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A fossil barite hot spring mound in the Holy Cross Mts.; a test of the isotope age hypothesis

A fossil barite hot spring mound of upper Lower Triassic age was discovered in the southwestern part of the Holy Cross Mts., Poland. It has been investigated using petrographic and isotopic methods. "The oxygen thermometer" has indicated 95–96°C as an average temperature of the examined barite formation. The lithostratigraphically established age of barite mineralization versus its host sandstones was confirmed by the mean $\delta^{34}S$ value (16.1‰) which corresponds to the upper Lower Triassic.

INTRODUCTION

The "smoker problem" discussed in many scientific publications was summarized by J. M. Edmond and K. von Damm (1983), P. A. Rona (1986) and in Polish literature by Z. M. Migaszewski (1989). This report follows the previous petrologic and isotopic investigations initiated by Z. M. Migaszewski (1991), and Z. M. Migaszewski and S. Hałas (1989) on various dolomite structural forms derived from submarine hydrothermal springs ("white smokers") in the Holy Cross Mts. Two aspects of this problem have been studied, i.e., hot springs as a potential source of either ore- or rock-forming deposits. Barite structural forms linked to hot springs have not so far been found in the Holy Cross Mts. The obtained results may have an impact on the age and the origin of barite- and ore-mineralization in the study area.

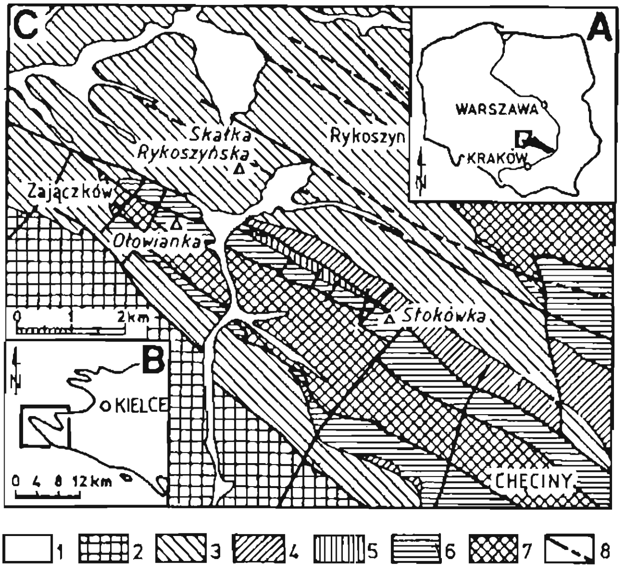

Fig. 1. Geologic sketch map of the study area with locations discussed

1 — Quaternary, 2 — Jurassic, 3 — Triassic, 4 — Permian, 5 — Carboniferous, 6 — Devonian, 7 — Cambrian, 8 — faults

Szkic geologiczny badanego obszaru

1 — czwartorzęd, 2 — jura, 3 — trias, 4 — perm, 5 — karbon, 6 — dewon, 7 — kambr, 8 — uskoki

MICROSCOPIC AND MASS-SPECTROMETRIC DETERMINATIONS

Microscopic examinations were performed with an *Amplival pol. — Carl Zeiss Jena* optical microscope. Stable sulphur and oxygen determinations were carried out on the modified mass spectrometer *MI-1305* (S. Hałas, W. Wołącewicz, 1981) on SO_2 gas. Large sulphate crystals were separated by hand-picking. The sulphate was reacted with $NaPO_3$ under vacuum at 850°C; SO_3 thus obtained was then reduced to SO_2 on copper heated to 750°C (S. Hałas, Z. Skorzyński, 1981).

DESCRIPTION OF THE FOSSIL BARITE HOT SPRING MOUND

Mount Skałka Rykoszyńska is located approximately 16 km west-southwest of Kielce within the Piekoszów Syncline that belongs to the so-called Permo-Mesozoic cover of the Holy Cross Mts. Palaeozoic inlier (Fig. 1). It consists of thick-bedded, red to light gray, poorly-sorted sandstones which dip several degrees northward. These sandstones, assigned to the middle Lower Triassic (M. Kuleta, unpubl. data), were formed under fluvial conditions. They are, in turn, overlain by marine red sandstones with bivalves ascribed to genus

Gervilleia. The central portion of the mount is enriched in barite which reaches as much as 20% of the whole rock.

