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The origin of lead and sulphur in Tulare ore field, Lece magmatic complex, SE Serbia

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Abstract. Lece magmatic complex in SE Serbia, part of the Serbo-Macedonian Metallogenic Province, is one of the most promising zones for lead, zinc and precious metals for the country. This complex was formed as a result of the post-collisional magmatic activity that lasted from Oligocene to Miocene. This study brings new lead and sulphur isotope data with an aim to constrain the origin of mineralizing fluids and to estimate the temperature of their formation. Galena from the Bakrenjača locality shows high $^{207}Pb/^{204}Pb$ values implying that the lead was dominantly derived from the upper continental crustal geochemical reservoir which was probably recycled within the mantle and erupted during Tertiary post-collisional magmatism. Sulfur isotope composition of galena, sphalerite and pyrite show overlapping $\delta^{34}S$ values in the range between 0 and 3‰ indicating a mantle origin of sulphur. Sulfur isotopes were also used to estimate the temperature under which the minerals were deposited forming a complex of veins. The calculated temperature is around 350 °C. Since this temperature is too high for epithermal deposits, it is probable that the associated minerals weren't deposited in isotopic equilibrium and other methods should be conducted for more precise temperature evaluation.

Key words: Lead and sulphur isotopes, Lece–Chalkidiki zone, Tulare, Bakrenjača.

Апстракт. Магматски комплекс Леце у југоисточној Србији, делу Српско-Македонске металогенетске провинције, је једна од најперспективнијих зона за истраживање олова, цинка и племенитих метала у тој земљи. Овај комплекс је формиран као резултат пост-колизионе магматске активности која је трајала од олигоцена до миоцена. Ова студија приказује нове резултате мерења изотопа олова и сумпора са циљем одређивања порекла флуида који су створили минерализацију и процене температуре њиховог формирања. Галенит са локалитета Бакрењача показује високе вредности $^{207}Pb/^{204}Pb$ што указује на то да је олово углавном пореклом из геохемијског резервоара горње континенталне коре која је вероватно рециклирана у мантлу и поново еруптирана током терцијарног пост-колизионог магматизма. Изотопи сумпора у галениту, сфалериту и пириту показују вредности $\delta^{34}S$ у распону између 0 и 3‰, што указује на порекло сумпора из омотача. Изотопи сумпора су такође коришћени за процену температуре формирања рудних минерала и комплекса жица. Израчуната температура је око 350 °C. Пошто је ова температура превише велика за епитермална лежишта, вероватно је да присутни минерали нису депоновани у изотопском еквилибријуму и треба користити друге методе за прецизније одређивање температуре.

Кључне речи: Изотопи олова и сумпора, Леце–Халкидики зона, Туларе, Бакрењача.

Introduction

Lead and zinc are currently two of the main metallic ores mined in Serbia. The major by-products of Serbian lead-zinc deposits are silver, copper, gold, bismuth and cadmium. Most of these Serbian deposits mined today genetically belong to the Serbo-Macedonian Metallogenic Province (Janković, 1990; Monthel et al., 2002; Janković et al., 2003). The position of this province on the geologic map of Balkan Peninsula is presented in Fig. 1.

This metallogenic province stretches through SW Serbia, Fyrom (Macedonia), NE Greece and S Bulgaria and is dominated by carbonate-replacement

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Pb-Zn-Ag-Au deposits, several porphyry Cu-Mo-Au deposits, stratiform volcano-sedimentary deposits, skarns, and various isolated magmatic-hydrothermal deposits.

