

JAN PARAFINIUK

Oxidation of native sulfur in the Fore-Carpathian sulfur deposits in the light of isotopic and mineralogical data

ABSTRACT: Secondary gypsum is formed as a result of sulfur oxidation in the native sulfur deposits of the Fore-Carpathian Depression, Southern Poland. Limestones containing native sulfur exposed to the activity of atmospheric weathering easily change into gypsum. The secondary gypsum occurs as fine, dispersed crystals, crusts and crystal groups growing on the surface of rocks, which are exposed for a longer period. The newly formed gypsum differs in the sulfur isotope composition from its older generations occurring in the deposits. The differentiation of isotopic composition of secondary gypsum in relation to native sulfur is much higher than it is indicated by the experimental data. There was recorded gypsum of both lighter and heavier isotopic composition than the native sulfur. The sulfur oxidation in the deposits can proceed either inorganically or by the sulfur bacteria. There was observed the secondary gypsum which crystallized from the formation waters collected in ephemeral pools in the bottom side of the sulfur mine and the formation of which is connected with the bloom of sulfur bacteria.

INTRODUCTION

The occurrence of elementary sulfur in nature is limited to the narrow range of redox potential and pH of environment (GARRELS & CHRIST 1965). In the strong reducing conditions and at the lower pH values the sulfide ion is stable. The rise of redox potential and/or pH values causes the native sulfur oxidation to the sulfate ion. The formation of native sulfur deposits undergoes only at a strictly determined, stable physico-chemical conditions. Changes of these conditions initiate processes of alteration or degradation of the deposits (CZERMIŃSKI 1968, NIEĆ 1984). Polish sulfur deposits are protected against the influence of atmospheric conditions by a thick cover of clayey sediments. Highly mineralized, hydrogen sulfide containing pore waters are an important factor of sulfur deposit preservation. In case the conditions in which the sulfur deposits were formed do not change, the degradation of the deposits as a result of the sulfur oxidation does not occur. The sulfur oxidation effects appear after

the exposure of the deposits or exchange of pore solutions into oxygenated infiltration waters.

The preparation of the deposits to the exploitation and the open mining (to lesser extent an underground melting) creates the conditions favoring the sulfur oxidation. Though even in the open mine the rate of the sulfur oxidation is small, the process itself has to be considered for the planned removal of the cover of the deposit and storage of sulfur ore (CZERMIŃSKI & PAWŁOWSKI 1961). The sulfur oxidation results in selfwarming of ore piles stored for a longer period, decrease of the sulfur content in the ore exposed to a longer influence of atmospheric conditions and crystallization of secondary gypsum, which is the subject of the present study.

GEOLOGICAL SETTING

Polish sulfur deposits are connected with the gypsum and anhydrite horizon deposited in the Middle Miocene (Badenian) in the Fore-Carpathian Depression. These deposits are mainly composed of layers of post-gypsum limestones (subordinately marls) with native sulfur, ranging in thickness from a few to several meters. They are located within the uplifted parts of tectonical structures or in the fault zones. In peripheral parts of some deposits or in their roof parts, the sulfur-bearing limestones pass into barren post-gypsum limestones from which sulfur has been removed by the secondary processes. The sulfur deposits

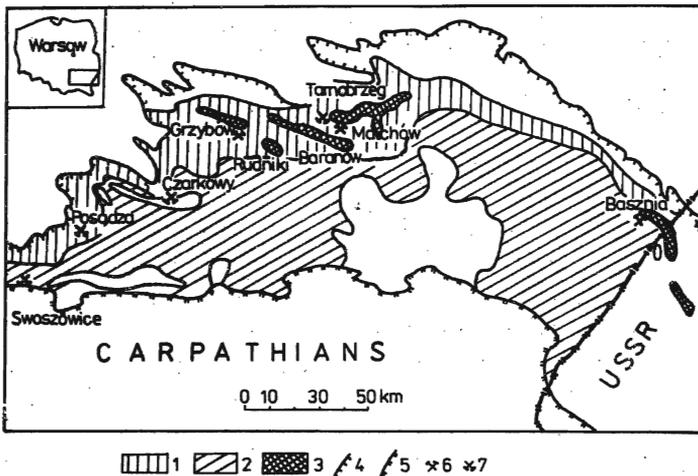


Fig. 1. Location of the native sulfur deposits within the Fore-Carpathian Depression, Southern Poland

- 1 — Extent of the Middle Miocene (Badenian) gypsum, 2 — extent of anhydrite, 3 — native sulfur deposits, 4 — extent of the Middle Miocene marine sediments of the Fore-Carpathian Depression, 5 — Carpathian overthrusts, 6 — operating sulfur mines, 7 — abandoned sulfur mines

are covered by marly sediments of the Pecten Beds (Badenian), Krakowiec Clays (Sarmatian) and Quarternary sediments. The total thickness of the cover of sulfur deposits ranges from several to more than 200 m. In the bottom of the deposits there occur sands and silts of the Baranów Beds (Badenian) deposited unconformably on the bedrock.

