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Sulfur isotope composition in the Plesenci native sulfur mineral deposit, Republic of Macedonia

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Abstract

For the first time, we present our findings of the origin of sulfur in the gypsum and native sulfur within the Plesenci deposit, R. Macedonia. There we made a series of complex research and analysis of the light isotope (^{32}S), heavy isotope (^{34}S), and their isotopic ratios ($\delta^{34}\text{S}$). For the gypsum within the ore deposit Plesenci, $\delta^{34}\text{S}$ values ranged from -7.1 up to -3.2‰ (standard deviation not higher than ± 0.9), averaging -5.5‰ , while those for native sulfur have shown range starting from -1.00 up to $+2.8\text{‰}$ averaging 0.5‰ (standard deviation not higher than ± 0.8), due to enrichment with lighter sulfur isotope and relative enrichment with heavy sulfur isotope, respectively. Those ranges of sulfur isotope ratios indicated that the origin of sulfur could be related to deep sources.

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1. Introduction

The Kratovo-Zletovo volcanic area was intimately associated with Tertiary volcanism along an active continental margin. The major rock types in the area are andesite, dacite, dacitic ignimbrite volcanic tuff [1, 2, 3]. Dacitic ignimbrite is the most common volcanic unit. The native sulfur and gypsum mineralization near the Plesenci village is apart of the aforementioned and well known Kratovo-Zletovo volcanic area (Figure 1a), which occupies an area of 1200 km², and it has been closely related with its metallogeny and other processes. This mineral resource is of volcanogenic origin, localized in redeposited Tertiary volcanogenic-sedimentary rocks. The mineralization morphology is mostly of vein-impregnations character. With this research we tried to find out the origin of sulfur and does it have been related with magmatic processes in the area, related to deep sources, or not.

2. Geology of the ore deposit

The native sulfur ore deposit has been closely related with trachy-andesite intrusions and formation of the hydrothermal quartzite. The intruded series has been built of re-deposited volcanogenic materials represented by different kinds of sand-tuffaceous and brecciated products. Volcanic activities such as these were, caused certain hydrothermal alterations of adjacent rocks (propylitization, alunization, pyritization, opalitization, kaolinitization etc.), that were used as a particular directions in the explorations of the sulfur mineralizations. Geological mapping and explorations of the Kratovo-Zletovo volcanic area determined that it is built of Miocene volcanic and volcano-sedimentary representatives (Figure 1b). The most important of them are: tuffaceous sandstones, limestones and bitumenous claystones, volcanic agglomerate-brecciated tuffaceous series, volcanic tuff, opalized tuff, hydroquartzite, andesite and trachy-andesite etc (Figure 1b).

