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Jan PARAFINIUK, Włodzimierz KOWALSKI, Stanisław HAŁAS

Stable isotope geochemistry and the genesis of the Polish native sulphur deposits — a review

The study summarizes earlier data concerning of sulphur, carbon, and oxygen isotope ratios in Polish native sulphur deposits of the Carpathian Foredeep. It characterizes isotope compositions of the Miocene evaporite rocks such as gypsum (the host-rocks for sulphur ores), native sulphur, postgypsum limestones, and residual sulphates (celestite, barite, and aqueous sulphates of ore water). Based upon available isotopic results the authors have proposed a model for genesis of Polish sulphur ores which includes: origin of ore-forming factors, mechanisms of ore-forming processes, capacity of sulphate-reduction process, origin of the ore water, how open the system was and the problem of sulphur ore disintegration.

INTRODUCTION

Analyses of sulphur, carbon, and oxygen isotope ratios have significantly advanced progress in the understanding of the origin of native sulphur ores connected with evaporite formations. A view of biogeochemical origin of the sulphur ores by means of bacterial reduction of solid sulphates (gypsum and anhydrite) with the use of hydrocarbons as a chemical reducing factor has been well established (e.g. H. G. Thode *et al.*, 1954; H. W. Feely, J. L. Kulp, 1957; A. P. Winogradov *et al.*, 1961; J. Dessau *et al.*, 1962; M. V. Ivanov, 1964; H. R. Krouse, R. G. L. McCready, 1979; R. Sassen, 1980). Although there is no doubt as to the bioepigenetic (*sensu* J. C. Ruckmick *et al.*, 1979) origin of the Polish sulphur ores (e.g. S. Pawłowski, 1970; S. Pawłowski *et al.*, 1965, 1979, 1985; B. Kubica, 1992; T. Osmólski, 1972; M. Nieć, 1982, 1992; M. Pawlikowski, 1982), and general features of the sulphate transformation are known, a great deal of detailed questions remain to be answered concerning geochemical conditions of the alteration process. Significant problems concerns the mechanisms involved in the process of sulphate transformation, conditions of ore-forming processes, and whether the reaction developed in open or closed system conditions.

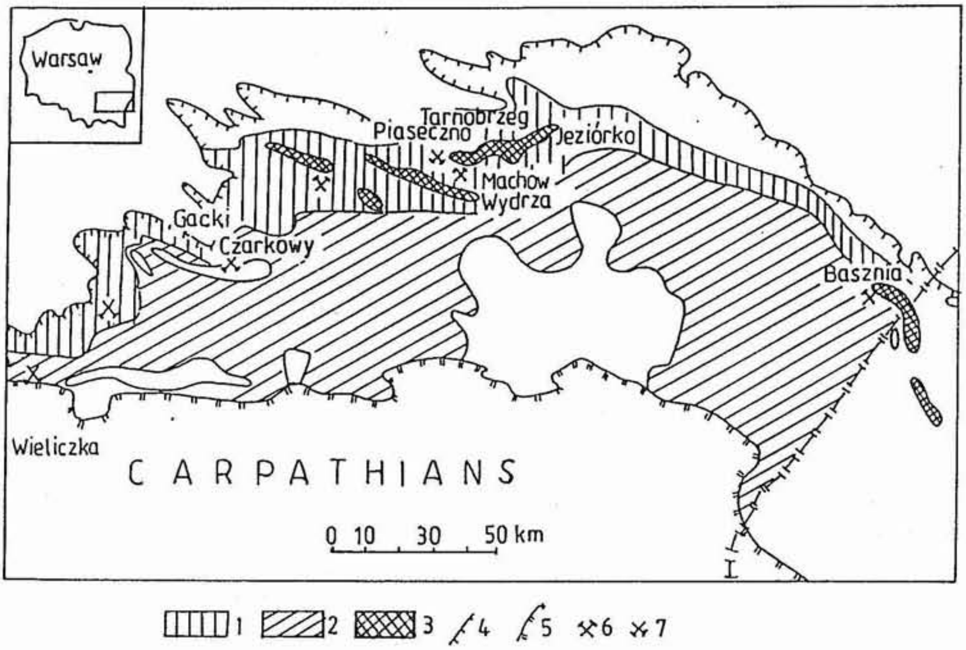

Fig. 1. Location of sulphur orebodies and investigated samples in the Carpathian Foredeep
1 — gypsum, 2 — anhydrites, 3 — sulphur ore, 4 — extent of the marine Miocene deposits of the Carpathian Foredeep, 5 — Carpathian Overthrust, 6 — active sulphur mines, 7 — closed sulphur mines
Lokalizacja złóż siarki zapadliska przedkarpackiego i miejsca pochodzenia próbek
1 — gipsy, 2 — anhydryty, 3 — siarka rodzima, 4 — zasięg morskich osadów miocenu zapadliska przedkarpackiego, 5 — nasunięcie karpackie, 6 — kopalnie siarki czynne, 7 — kopalnie siarki nieczynne

This work, based on the available published data and extensive original isotopic research, presents an attempt to solve the above mentioned problems. It also attempts to summarize earlier results, mainly in order to complete a geochemical model of the genesis of Polish sulphur ores.

MATERIALS AND METHODS

Samples for the study were mainly taken from the Tarnobrzeg sulphur orebody; it is the biggest in Poland and is located in the northern part of the Carpathian Foredeep. Most of the samples were taken from open-pit mines at Machów and Piaseczno. Selected boreholes from underground-melting mines at Jeziórko and Wydrza (ore fields located in the central and southern parts of the Tarnobrzeg deposit) were sampled as well. Borehole cores of the Basznia underground-melting mine (eastern part of the foredeep) as well as old open-pit mine at Czarkowy (western part of the foredeep) were examined only to a limited extent

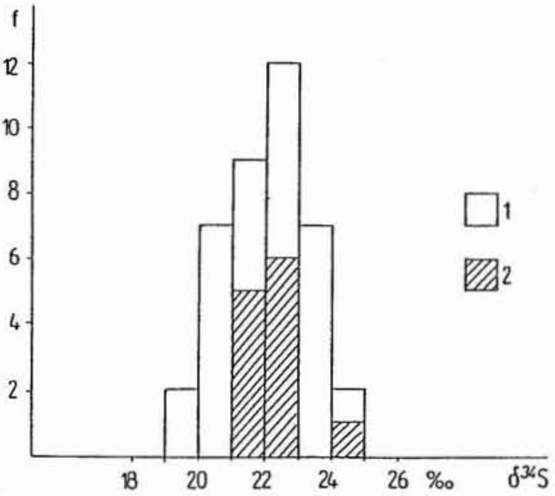

Fig. 2. Sulphur isotopic composition of Miocene gypsum
1 — gypsum samples taken from unaltered sulphate deposits, 2 — gypsum samples taken from sulphur ores and their direct surrounding
Skład izotopowy siarki gipsów mioceńskich
1 — próbki gipsu z obszarów zapadliska nie objętych redukcją, 2 — próbki gipsu ze złóż siarki i ich bezpośredniego otoczenia

(Fig. 1). Samples of gypsum and anhydrite from Ponidzie (northern, marginal part of the basin) and Wieliczka (salt mine in Kraków region) were analysed as well.

Most isotopic analyses were done by means of a modified bicollector mass-spectrometer *MI-1305* (S. Hałas, 1979; S. Hałas, Z. Skorzyński, 1980). Isotope ratios of $^{34}S/^{32}S$, $^{13}C/^{12}C$ and $^{18}O/^{16}O$ are given in δ values relation to the international CDT, PDB, and SMOW standards respectively.