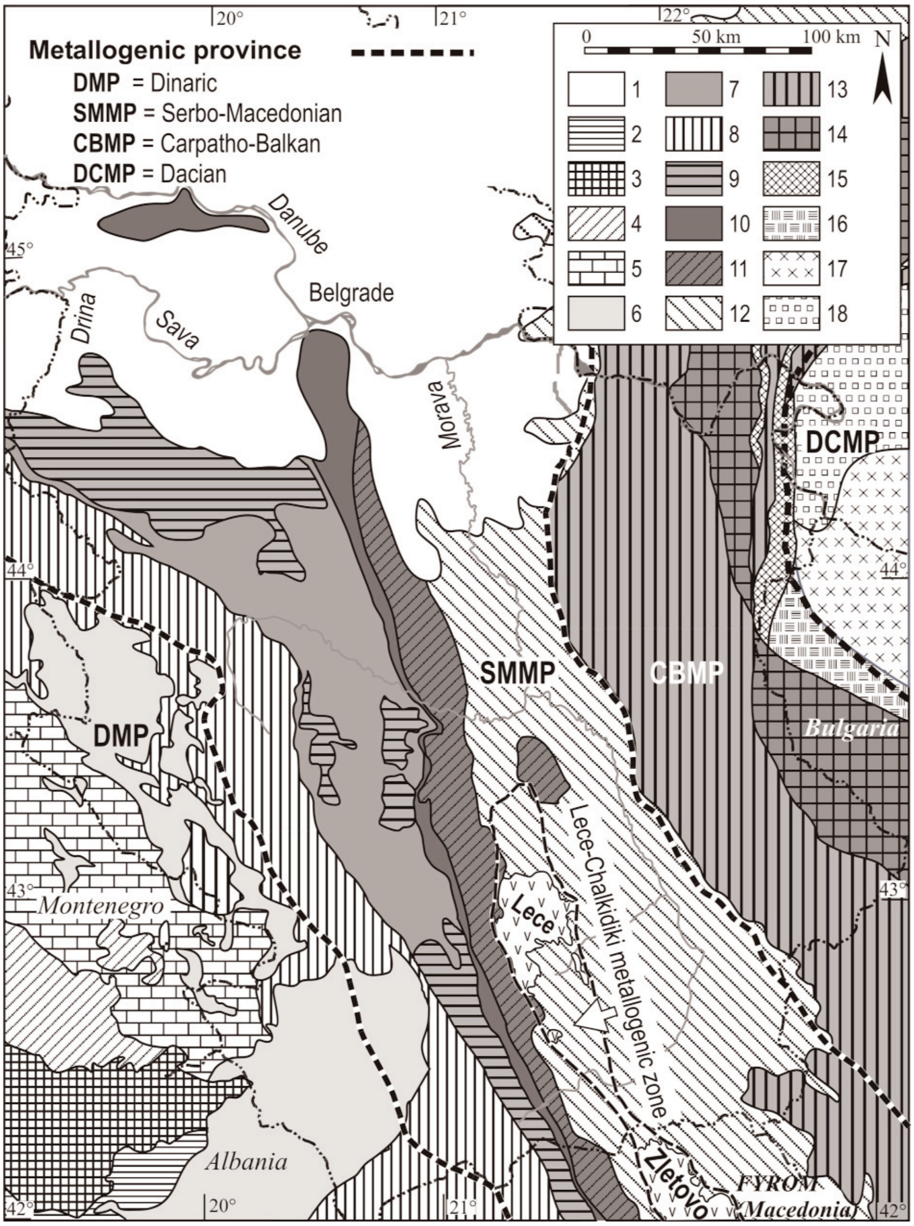

Fig. 1. Main geotectonic units of Serbia (modified after DIMITRIJEVIĆ, 1997; SCHMID et al., 2008; CHIARI et al., 2011) with marked position of main Metallogenic Provinces. Lece–Chalkidiki metallogenic zone and Lece and Zletovo volcanic complexes are shown too. **1)** Pannonian Basin, **2)** Budva-Cukali Zone, **3)** High Karst Unit, **4)** Pre-Karst and Bosnian Flysh Unit, **5)** East Bosnian–Durmitor Thrust Sheet, **6)** Dinaric Ophiolitic Belt, **7)** Western Vardar Ophiolitic Unit, **8)** Drina–Ivanjica Thrust Sheet, **9)** Jadar–Kopaonik Thrust Sheet, **10)** Sava Zone, **11)** Eastern Vardar Ophiolitic Unit, **12)** Serbo-Macedonian Unit, **13)** Getic Unit, **14)** Danubian Nappes, **15)** Ceahlau-Severin Unit, **16)** Central Balkan and Prebalkan Units, **17)** Moesian Platform, **18)** External Moesian Foredeep.

