

## On the chemism of barite from Petrova gora and its comparison with the chemism of barite from other deposits in Croatia

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Strontium content of barite and the isotopic composition of sulfate sulfur from epithermal barite veins in Petrova gora are determined. An attempt is made to establish the sources of mineral material. Each barite deposit in Croatia has its own characteristics of the chemism expressed in terms of strontium content and  $\delta^{34}\text{S}$  values.

### INTRODUCTION

The metallogeny of Petrova gora Mountain in south-western Croatia was thoroughly studied by Jurković (1958). The hydrothermal ore occurrences are situated in the eastern part of the palaeozoic horst of Petrova gora, forming a relatively narrow belt of some 13 km in length. The epithermal barite veins containing some siderite from younger phase of mineralization form the southern part of the ore belt. The increasing quantities of the siderite in the northern part of the barite vein sets indicate a transition to the zone of mesothermal quartz-siderite veins; this zone ends with rare quartz veins. In the latter one can find insignificant quantities of sulfides, particularly pyrite and chalcopyrite.

According to Jurković (1958) the barite veins originated by filling open cracks and fissures in the quartzose sandstones and conglomerates of the Upper Palaeozoic age. These brittle sediments of the outer zone cracked during one phase of the Variscian orogeny, whereas the sediments of the inner zone (subgraywackean sandstones and shales) were only subject to folding. The tectonically deformed layers of sediments served as pathways for the ascending mineralizing fluids and as the loci of deposition of the ore material.

The simple mineralogy and the spatial zonality of the ore occurrences are the characteristics of the plutonic-hydrothermal parageneses at the cryptobatholithic level.

The plutonic body in Petrova gora is not discovered, but the detrital particles in the subgraywackean sandstones are indicating a granitic type pluton. A large batholite of this type is discovered in the region between

the rivers Drava and Sava, north-east of Petrova gora. One can conclude that this pluton is younger than Silurian but older than uppermost part of Carboniferous.

The formation of barite was possible under conditions of the high oxidation potential during an arid climate prevailing after the deposition of Upper Palaeozoic sediments and after the regression of the sea in the Permian (Jurković, 1958).

Some tectonic phases caused the recrystallization of the barite under influence of pressure. The primary barite of the first generation (the crystal size averaging 1 to 3 mm) passed partly to the second generation barite with finer grains (50 to 150  $\mu\text{m}$ ); the very fine-grained barite of the third generation is also observed.

The strontium content and the isotopic composition of sulfate sulfur in the barites from Petrova gora are determined in order to obtain genetic relevant data and to make a comparison with the corresponding data for the barites of the marine sedimentary type in Gorski Kotar and Lika (previously described by Šiftar, 1981).

## RESULTS AND DISCUSSION

The samples analyzed originate from the whole barite belt, but predominantly from the northern part (Kijak) and the southern part of the belt (Crkvine, situated in Bosnia).

The strontium content is determined by the emission spectrochemical analysis and by the chemical analysis after the precipitation of barium from homogeneous solution as barium chromate. The results are expressed as  $\% \text{SrSO}_4 = 100 \text{SrSO}_4 / (\text{BaSO}_4 + \text{SrSO}_4)$ .

The isotope analysis of sulfur is performed using the mass spectrometer Varian CH7. The barite samples are fused with sodium carbonate, the water extracts are neutralized with hydrochloric acid and taken to dryness; the soluble sodium sulfate is reduced by the acid mixture (HJ, HCl,  $\text{H}_3\text{PO}_2$ ), the hydrogen sulfide is precipitated as cadmium sulfide and finally converted to silver sulfide. The latter is oxidized to sulfur dioxide by copper(I)-oxide at 800 °C in vacuum. The results are expressed in the usual manner as  $\delta^{34}\text{S}(\text{CDT})$ .

The strontium content for all analysed samples is shown on Fig. 1.

In Table 1 the data of samples analyzed for sulfur isotopes are presented.

The values of strontium content are similar to those registered in numerous barite deposits of similar type. In general one can observe a slight decrease of strontium content from the first to the second generation of barite, with a more expressed decrease in the third generation, but exceptions are registered, too. Naturally, in some parts of barite veins strontium is enriched above the average percentage in the primary barite of the first generation. However, one must take into consideration the possible changes of Ba/Sr ratio in the particular portions of the mineralizing solutions.

The source of barium and strontium is usually assumed to be connected with the (undiscovered) pluton of the granitic type.