Earlier sulphur isotope analyses were done by means of direct oxidation of elemental sulphur to SO_2 in free oxygen. In recent analyses, elemental sulphur was oxidized to sulphate in a concentrated mixture of HCl and HNO_3 with an admixture of Br_2; subsequently the sulphate was then converted to SO_2 by the method of S. Hałas and W. Wołącewicz (1981). The same method applied to the isotope analyses of celestite, barite, and gypsum. However, the gypsum was first dissolved and precipitated as $BaSO_4$ and then analysed according to procedure described above. Carbonate samples for $\delta^{13}C$ and $\delta^{18}O$ analysis were converted to CO_2 by means of reaction with 100% phosphoric acid with some admixture of P_2O_5. Isotopic analyses of the oxygen contained in sulphates were done by means of the reduction of $BaSO_4$ to pure CO_2 with the aid of graphite (Y. Mizutani, 1971). The $\delta^{13}C$ values are accurate to ±0.1‰ in carbonate samples and both $\delta^{34}S$ and $\delta^{18}O$ values are accurate to ±0.2‰ in sulphate samples.

In addition, all available (published) isotopic data on the Polish sulphur-bearing formation are included in the diagrams presented below while the original results are given in Tables's.

Table 1

Isotopic composition of the Miocene gypsum and anhydrite of the Carpathian Foredeep

Sediments	Sample	$\delta^{34}S_{CDT}$ [‰]	$\delta^{18}O_{SMOW}$ [‰]
Gypsum Gacki – Ponidzie	BS–9 BS–19 BS–11	23.0 22.9 22.4	13.9 13.0 13.1
Gypsum-anhydrite Horyniec	H–5	23.2	12.9
Anhydrite Wieliczka	W–1002 W–1005 W–1008 W–1010	22.2 21.9 22.7 22.8	12.9 10.6 14.2 14.2
Gypsum Piaseczno sulphur mine	T–30a T–31 T–39 T–40	24.6 22.4 23.6 23.0	14.4 13.6 13.3 13.6

MIOCENE SULPHATES

Sulphur isotopic analyses of gypsum and anhydrite presented in Figure 2 and Table 1 demonstrate a distinct homogeneity of the isotope composition: $\delta^{34}S$ ranges from 19 to 25‰ with a mean of 22–23‰. These results correspond very well to those of Miocene gypsum found in the Mediterranean basin (e.g. A. Longinelli, 1979/1980) as well as to other Tertiary evaporite formations (G. E. Claypool *et al.*, 1980). Taking into account sulphur isotope fractionation occurring during gypsum crystallization from sea water (experimentally fixed as 1.65‰) — H. G. Thode, J. Monster (1965), one may assume that the gypsum precipitated from a brine would have $\delta^{34}S$ equal to about 20‰. This value is analogous to the value of aqueous sulphate of recent sea water (A. Sasaki, 1972).

This study reveals that there is no significant differentiation in the isotopic composition of various gypsum lithofacies like: coarse-crystalline selenite (*szklica* gypsum), sabre-like gypsum, or fine-crystalline laminated gypsum. Additionally, there is no substantial isotopic difference between gypsum and anhydrite. Small isotopic differences (up to few permilles) found within sulphates may be the result of later diagenetic recrystallization processes which commonly affected gypsum deposits. Furthermore, there is no difference in the isotopic composition between gypsums directly surrounding sulphur ores or isolated gypsum lenses found within the ore series and the gypsum occurring in areas unaffected by the transformation processes.

Earlier data on the oxygen isotopic composition of the sulphate ion from Miocene gypsum and anhydrite are listed in Table 1. $\delta^{18}O$ values of these sulphates are found to be in a relatively narrow range, from 10.6 to 14.4‰ (mean = 13.3‰). These results clearly indicate the isotopic homogeneity of the Miocene sulphates from the Carpathian Foredeep. Because gypsum precipitation from sea water is associated with an isotope fractionation

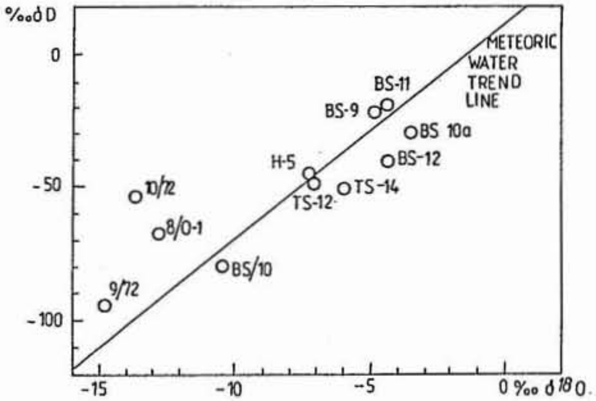

Fig. 3. $\delta^{18}O$ values and δD values of water estimated from the isotopic composition of gypsum water of crystallization (after S. Hałas, H. R. Krouse, 1982)
Wartości $\delta^{18}O$ i δD wody określone ze składu izotopowego wody krystalizacyjnej gipsu (według S. Hałasa i H. R. Krousego, 1982)

effect of sulphate oxygen equal to 3.5‰ (R. M. Lloyd, 1968), one may assume that $\delta^{18}O$ value of sulphates precipitated from the Miocene sea water was equal to about 10‰. This value is analogous to the value of aqueous sulphate of recent sea water (G. E. Claypool *et al.*, 1980).

Opposite to the oxygen of sulphates, both oxygen and hydrogen from crystallization water of gypsum are easily isotopically exchanged. Both the isotopic exchange of crystallization water with meteoric waters and gypsum dehydratation followed by anhydrite rehydratation are responsible for occasional preservation of gypsum crystallization water in deposits older than recent evaporites (Z. Sofer, 1978). Crystallization water of gypsum in equilibrium with sea water should be characterized by $\delta^{18}O = 4‰$ and $\delta D = -20‰$, which fit well with fractionation factors established experimentally (R. Gonfiantini, J. C. Fontes, 1963). The isotope values obtained for gypsum of the Carpathian Foredeep (Fig. 3) are distinctly lower than the values presented above. This fact unequivocally suggests that the gypsum, at least partly, exchanged its crystallization water with groundwater of meteoric origin. In addition, using these results, one may remark that the exchange process affected the laminated gypsum lithofacies (which commonly makes up the upper part of the sulphate sequence) more than the coarse-crystalline gypsum lithofacies (usually located in the lower part of the sequence). The isotopic values of most of the investigated gypsum samples occur close to the Craig's meteoric water trend line and thus correspond to an isotopic equilibrium with groundwater, or occur just below this line which fits with the mixing of sea and meteoric waters. A few isotopic results obtained from gypsum samples taken from the Basznia sulphur orebody occur just above the meteoric water line and their isotopic composition may be explained as the effect of anhydrite rehydratation with only limited access the groundwater (S. Hałas, H. R. Krouse, 1982; A. H. Bath *et al.*, 1987).