There is a general agreement that all these ore deposits are genetically related to Oligocene-Miocene magmatism (JANKOVIĆ, 1990; TSIRAMBIDES & FILIPPIDIS, 2016), which followed the closure of the branch of Tethyan Ocean along the Vardar–Izmir–Central Anatolia Zone (JELENKOVIĆ, 2014). The magmatism is dominantly calc-alkaline, with subordinate shoshonitic and ultrapotassic occurrences of magmatic rocks (CVETKOVIĆ et al., 2004). It is a typical post-collisional volcanism (HEINRICH & NEUBAURER, 2002; CVETKOVIĆ et al., 2004), geodynamically related to delamination of the thickened lithosphere (DEWEY, 1988). The delamination triggered melting and upwelling of different mantle materials. SERAFIMOVSKI & JANKOVIĆ (2000) proposed that the parental magma was partially derived from the lowest part of the continental crust, above the upper mantle, since the measured strontium isotope ratios indicate a contamination of magma by material from the continental crust. The seismic tomography models of this part of Alpine orogenic belt suggest that post-collisional slab break-off and following asthenosphere uprising have led to magmatism and the formation of hydrothermal deposits (DE BOORDER et al., 1998).

The Lece magmatic complex in SW Serbia is one of the most promising zones for lead, zinc and precious metals in the Serbo-Macedonian Metallogenic Province (TSIRAMBIDES & FILIPPIDIS, 2016). The contact zone at the eastern rim of Vardar zone extends around 700 km in length and it is called Lece–Chalkidiki metallogenic zone (Fig. 1) (SERAFIMOVSKI, 1990). Several different ore fields can be distinguished in this metallogenic zone, including Djavolja Varoš, Lece, Tulare, Dražnja-Propastica, Novo Brdo and Bujanovac ore fields, as well as Sijarinska Banja, Kravarske Planine, Glama and Crni Vrh mineralization zones (JELENKOVIĆ, 2011).

In this study we analyzed samples from Tulare ore field (Fig. 2), where geological exploration was performed by Dunav Resources Co. in late 2012. A carbonate-base metal gold epithermal vein system at Bakrenjača and Gubavce localities, located approximately 3 km south of the Kiseljak porphyry deposit has been identified (Fig. 2) (VELOJIĆ, 2015; TSIRAMBIDES & FILIPPIDIS, 2016).

The main aim of this research was to better understand the origin of this interesting ore field which was previously not extensively studied and to compare the results with similar deposits in Lece-Chalkidiki metallogenic zone to ensure if the isotope ratios confirm the genetic connection between them. Samples were taken from both low-sulphidation and presumed high-sulphidation veins to examine if there are genetic similarities between the different vein generations.