Large sulfur deposits in the Fore-Carpathian Depression were discovered in the northern marginal zone of the evaporated area, though appearances of sulfur are also known from the central part of the Depression. The largest documented deposit of native sulfur is at Tarnobrzeg, with its length 35 km and width 0.5–4.5 km (see Text-fig. 1). To the SW of the Tarnobrzeg deposit there are situated smaller ones, namely: the Osiek – Baranów, the Grzybów, and the Rudniki deposits. In the eastern edge of the Polish part of the Fore-Carpathian Depression the sulfur-bearing limestones occur in the area of Basznia being the continuation of the Ukrainian deposits. Small deposits and sulfur appearances occurring in the western part of the Depression (Swoszowice, Pośadza, Czarkowy; see Text-fig. 1) have only historical importance.

The origin of the Polish native sulfur deposits is connected with the bacterial reduction of sulfates under the influence of hydrocarbons as an energy source. There exist some data indicating an epigenetic nature of alteration processes of lithified gypsum rocks into sulfur-bearing limestones (PAWŁOWSKI & *al.* 1979).

MATERIALS AND METHODS

For the study purposes the Czarkowy and Machów deposits (see Text-fig. 1) were chosen. They differ in the oxidation process advancement. The Czarkowy deposit was exploited periodically since 18th century till 1918 and played an important role in sulfur supply of Russia in 19th century and Austria during the 1st World War. Analyzed samples were taken from the outcrop of the Czarkowy deposit itself, and from the dump, the both of which have been exposed to the activity of atmospheric conditions at least since the last 70 years.

The Machów mining field is situated in the SW part of the Tarnobrzeg deposit, which has been discovered in 1953. The exploitation is run by the open-pit mine working continuously from the 60's. Analyzed samples were taken from the western wall of the open-pit in the zone ranging from recently exploited spots to those exposed for several years. To the present studies included were also samples of gypsum which forms in the ephemeral pools at the deposit bottom.

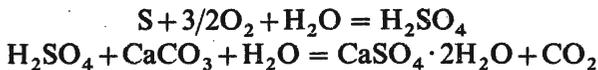
The replacement of native sulfur and calcite by the secondary gypsum has been observed in thin sections under the polarizing microscope and scanning electron microscope (SEM).

For the isotope studies sulfates were converted to SO_2 using procedure of HALAS & WOLAŃCIEWICZ (1981). Barium sulfate precipitated from the oceanic water, correlated with the troilite standard (CDT), has been used as the determination standard. Samples of the sulfur ore were ground and leached with the distilled water for a period of 24 hours. After the dissolution of gypsum, the samples were filtered and then sulfates as BaSO_4 were precipitated from the filtrate. Isotopic composition of the native sulfur was determined in the same samples after having carbonates (and celestite if necessary) removed by means of hot HCl (1:1 v/v). Sulfur was oxidized using mixture of concentrated HNO_3 and HCl (3:1) with an admixture of bromine. After the separation of insoluble silicate residuum, BaSO_4 was precipitated and then treated similarly as in the case of gypsum samples. In the course of sample preparation for isotopic analysis, the gypsum and sulfur content were determined by weight method. The error of isotopic determinations in the $\delta^{34}\text{S}$ values did not exceed $\pm 0.2\text{‰}$.

MINERALOGY OF THE SECONDARY GYPSUM

The secondary gypsum, crystallized as a result of native sulfur oxidation, is often encountered although usually in small amounts, as a component of sulfur-bearing limestones exposed to a longer contact with an oxidizing environment. However, it was not until now described in details because of difficulties in differentiation of the secondary gypsum from older generations of this mineral, occurring in the sulfur deposits.