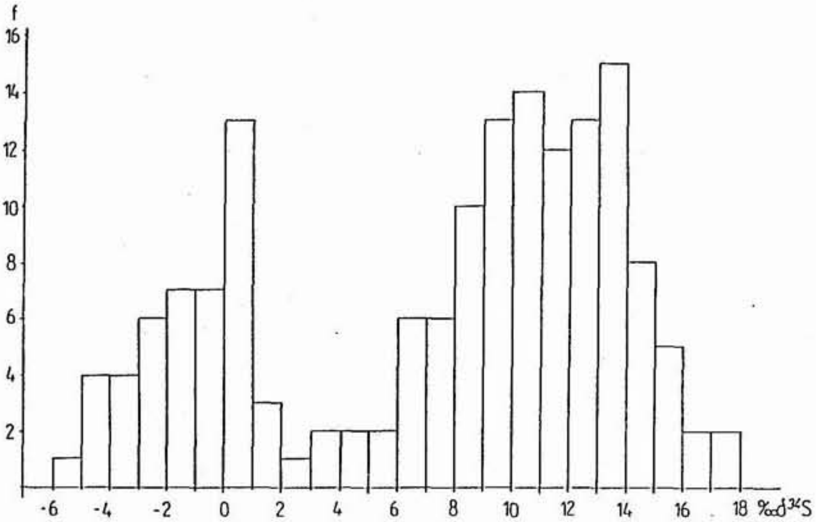

Fig. 4. Isotopic composition of native sulphur
Skład izotopowy siarki rodzimej

NATIVE SULPHUR

From laboratory experiments and field observations (see L. A. Chambers and P. A. Trudinger for further references, 1979), there is evidence of distinct fractionation of sulphur isotopes due to bacterial sulphate reduction. The main role in the sulphate reduction processes is commonly ascribed to heterotrophic bacteria of the species *Desulfovibrio*, which are active in anaerobic environments. Enrichment in the ^{32}S of hydrogen sulphide as a product of sulphate reduction relative to the value measured in sulphate depends on the reduction rate and may reach as much as 46‰ (I. R. Kaplan, S. C. Rittenberg, 1964) although, in most experiments it usually does not exceed 25‰. The isotopic composition of both hydrogen sulphide and elemental sulphur (formed from H_2S) substantially depends on whether open or closed (i.e. with a limited supply of sulphates) system conditions operated in the environment of alteration.

Native sulphur of the Polish sulphur ores is distinctly enriched in the isotope ^{32}S in comparison to the sulphur of host gypsum rocks. In addition, it has been established that the sulphur isotopic composition distinctly changes in particular sulphur ores from –6 to 18‰ (Fig. 4). The isotopic values distribution is bimodal with the first mode close to 0‰ and the second one close to 11‰. A similar pattern of the isotopic value distribution has been obtained by J. Czermiński and T. Osmólski (1974) (their data are not included in Fig. 4). Native sulphur of shallow buried (peripheral parts of the foredeep) sulphur ores, native sulphur of aggregates dispersed within unaltered gypsum deposits, in claystones of the Upper Badenian ore cover, and in sands underlying the evaporite horizon (the Baranów Beds) are characterized by low $\delta^{34}S$ values. The origin of isotopically light sulphur is connected with the initial phase of sulphate reduction and migration of isotopically light H_2S (formed in the same phase of the alteration) into marginal parts of the sulphur ores or into the deposits surrounding sulphur ores. Hydrogen sulphide migrated in both vertical and horizontal directions and later was oxidized to elemental sulphur. Isotopically heavier native sulphur occurs in deeper parts of the sulphur orebodies and most likely is connected with *in situ* oxidation of hydrogen sulphide. Because isotopically light sulphur is quantitatively insignificant, the average $\delta^{34}S$ for all elemental sulphur in Polish sulphur ores may be calculated as equal to about 11‰. The same value has been obtained for sulphuric acid produced from native sulphur exploited in the Machów mine. Thus, it indirectly confirms the course of calculation presented above.

Native sulphur varieties such as macro- and cryptocrystalline waxy or dusty sulphur cannot be categorized with regard to their isotopic signatures, although, in general the coarse-crystalline variety often has higher $\delta^{34}S$ values.

POSTSULPHATE LIMESTONES

$\delta^{13}C$ values of the postsulphate limestones differ significantly (by a distinct depletion) from normal-marine limestones. The isotope results presented in Figure 5 and in Table 2 exhibit a great variety of carbon isotopic composition in the sulphur-bearing limestones. Based upon the carbon isotopic composition, the postsulphate limestones may be divided into two distinct groups. A larger group is characterized the values ranging from –40 to –45‰ while the smaller one is more inhomogenous (with a broad $\delta^{34}S$ range) and characterized by higher $\delta^{13}C$ values (sometimes up to –20‰). The first group is typical for the central parts of the sulphur ores while the second one for the peripheral parts of the ores as well as for the transitional zones associated with non-altered gypsum deposits. Such low $\delta^{13}C$ values unequivocally indicate hydrocarbons as the source of carbon for the formation of postsulphate limestones. Some interpretations have been proposed to explain the observed variability of the carbon isotopic composition of the postsulphate limestones. For instance, S. Hałas (1973) has linked this fact with a differentiation of the reducing agents composition. According to him, the isotopically lightest postsulphate limestones formed by means of oxidation of the lighter hydrocarbon fractions, particularly methane, while isotopically heavier limestones originated due to oxidation of oils or bitumens dispersed in the Miocene formation. This interpretation fits well with the isotopic composition of Miocene hydrocarbons, which have $\delta^{13}C$ values ranging from –61.6 to –71.0‰ for methane, and from –27.6 to –23.4‰ for dispersed bitumens (J. J. Głogoczowski, 1976). J. Czermiński and T. Osmólski (1974) assumed methane as the main factor in sulphate reduction for the central parts of the sulphur deposits, whereas for the peripheral parts of sulphur ores they suggested an admixture of marine-confined limestones. These authors found isotopically extremely light postsulphate limestones characterized by $\delta^{13}C$ values of –59.9‰ in the Czarkowy sulphur ore and interpreted them as having originated due to the oxidation of methane. J. Czermiński and T. Osmólski postulated an interfingering of marine and postsulphate limestones as the possible cause for the origin of sulphur-bearing limestones with $\delta^{13}C$ values from –27.4 to –18.6‰ exposed in the northern part of the Piaseczno ore.

Table 2

Isotopic composition of the sulphur-bearing limestones

Sulphur mine	Sample	$\delta^{13}C_{PDB}$ [‰]	$\delta^{18}O_{SMOW}$ [‰]
Machów	TS–1	–42.8	27.0
	TS–2	–44.3	27.0
	TS–3	–43.0	27.0
	TS–4	–44.3	27.2
	TS–5	–43.1	27.2
	TS–7	–39.3	24.6
	MW–7	–42.5	26.8
Jeziórko	TS–10	–46.7	26.9
	TS–11	–43.7	26.2
	TS–12	–29.1	25.9
Basznia	TS–13	–42.4	27.3

According to the present authors, it seems to be clear that the development of the carbon isotopic composition of the postsulphate limestones during the transformation events was more complex than it has been assumed so far. Namely, the hypotheses mentioned above with regard to particular sulphur ores assumed that the processes of sulphate reduction and hydrocarbon oxidation took place in closed system conditions (i.e. all methane was used in the reactions and CO_2 formed during the alteration was completely bound by calcium ions to precipitate $CaCO_3$). However, there is a possibility that a part of CO_2 could be carried away from sulphur ores, and this could have strongly influenced the observed isotopic