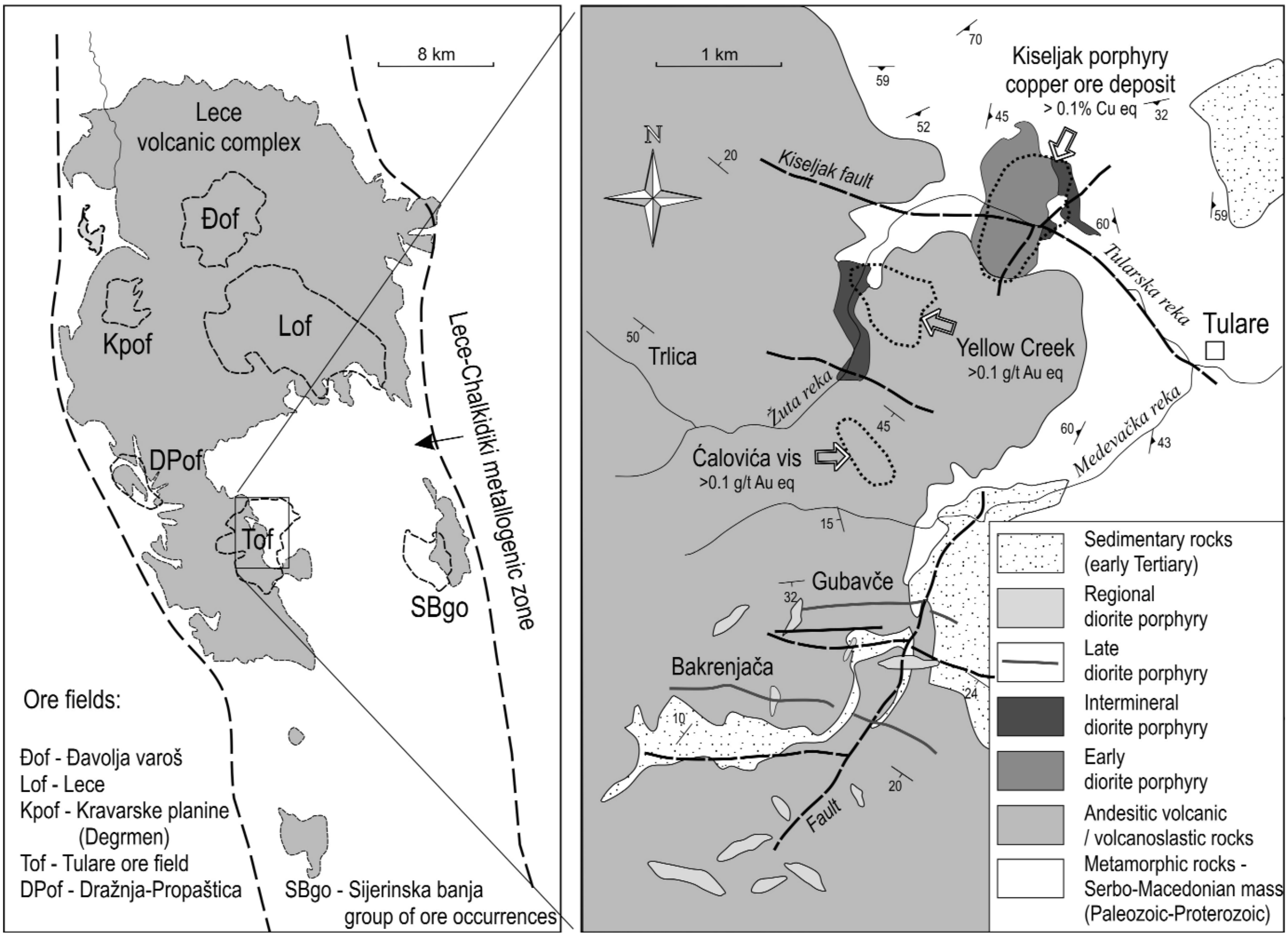

Fig. 2. Simplified map of Lece magmatic complex and of Tulare ore field with marked position of the Kiseljak porphyry copper ore deposit and zones of ore occurrences: Yellow Creek, Ćalovića vis, Bakrenjača and Gubavče.

Samples and methods

The main type of mineralization in this area is carbonate-filled lead-zinc ore veins. Ore microscopy has indicated that the main ore minerals in Bakrenjača–Gubavce system are galena, sphalerite, pyrite, chalcopyrite and tetrahedrite (PEŠUT, 1960; SERAFIMOVSKI, 1990).

Several generations of veins can be distinguished in this hydrothermal system (by the order of formation, fig. 3):

1) Primary pyrite veins - often occur as tensional or stockwork veins 1–2 mm thick. These veins often contain pyite and chalcopyrite.

2) Quartz- carbonate veins- occur as network or massive veins from 1–10 cm thick. They are the main ore-bearing veins in this ore deposit, often containing chalcopyrite, galena and sphalerite. Unlike the other veins, they often contain adularia or small geodes in their central parts and often exhibit epithermal colomorph or vuggy textures.

3) Secondary pyrite- chalcopyrite veins - are up to 3 mm thick and they are crosscuting quartz-carbonate veins. Unlike P1 veins, these veins are darker and contain more chalcopyrite. They mostly occur in BKDD001 drill hole.

4) Brown carbonate veins (BC) – are up to 5 mm thick and they are crosscuting all the previous veins.

Fig. 3. Examples of vein types from Gubavče–Bakrenjača epithermal system. Upper picture: Quartz-carbonate veins with galena and sphalerite and thin brown primary pyrite veins from BKDD003 drill core Lower picture: Secondary pyrite-chalcopyrite vein crosscuting quartz- carbonate vein from BKDD001 drill core.

These veins rarely occur and they do not contain ore minerals.

This is a low-sulphidation epithermal system, but there is an indication that a part of this system was formed under high-sulphidation conditions (Velojić, 2015). One of the samples from a supposed high-sulphidation vein is D50032.

Four samples from the exploration area were selected for lead isotope analysis:

1) D50028 (drill hole BKDD001- 102.1 m)
2) D50032 (drill hole GUDD001- 187.1 m)
3) D50033 (drill hole GUDD001- 297.1 m)
4) D50037 (drill hole GUDD002- 37.1 m)

Lead isotope analyses on galenas were carried out at the Institute of Geosciences, University of Mainz (JGU), using an Agilent 7500ce quadrupole ICP-MS equipped with an ArFExcimer laser ablation system (193 nm wavelength, NWR193 by esi/NewWave). The LA-ICP-MS was optimized before the isotope measurements to ensure high sensitivity and low oxidation rates.