Petrographically, the aforementioned sandstones can be assigned to typical quartz and sublithic arenites and are composed primarily of well-rounded quartz grains about 0.5 mm in diameter (Pl. I, Figs. 2 and 3), in some places with an admixture of clay and crypto/micro-crystalline siliceous rock, dacite and rhyolite particles, as well as muscovite flakes as much as 2 cm in size. The shape and nearly monomineral composition of grains and particles indicate that these sandstones were formed in a high-energy environment apparently through redeposition of older terrigenous sediments. However, most of these components were transported from the south. The clastic material is cemented primarily by coarse barite crystals up to 1.4 mm long. The latter feature tabular habit. In some places these crystals contain liquid-gaseous inclusions which indicate that their growth was controlled by hydrothermal action. A small amount of iron-clay-silica early-diagenetic cement (slightly older than barite) is present, too. This indicates that the barite generally crystallized within loosely-packed sands. It should be emphasized here that Triassic sandstones that occur in the examined area are commonly bound by clay minerals associated with iron oxides and hydroxides, and silica; no barite is present here.

DISCUSSION OF ISOTOPIC RESULTS

The $\delta^{34}S_{PDB}$ and $\delta^{18}O_{SMOW}$ values of 7 barite samples range from 15.5 to 16.5‰ and from 14.70 to 14.58‰, respectively. "The oxygen thermometer" indicates the temperatures from 95 to 96°C (R. Bowen, 1988). These values support the results of lithologic and petrographic investigations as to the hydrothermal origin of this barite. The mean $\delta^{34}S$ (16.1‰) is characteristic of that for the middle/upper Lower Triassic evaporate sulphates (G. E. Claypool *et al.*, 1980). The isotopic data from Germany indicate a sharp increase of the $\delta^{34}S$ mean values of evaporates from the lower Lower Triassic (Unterer Buntsandstein) 10‰ through the middle Lower Triassic (Mittlerer Buntsandstein) 12.5‰ to the upper Lower Triassic (Röt) 24‰ (G. E. Claypool *et al.*, 1980). It seems that in a well oxidized environment (lack of organic matter), the barite was not substantially enriched in ^{34}S isotope (M. P. Cecile *et al.*, 1983), hence the derived values likely fall close to the sulphur isotope age curve for evaporites. The obtained mean $\delta^{34}S$ value indicates the upper Lower Triassic age of the examined barite. This inference has also been confirmed by the results of lithologic and petrographic investigations. The barite mound was then formed within loosely-packed, in some places slightly cemented, sands through the reaction of hydrothermal barium with seawater sulphate.

CONCLUSIONS

The results of investigations performed on barites derived from other sites in the Holy Cross Mts. indicate that at least some of them were formed in the late Early Triassic period. At that time the study area was at least partly covered by a shallow sea, the extent of which seems to have been locally controlled by extensional tectonics that triggered hydrothermal action. Ba-rich fluids (recycled hybridized water) were discharged periodically along local faults forming irregular mound(s) within Lower Triassic uncemented clastics (sort of "sieve") or veins which pierced older rocks, i.e., Devonian and Permian limestones. The obtained isotopic values are fairly close to those from veined barites in the nearby Devonian abandoned quarry in Mount Ołowianka and the Zechstein open pit in the northern part of Mount Stokówka (Fig. 1).

The $\delta^{34}S$ and $\delta^{18}O_{SMOW}$ of barite from Ołowianka are 19.69 and 14.17‰ (temp. = 111°C). The $\delta^{34}S$ value of barite from Stokówka varies from 17.60 to 21.03‰, whereas $\delta^{18}O_{SMOW}$ is 16.90‰ (84°C), respectively. In addition, the $\delta^{18}O_{PDB}$ values of accompanying calcites are –10.49 (Ołowianka) and –9.32‰ (Stokówka), which corresponds to temperatures 78 and 69°C (assuming that the $\delta^{18}O_{SMOW}$ of hydrothermal fluids was ±1‰).

Compared to barites, the temperatures of crystallization of calcites were somewhat lower. Nonetheless, lithologic and petrographic investigations of calcite mineralization in the Holy Cross Mts. allowed this calcite to be assigned to one of the youngest generations of middle/upper Lower Triassic age (Z. M. Migaszewski *et al.*, 1994). These barites are probably slightly younger (upper Lower Triassic), even though the present sulphur isotope composition may have been connected with that of coeval galena (–10.02‰ in Ołowianka and –9.09 to –9.50‰ in Stokówka). The precipitation of barite and galena apparently took place in a fault-controlled "normal" seawater-submarine brine pool environment. The produced H_2S, enriched in ^{32}S isotope, reacted with Pb^{2+} to form "light" galena. Ba^{2+} released during this process then diffused back to the more oxidized zone where it was reprecipited as "heavy" barite.