The biggest amounts of secondary gypsum were found in the Czarkowy deposit outcrop. This outcrop constitute porous, fragile limestones containing numerous fine, dispersed gypsum crystals. The surface of limestones is covered by groups of crystals or gypsum crusts. In the interior of the rocks there were observed remnants of native sulfur aggregates surrounded by gypsum crystals. It was possible to trace under the microscope the gradual replacement of sulfur by gypsum which was accreting from the edges of sulfur aggregates and penetrating their interior along fissures. The surface of sulfur aggregates is uneven and possesses many corrosive concavities, whereas the accreting gypsum forms well developed euhedral crystals (*see* Pl. 1, Figs 1–2). Some bigger gypsum crystals show poikilitic texture. They contain in their interior besides sulfur and calcite relicts also smaller, randomly placed gypsum crystals. There were also observed strongly corroded calcite crystals. In places where gypsum is more abundant, calcite disappears dissolved by sulfuric acid according to the equations:

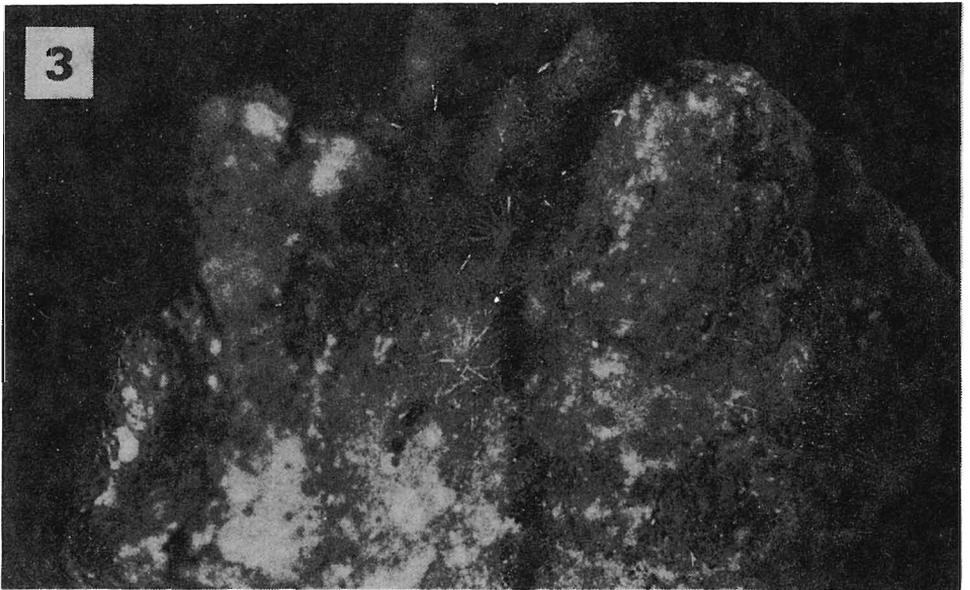
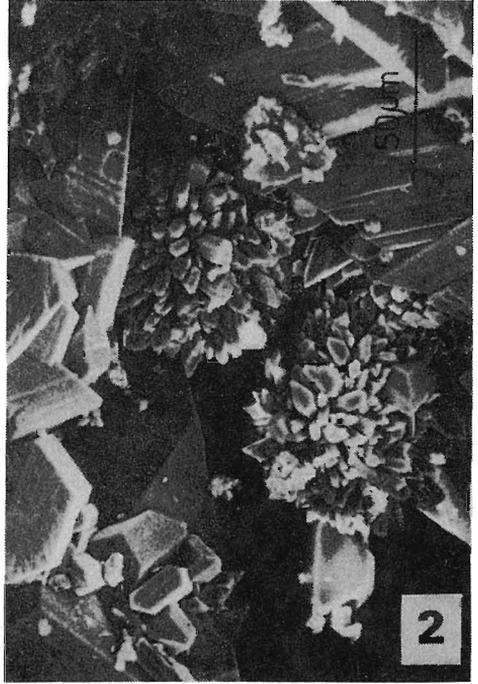
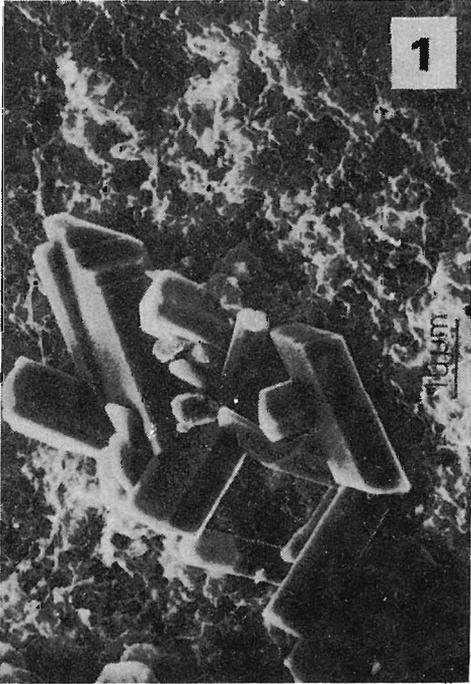