In total 62 spots on 26 galena crystals were analyzed. The following isotopes were monitored: ^{202}Hg, ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb. Reference materials used as standards for these measurements were NIST610 basalt glass and GSE-1G. The procedure of measurements was: 3 measurements on NIST610→ 3 measurements on GSE-1G→10 measurements on galena samples→ 3 measurements on NIST610→ 3 measurements on GSE-1G→10 measurements on galena samples→ 10 measurements on NIST610 (5 with 50 μm diameter and 5 with 10 μm diameter) → 3 measurements on GSE-1G → 10 measurements on galena samples→ repeat.

The measured ratios related to ^{204}Pb were corrected for isobaric interferences with ^{202}Hg using the equation:

$$^{204}\mathrm{Pb}_{\mathrm{corrected}} = {}^{204}\mathrm{Pb}_{\mathrm{measured}} - 0.23\times{}^{202}\mathrm{Hg}_{\mathrm{measured}}$$

NIST610 was used for calibration and obtaining correction factors, which were calculated by dividing measured values of ^{208}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, ^{206}Pb/^{204}Pb, ^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb with recommended values. Real values were taken from GeoRem database (compiled values for NIST610 and GSE-1G) (Jochum et al., 2005).

GSE-1G reference material was used for checking the accuracy of the measurements by dividing measured values by correction factor (calculated from NIST610) and comparing the new values with recommended values (taken from GeoRem). Most of the measured values for all isotope ratios had accuracy better than 0.2% (1RSD).

Measured ratios of isotopes in the samples were corrected by eliminating values with anomalous data (which have the aberration of more than 3 standard deviations) and after that divided by correction factor from standards. The final correction was the elimination of data for the samples which have a slope of the ratio of isotopes higher than 0.0005 (which indicates a change of conditions during the measurements). Thus, the final number of acceptable measurements which were used in this research is 36.

Sulphur isotope measurements were conducted at the Scientific and Technological Center of the University of Barcelona.

Five samples from the exploration area were selected for sulphur isotope analysis:

1) D47918 (drill hole BKDD003- 45 m)
2) D50026 (drill hole BKDD001- 15.5 m)
3) D50030 (drill hole GUDD001- 37.8 m)
4) D50032 (drill hole GUDD001- 187 m)
5) D50033 (drill hole GUDD001- 297 m)

Hand- picked grains of galena, sphalerite and pyrite were weighed inside individual tin boats for 0.150 mg. Samples were then wrapped and loaded into the autosampler coupled to Elemental Analyzer Carlo Erba EA 1108 and IRMS Delta plus xp Thermofisher.

Reference standards used were: IAEA SO-5 ($\delta^{34}S$ = +0.5), IAEA SO-6 ($\delta^{34}S$ = –34.1), BS127 ($\delta^{34}S$ = +20.3). Reference material used was: YCEM ($\delta^{34}S$ = +12.8). Results are related to the standard VCDT (Vienna Canyon Diablo Troilite) and are expressed in permil in the typical delta notation.

Results and Discussion

The results of measurements of Pb isotopes and their average values are presented in Tables 1–4.

Table 1. Ratios of Pb isotopes in sample D50028.

Spot number	207/206	208/206	206/204	207/204	208/204
178	0.83	2.03	18.47	15.16	37.15
179	0.83	2.05	18.62	15.51	37.54
181	0.84	2.05	18.40	15.44	37.51
182	0.84	2.08	18.52	15.45	38.34
198	0.85	2.08	18.73	15.90	39.19
199	0.85	2.06	19.03	16.15	38.92
200	0.85	2.08	18.88	16.16	39.11
204	0.85	2.10	18.75	16.04	39.35
Average	**0.84**	**2.07**	**18.67**	**15.73**	**38.39**
SD	0.01	0.02	0.22	0.38	0.88
Error (%)	0.00	0.01	0.08	0.13	0.31

SD=Standard Deviation.

Table 2. Ratios of Pb isotopes in sample D50032.

Spot number	207/206	208/206	206/204	207/204	208/204
234	0.84	2.06	18.43	15.61	38.12
235	0.85	2.04	18.54	15.84	37.57
236	0.84	2.04	18.71	15.89	38.36
239	0.87	2.13	18.18	15.75	38.56
240	0.85	2.08	18.54	15.67	38.55
Average	**0.85**	**2.07**	**18.48**	**15.75**	**38.23**
SD	0.01	0.04	0.20	0.12	0.41
Error (%)	0.00	0.02	0.09	0.05	0.18

SD=Standard Deviation.