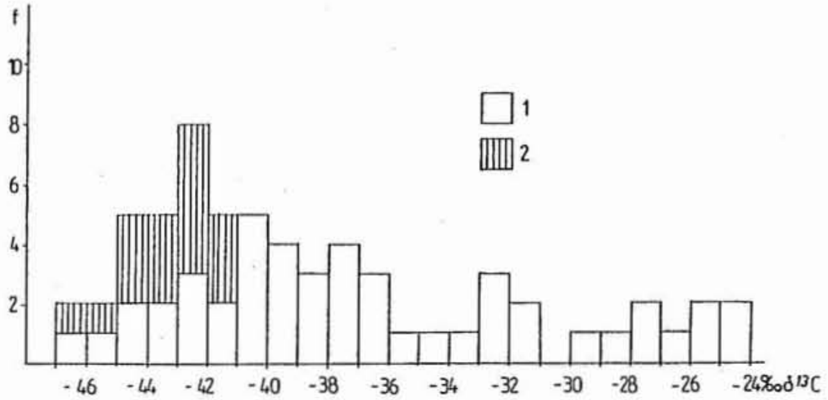

Fig. 5. Carbon isotopic composition of sulphur-bearing limestones
1 — sulphur-bearing limestones, 2 — coarse-crystalline calcite, aragonite, and strontianite
Skład izotopowy węgla wapieni osiarkowanych
1 — wapienie osiarkowane, 2 — kalcyt grubokrystaliczny, aragonit i stroncjanit

ratios. Anaerobic methane oxidation is commonly linked with depletion in ^{13}C isotope of residual gas. Fractionation factors for such a reaction range between 1.002 and 1.014 (M. J. Whiticar, E. Faber, 1986). Consequently, if methane oxidation was not complete originating by this process CO_2 would have a more negative value than the initial methane. A distinct fractionation occurs in the $CO_2 - CaCO_3$ system and depends on the temperature. For each stage of dissociation:

$$CO_2 + H_2O = H_2CO_3 = HCO_3^- + H^+ = CO_3^{2-} + 2H^+$$

an equilibrium fractionation of the carbon isotopes through isotopic exchange is established. In the $CO_3^{2-} - CO_2$ system this fractionation is equal to 5.0‰ at 25°C (S. Hałas *et al.*, in preparation), and in the $HCO_3^- - CO_2$ system it is equal to 9.3‰ (W. G. Mook *et al.*, 1974; J. Szaran, 1983). The precipitation of calcite and aragonite is also connected with the carbon isotope fractionation and it causes the enrichment of a stable phase in ^{13}C which is about 0.8 and 2.7‰ respectively (C. S. Romanek *et al.*, 1992). The data presented above indicate that the unbound CO_2 should have a much lighter carbon isotopic composition than that found in the precipitated carbonates. Consequently, if a part of CO_2 produced in this way migrated outside the system (such conditions probably existed in the peripheral parts of the sulphur ores), then the limestones precipitated there would have higher $\delta^{13}C$ values than the limestones of the central parts of sulphur ores. This suggestion is confirmed by the isotopic ratios of the limestones occurring above and below the sulphur-bearing series (M. Pawlikowski, W. Przybyłowicz, 1979). They found that the carbonates overlying the Wydrza ore have $\delta^{13}C$ ranging from –14.9 to –5.7‰. These values are distinctly lower than those obtained for the limestones occurring above unaltered gypsum deposits. This may be best explained by the access of the light CO_2 coming from the sulphur ores. The *Lithothamnium*-bearing limestones underlying the sulphur series appear isotopically less changed: $\delta^{13}C$ values range from –6.8 to –4.2‰. Similarly, coarse-crystalline calcite and rarely aragonite and strontianite, which precipitated in caverns and vugs of the postsulphate limestones during the later ore-forming stages, belong to the carbonate mineral group characterized by the isotopically lightest carbon. They were formed at the expence of

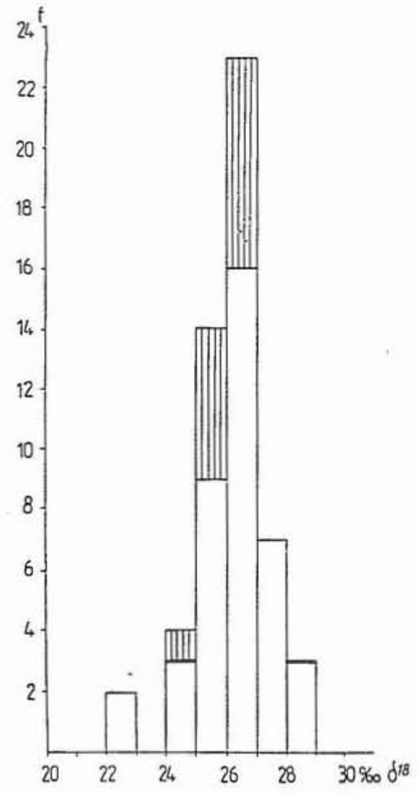

Fig. 6. Oxygen isotopic composition of sulphur-bearing limestones
Explanation as in Fig. 5
Skład izotopowy tlenu wapieni osiarkowanych
Objaśnienia jak na fig. 5

Table 3

Isotopic composition of the residual sulphates

Celestite				Barite			Sulphates of ore water		
sample		$\delta^{34}S_{CDT}$	$\delta^{18}O_{SMOW}$	sample		$\delta^{34}S_{CDT}$	sample		$\delta^{34}S_{CDT}$
Machów	TS–7a	41.7	18.5	Machów	M–01	54.1	Machów	st 66	32.0
	TS–7b	35.9	16.7		M–02	54.7		st 68	33.3
	TS–8	35.9	17.0		M–03	56.7		st 150	32.7
	TS–9	36.9	17.0		M–05	55.0		st 152	33.8
	CM–1	58.6	23.6		M–05	53.8		rz-1	31.5
	CM–5	53.1	27.0		BM–2	67.6		k-1	33.1
	M–50	38.8	22.1		BM–3	71.0			
	M–51	59.3	24.6		BM–4	66.6			
	M–52	38.7	19.2		BM–5	64.1			
	M–53	56.8	22.6		BM–6	66.0			
	M–54	51.4	26.1		BM–1	42.2			
	M–55	35.4	19.0		RM–2	36.3			
	M–56	56.4	24.0		tr 1	39.2			
	M–57	45.1	24.7		tr 2	39.8			
	M–58	39.7	18.5		tr 3	39.0			
	M–59	37.2	18.1		tr 4	39.6			
Piaseczno	S–1	47.4	19.0		tr 5	39.5			
	S–2	57.7	23.6		tr 5	39.8			
					tr 7	39.2			
Czarkowy	CZ–21	39.8	20.7						
	CZ–22	40.3	18.3						
	CZ–23	40.4	19.6						

residual and light carbon dioxide (W. Kowalski *et al.*, 1980; M. E. Böttcher *et al.*, in preparation).

The oxygen isotope composition of the postsulphate limestones is much more homogeneous (Tab. 2; Fig. 6) than the carbon isotopic composition. The $\delta^{18}O$ values range from 24.8 to 27.3‰. With regards to equilibration, oxygen isotopic composition of carbonates is a function of temperature and isotope composition of the water occurring in the environment of mineral precipitation. Low fluctuations of the $\delta^{18}O$ values of the postsulphate limestones indicate a stable temperature of the ore-forming processes which developed in a aqueous environment characterized by rather uniform oxygen isotope composition.

RESIDUAL SULPHATES

All sulphate minerals and aqueous sulphates which formed from the un-reduced (i.e., unaltered and thus residual) part of the initial solid sulphates are defined here as the residual

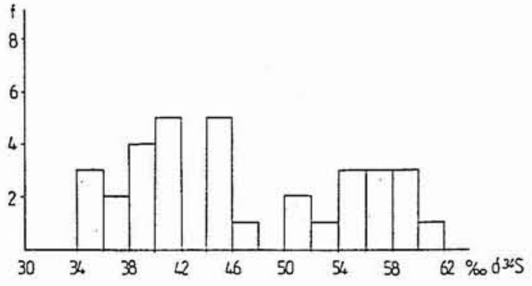

Fig. 7. Sulphur isotopic composition of celestite
Skład izotopowy siarki celestynu

sulphates. They include: celestite, barite, and one of the gypsum generations. Celestite and barite occur in the ore series in quantities which do not exceed one percent by weight, although locally they may form larger aggregates. They are characterized by a variety of morphological forms: from small grains dispersed in the postsulphate limestones to monomineral imprints, veins, and larger druses preserved in cavernous sulphur-bearing carbonate series. These minerals are commonly composed of several generations of crystals (J. Parafiniuk, 1989*a*; E. Pilichowska, 1984).

