Sulfur- and oxygen-isotope composition as the genetic indicator for celestite from the Miocene evaporites of the Carpathian Foredeep

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Abstract. New results of sulfur- and oxygen-isotope analysis of celestite point to two different origins for the celestite in the Carpathian Foredeep. Celestite from the salt mine at Wieliczka has $\delta^{34}S$ values ranging from 21.2 to 22.1‰ and $\delta^{18}O$ from 9.6 to 15.8‰, values similar to those found in gypsum and anhydrite of Miocene evaporites. In native sulfur deposits, two genetically different groups of celestite have been observed. The oldest generation with $\delta^{34}S$ from 55 to 60‰ records residual sulfates strongly enriched by ore forming processes. The younger generation with $\delta^{34}S$ from 35 to 40‰ was formed during mixing of residual sulfates and those from leaching of original evaporites.

Keywords: Miocene, evaporites, sulfur deposits, celestite, sulfur isotopes, oxygen isotopes.

Introduction

Celestite is a relatively common mineral which occurs in Miocene evaporitic sediments of the Carpathian Foredeep (see Parafiniuk, 1989). Attention was paid by various investigators and mineral collectors to nicely developed crystals of celestite which were found in many locations within native sulfur deposits. In a microcrystalline form celestite occurs also in sulfate and halite facies of evaporites (see Kasprzyk, 1989). Its occurrence in the salt deposit in Wieliczka mine has been reported by Prochazka *et al.* (1969).

Here we demonstrate the use of $\delta^{34}S$ and $\delta^{18}O$ of celestite as an indicator of its genesis. The isotope data published so far refer to celestite from sulfur deposits only (Hałas & Kurpiewski, 1982; Parafiniuk, 1989). No isotope data have been published for celestite which occurs in evaporitic gypsum or halite, and no experimental data on isotope fractionation between celestite and sulfate ion in a mother solution have been reported so far. For these reasons a comparison of the isotopic ratios of celestite from evaporites and from sulfur deposits should lead to better understanding of some aspects of sulfur deposit formation.

Mode of occurrence of celestite

As a rule, celestite occurs in Miocene evaporites of the Carpathian Foredeep in the form of scattered, very irregularly distributed crystals averaging hundredths of millimetres in size. The strontium content in gypsum of the Nida Valley is 0.18 wt% (Parafiniuk, 1987), whereas in the Staszów region it is 0.67 wt% (Kasprzyk, 1989). Gypsum in some localities contains up to 3 wt% strontium. Residual material which results from the karstic solution of gypsum is distinctly enriched in strontium. Celestite present in gypsum forms minute xenomorphic grains, at some places prismatic or tabular crystals, reaching 0.03 mm in size. They occur on surfaces of gypsum crystals or in the interstices around carbonate and clay minerals.

In one of the rock salt varieties in the Wieliczka deposit Prochazka *et al.* (1969) reported up to 2.8 wt% strontium. It was linked to the abundant content of irregular grains or tabular crystals of celestite ranging from 0.03 to 0.06 mm in diameter. Celestite crystals coated carbonate and anhydrite aggregates, forming intergrowths with surrounding halite.

Celestite-rich rock salt constitutes the oldest beds of the Wieliczka deposit, reflecting the view that during seawater evaporation, maximum celestite precipitation occurs before halite precipitation (Usdowski, 1973), or in the final phase of carbonate precipitation and at the beginning of sulfate crystallization (Müller, 1962; Butler, 1973). Such regularities are less visible in the gypsum profiles of the Carpathian Foredeep. The celestite content is more distinctly dependent on the admixture of carbonate and clay minerals what may be connected with the

solution of gypsum rocks and an accumulation of celestite residual material. Nevertheless, the mode of occurrence of celestite in salt or gypsiferous rocks indicates its evaporitic origin. Subsequent recrystallization in the form of idiomorphic crystals sometimes has been observed.