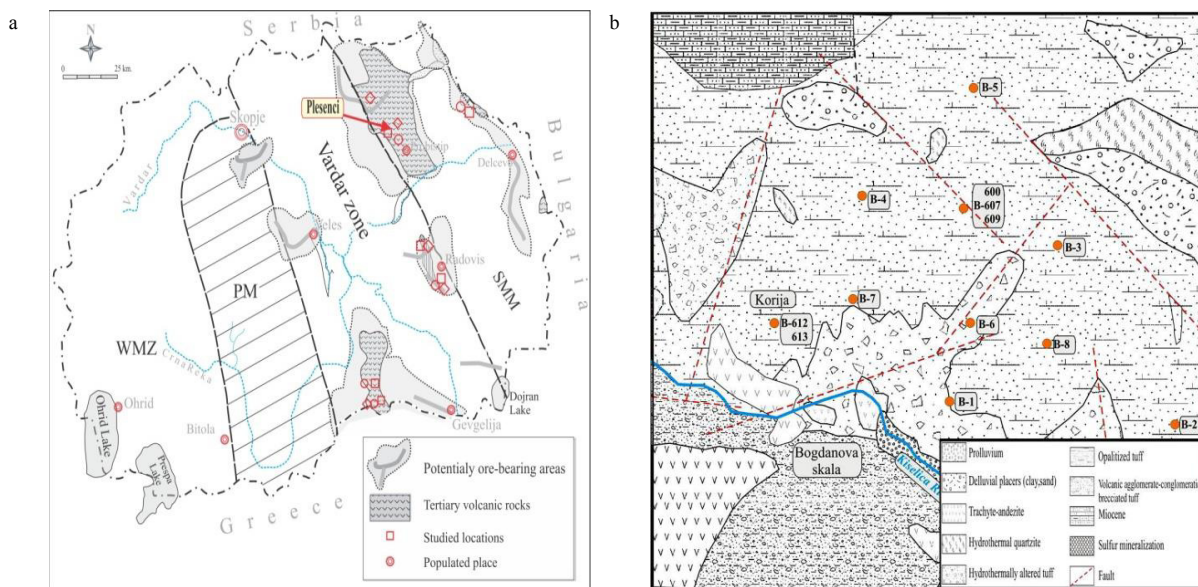


Fig. 1. (a) Simplified regional map with position of the Plesenci deposit (WMZ-Western Macedonian Zone; PM-Pelagion Massif; SMM-Serbo-Macedonian Massif); (b) Geological map of the Plesence area, R. Macedonia (scale 1 : 2 500).

From the metallogenetic point of view the most important is the volcanic agglomerate-brecciated tuffaceous series, which is built of volcanic rocks of different composition that interchange with sand-clay material. There can be found dacite-andesite, opalized tuffs, quartzite etc. Within this series were determined intrusions of andesite-trachyte dykes where on the contacts with them were distinguished hydrothermal alterations and mineralization of vein-impregnations occurred. The mineralization mainly consists of native sulfur, pyrite, gypsum and anhydrite. From the

geotectonic point of view this terrain is a part of the Kratovo-Zletovo area, which have been enclosed in frame of the geotectonic processes that occurred in it (synclinal form, additionally faulted by linear faults of NW-SE and NE-SW direction). Along the faults were determined traces of movement and hydrothermal alterations, which in general complies with the direction of volcanic intrusions. Such tectonic movements allowed space for circulation of ore solutions and waters enriched with oxygen, which caused native sulfur deposition of vein-impregnation type.

3. Analytical methods

Within this study were analyzed gypsum and native sulfur samples from the Plesenci deposit (25 samples in total). Samples were obtained from locations given at Figure 1b, no pretreatment was needed while minerals were isolated easily due to their massive nature. The analyses were performed at the analytical facilities of the Geology Department at the Royal Holloway, University of London. The Fisons Instruments “Isochrom-EA” system used here consists of an elemental analyzer (EA1500 series 2), on line to an Optima mass spectrometer operating in continuous flow mode [4]. Measured sulfur contents are within 1–1.5% of expected values and the reproducibility of $\delta^{34}\text{S}$ values is 0.1‰ (1s). In order to obtain unbiased results we repeated analyses for each sample (three repeats), which resulted in reported different standard deviations for the various samples (Table 1).

4. Results and discussion

During the execution of this project study of stable isotopes of sulfur in gypsum and native sulfur from the Plesenci area was performed. Samples were taken in a random manner. The analysis performed at the analytical facilities mentioned above gave us the results shown in Table 1.

Table 1. Sulfur isotopic composition of native sulfur (1-11) and gypsum (12-25) from the Plesenci area.

Sample	$\delta^{34}\text{S}$ [‰ VCDT]	±std	Sample	$\delta^{34}\text{S}$ [‰ VCDT]	±std
1	-0.4	0.1	12	-6,6	0,5
2	-1.0	0.2	13	-7,1	0,1
3	-0.3	0.7	14	-6,5	0,6
4	0.4	0.2	15	-5,7	0,8
5	2.8	0.6	16	-3,6	0,8
6	1.6	0.8	17	-5,7	0,2
7	-0.4	0.4	18	-6,9	0,9
8	0.2	0.3	19	-3,6	0,5
9	2.1	0.5	20	-6,9	0,6
10	0.7	0.8	21	-6,9	0,1
11	-0.6	0.5	22	-7,0	0,3
			23	-4,9	0,1
			24	-3,2	0,1
			25	-3,3	0,1

Sulfur stable isotopic composition of gypsum as shown in Table 1 lead us to consider the origin of these minerals in the Plesenci area. Namely, bearing in mind that initial study of stable isotope composition of sulfur in gypsum in Macedonia was performed by [5] and their results have proven an evaporitic origin of that gypsum in the area Kosovrasti-Debar ($\delta^{34}\text{S}$ range from +16.6 up to +20.6‰). Our data significantly are different than for gypsum from the Kosovrasti-Debar area. Our $\delta^{34}\text{S}$ values for gypsum ranged from -7.1 up to -3.2‰ (standard deviation not higher than ±0.9), Figure 2a. As can be seen from the Figure 2a such low $\delta^{34}\text{S}$ values do not support an evaporitic origin of gypsum minerals in the Plesenci area. The negative $\delta^{34}\text{S}$ values and their relatively wide range suggest that the sulfur in these gypsum samples was not derived from the simple dissolution and re-precipitation of marine evaporite sulphate within the stratigraphic section. Instead, the sulfate-sulfur was probably derived from the oxidation of diagenetic sulfide minerals and/or eventually from organically bound sulfur in nearby strata. Such a conclusion has been supported by latest sulfur isotope data determined in native sulfur from the same area (Table 1; samples 1-11).