The $\delta^{34}S$ values of both celestite and barite vary across a wide range: from 36 to 61‰ and from 36 to 71‰, respectively (Tab. 3). Hence, both these minerals are distinctly enriched in the heavier sulphur isotope in comparison to the initial gypsum deposits. In spite of this large isotopic range, it is possible to distinguish (Figs. 7, 8) two distinct groups of $\delta^{34}S$ values for both celestite and barite. The first group of values concentrates around $\delta^{34}S = 40‰$ while the second one occurs between 54 and 60‰ (mean value of 54‰ for celestite and mean value of 68‰ for barite). However, the mean value of barite is relatively less accurate due to a smaller number of analyses. Such a high variability of the sulphur isotopic composition of both these minerals cannot be simply explained as a result of isotopic effects induced by the crystallization process. For example, both celestite and co-occurring anhydrite found in the salt mine at Wieliczka have the same sulphur isotopic composition (J. Parafiniuk, S. Hałas, in preparation). It clearly indicates that a similar isotopic fractionation effect operated during the precipitation of these minerals. According to the present authors, the observed variability of the sulphur isotopic composition of celestite and barite of the Polish sulphur ores may be best explained by variability in the isotopic composition of ore water responsible for the precipitation of celestites and barites. This suggestion is supported by the results of the isotopic analyses. In the case of barite, the heaviest sulphur isotopic values were found in coarse-crystalline forms which are sometimes coloured brown

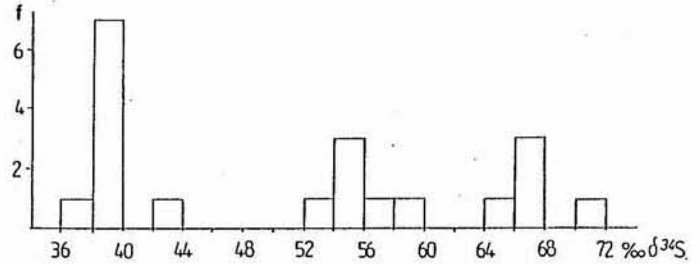

Fig. 8. Sulphur isotopic composition of barite
Skład izotopowy siarki barytu

by bitumens. Younger barite generations, which are white or greyish and sometimes developed as sinters, commonly have lower $\delta^{34}S$ values.

Barite precipitation has recently been observed within the pipes of the Machów mine drainage system as well as locally in the lowest part of the exploited ore series. Barite crusts occurring in the pipes have $\delta^{34}S$ values from 36.3 to 42.2‰ (Tab. 3) which are similar to the values obtained for barite sinters found in the lowest part of the exploited series. A similar interpretation can be called upon the origin of celestite with the $\delta^{34}S$ value about 40‰ (J. Parafiniuk, S. Hałas, in preparation). This celestite generation had to be formed relatively late, possibly its origin was connected with the industrial penetration of the ore series. Unfortunately, modern precipitation of celestite has not been documented in the Machów mine and a sinter celestite variety has been documented only from the Piaseczno mine so far (T. Tyniec, 1961). Generally, the formation of sinter crusts, especially those developed as stalactites, could only take place in an evironment subjected to gravitational flow. Certainly, such a water flow could develop after artificial exposure of the ore series by exploitation and pumping of ore water. In general however, the age of karstification of the Polish sulphur ores is still controversial (comp. T. Osmólski, 1976 and discussion of M. Nieć, 1977 with T. Osmólski, 1977). A trend toward a gradual decrease in the $\delta^{34}S$ values of the aqueous sulphates is additionally supported by successive celestite generations which become progressively less isotopically depleted. In two analysed samples, the older celestite generations with $\delta^{34}S$ values from 45.4 to 44.4‰ were covered by the younger ones with $\delta^{34}S$ between 41.7 and 35.9‰.

Assuming the same fractionation effect as gypsum and based on the younger celestite and barite generations, it is possible to calculate the mean $\delta^{34}S$ values of aqueous sulphates as equal to 38‰. This value represents the youngest stage of the sulphur ore's history, i.e. the chemical ore water regime characterizing ore series before exploitation. Unfortunately, isotopic analyses of ore water at the beginning of exploitation were not carried out. A few analyses of ore water samples taken after several years of exploitation already had lowered $\delta^{34}S$ values ranging from 31.5 to 33.8‰ (Tab. 3). Undoubtedly, these results indicate intensive infiltration of meteoric water into sulphur-bearing series which led to the mobilization of native sulphur by means of oxidation.

Isotopically heavy sulphur of residual origin was found in a few gypsum samples from the Machów mine. This gypsum developed as transparent selenites, was partly brown stained by bitumens and contained native sulphur inclusions. The $\delta^{34}S$ values of this gypsum ranged from 32 to 42‰. These values correspond well to the isotopic composition of the younger celestite and barite generations.

The isotopic composition of aquaeous sulphate (of the ore water) calculated for the end of sulphate reduction is much more difficult to estimate. This process could develop with varying intensity in particular parts of the sulphur ores and thus should be reflected by the isotopic composition of residual sulphates. Using all available data on the isotopic composition of the older celestite and barite generations, it is possible to calculate the mean $\delta^{34}S$ values at about 60‰ for aqueous residual sulphates remaining after the sulphate reduction.

A residual character is also supported by the oxygen isotopic composition of these sulphates (Tab. 3). The $\delta^{18}O$ values of celestite range from 16.7 to 27.0‰ and are distinctly higher than those found for the Miocene evaporites. The analyses show a correlation between both the sulphur and oxygen isotopic compositions. Older celestite generations have higher values of $\delta^{34}S$ and $\delta^{18}O$ than younger generations.

Oxygen isotopic exchange between sulphate ions and water in shallow subsurface temperature conditions is very slow (H. Chiba, H. Sakai, 1985). For this reason, the enrichment of residual sulphate in ^{18}O has to be a result of bacterial sulphate reduction. As one may suppose (Y. Mizutani, T. A. Rafter, 1973; P. Fritz *et al.*, 1989), the oxygen exchange reaction takes place between sulphate – enzyme complexes and water, the latter being the evironment of reaction. Note that opposite to the sulphur isotopic composition, the oxygen isotopic composition of the residual sulphates does not depend on the rate of sulphate reduction but instead depends only on the temperature and water's isotopic composition. In experimental conditions the oxygen fractionation factor between sulphate and water reached 25‰ at 30°C and 27‰ at 17°C (P. Fritz *et al.*, 1989). Thus, the results of complex sulphate isotopic composition analyses may be used to estimate the genesis and geochemical history of the ore waters.

SULPHUR ISOTOPIC BALANCE IN SULPHUR ORES

Assuming that sulphate reduction developed in closed system conditions, it is possible to compute the equation which balances the sulphur isotopic composition (W. Kowalski *et al.*, 1990):

$$M_g\,\delta^{34}S_g = M_s\,\delta^{34}S_s + M_r\,\delta^{34}S_r \qquad [1]$$

where: M_g — the mass of elemental sulphur contained in a mass of gypsum (it has been assumed here that the mass of gypsum is 1000 g); M_s — the mass of native sulphur originated from the mass of gypsum; M_r — the mass of sulphur contained in sulphates derived from residual as well of aqueous and solid minerals.