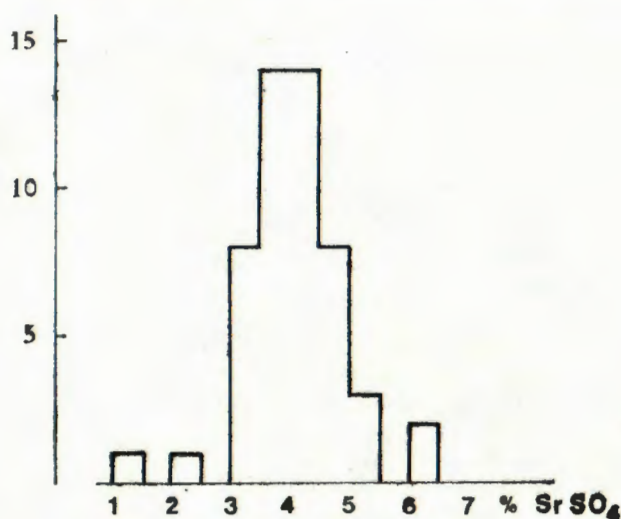


Fig. 1. Distribution of SrSO<sub>4</sub> content in barite samples  
Sl. 1. Razdioba udjela SrSO<sub>4</sub> u uzorcima barita

However, Dunham and Hanor (1967) stated that the appearance of barite contradicts to the earlier opinion that the ores of an element are to be found primarily in the provinces represented by rocks enriched in the given element. Namely, barium will mostly pass into magmatic fluids if not captured by minerals crystallizing from magmatic melts. A low Na<sub>2</sub>O/K<sub>2</sub>O ratio and the low content of CaO in magma is resulting in early crystallization of K-feldspar capturing barium. If the calcium content is high (usually accompanied by the Na<sub>2</sub>O/K<sub>2</sub>O ratio higher than unity), then the plagioclase will crystallize first leaving barium in the melt respectively in the fluids if the melt becomes saturated with water before the K-feldspar begins to crystallize. Of course, the water content of magma is important. According to Dunham and Hanor (1967) the barite mineralization can be associated with some rocks of the granitic type (e. g., quartzdiorite, quartzmonzonite) but not with the granite itself because its content of K<sub>2</sub>O is too high and the content of CaO is too low.

If such considerations hold for barium, they could also be applied for strontium. However, the diadochy of strontium with calcium and potassium seems to exclude the possibility of such relatively simple explanation as in the case of barium distribution between K-feldspars and Ca-rich plagioclases. Assuming the magmatic fluids are the common source for both barium and strontium, a particular combination of major elements content in the magma and a certain process of crystallization should exist leading to the specific Ba/Sr ratio in the mineralizing fluids. Such explanation is not easy to make for both Ba and Sr, therefore the direct derivation of Ba and Sr from magmatic fluids seems to require a stronger foundation. Of course, one can assume a separate source of strontium of another nature to exist, but such a source would be possible for barium, too.

Table 1. Isotopic composition of barite sulfur (including data for strontium content)  
 Tablica 1. Izotopni sastav baritnog sumpora (s podacima o udjelu stroncija)

Sample Uzorak	Description — Opis	$\delta^{34}\text{S}$ ‰	$\text{SrSO}_4$ % <sub>d</sub>
K 386m	White barite, coarsely crystallized, with distinct cleavage Bijel, krupnokristalast, izrazito kalav barit	+ 8,3	4,81
K 374m	Coarse-grained, transparent barite Krupnozrnast, proziran barit	+ 5,0	3,67
K 360m	Tabular shaped barite with some limonite matter Pločasti kristali barita s nešto limonitne tvari	+ 5,5	5,03
K 350m	Somewhat finer grained barite, close to the wall rock Barit nešto sitnijeg zrna, na rubu žile	+ 10,6	3,83
K 336m	Coarse-grained barite, with fine dispersion of limonite Krupnozrnast barit s fino dispergiranim limonitom	+ 7,5	4,26
K 336m	Aggregate of thin barite platelets Nakupina tankih baritnih pločica	+ 11,0	4,67
KJ	Coarsely grained barite with some siderite Krupnokristalast barit s nešto siderita	+ 11,4	4,86
S	Coarse-crystallized, distinctly cleavable barite Krupnokristalast, dobro kalav barit	+ 9,6	3,69
C O,a	Sugar-like barite, somewhat fragile close to the wall rock Šećerast, pomalo krhak barit uz rub žice	+ 9,3	1,36
C O,c	Similar (the same handstick), but separated from (a) by a tiny layer of grayish mineral dust Sličan baritu (a), ali odvojen od njega finom disperzijom sivkastog mineralnog praha	+ 11,2	6,33
C 53	Coarse-crystallized, hard barite with some siderite Krupnokristalast, tvrd barit s nešto siderita	+ 7,1	4,72
C 63	Coarsely grained, somewhat fragile barite Krupnozrnast, ponešto drobljiv barit	+ 7,9	3,47

Sample location — Nalazište uzoraka

K	Kijak, northern hill-side — Sjeverna Kijačka kosa
KJ	Klokočev jarak, incline — Klokočev jarak, niskop
S	Sivac, lower adit — Sivac, donji potkop
C	Crkvine, »Main vein« — Crkvine, »Glavna žica« Shaft (incline) Nr. 6 — Niskop br. 6
O	Entry — Ulaz
53	53 <sup>rd</sup> horizon — 53. horizont
63	63 <sup>rd</sup> horizon — 63. horizont

Barium can be leached from granitic rocks during alteration. However, Solomon (1966) proved barium could be brought in the granitic rock from the outside.