The sulfur-bearing limestones, which were formed from evaporitic gypsum, are particularly celestite-rich rocks. The average content of celestite in Polish sulfur deposits may be only roughly estimated as 1 to 1.5 wt% due to its nonuniform distribution. Celestite forms as tiny grains scattered in limestones or native sulfur and as clusters up to several kilograms in weight which may be found in limestone fissures and caverns. Moreover celestite occurs in a huge diversity of forms and varieties, *i.e.* massive, veined, nested and perfectly shaped crystal druses. Celestite crystals may be totally translucent and colourless, or white and greyish, as well as coloured in various tints of yellow through brown to nearly black. The white and greyish colour comes from numerous liquid inclusions while other tinges are due to an admixture of bituminous substances and/or native sulfur inclusions. Pale blue varieties of celestite have also been found. The crystals commonly have a prismatic habit and range from a couple of millimetres to several centimetres in diameter. More bituminous varieties often yield a more needle-like habit. Several celestite generations can be distinguished here. Their origin was connected either to formation processes of native sulfur deposits or their consecutive transformation. Based upon its development, celestite from sulfur deposits does not seem to have been derived directly from host evaporites, but it has been formed epigenetically.

Materials and methods

The following set of samples has been selected for this study: 12 samples of celestite from a native sulfur deposit at Machów, 3 samples from an abandoned sulfur mine at Czarkowy and 5 samples from the salt mine at Wieliczka (Fig. 1). Coarsely crystalline celestite from sulfur deposits was powdered in an agate mortar and subsequently treated by HCl to remove traces of carbonates. Finely crystalline celestite from the salt mine was separated from halite and carbonates by dissolution in distilled water and subsequent treatment by HCl. Finally celestite was separated from anhydrite and other minerals by mean of methylene iodide. Attempts at celestite separation from gypsum in the same manner were fruitless, although some gypsum samples contained considerable amounts of Sr.

Splits of prepared celestite samples were melted with a mixture of $Na_2CO_3 + K_2CO_3$ and then dissolved for determination of Ba concentration by the AAS and ICP/IAS methods. Celestite for sulfur isotope analysis
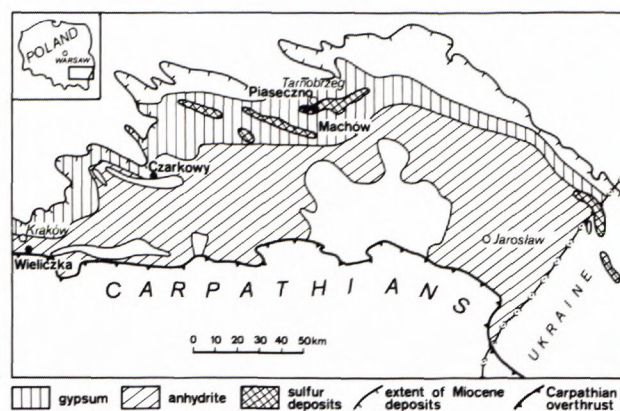

Fig. 1 Location of studied localities in the Carpathian Foredeep

was converted to SO_2 by means of $NaPO_3$ (Hałas & Wołącewicz, 1981). Oxygen isotope analysis was performed on CO_2 obtained by reduction of $SrSO_4$ with graphite (Mizutani, 1971).

Results

The analysis for barium in celestite demonstrates that no solid solution barite - celestite occurs in the Carpathian Foredeep, though the complete series in the binary system $SrSO_4$-$BaSO_4$ is known (Burkhard, 1973; Wieser, 1982). Barium content in celestite in the investigation was rather low, from 0.17 to 0.54 wt% (Table 1). Celestite from Wieliczka has a more homogeneous Ba content (at 0.20 wt%) than that from sulfur deposits.

The results of sulfur and oxygen isotopes analysis are listed in Table 1 and plotted in Fig. 2. A major difference in the isotope ratios of celestite from Wieliczka and that from native sulfur deposits is clearly seen. Celestite from Wieliczka is rather isotopically homogeneous in comparison to that from sulfur deposits. Moreover, its isotopic composition is close to that of gypsum (or anhydrite) of Miocene evaporites in the Carpathian Foredeep (Halas & Krouse, 1982).