The same indices apply to the isotopic signatures of sulphur in gypsum, native sulphur, and residual sulphates. In these considerations hydrogen sulphide of the ore water has been omitted for two reasons: its insignificant quantities compared to the amount of ore and its uncertain genesis. H_2S may be a relic of the sulphate reduction process or may be a product of the hydrolysis of native sulphur. Based upon the findings of sulphur isotopic ratios of all components included in equation [1] and the value of M_g (equal to about 180 g), it is possible to evaluate a mass of elemental sulphur obtained in this way. The $\delta^{34}S_g$ and $\delta^{34}S_s$ values may be estimated with adequate accuracy as 22 and 11‰ respectively. The mean sulphur isotopic composition of residual sulphates is much more difficult to calculate due to a lack of measured data of aqueous sulphates left after sulphate reduction. Substituting a value of 33‰ for $\delta^{34}S$, which corresponds to the mean isotopic composition of sulphates from the ore water currently conducted away the Machów mine by a drainage system, we get:

$$180\text{ g } 22‰ = M_s\ 11‰ + (180\text{ g} - M_s)\ 33‰$$

from the above: $M_s = 90$ g, and the capacity of sulphate reduction is as high as 50%. It is evident that this value is extremely low. More detailed calculations may be obtained by the estimation of sulphate isotopic composition of ore waters deciphered from the composition of residual sulphates. For younger celestite and barite generations, for which the original host fluids should have $\delta^{34}S$ value equalling ≈ 38‰, we obtain capacity equal to 59%. For the older generations, closer to the end of the sulphate reduction and characterized by $\delta^{34}S$ value equalling ≈ 60‰, the capacity is 77%. It seems likely that the latter value is the closest to the real one. Hence, it means that at least 1/4 of the original sulphate bulk has remained in the solution as non-reduced sulphates. A part of these sulphates has been preserved in the ore waters until the present while another part has been carried outside the orebody and only a small part has been bound into sulphate minerals such as celestite and barite.

MECHANISM OF ORE-FORMING PROCESSES IN THE LIGHT OF ISOTOPIC STUDIES

A model of bioepigenesis for the Polish sulphur ores of the Carpathian Foredeep, worked out on the basis of various geological data (e.g. S. Pawłowski *et al.*, 1965, 1979, 1985; T. Osmólski, 1972; M. Nieć, 1982, 1992; B. Kubica, 1992) is also confirmed by the isotopic data. The sulphate reduction could not have taken place syngenetically with gypsum deposition in marginal part of the Miocene basin, because the observed enrichment in ^{34}S of residual sulphates could not have occurred in such open system with an unlimited supply of sulphate ions. One may assume that the sulphate reduction in the basin took place syngenetically with gypsum precipitation in lagoons isolated from open-marine conditions. However, in such cases the gypsum deposits preserved at the contacts with the sulphur-bearing limestones should be noticeably enriched in the heavier sulphur isotope. Meanwhile, all gypsum deposits overlying, or underlying, or adjacent to the sulphur-bearing series are isotopically homogenous with the isotope composition typical for non-altered Miocene evaporites. This is interpreted by the present authors as support for the epigenetic course of sulphate reduction developed from the solution containing sulphate ions which came from dissolved solid gypsum. It is obvious that the isotopic results do not precisely match the age of the sulphate transformation developed in the Carpathian Foredeep. However, all collected geological data (ref. *op. cit.*) suggest that the process already took place in Tertiary time, certainly after substantial burial of the evaporite horizon by impermeable clayey series which isolated the ore-forming environments. In the light of these data, the sulphur ore origin may be linked with the Late Alpine orogenic movements developed in the Carpathian belt and in its foredeep. These tectonic movements were responsible for the formation of suitable pathways conducive to hydrocarbon migration into marginal and shallow parts of the Carpathian Foredeep.

Sulphur isotope fractionation found in the sulphate-native sulphur system heavily argues for bacterial sulphate reduction. Inorganic sulphate reduction cannot effectively develop in low temperatures and commonly is connected with a much lower sulphur isotope signature than is observed in the Polish sulphur ores. For anaerobic heterotrophic bacteria like *Desulfovibrio*, which, most probably played the main role in the formation of the Polish sulphur ores, sulphate reduction to hydrogen sulphide was connected with their metabolic activity. These bacteria are active at a pH between 5.5 and 9 and a temperature between 5 –75°C, with a maximum activity at 30–55°C (M. V. Ivanov, 1964). They use (by means of oxidation) organic matter, for instance hydrocarbons, as an energy donor. If these bacteria use methane according to the equation:

$$SO_4^{2-} + CH_4 = HS^- + HCO_3^- + H_2O \qquad [2]$$

then the environment becomes highly enriched in hydrogen sulphide and carbonate ions. Consequently, calcite is precipitated. In the light of the isotopic investigations discussed elsewhere in this paper, it seems clear that there is no need to assume any reducing factor other than methane. Oils or other bitumens may have played a subordinate role.

The oxidation of hydrogen sulphide (produced by sulphate reduction) is a requisite for the formation of elemental sulphur. There are two possible mechanisms of oxidation. The first one assumes reaction between hydrogen sulphide and a sulphate ion:

$$4H_2S + SO_4^{2-} = 5S + 4H_2O \qquad [3]$$

However, this reaction occurs too slowly in shallow subsurface temperatures to account for much of the necessary oxidation (J. B. Davis, D. W. Kirkland, 1979). The second possibility assumes the oxidation of hydrogen sulphide by oxygen dissolved in meteoric waters infiltrating sulphur ores (T. Osmólski, 1973) according to the equation:

$$H_2S + 1/2O_2 = S + H_2O \qquad [4]$$

This mechanism strongly implies a huge, subterranean, fresh-water flow through the ore series. However, this assumption is not supported by the chemistry of the ore water or by the results of the isotopic studies. Additionally, such a flow should result in almost complete freshening of the ore water and a removal of residual sulphates. Moreover, it is difficult to accept of oxygen diffusion through a hydrochemical barrier formed at the ore boundaries mainly because the low rate of oxygenated water flow throughout the thick, impermeable, clayey cap covering the sulphur ores would have been too low.

According to the present authors, a more appropriate hypothesis assumes the oxidation of hydrogen sulphide by autotrophic bacteria which can synthetize organic substances from carbon dioxide or bicarbonate. This reaction may be schematically written as follows:

$$2H_2S + CO_2 = 2S + (CH_2O) + H_2O \qquad [5]$$

Elemental sulphur may be deposited intracellulary in bacterial cells and then, after their post-mortem decomposition, this mineral may be accumulated into larger, pure sulphur aggregates. Relics of microfossils preserved within sulphur granules and resembling sulphur bacteria were well illustrated by J. Czermiński (1960) and more recently, sulphur grains of sizes corresponding to cells of bacteria have been described by W. Ryka (1988). Microbial ecosystems formed various organic complexes which in turn might have been used by sulphate-reducing bacteria and were not preserved in the ore sequences. This hypothesis requires a close co-operation between both the reducing and oxidizing bacteria and is commonly described from natural marine, continental-water, and soil systems. This microbial ecosystem, defined as *sulfureta*, consists of sulphate-reducing bacteria like

Desulfovibrio and sulphur-oxidizing microbes like photosynthetic sulphur bacteria of *Chromatium* species (P. A. Trudinger, 1979). However, this model cannot be easily applied to the formation of Polish sulphur ores because of the environmental demands of phototrophic bacteria.

