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Mass-spectrometric examinations ($\delta^{34}S$) of different baryte, pyrite, galena, sphalerite samples from the ore occurrences in the mixed series at Nežilovo village, Macedonia

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Abstract

In this paper we present the results of the $\delta^{34}S$-mass spectrometric examinations of different baryte, pyrite, galena and sphalerite samples from the ore occurrences in the mixed series at Nežilovo village, Macedonia. The examined baryte samples (fine-grained and coarse-grained generations in total number of 16 samples) show a very narrow span of the $\delta^{34}S$ (+22.5 to +28.3 ‰ for the fine-grained barytes and +21 to +26 ‰ for the coarse-grained baryte generations). These $\delta^{34}S$ values for the examined barytes samples show a homogenous S-source probably of marine origin—marine sulphates. In five samples of different sulphide minerals: galena, sphalerite, cleiophane (from baryte schists), pyrite (from cymrite-quartz schists) were found very close $\delta^{34}S$ values, varying of +3.3 ‰ to +11.6 ‰. These values for examined sulphides show probably an endogenous-juvenile origin representing volcanic sulphides. Examined pyrite sample with hexahedral forms (from the albite-augen gneisses) shows $\delta^{34}S$ values of -10.5 ‰, being typical for S-source of sedimentary origin.

Key words: baryte, cleiophane, galena, mass-spectrometric, pyrite, sphalerite

Introduction

The mixed series at the Nežilovo village area is situated about 40 kilometers westward from the town Veles and belong to the central part of the Pelagonian massif in Macedonia (Arsovski 1960). This series is treated as a former volcano-sedimentary formation, later metamorphosed by the very complex poly-metamorphic processes (Arsovski 1960, Jančev 1975). As result of the those volcano-metamorphic processes, this series show very complex petrological composition, containing mainly albite-augen gneisses, micaschists, banded microcline gneisses, meta-rhyolites, dolomitic marbles, baryte schists, cymrite-quartz schists, tilasite veins etc. The aforementioned petrological members are very intimately connected among themselves, varying very intensively in vertical and lateral sense as a very common characteristic of this series. The complex mineral paragenesis from the ore occurrences in the mixed series are characterized by quantitative predomination of the oxide minerals, including gahnite, franklinite, hetaerolite, zincohoegbomite, rinmanite, ferricoronadite, nežilovite, zincovelesite in relation to the sulphide minerals (galena, sphalerite, pyrite, cleiophane) of subordinate importance (Chukanov et al. 2017). Very rare complex and oxide-mineral paragenesis as well as Pb, Zn, Fe-sulphide mineral paragenesis are enclosed in baryte schists and dolomitic marbles (Stojanov 1960, Ivanov 1961, Jančev 1975, 1990, Bermanec et al. 1996). We expect that $\delta^{34}S$-mass spectrometric examinations of baryte and sulphide samples (galena, sphalerite, pyrite) will help us to determine the S-source origin.

Material and methods

Examined baryte samples as well as sulphide minerals (pyrite, galena, sphalerite) are taken from the ore-bearing petrological members (baryte, cymrite-quartz schists, tilasite vein) and rarely from the albite-augen gneisses in a total distance od 3 km) inside the mixed series of treated area (Tab. 1). All examined mineral samples were prepared as monomineral fractions by