In the western wall of the Machów open pit-mine, which is for a shorter time exposed to the activity of atmospheric conditions, the oxidation process is by far less advanced. The macroscopically visible secondary gypsum is only in the oldest part of the wall sporadically observed here. However, as mineralogical analyses indicate (Table 1), the scattered gypsum is the common component of the sulfur-bearing limestones. In small amounts it also occurs in the presently mined sulfur ore. The comparison of the gypsum content in limestones (Table 1) from the current front of exploitation to the part exposed

Table 1

Mineral composition of the weathering sulfur-bearing limestones from the western wall of the Machów open-pit mine (wt. %)

Sample	Gypsum	Native sulfur	Calcite
M 87/1	0.02	21.2	75.6
M 87/2	0.9	19.8	63.8
M 87/3	1.0	63.3	30.9
M 87/4	3.1	38.1	43.5
M 87/5	7.4	31.1	49.5
M 87/6	3.9	22.0	66.9



- 1 – Secondary gypsum crystals on the weathering native sulfur; Czarkowy, SEM
- 2 – Euhedral secondary gypsum crystals in the fissure of sulfur-bearing limestone; Czarkowy, SEM
- 3 – Acicular secondary gypsum overgrowing calcite and native sulfur; Machów, nat. size

for over a dozen years, indicates that the degree of sulfur oxidation first of all depends on the time of the atmospheric influence. The structure of sulfur-bearing limestones and shape of sulfur aggregates play also a certain role. The fissured and strongly cavernous limestones containing aggregates of fine-crystallized sulfur are less resistant to oxidation than compact rocks with a coarse-crystallized sulfur. However, the secondary gypsum content is only an approximate measure of the oxidation degree, because of the possibility of partial sulfate drainage by rainfall.

The weathering sulfur-bearing limestones are becoming fragile and strongly porous. The presence of fine, dispersed pyrite gives them gray color. Its oxidation changes the limestone color to white, somewhere covered with the brown patches of iron oxides. The sulfur crystals in the caverns in limestone at the first stage suffer the internal fissuring because of exceptional sensitivity to the temperature change, and the crystal surface becomes partially corroded and frosted.

The products of chemical weathering of the sulfur-bearing limestones has to be differentiated from the much more common barren ones. The barren limestones do not differ by their texture from those of sulfur-bearing. They were formed as a result of dissolution and replacing of sulfur from some parts of the deposits. This process probably underwent in the reducing conditions with the share of hydrocarbons (NIEĆ 1984), as it is indicated by the brown color of calcite and barite crystals, which precipitated in postsulfur caverns. In the barren limestones gypsum does not occur.

Another of secondary gypsum has been recorded in the bottom of the Machów open-pit mine. It occurs as a few millimeters long, euhedral, needle-shaped crystals densely overgrowing sulfur or calcite crystals (*see* Pl. 1, Fig. 3). Its relation to the occurring minerals indicates that this is the youngest mineral crystallizing from the pore waters. The acicular gypsum cannot have any connection with the ore-forming processes, therefore it is the product of the recent sulfur oxidation. Details concerning the origin of this secondary gypsum are discussed hereafter.

SULFUR ISOTOPE COMPOSITION OF GYPSUM

The determination of sulfur isotope ratios appear to be a convenient method of solving the origin problem of gypsum in the sulfur deposits. On the basis of these investigations and mineralogical observations three gypsum generations may be distinguished.

The oldest generation is gypsum, which is being parent rock for the sulfur deposits. This is the product of the evaporation in hypersaline conditions, which has been deposited over a large area of the Fore-Carpathian Depression in the Middle Miocene (*see* Text-fig. 1). Its lithology varies from laminated, fine-crystalline rocks to giant, several meters long selenite crystals (KWIATKOWSKI 1972, BABEL 1987). This gypsum surrounds the sulfur deposit, and it occurs either in the bottom side, or at the top, or as isolated remnants in the peripheral parts of the deposits.