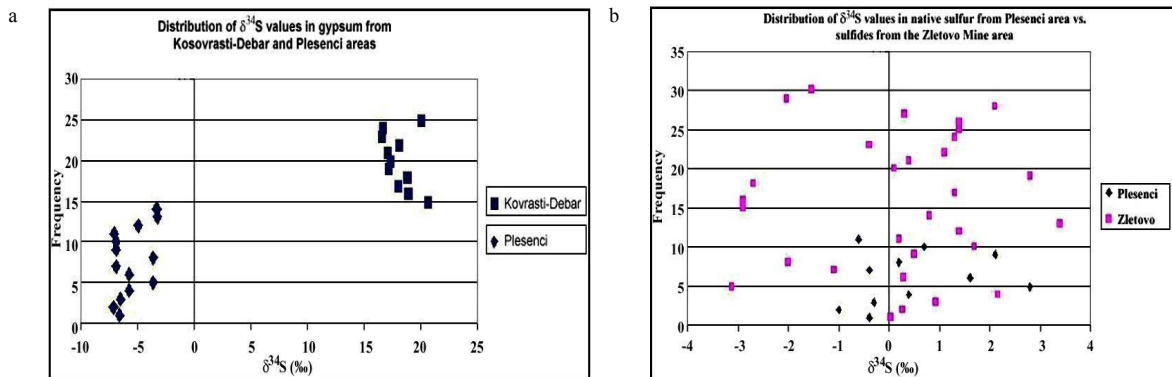


Fig. 2. (a) Distribution of $\delta^{34}\text{S}$ values in gypsum from the Plesenci area vs. $\delta^{34}\text{S}$ values in gypsum from the Kosovrasti-Debar area; (b) Distribution of $\delta^{34}\text{S}$ values in native sulfur from the Plesenci area vs. $\delta^{34}\text{S}$ values in sulfides from the Zletovo mine area.

Data as shown in Table 1, range of values from -1.0 to $+2.8\%$ in native sulfur, suggests the endogene origin of sulfur without any doubts related with magmatic processes in the area. Slightly increased $\delta^{34}\text{S}$ values in only few samples, most probably, were due to oxidation of diagenetically introduced sulfur. Data for native sulfur from the Plesenci area and its endogene origin is quite compatible with data for sulfides in the Zletovo Mine (Figure 2b), both being enclosed into the Kratovo-Zletovo volcanic area (Figure 2b). Most probably there is not a significant fractionation of mantle and lower crust sulfur, since this data are in compliance with $\delta^{34}\text{S}$ (magma sulfide) $\approx \delta^{34}\text{S}$ (magma) $\approx \delta^{34}\text{S}$ (primary rocks) $\approx 0\%$ [6]. It is noteworthy that sulfur isotope compositions data of gypsum and native sulfur from the Plesenci area were compared with those given in [6, 7, 8], for a better understanding of an elaborated facts above. It is noticeable that all the sulfur stable isotope data from gypsum and native sulfur samples from the Plesenci deposit are compatible with widely accepted ranges for diagenetic sulfide minerals (and/or eventually from organically bound sulfur in nearby strata) and endogene origin related with magmatic processes types of sources of S, respectively, which once again confirmed our conclusions related with sulfur origin in analyzed samples.

5. Conclusion

The study of stable isotopes of sulfur in gypsum and native sulfur from the Plesenci have shown relatively narrow $\delta^{34}\text{S}$ ranges from -7.1 to -3.2% and from -1.0 to $+2.8\%$, respectively. Values for gypsum suggest that sulfur probably derived by oxidation of diagenetic sulfide minerals and/or eventually from organically bound sulfur in nearby strata. Native sulfur isotope ratios data suggest an endogene origin that has been related with magmatic processes in the area related to deep sources.

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