Results of the isotopic researches may be used as a geological thermometer that could help to estimate the temperature of sulphur ore formation. In the equilibrium state the oxygen isotopic composition of calcite is mainly controlled by the water composition of the precipitation environment and the temperature, according to the formula established by I. Friedman, J. R. O'Neil (1977):

$$1000 \ln[(\delta^{18}O_{CaCO_3} + 1000) : (\delta^{18}O_{H_2O} + 1000)] = 2.78\,(10^6\,T^{-2}) - 2.89 \qquad [6]$$

Of course, at present, it is impossible to precisely evaluate the isotopic composition of the ore water which has been created by the ore-forming processes. Assuming that this water had an isotopic composition similar to recent marine waters then it is possible to obtain a temperature of sulphur ore formation equal to 39°C. Assuming that ore waters had an isotopic composition like recent groundwaters (with $\delta^{18}O$ value = –7‰) then the temperature was equal to 6°C. Thus, the most realistic temperature for the alteration of sulphate deposits and responsible for the formation of the Polish sulphur ores was in the range between 6 and 39°C. Certainly, it seems more likely that the formation temperature was closer to the higher limit of the range. This corresponds well to the optimal environmental conditions for the development of sulphate-reducing bacteria. Similar results have recently been reported by A.W. Pobierieżski (1993) for the West Ukraine sulphur ores. He used the thermobarogeochemical method and found that the temperature of the sulphur mineralization environment was not higher than 35–37°C.

ORIGIN OF THE ORE WATERS

Origin and evolution of ore water composition of the Polish sulphur ores is essential to evaluation whether the transformation process developed in closed or open system conditions. Although, both hydrogeochemical and isotopic analyses contributed substantial data, a final conclusion at the present stage of knowledge seems to be impossible. Currently, detailed chemical characteristics of the ore waters are available and were already established during the documenting research as well as by the hydrogeological mine service of the Tarnobrzeg ore (e.g. S. Turek, 1965, 1979; A. Smuszkiewicz, 1969). These waters occur elsewhere in sulphur-bearing and barren limestones, in gypsum deposits found in the ore series as well as in the underlying carbonate-siliciclastic sequence of the Baranów Beds. The ore waters are mineralized and the extent of the mineralization increases along with increasing depth of the ore series occurrence. The chemistry of these waters changes in the same direction. For example, in the shallowest part of the Piaseczno ore they were mineralized up to 1–2 g/l with bicarbonate 50 and 35% mval/l of sulphate while chloride only comprised 15% mval/l. As to the cations, these waters were calcium-dominated (80% mval/l) with an admixture of magnesium and sodium (10% mval/l per each element). In the deeper-buried part of the ore series, where the Machów mine is located, the mineralization of the ore waters increases up to about 10 g/l and at the same time a decrease of bicarbonate content (up to 10% mval/l) was observed there. In the ore water of this region, there is a high concentration of aqueous sulphate, sodium predominates over calcium and magnesium among the cations, and bicarbonate is replaced by chloride comprising about 50–60% mval/l. The highest ore water mineralization up to 18 g/l is observed toward the southeast direction where chloride and natrium predominate (80% mval/l per each) while sulphate comprise about 15% mval/l and bicarbonate is about 5% mval/l. Similar proportions in the ore water were found for calcium and magnesium (both 5% mval/l). In general, the ore waters also contain free carbon dioxide and hydrogen sulphide occurring in various amounts: from few tens up to a few hundred mg/l.

The ore water chemistry presented above clearly shows that the ore waters were not developed only via the infiltration of surface waters into ore the series. Their chemical composition is similar for the brines accompanying hydrocarbon fields and the proportions between the main ore water components developed due to extended contact of residual marine water with the rock environment. According to the present authors, it is difficult to decide whether these waters are of a depositional origin linked with a stage of gypsum precipitation or whether they migrated (along with hydrocarbons) from deeper parts of the foredeep, as is commonly assumed by other workers. Certainly, the origin of these waters was complex. Undoubtedly, they were partly replaced by meteoric waters descending from a recharge area (occurring beyond the sulphur ores) and passing over the sulphur-bearing formation along a regional dip. Based upon the extent of ore water mineralization, it is possible to compute that at the depth of the Machów ore the residual and meteoric waters mixed at a ratio of 1:1. Generally, the infiltration water predominated in the shallow part of the orebody while the original brines predominated in the deeper part.

The model of ore water genesis outlined above is supported by the isotopic results. The sulphate isotopic composition indicates a residual character of the ore water and this, in turn, evidences a limited exchange between the ore water and its environment at the time of the sulphur ores' formation. It also allows reconstruction the evolution of the ore water isotopic composition from the initial ore formation stage untill the present day. If it is assumed, as suggested by the sulphur isotopic composition of the older celestite and barite generations, that the sulphur ore water isotopic composition was equal to 60‰ at the time the Machów ore was formed, then the sulphur isotopic composition of the younger generations (equal to 40‰) means that the original residual sulphates mixed together with an equal amount of unaltered sulphates of evaporitic origin. A part of these residual sulphates could be the result of direct contact between the ore waters and unaltered gypsum deposits. However, most of the aqueous sulphate got to the ore series by infiltration of surface meteoric waters flowing through gypsum rocks surrounding the sulphur ores. A local increase in the ore water aqueous sulphate content could induce the binding of Sr and Ba ions into precipitated sulphate minerals i.e. celestite and barite. A further decrease in the $\delta^{34}S$ value to about 33‰ of aqueous sulphates found in recent ore waters at Machów

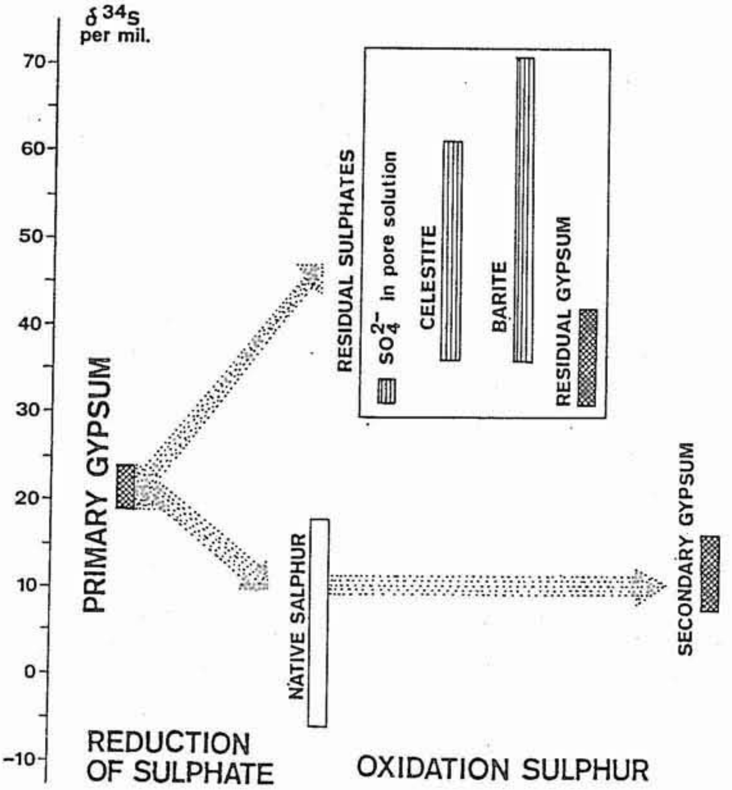

Fig. 9. Fractionation of sulphur isotopes in both gypsum reduction and native sulphur oxidation processes in the Machów ore

Frakcjonowanie izotopów siarki w procesach redukcji gipsu i utleniania siarki rodzimej w złożu Machów

was presumably connected with the development of both anthropogenic exposure and ore water drainage.