Compared to the precision estimated by GSE-1G reference measurements, the standard deviations of isotope ratios of galena crystals are much higher. For ^{206}Pb/^{204}Pb the average standard deviation is 0.298 with a maximum deviation of 0.4 (sample D50033). For ^{207}Pb/^{204}Pb ratios, the average standard deviation is 0.267 with a maximum deviation of 0.38 (sample D50028). For ^{208}Pb/^{204}Pb ratios the average deviation is 0.593 with a maximum deviation of 0.88 (sample D50028).

Figures 4, 5, 6 and 7 show the average values of corrected ratios for each sample plotted on ^{207}Pb/^{204}Pb vs ^{206}Pb/^{20}4Pb and ^{208}Pb/^{204}Pb vs ^{206}Pb/^{204}Pb diagrams.

Although there are certain deviations, the average values for isotopic ratios show that the analyzed gale-

Table 3. Ratios of Pb isotopes in sample D50033.

Spot number	207/206	208/206	206/204	207/204	208/204
140	0.79	1.97	19.73	15.49	38.91
141	0.84	2.10	18.45	15.50	38.68
142	0.82	2.08	18.84	15.74	39.13
143	0.85	2.03	18.73	15.97	37.83
144	0.83	2.06	18.13	15.09	37.41
147	0.82	2.02	19.29	15.79	38.85
149	0.84	2.02	18.96	15.99	38.22
158	0.85	2.02	18.99	15.90	38.49
159	0.84	2.03	18.78	15.66	37.74
160	0.87	2.10	18.69	16.24	38.84
162	0.82	2.01	19.28	15.68	38.64
163	0.83	2.03	19.11	15.47	38.77
164	0.83	2.01	19.27	15.87	38.85
166	0.84	2.10	18.29	15.44	38.43
167	0.84	2.06	18.51	15.71	38.17
174	0.81	2.02	19.32	15.38	38.68
176	0.82	2.07	18.85	15.47	38.64
177	0.84	2.00	18.93	15.80	37.91
Average	**0.83**	**2.04**	**18.90**	**15.68**	**38.45**
SD	0.02	0.04	0.40	0.27	0.47
Error (%)	0.00	0.01	0.10	0.06	0.11

SD=Standard Deviation.

Table 4. Ratios of Pb isotopes in sample D50037.

Spot number	207/206	208/206	206/204	207/204	208/204
216	0.83	2.02	18.58	15.40	37.63
223	0.85	2.04	18.98	15.97	38.12
230	0.85	1.97	18.98	16.08	37.53
231	0.86	2.07	18.46	15.84	38.61
232	0.85	2.10	18.67	15.84	39.19
Average	**0.85**	**2.04**	**18.73**	**15.83**	**38.22**
SD	0.01	0.05	0.23	0.26	0.70
Error (%)	0.01	0.02	0.10	0.11	0.31

SD=Standard Deviation.

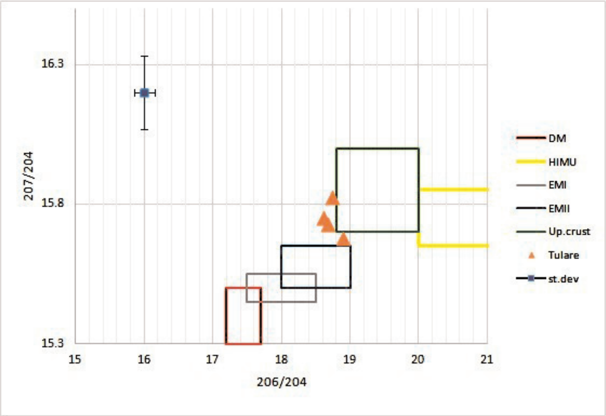

Fig. 4. Average values of isotope ratios plotted on ^{207}Pb/^{204} Pb vs ^{206}Pb/^{204}Pb diagram. Fields for geochemical reservoirs (DM, HIMU, EMI, EMII) are taken from Zindler & Hart (1986). Analytical precision (one standard deviation of average ratios) is given in the upper left corner.