The surrounding rocks of the barite veins in Petrova gora are not taken in consideration as a source of barium being without signs of alteration required for mobilisation of barium if present at all in necessary quantities. The same can be said for strontium, though this possibility could be checked by the method of strontium isotope analysis (Reesman, 1968).

It is not excluded that both Ba and Sr were leached from some deeper sediments (shales?) or from some earlier concentrations of these elements. They can be mobilized by the action of chloride solutions present in the deep layers of sediments, originating predominantly from ancient sea-water (Waljaschko, 1965). The ascension of these solutions to the surface is not a common occurrence, but is restricted to areas representing tectonically deformed zones. Even the sulfates of Ba and Sr dispersed in sediments could be mobilized from them owing to the increased solubility in sodium chloride solutions, supported by higher temperature and pressure (Templeton, 1960; Scherp and Strübel, 1974). The permeation of rocks by such solutions, their accumulation and concentration can be done by producing the microfissuration in the rocks under action of tectonic movements, as showed by Dandurand & al. (1972).

The deposition of strontium-containing barite can be generally caused by the decrease of temperature and pressure followed by the decomposition of simple chloride complexes, by the decrease of the salinity of the brines carrying both metals and sulfate, by the mixing with sulfate bearing ground water or in some cases by the oxidation of the sulfide components present.

It must be noted that the solubility of the strontium-containing barite is not the same as the solubility of the pure barite, both in water and in sodium chloride solutions (Gundlach & al., 1972). The concentration of Ba in the solution obtained by solving Sr-containing barite is about one order of magnitude smaller than in the case of solving pure barite. The concentration of Sr is smaller too, but in reverse to the solubility of pure celestite the solubility of Sr is increased by increasing temperature achieving a maximum at 130 °C. By the increased concentration of Sr in the solution and therefore by the corresponding increase of sulfate concentration one can explain the decreased solubility of Ba from Sr-containing barite. These facts must be born in mind when considering the changes in Ba/Sr ratios during the recrystallization of barite.

The relatively coarse grained masses of barite (the sugar-like barite) and the more rare aggregates of small tabular crystals are indicating a moderately rapid crystallization of the primary barite. One can conclude that the changes in conditions leading to the deposition generally were not to abrupt; therefore the strontium content of barite is fairly uniform. However, it is clear that in the whole area of the barite belt and in the whole time during the barite mineralization some variations in the depositional conditions occurred.

The distribution of the  $\delta^{34}\text{S}$  values cannot indicate a distinct source of the sulfate sulfur. Some values correspond to the values for the marine

sulfate of the Permian age, but the others are too low. The magmatic fluids can be excluded as the only or the predominant source, some of the  $\delta^{34}\text{S}$  values being too high. The lack of sulfide sulfur makes the attempts of explanation more difficult. It is possible that several sources of sulfate sulfur existed: the chloride solutions, possibly partly of magmatic origin, which extracted, mobilized and carried sulfate (together with barium and strontium) from deep-sited rocks, the connate waters of sediments and finally the ground water or the meteoric water in general. The sulfates of the latter have usually low positive values of  $\delta^{34}\text{S}$  (e. g., Čukhrov, 1970). Somewhat variable amounts of the particular solutions having its own sulfur isotope features caused somewhat different isotope values of the deposited barite.

In all that one cannot neglect the role of tectonic events in accumulating, mobilizing and depositing the mineral material.

A comparison of the barite deposit types in Croatia can be made using the strontium content and the isotopic composition of sulfate sulfur as parameters.

The data for the barites from Gorski Kotar and Lika are taken from a previous article (Šiftar, 1981). These deposits are of marine sedimentary type. In the barites one can find the preserved remnants of the primary gel structures, especially in the deposits of Gorski Kotar. The deposits are of different age; in Gorski Kotar it is Lower Triassic, in Lika probably Upper Carbonaceous. The source of sulfate sulfur seems to be the marine sulfate of the coeval sea; the contribution from another source in Lika is possible, too.

In the diagram %  $\text{SrSO}_4$  vs.  $\delta^{34}\text{S}$  (Fig. 2) one can notice that each group of barite deposits covers a distinct area, almost without overlapping. Such grouping is evidently caused by differences in age of mineralization, by different sources of ore material and composition of mineralizing fluids and by various conditions prevailing during deposition and diagenesis; briefly, there existed a distinct combination of these variables in each group.