DISINTEGRATION OF SULPHUR ORES

The isotopic results are also helpful for the evaluation of sulphur ore disintegration induced by anthropogenic subaerial exposure (comp. R. Blajda *et al.*, 1975). As is commonly known (see e.g. S. V. Kushnir, 1988 with references therein), elemental sulphur is only stable in narrow pH and Eh conditions. Generally, a long-term preservation of the sulphur ores is possible only in slightly reducing conditions assured by a thick cover of impermeable clay. The exploitation of sulphur ores by both the open-pit and underground melting methods induced a drastic change in conditions and caused the oxidation of sulphur ores. Consequently, the oxidation produced sulphuric acid which immediately reacted with calcium carbonate to precipitate secondary gypsum (a reverse process to the sulphur ore formation). The precipitation of secondary gypsum is commonly observed in the open-pit mine at Machów, and it is also intensively developed in old dumps and outcrops of the closed Czarkowy open-pit mine (S. Hałas, A. Kurpiewski, 1982; J. Parafiniuk, 1989*b*). The analysis of sulphur isotopic composition is the best method for the identification of secondary gypsum. The oxidation of native sulphur through either organic (by the activity of *thiobacillus* — G. A. Sokolova, G. I. Karavaiko, 1968; M. V. Ivanov, 1964) or inorganic means is associated with a slight isotopic fractionation (N. Nakai, M. L. Jensen, 1964; W. A. Grinenko, L.N. Grinenko, 1974). Because elemental sulphur is characterized by the light isotopic composition, the secondary gypsum formed by native sulphur oxidation is also enriched in the ^{32}S. The $\delta^{34}S$ values of both the dispersed secondary gypsum crystals (up to few percentage of rock volume) preserved in sulphur-bearing limestones of the Machów mine and the gypsum encrusting exposed limestones with native sulphur at Czarkowy have the isotopic range between 7.7 and 15.7‰. These values are distinctly lower than the values typical for Miocene evaporites and lower than those obtained for residual gypsum. Thus, the isotopic composition allows easy distinction among these three (primary solid, aqueous, and secondary solid) generations of gypsum (Fig. 9)

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Instytut Geochemii, Mineralogii i Petrografii
Uniwersytetu Warszawskiego
Warszawa, al. Żwirki i Wigury 93
Instytut Fizyki
Uniwersytetu M. Curie-Skłodowskiej
Lublin, Plac M. Curie-Skłodowskiej 1
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Jan PARAFINIUK, Włodzimierz KOWALSKI, Stanisław HAŁAS

GEOCHEMIA IZOTOPÓW TRWAŁYCH A GENEZA ZŁÓŻ SIARKI — ZARYS

Streszczenie

Przedstawiono model genezy polskich złóż siarki rodzimej zapadliska przedkarpackiego oparty na wynikach analiz stosunków izotopowych siarki, węgla i tlenu w gipsach, siarce rodzimej, wapieniach pogipsowych i siarczanach rezydualnych (celestyn, baryt, siarczany wód złożowych).

Gipsy mioceńskie całego obszaru zapadliska przedkarpackiego, macierzyste dla złóż siarki, cechują się homogenicznym składem izotopowym siarki i tlenu (tab. 1, fig. 2). Wartości $\delta^{34}S$ wynoszą dla nich 22–23‰, a $\delta^{18}O$ ok. 13‰. Są one typowe dla ewaporatów mioceńskich, a także analogiczne jak dla siarczanu współczesnej wody morskiej. Badania izotopowe wody krystalizacyjnej gipsu wykazały znaczny stopień jej wymiany z wodą gruntową (fig. 3).

Siarka rodzima w porównaniu z gipsami jest wyraźnie wzbogacona w izotop ^{32}S, a średnia wartość $\delta^{34}S$ wynosi dla niej ok. 11‰, przy zmienności od –6 do 18‰ (fig. 4). Lżejsza izotopowo siarka występuje w peryferyjnych częściach złóż lub jest rozproszona w skałach otoczenia.

Wapienie pogipsowe różnią się od typowych wapieni morskich dużym wzbogaceniem w izotop ^{12}C (tab. 2, fig. 5). Dla wapieni centralnych części złóż wartości $\delta^{13}C$ są skupione w przedziale od –40 do –45‰, podczas gdy dla partii marginalnych mogą dochodzić do –20‰. Dotychczas zróżnicowanie to tłumaczono odmiennym źródłem pochodzenia węgla (lekki izotopowo metan w częściach centralnych, cięższa ropa naftowa lub bituminy w częściach peryferyjnych) lub kontaminacją izotopowo cięższymi, pierwotnymi wapieniami morskimi. Wydaje się, że bardziej prawdopodobną przyczyną zróżnicowania składu wapieni była migracja części CO_2 ze środowiska formowania się złóż. W przeciwieństwie do węgla skład izotopowy tlenu wapieni pogipsowych jest jednorodny z wartościami $\delta^{18}O$ od 24,8 do 27,5‰.

Celestyn, baryt, jedna z generacji gipsu oraz siarczany wód złożowych zostały zaliczone do siarczanów rezydualnych, gdyż utworzyły się z niezredukowanej części siarczanów wyjściowych. Charakteryzują się wybitnym wzbogaceniem w izotop ^{34}S (tab. 3, fig. 7, 8). Wartości $\delta^{34}S$ celestynu zmieniają się od 36 do 61‰, a barytu od 36 do 71‰. Na podstawie składu izotopowego siarki można wyróżnić starsze generacje obu tych minerałów o wartościach $\delta^{34}S$ ok. 60‰, które krystalizowały w końcowych stadiach etapu redukcji, oraz młodsze, o wartościach $\delta^{34}S$ ok. 40‰, utworzone później, aż do początków eksploatacji złóż. Siarczany rezydualne zostały zachowane do naszych czasów w wodach złożowych, na co wskazują ich wartości $\delta^{34}S$ wynoszące od 31,5 do

33,8‰. Siarczany rezydualne są również wzbogacone w cięższy izotop tlenu. Dla celestynu wartości $\delta^{18}O$ wynoszą od 16,7 do 27,0‰.

Z bilansu izotopów siarki (równanie [1]) można określić wydajność procesu redukcji. Nie była ona wyższa niż 77%, co oznacza, że co najmniej 1/4 masy pierwotnych siarczanów pozostała niezredukowana w roztworze.

Dane izotopowe potwierdzają — wypracowaną na podstawie innych przesłanek — tezę epigenetycznego pochodzenia omawianych złóż siarki. Stanowią one ważny argument na rzecz bakteryjnego przebiegu procesu redukcji siarczanu do siarkowodoru. Także utlenienie H_2S do siarki rodzimej odbyło się zapewne przy udziale mikroorganizmów. Kluczowy dla rozstrzygnięcia, czy środowisko powstania złóż siarki miało charakter otwarty czy też zamknięty, jest problem pochodzenia wód złożowych. Ich chemizm oraz wyniki badań izotopowych skłaniają do przyjęcia poglądu, że były to solanki wzbogacone w siarczany z rozpuszczania gipsu. Wody te były stopniowo wymieniane przez infiltrujące wody powierzchniowe, ale wymiana ta wyraźnie zaznaczyła się tylko w płytszych, słabiej izolowanych częściach złóż.

Eksploatacja złóż siarki wywołała ich degradację. W efekcie przejścia środowiska złóż w utleniające został uruchomiony proces utleniania siarki rodzimej i lokalnie utworzył się wtórny gips. Cechuje się on wartościami $\delta^{34}S$ w granicach 7,7–15,7‰, co umożliwia jego odróżnienie od innych generacji gipsu występujących w tych złożach.