The isotopic composition of the Miocene gypsum is fairly uniform with an average $\delta^{34}\text{S}$ value close to 22‰ (HALAS & KROUSE 1982, PARAFINIUK & *al.* 1989). This value is typical of Miocene evaporites (see CLAYPOOL & *al.* 1980, LONGINELLI 1980) and it indicates that the crystallization of gypsum proceeded from brines with sulfur isotope ratios analogous as in the recent marine water.

The second generation constitutes the rarely occurring crystals of selenite, from a few to several centimeters long, which are found in peripheral parts of the sulfur deposits, *i.e.* in the intermediate zone of sulfur-bearing limestones and nonaltered gypsum. Gypsum crystals of this generation, often stained by hydrocarbons to the yellow or brown color, can also contain native sulfur inclusions. These gypsum crystals are genetically connected with the bacterial sulfate reduction, which led to the sulfur deposits origin. This gypsum crystallized from the pore solutions containing still unreduced, residual sulfates of the incompletely proceeded ore-forming processes. Since bacterial reduction leads to the distinct sulfur isotope fractionation, the hydrogen sulfide and then the developing elementary sulfur are enriched in lighter isotope, whereas in residual sulfates the heavier sulfur isotope cumulates (see Text-fig. 2). Hence, sulfur of residual gypsum is isotopically heavier than that of evaporate origin and $\delta^{34}\text{S}$ values are ranging from 32 to 42‰ . Still higher enrichment with the heavier sulfur isotope is typical of celestite ($\delta^{34}\text{S}$ values changes from 41 to 61‰) and barite ($\delta^{34}\text{S}$ changes from 54 to 71‰), which crystallized from pore solutions containing residual sulfates (PARAFINIUK 1989). The formation waters retain the residual sulfates until nowadays what indicates their isotopic analysis with $\delta^{34}\text{S}$ average value of 33‰ .

The third, youngest gypsum generation is the product of native sulfur oxidation. Amongst all of the generations this one has the isotopically lightest sulfur, which reflects the isotopic composition of the native sulfur. The $\delta^{34}\text{S}$ values of the investigated native sulfur deposits range from -6 to $+18\text{‰}$ with the average value estimated as 11‰ (HALAS 1986).

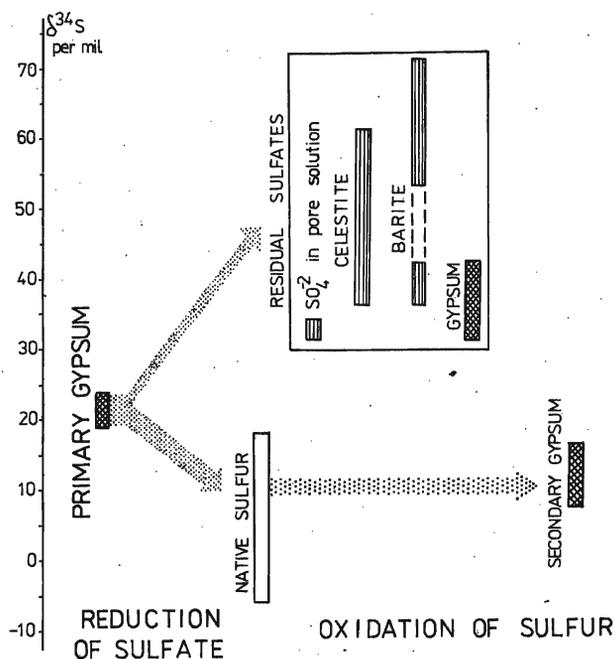


Fig. 2. Sulfur isotope fractionation in the Polish native sulfur deposits (partly based on the data from PARAFINIUK & *al.* 1989)

Table 2
Sulfur isotope composition of secondary gypsum in comparison with native sulfur

Sample	Gypsum $\delta^{34}\text{S}$ (‰)	Native sulfur $\delta^{34}\text{S}$ (‰)
Czarkowy:		
Cz-1 gypsum in limestone with relics of sulfur	13.9	10.1
Cz-2 gypsum in limestone with relics of sulfur	13.1	12.2
Cz-3 gypsum in limestone with relics of sulfur	14.2	12.2
Cz-4 gypsum in limestone with relics of sulfur	13.4	10.8
Cz-5 gypsum in limestone with relics of sulfur	13.3	11.5
Cz-11 gypsum crust	10.4	
Cz-12 gypsum crust	10.9	
Cz-13 gypsum crust	12.1	
Cz-14 gypsum crust	10.9	
Cz-15 gypsum crust	11.9	
Machów:		
M 87/1 dispersed gypsum in limestone with sulfur	15.7	9.3
M 87/2 dispersed gypsum in limestone with sulfur	8.8	10.3
M 87/3 dispersed gypsum in limestone with sulfur	12.5	16.0
M 87/4 dispersed gypsum in limestone with sulfur	9.5	10.4
M 87/5 dispersed gypsum in limestone with sulfur	7.7	8.9
M 87/6 dispersed gypsum in limestone with sulfur	8.5	9.9
GM-1 acicular secondary gypsum	13.1	