The $\delta^{34}S$ and $\delta^{18}O$ values of Miocene evaporites from the Carpathian Foredeep are also summarized in Table 2. From the comparison of these data and δ values of celestite from Wieliczka, one may state that during celestite crystallization from sea water in the halite facies the isotope fractionations do not exceed those for gypsum. The experimentally determined fractionations of sulfur and oxygen isotopes during crystallization of gypsum are 1.65‰ and 3.5‰, respectively (Thode & Monster, 1965; Lloyd, 1968). Although there are no data on fractionations for celestite, it seems reasonable to assume that celestite which precipitated in the sulfate facies has similar $\delta^{34}S$ and $\delta^{18}O$ values as gypsum formed in these facies. It should be emphasized that $\delta^{34}S$ in gypsum

Table 1. Isotopic compositions and Ba contents of celestite

Sample	Ba content [wt.%]	δ^{34}S CDT [‰]	δ^{18}O SMOW [‰]
Wieliczka:			
W-1001	0.19	22.1	9.6
W-1003	0.19	21.3	10.5
W-1011	0.20	21.4	13.2
W-1012	0.21	21.2	15.8
W-1013	0.20	21.4	11.3
Czarkowy:			
CZ-21	0.30	39.8	20.7
CZ-22	0.27	40.3	18.3
CZ-23	0.26	40.4	19.6
Machów:			
CM-1	0.31	58.6	23.6
CM-5	0.40	53.1	27.0
M-50	0.54	38.8	22.1
M-51	0.31	59.3	24.6
M-52	0.54	38.7	19.2
M-53	n.d.	56.8	22.6
M-54	0.42	51.4	26.1
M-55	0.34	35.4	19.1
M-56	0.22	56.4	24.0
M-57	0.27	45.1	24.7
M-58	0.43	39.7	18.5
M-59	0.17	37.2	18.1
TS-7a *	n.d.	41.7	18.5
TS-7b *	n.d.	35.9	16.7
TS-8 *	n.d.	35.9	17.0
TS-9 *	n.d.	36.9	17.0
Piaseczno:			
S-1 *	n.d.	47.4	19.0
S-2 *	n.d.	57.7	23.6

n.d. not detected
* data from Hałas & Kurpiewski (1982)

Table 2. Isotopic composition of CaSO₄ from the Miocene evaporites from the Carpathian Foredeep.

Sample	δ^{34}S CDT [‰]	δ^{18}O SMOW [‰]	Data source
Wieliczka:			
W-1002	22.2	12.9	3
W-1005	21.9	10.6	3
W-1008	22.7	14.2	3
W-1010	22.8	14.2	3
29664-1	21.8	12.9	1
29664-2	21.9	10.8	1
29664-3	21.6	12.9	1
Gacki:			
BS-9	23.0	13.9	2
BS-10	22.9	13.0	2
BS-11	22.4	13.1	2
Piaseczno:			
T-30a	24.6	14.4	2
T-31	22.4	13.6	2
T-39	23.6	13.3	2
T-40	23.0	13.6	2
Horyniec:			
H-5	23.2	12.9	2

Data source: 1. Claypool et al. (1980), 2. Hałas & Kurpiewski (1982), 3. This paper
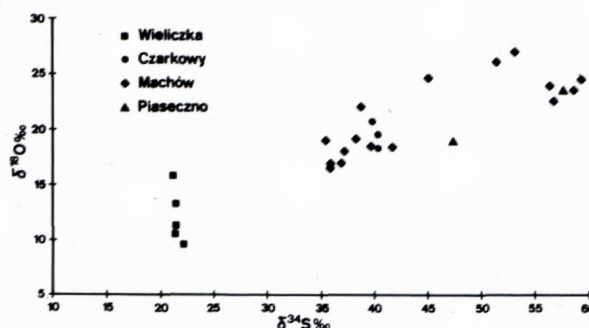

Fig. 2. Spread of isotope data for celestites from the Carpathian Foredeep.

that crystallized at the beginning and at the end of the sulfate facies differed by less than 1‰ (Raab & Spiro, 1991).