Table 1. Analysed sulphate and sulphide minerals

BARYTE samples, description	**$\delta^{34}S$‰**	**T°C**	**$SrSO_4$%**
1. Coarse-grained (1cm) baryte associated with tilasite	+21.1	320	2.53
2. Coarse-grained (1-2cm) baryte associated with cymrite	+20.6	325	1.92
3. Coarse-grained (1cm) baryte from the banded gneisses	+26.5	255	2.41
4. Coarse-grained (1cm) baryte associated with hydrothermal dolomite	+28.0	235	2.47
5. Coarse-grained (2cm) baryte associated with hydrothermal dolomite	+26.20	252	2.51
6. Coarse-grained (1cm) baryte associated with tilasite	+21.03	320	1.67
7. Fine-grained (1mm) baryte associated with tilasite	+22.5	300	2.07
8. Fine-grained (0.5mm) baryte from ore occurrence No 9	+24.06	280	2.32
9. Fine-grained (1mm) baryte from ore occurrence No 13	+28.3	230	1.86
10. Fine-grained-fibrouse baryte from ore occurrence No 6	+26.8	255	2.07
11. Fine-grained (1mm) baryte – contact area with cymrite	+24.8	280	-
12. Fine-grained (1mm) baryte from ore occurrence No 2	+30.7	205	2.20
13. Fine-grained (1mm) baryte associated with cleiophane from ore occurrence No 1	+23.0	290	-
14. Fine-grained (2mm) baryte from the banded gneisses	+26.5	255	2.74
15. Fine-grained (1mm) baryte from ore occurrence No 5	+28.2	230	2.15
16. Fine-grained (1mm) baryte from ore occurrence No 4	+25.3	275	2.55
GALENA, SPHALERITE, PYRITE samples, description			
17. Galena from Plavnik, microlocality	+3.3	-	-
18. Galena from ore occurrence No 1	+6.4	-	-
19. Sphalerite-cleiophane from ore occurrence No 1	+7.9	-	-
20. Pyrite from cymrite-quartz schists	+11.6	-	-
21. Pyrite associated with cymrite	+10.78	-	-
22. Pyrite-metamorphic from albite-augen gneisses	-10.5	-	-

means of a binocular microscope (Leitz, Wetzlar, Germany). The monomineral fractions of baryte, pyrite, galena, cleiophane (sphalerite) were directed in the mass-spectrometric procedures.

$\delta^{34}S$ contents in baryte and sulphide minerals (pyrite, galena, sphalerite, cleiophane) were analysed by standard mass-spectrometric procedures and technical equipment at the institutes "Ruđer Bošković", Zagreb (Croatia) and "Jožef Stefan", Ljubljana (Slovenia).

Sixteen barytes and six sulphides samples from the ore occurrences composed of baryte schists, quartz-cymrite schists, dolomitic marbles were analysed for $\delta^{34}S$ ‰.

Results and discussion

On the bases of the values of $\delta^{34}S$ ‰ obtained from the analysed samples (Tab. 1), we can conclude the following:

In nine samples of the fine-grained barytes $\delta^{34}S$ values of +22.5 ‰ to +28.3 ‰ were found, with a very narrow span (of ca. +5.8 ‰), instructing us to a conclusion for a homogenous S-source. Only in one sample (No 12) a value of $\delta^{34}S$ of +30.7 ‰ was found.

In five samples of coarse-grained baryte samples $\delta^{34}S$ values of +21 to + 26 ‰ were found, representing also a very narrow span, indicating also to a homogenous S-source.