It was found experimentally that the sulfur isotope fractionation in the process of native sulfur oxidation is minimal. According to NAKAI & JENSEN (1964), bacterial oxidation of native sulfur causes slight (from 0.3 to 1.7‰) enrichment of the originating sulfate with ^{32}S isotope. Similar slight enrichment of sulfate with the light sulfur isotope was observed in the experiments of inorganic native sulfur oxidation (*vide* GRINENKO & GRINENKO 1974).

The secondary gypsum of the sulfur deposits indicates greater variability with respect to co-existing native sulfur than it is indicated by the experimental data (Table 2). There were recorded gypsum samples of both enriched in lighter sulfur isotope up to 3.5‰ and enriched in the heavier one up to 6.4‰. In fact, the secondary sulfate enrichment with ^{32}S isotope may be still higher since it is partly marked by the fractionation effect connected with the gypsum crystallization. According to THODE & MONSTER (1965) the $\delta^{34}\text{S}$ of gypsum is 1.6‰ higher than

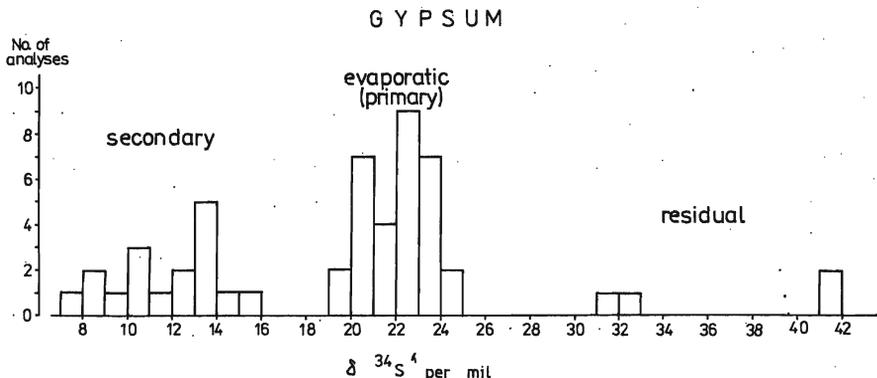


Fig. 3. Histogram of sulfur isotope composition of three gypsum generations from the Polish native sulfur deposits

this of parent brine. The fractionation of sulfur isotopes of bigger extent in the course of oxidation process was recorded by HAŁAS & KURPIEWSKI (1982) in a few samples from the Machów and Jeziórko deposits. The secondary sulfates, which they isolated by means of NaCl solution were up to 7–8‰ lighter than native sulfur. It is still an open question, whether so significant differences of isotopic composition are the result of the fractionation in the course of native sulfur oxidation or they are connected with the heterogeneity of native sulfur isotopic composition and selectivity of oxidation.

The secondary gypsum, which is isotopically heavier than the native sulfur, was probably formed with the share of heavy residual sulfate of the formation waters. This influence is the most distinct in a sample taken from the part of the Machów mine, which is exploited at present. Here, the small amounts of secondary sulfates still are in contact with the remnants of undrained formation waters. In the older part of the open-pit mine, devoid of the formation water inflow, the isotopic composition of gypsum is closer to the native sulfur.

Despite the contamination, the sulfur isotopic composition enabled to distinguish in all studied samples the secondary gypsum from its older generations (Text-fig. 3).

MECHANISM OF THE NATIVE SULFUR OXIDATION

It is known that the native sulfur can be oxidized both inorganically or microbiologically. In favorable conditions (high partial pressure of oxygen and pH of the environment between 3.0 and 6.0) bacterial oxidation of sulfur might run with the considerable rate. According to NAKAI & JENSEN (1964), a mixed culture of sulfur bacteria at 32°C oxidized from 4.1 to 5.3 mg S in 100 ml medium per day. The inorganic oxidation, though slower, might also be productive. In the experiment of VINOGRADOV & GRINENKO (*vide* GRINENKO & GRINENKO 1974), a flow of the oxygen stream through the water containing fine-dispersed sulfur, caused after 3–4 months the alteration of nearly all sulfur in sulfate.

