur isotope compositions of sulfides from the Losen ore field.

The isotope fractionation data between the minerals in sample L-129 (Tab. 3) were used to determine the equilibrium temperatures recorded by the sample. The geothermometers derived for the pairs sphalerite-chalcopyrite and sphalerite-galenite gave the temperatures of formation of polymetallic sulfides in a sample typical of this deposit. The resultes are presented in Tab. 4.

The temperature measurements carried out for three different sulfide pairs show a good agreement within the experimental error limits. The isotope ratio determinations indicate that the temperature at the productive stage was equal to 290 ± 25 °C.

The above results agree well with the available geological evidence and earlier isotope studies (Антимова, 1978; Bogdanov—Zairi, 1985). The isotope composition of the productive galenite-sphalerite-chalcopyrite mineral assemblage (δS^{34}) varies within 6—7 to 3—4 ‰.

A somewhat heavier sulfur isotope composition relative to the meteoritic compositions makes one suggest that the crustal sulfur had been trapped at the ore deposition stage.

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