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KOPALNA FORMA BARYTOWEGO ŹRÓDŁA HYDROTERMALNEGO Z GÓR ŚWIĘTOKRZYSKICH; TEST HIPOTEZY WIEKU IZOTOPOWEGO

S t r e s z c z e n i e

Nieregularna forma strukturalna barytu hydrotermalnego została odkryta w osadach środkowego pstrego piaskowca odsłaniających się w Skałce Rykoszyńskiej (południowo-zachodnia część Gór Świętokrzyskich). Baryt tworzy tutaj spoiwo piaskowców (arenitów kwarcowych i sublitycznych) osiągając 20% objętości skały. Badania izotopowe 7 próbek wykazały wartości $\delta^{34}S_{PDB}$ i $\delta^{18}O_{SMOW}$ w zakresie od 15.5 do 16.5‰ i od 14.70 do 14.58‰. Ostatnie z wymienionych odpowiadają zakresowi temperatur od 95 do 96°C. Hydrotermalne pochodzenie barytu potwierdza również obecność inkluzji gazowo-ciekłych. Wyniki badań litologicznych i petrograficznych oraz oznaczeń $\delta^{34}S$ w zestawieniu z krzywą wieku izotopowego siarki siarczanów morskich (G. E. Claypool i in., 1980) wskazują na górny pstry piaskowiec, jako najbardziej prawdopodobny wiek mineralizacji barytowej. Roztwory hydrotermalne (zhybrydyzowana woda morska) zawierające jon Ba^{2+} wnikały w słabo spojone piaski, tworząc nieregularnie rozprzestrzenione spoiwo barytowe.

PLATE I

Fig. 2. Quartz grains showing light wavy extinction cemented by barite crystals (crossed nicols); scale bar is 0.1 mm

Ziarna kwarcu o falistym wygaszaniu światła scementowane kryształami barytu (nikole skrzyżowane); skala 0,1 mm

Fig. 3. Same (one nicol)

Jak wyżej (jeden nikol)

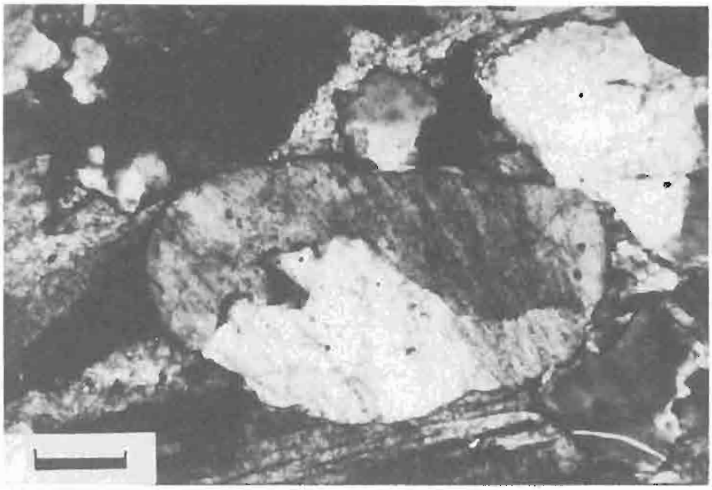

Fig. 2

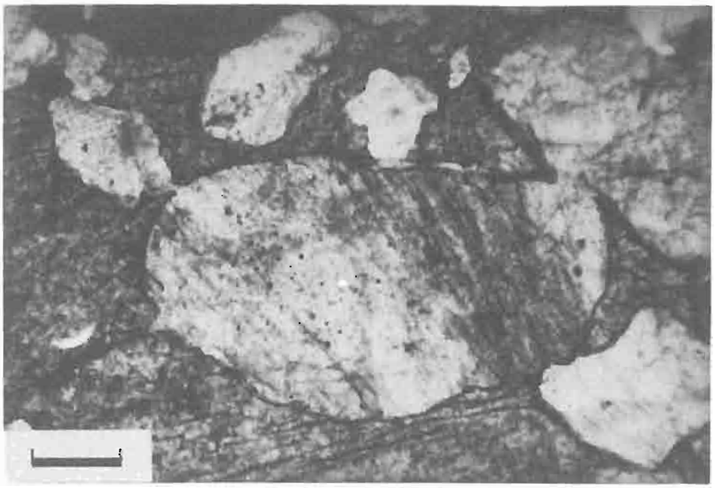

Fig. 3

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