In the case of the sulfur deposits both mechanisms of oxidation are possible, though the rate of the process itself in the laboratory conditions is commonly much slower. It also does not attain the oxidation intensity recorded by BLAJDA & *al.* (1975) for the cores stored in an open air, which after a year of storage indicated the sulfur content decrease by 20–25%. It seems that sulfur-bearing limestones exposed in the dry scarps of the Machów mine and in the outcrops of the Czarkowy deposit are mainly inorganically oxidized. These locations have environmental conditions unfavorable for mass development of sulfur oxidizing bacteria and thus slow oxidation rate has been observed there. The oxidized sulfur-bearing limestones exposed at Czarkowy have presently a similar preservation state as they had 50 years ago (KRAJEWSKI 1935). The low oxidation rate was partially caused by compact structure of the limestones and crusts of secondary gypsum, which isolated relics of native sulfur from the influence of oxidizing factors.

Bacterial oxidation of sulfur can be more effective in these parts of the

deposits which are under exploitation and in the bottom deposit remnants contacting continuously with formation waters. The sulfur oxidizing bacteria belonging to the genus *Thiobacillus* (the species *T. thiooxidans* and *T. thioparus*) are well known from the formation waters of the sulfur mines (IVANOV 1964, FISCHER & DOWGIALŁO 1965). These bacteria find the most favorable conditions of their development in small ephemeral pools of formation waters which contain all inorganic components essential for the bacteria development. Life activity of sulfur bacteria in the warm season of the year can lead to such an increase of sulfates originating from sulfur oxidation that the gypsum crystallization is triggered in the form of acicular crystals overgrowing sulfur and calcite (see Pl. 1, Fig. 3). The isotopic composition of this gypsum ($\delta^{34}\text{S}$ value is 13.1‰) suggests its post-sulfur origin, despite the crystallization from the solution containing considerable amounts of residual sulfate, which $\delta^{34}\text{S}$ exceed 30‰. Negligible contamination degree of the secondary gypsum by residual sulfates of formation waters points out large intensity of bacterial sulfur oxidation, which bears features of bacterial bloom.

Acknowledgements

The author wishes to thank Dr. A. WITKOWSKI and Dr. A. KOZŁOWSKI for their kind help in preparation of the English text of this paper.

Institute of Geochemistry,
Mineralogy and Petrography,
University of Warsaw,
Al. Zwirki i Wigury 93,
02-089 Warszawa, Poland

REFERENCES

- BĄBEL, M. 1987. Giant gypsum intergrowths from the Middle Miocene evaporites of Southern Poland. *Acta Geol. Polon.*, 37 (1/2), 1–20. Warszawa.
- BLAJDA, R., NIEĆ, M. & SKÓRSKI, W. 1975. Variations of the sulphur contents in ore samples due to weathering. *Kwart. Geol.*, 19 (4), 691–700. Warszawa.
- CLAYPOOL, G. E., HOLSER, W. T., KAPLAN, I. R., SAKAI, H. & ZAK, I. 1980. The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. *Chem. Geol.*, 28, 199–260. Amsterdam.
- CZERMINSKI, J. 1968. Epigenetic processes within Tortonian sulphur-bearing series. *23rd Intern. Geol. Congr., Rep. 23rd Session*, 8, 121–127. *Academia*; Prague.
- & PAWŁOWSKI, S. 1961. Processes contemporarily appearing within the sulphur deposits and their significance for exploitation. *Przełł. Geol.*, 1, 5–6. Warszawa.
- FISCHER, E. & DOWGIALŁO, A. 1965. Uwagi o bakteriach siarkowych wód odkrywkowej kopalni siarki w Piasecznie na tle cech środowiska. *Przewodnik 38 Zjazdu PTG*, 153–160. Warszawa.
- GARRELS, R. M. & CHRIST, C. L. 1965. *Solutions, Minerals and Equilibria*. Harper and Row; New York.
- GRINENKO, V. A. & GRINENKO, L. N. 1974. *Sulphur Isotope Geochemistry [in Russian]*. Nauka; Moskva.
- HAŁAS, S. 1986. Stable isotopes as the source of information on deposit-forming processes at the example of the Tarnobrzeg native sulfur deposits. *Przełł. Geol.*, 7, 374–379. Warszawa.