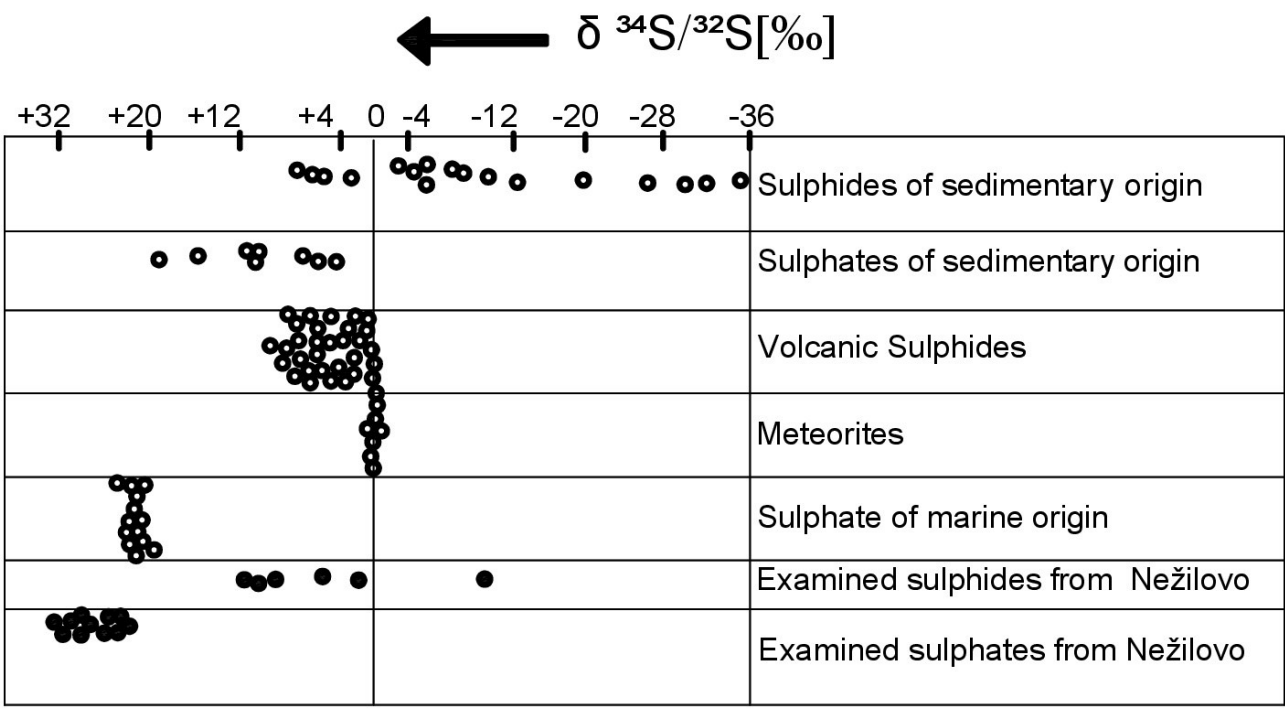


Figure 1. δ ^{34}S contents in different geological materials from different origin (by Mayne 1960, in Smales and Wager 1960) and examined sulphates (barytes), sulphides (galena, sphalerite, pyrite) from treated area at Nežilovo

Fine-grained and coarse-grained baryte samples show very similar δ ^{34}S-values, with a characteristic that fine-grained baryte samples are slightly enriched in δ ^{34}S.

According to Mayne (1960, in Smales and Wager 1960), it could be concluded that examined baryte samples are characterized with S from marine origin— marine sulphates (Fig. 1).

The measured temperatures (Tab. 1) starting from 200-320^{o}C confirm the hydrothermal origin for the examined baryte samples.

The examined baryte samples from the study area near Nežilovo village show values of δ^{34}S comparable with the baryte occurrences from Gorski Kotar (Šiftar 1984) (Fig. 2).

Some stable isotopes of Sulphur were examined by Jančev et al. (1999) in the gypsum from Kosovrasti, Debar, Western Macedonia, where δ ^{34}S ranges from +16.6 to +20.6 ‰. These results show an evaporitic origin of the gypsum from the Kosovrasti microlocality. However, presented data from Nežilovo area are much-higher than 20 ‰ for δ ^{34}S.

According to their δ ^{34}S values, the baryte samples from Nežilovo area are comparable with the baryte occurrences from Vareš, Megen and Ramelsberg (Fig. 2).

Examined sulphides from Nežilovo area are similar to the sulphides of endogenous-juvenile origin from different areas (Fig. 3) whereas the pyrite from the albite-augen gneisses show sedimentary origin.

Conclusions

According to the literature data from the previous studies, as well as the results of the present analyses, we can conclude:

The mass-spectrometric values of δ ^{34}S range from +21 ‰ to +28 ‰ for the examined baryte ($BaSO_4$) samples from Nežilovo area are showing a homogenous S-source of marine origin.

The mass spectrometric values (δ ^{34}S = +3.3 ‰ to +11.6 ‰) for the examined sulphide (pyrite from quartz-cymrite schists and galena, sphalerite from baryte schists) show also a homogenous S-source of narrow span, comparable with sulphides of volcanic origin.

δ ^{34}S value (-10.5 ‰) for pyrite from albite-augen gneisses show typical value for S-source of sedimentary origin.