Celestite from native sulfur deposits has significantly higher δ values than evaporitic sulfates, what has been noted by Parafiniuk et al. (1994). The δ^{34}S values determined for this celestite vary from 35.0 to 59.3‰, the δ^{18}O from 17 to 27‰. Two diverse groups of celestite can be noted from Fig. 2, one with δ^{34}S from 55 to 60‰ and the other with δ^{34}S from 35 to 40‰. Only a few samples have δ^{34}S values between these ranges. These groups also can be distinguished with respect to the oxygen isotopes ratio, although differences in δ^{18}O values are smaller. There is no correlation between habit and size of celestite crystals and their isotopic composition.

The most likely lanation of the two groups of celestite seems to be linked with different generations of this mineral. The first generation with higher δ^{34}S values was related to the conversion of gypsum to native sulfur. A strong isotope fractionation during bacterial reduction of sulfate results in high δ values of the remaining sulfate in the solution. That remnant sulfate has been fixed predominantly in the first generation of celestite.

The second generation probably contains sulfate ion fixed later, most likely during processes of transformation of the native sulfur deposits. A trend in increased δ^{34}S values with age was observed directly. In two specimens in which a celestite cluster subsequently grew on another we noticed δ^{34}S values of 45.4 and 44.4‰ for the older, while 41.7 and 35.9‰ for the younger cluster, respectively.

Isotopic composition of celestite and the formation of sulfur deposits

The isotopic composition of sulfur and oxygen in celestite seems to be a valuable indicator of the conditions in which sulfur deposits were formed. The isotopically heavier (older) celestite represents compositions of

SO_4^{2-} ion of residual sulfates. Its isotopic composition can be used for estimation of sulfur isotope balance and hence of the capacity of the gypsum reduction process (Parafiniuk *et al.,* 1994). A large enrichment in ^{34}S implies that the ore forming process went on with limited mass exchange, at nearly closed system conditions, excluding supply of hydrocarbons. The estimated capacity of reduction did exceed 75 to 77% (see Parafiniuk *et al.,* 1994).

The younger generation of celestite with lower δ values seems to be a product of various processes which have gone after formation of the sulfur deposit, including recent processes. Although recent crystallization of celestite was not reported, investigations of recently formed barite were reported by Parafiniuk *et al.* (1994). Its $\delta^{34}S$ values vary from 42.2 to 36.3‰ close to values of the younger generation of celestite. Recent barite precipitation has been noted within the pipe of the Machów mine drainage system as well as in sulfur bearing limestones. Also sulfate dissolved in formation waters shows residual feature with $\delta^{34}S$ from 31.5 to 33.8‰ (Parafiniuk *et al.,* 1994).

It seems that a drop of $\delta^{34}S$ values which is observed between two generations of celestite may be interpreted as a record of evolution of the ore water composition due to influence of ambient water containing sulfate from freshly dissolved gypsum. Such an interpretation is suggested by correlation between the isotopic composition of sulfur and oxygen in celestite from evaporites and sulfur deposits (Fig. 2). Contrary to sulfur isotopes, oxygen isotope ratios do not depend on the degree of sulfate reduction but on the isotopic composition of water in which the reduction took place (Fritz *et al.,* 1989).

The intensity of crystallization of younger celestite was probably controlled by a growing sulfate concentration which came from dissolution of surrounding gypsum. In the Machów mine conditions one may estimate from the isotopic compositions of both generations of celestite that sulfates of the deposit waters are a mixture of residual and primary evaporitic sulfates in proportion *ca.* 1:1. The isotopic ratios of sulfates in recent deposit water have been found to be remarkably lower than that in younger celestite. The main reason for the decrease of $\delta^{34}S$ of dissolved sulfates may be reoxidation of isotopically lighter native sulfur.

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