- & KROUSE, H. R. 1982. Isotopic abundances of water of crystallization of gypsum from the Miocene evaporite formation, Carpathian Foredeep, Poland. *Geochim. Cosmochim. Acta*, **46** (2), 293–296. Oxford.
- & KURPIEWSKI, A. 1982. Isotopic composition of oxygen and sulphur in sulphur ore sulphates in the Tarnobrzeg deposits. *Przegl. Geol.*, **2**, 69–73. Warszawa.
- & WOŁĄCEWICZ, W. P. 1981. Direct extraction of sulfur dioxide from sulfates for isotopic analysis. *Anal. Chem.*, **53** (4), 686–689.
- IVANOV, M. V. 1964. The role of microbiological processes in the formation of sulfur deposits [in Russian]. *Nauka*; Moskva.
- KRAJEWSKI, R. 1935. Die Schwefellagerstaette in Czarkowoy. *Bull. Serv. Geol. Pol.*, **8** (2). Warszawa.
- KWIATKOWSKI, S. 1972. Sedimentation of gypsum in the Miocene of Southern Poland. *Prace Muzeum Ziemi*, **19**, 3–93. Warszawa.
- LONGINELLI, A. 1979. Isotope geochemistry of some Messinian evaporites: paleoenvironmental implications. *Palaeogeogr., Palaeoclimatol., Palaeoecol.*, **29**, 95–123. Amsterdam.
- NAKAI, N. & JENSEN, M. L. 1964. The kinetic isotope effect in the bacterial reduction and oxidation of sulfur. *Geochim. Cosmochim. Acta*, **28** (2), 1893–1912. Oxford.
- NIEĆ, M. 1984. Secondary processes in the genesis of biogenic native sulphur deposits. *27th Intern. Geol. Congr. Abstr.*, **2**, sect. 0.4–0.5. Moscow.
- PARAFINIUK, J. 1989. Strontium and barium minerals in the sulphur deposits from Tarnobrzeg region (SE Poland). *Archiwum Mineral.*, **43** (2), 41–60. Warszawa.
- , KOWALSKI, W. & HAŁAS, S. 1989. Model of sulfur isotope fractionation in the Polish native sulfur deposits. *Freiberger Forschungsheften* (in press).
- PAWŁOWSKI, S., PAWŁOWSKA, K. & KUBICA, B. 1979. Geology and genesis of the Polish sulfur deposits. *Econ. Geol.*, **74** (2), 475–483. Lancaster.
- , — & — 1985. Geology of the Tarnobrzeg native sulfur deposit. *Prace Instytutu Geologicznego*, **114**. Warszawa.
- THODE, H. G. & MONSTER, J. 1965. Sulfur isotope geochemistry of petroleum, evaporites and ancient seas. *Amer. Assoc. Peter. Geol. Mem.*, **4**, 367–377.

J. PARAFINIUK

UTLENIANIE SIARKI RODZIMEJ POLSKICH ZŁOŻ SIARKI W ŚWIETLE BADAŃ IZOTOPOWYCH I MINERALOGICZNYCH

(Streszczenie)

Siarka rodzima wystawiona na działanie czynników atmosferycznych stosunkowo łatwo ulega utlenianiu przechodząc we wtórny gips. Przedmiotem badań był wtórny gips z odsłonięcia złoża siarki w Czarkowych oraz z odkrywkowej kopalni siarki w Machowie (fig. 1). Tworzy on drobne, rozproszone kryształy w wapieniach siarkonośnych, a także skorupy i szczotki krystaliczne na powierzchni wietrzejących skał (pl. 1, fig. 1–2). Stopień utlenienia siarki mierzony ilością wtórnego gipsu zależy od czasu oddziaływania czynników atmosferycznych, w mniejszym zaś stopniu od tekstury wapieni siarkonośnych i wykształcenia skupień siarki (tabela 1). Wtórny gips można łatwo odróżnić od starszych generacji tego minerału w badanych złożach na podstawie składu izotopowego siarki (fig. 2–3). Zaobserwowano większe zróżnicowanie składu izotopowego siarki wtórnego gipsu względem siarki rodzimej (tabela 2), niż to wynika z danych eksperymentalnych. Proces utleniania siarki może zachodzić na drodze nieorganicznej oraz przy udziale bakterii siarkowych. Stwierdzono tworzenie się gipsu (pl. 1, fig. 3) w efekcie zakwitu bakterii w wodach złożowych kopalni Machów.