The obtained δ ^{34}S results for the examined samples of baryte are in quite good concordance with the geological facts that the examined mixed series actually

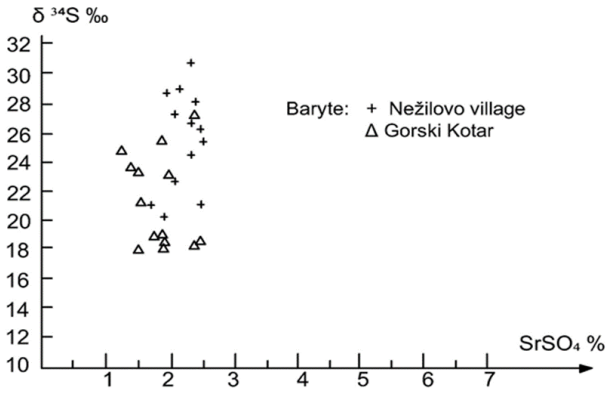


Figure 2. Comparative analysis of δ ^{34}S between baryte from Gorski Kotar (Šiftar 1984) and baryte from Nežilovo area

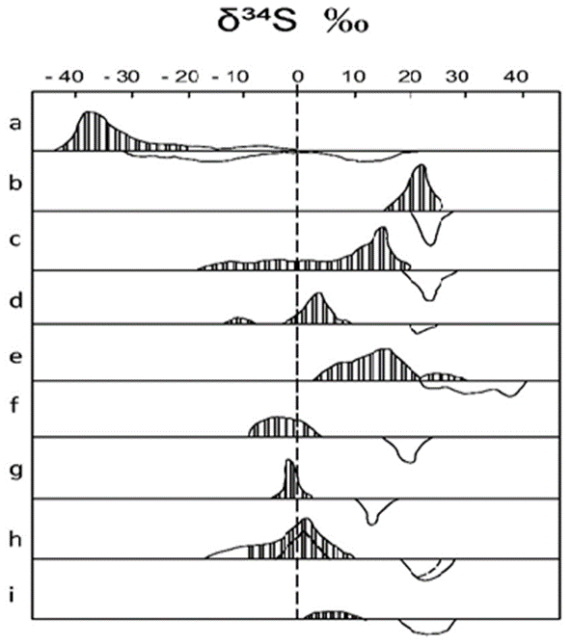


Figure 3. δ ^{34}S-Distribution in sulphides (shaded area) and barytes from the ore occurrences: Cu-schists (a), Meggen (Germany) (b), Rammelsberg (Germany) (c), Shakanai (Japan) (d), Mississippi (USA) (e), Barytes-North Pennines (England) (f), Bad Grund, Harz (Germany) (g), Vareš, Bosnia and Herzegovina (h), Barytes and sulphides from Nežilovo (Macedonia) (i). Histograms are not in measure.

represents a transgresive series i.e. a volcano-sedimentary series originated in extremely elevated conditions at very high positive oxidation potentials.

Examined δ ^{34}S results for the treated galena, sphalerite and pyrite are characteristic for sulphides of volcanic origin associated to the aegirine-meta-rhyolites from the mixed series of Nežilovo village area.

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Масино спектрометриски испитувања (δ ^{34}S) во различни минерални примероци на барит, галенит, пирит, сфалерит од рудоносните појави на мешаната серија во село Нежилово, Македонија

Симеон Јанчев и Билјана Карамачоска

Резултатите добиени од испитаните шеснаесет примероци на барит од мешаните серии кај Нежилово со различна грануларност (ситно зрнести и крупни зрнести генерации) укажаа на многу блиска вредност на δ ^{34}S (+22.5 до +28.3 ‰ за ситно зрнестите барити и +21 до +26 ‰ за крупно-зрнести барити од различна генерација). Овие $\delta^{34}S$ вредности на испитаните баритни примероци покажуваат хомогеност во изворот на сулфур, со што се смета дека тој најверојатно има морско потекло и потекнува од морски сулфати. Испитаните пет примероци од различните минерали (галенити, сфалерити во примероци од баритните шкрилци како и на пиритот од кумритно-кварцни шкрилци) покажуваат променлива содржината на δ ^{34}S во граници од +3.3 ‰ до +11.6 ‰. Овие δ ^{34}S резултати од испитуваните сулфиди покажуваат ендогени-јувенилни вредности што укажува дека тоа се вулкански сулфиди. Испитаниот пиритен примерок (со хексагонални форми) од албитните-аугенските гнајсеви покажува вредност на δ ^{34}S од -10.5‰ што претставува типичен индикатор дека содржина на сулфур е од седиментно потекло.

Клучни зборови: барит, галенит, клеофан, масен-спектрометар, пирит, сфалерит