It must be noted that each of the groups of deposits is connected with the uplifted areas of the Upper Palaeozoic age, appearing in the peripheral parts or in the flanks of such structures. Although of a spatially restricted scale, these positive structures are indicating a genetic link between tectonic movements and barite mineralization. Gunzert (1961) stated that barite veins appeared predominantly on the uplifted large-scale areas of the Variscian bedrocks in Central and West Europe. Dunham and Honor (1967) came to the same conclusion for barite districts of younger age in the Western United States, considering that regional magmatic activity is necessary, too. However, the authors do not state that a genetic link between any barite deposit and particular igneous body must exist.

#### CONCLUSIONS

The strontium content and the  $\delta^{34}\text{S}$  values of sulfate sulfur in epithermal barite veins from Petrova gora are determined. An attempt is made to establish the origin of the mineral material. When considering a dis-

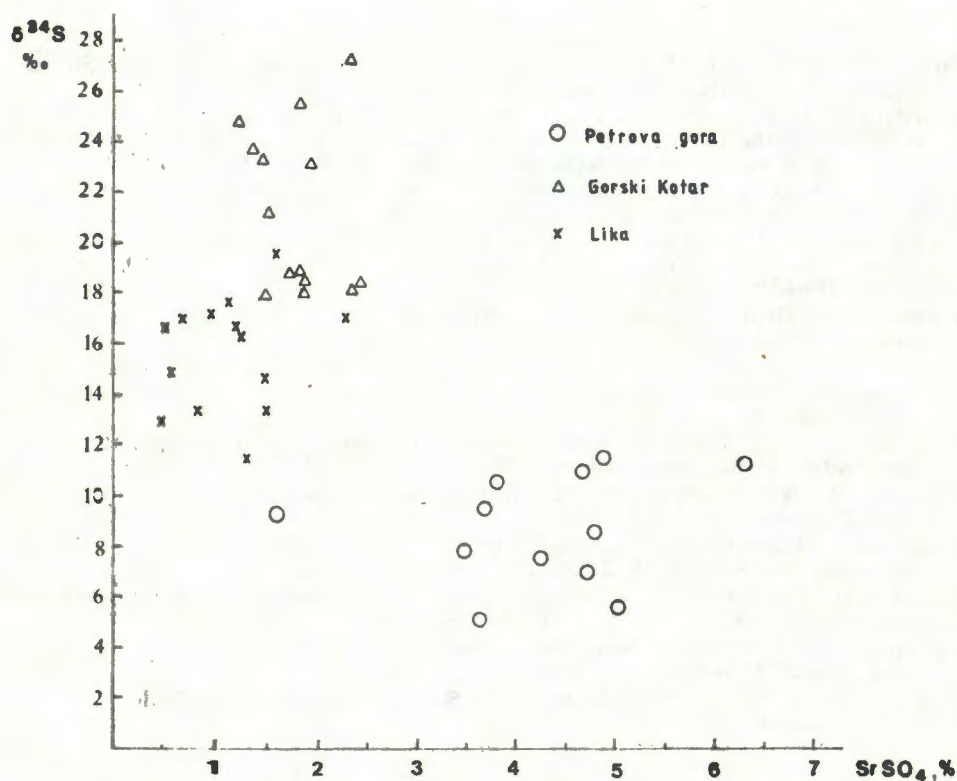


Fig. 2. Plot of  $\delta S$  values for sulfate sulfur vs.  $SrSO_4$  content in barites from barite deposits in Croatia

Sl. 2. Izotopni sa-stav sulfatnog sumpora prema udjelu  $SrSO_4$  u baritima iz baritnih ležišta u Hrvatskoj

tinct type of magma to be the source of barium, one cannot neglect strontium; the difference in crystal chemistry of both elements would require a particular combination of the major element content in the magmatic melts as well as a specific process of magmatic crystallization resulting in the given primary Ba/Sr ratio in the magmatic fluids. The deeper sediment layers can be also regarded as sources (or at least as additional sources) of both Ba and Sr, whereat the mobilizing role of the chloride solutions of the deep circulation must be born in mind. The sulfate sulfur does not seem to be from one source only.

By using strontium content and  $\delta^{34}S$  values as parameters one can show that each of the economically exploited barite deposits in Croatia has its own characteristics. All three groups of barite deposits appear in the uplift areas.

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### O kemizmu barita iz Petrove gore i njegovoj usporedbi s kemizmom barita iz ostalih ležišta u Hrvatskoj

D. Šiftar

Određen je udio stroncija i izotopni sastav sulfatnog sumpora u uzorcima barita iz Petrove gore. Uzimajući ove podatke kao parametre za usporedbu proizlazi da bariti triju velikih ležišta u Hrvatskoj čine tri odvojene skupine između kojih gotovo nema preklapanja. Zajednička je značajka tih ležišta povezanost s p-odručjima pozitivnih struktura.