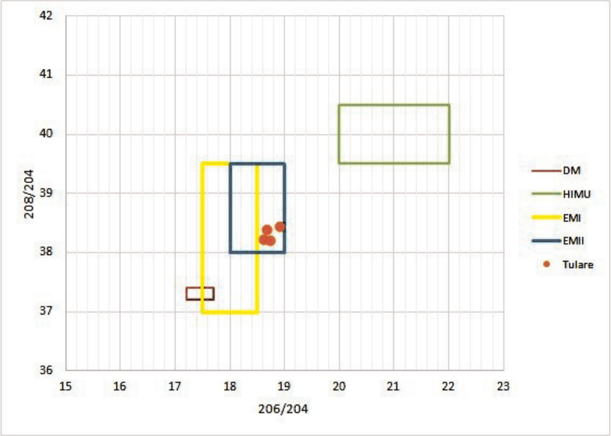

Fig. 5. Average values of isotope ratios plotted on ^{208}Pb/^{204} Pb vs ^{206}Pb/^{204}Pb diagram. Fields for geochemical reservoirs (DM, HIMU, EMI, EMII) are taken from ZINDLER & HART (1986). Analytical precision (one standard deviation of average ratios) is given in the upper left corner.

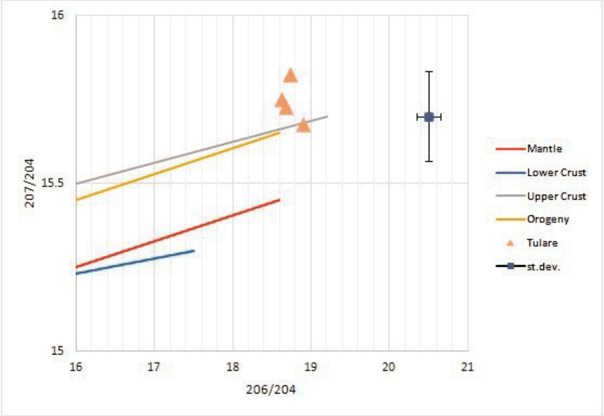

Fig. 6. Average values of isotope ratios plotted on ^{207}Pb/^{204} Pb vs ^{206}Pb/^{204}Pb plumbotectonic diagram. Values for different reservoirs (mantle, lower crust, upper crust and orogeny) are taken from ZARTMAN & HAINES (1988). Analytical precision (one standard deviation of average ratios) is given in the upper right corner.

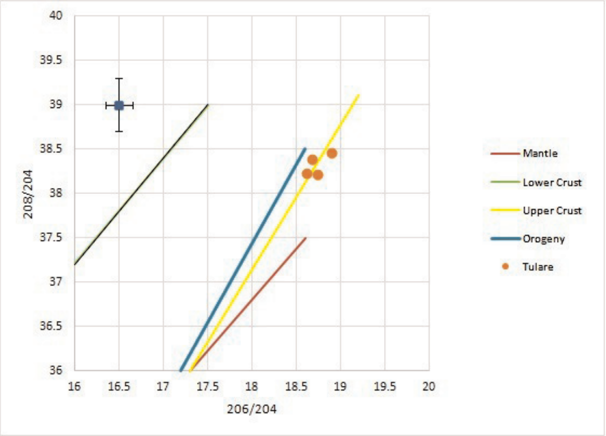

Fig. 7. Average values of isotope ratios plotted on ^{208}Pb/^{204}Pb vs ^{206}Pb/^{204}Pb plumbotectonic diagram. Values for different reservoirs (mantle, lower crust, upper crust and orogeny) are taken from ZARTMAN & HAINES (1988). Analytical precision (one standard deviation of average ratios) is given in the upper left corner.

nas present relatively high ^{207}Pb/^{204}Pb ratios (higher than 15.65), which is characteristic for the upper continental crust (ROLLINSON, 2014). In Figs. 4 and 5, average values of lead isotope ratios plot close to upper continental crust field and inside EMII field respectively, implying mantle enriched with recycled continental crust, continentally derived sediment or ocean-island crust. In Figs. 6 and 7, these ratios plot either on or very close to the upper crust evolution curves (ZINDLER & HART, 1986; ROLLINSON, 2014).

Similar lead isotope measurements were conducted in other lead-zinc deposits in Lece-Chalkidiki zone, such as Zletovo in Fyrom (Macedonia) and Olympias in Greece (JANKOVIĆ, 1978; CHALKIAS & VAVELIDIS, 1988; SERAFIMOVSKI, 1993). Their results are presented in Tables 5, 6 and 7. The average values of lead isotope ratios of these studies, together with the average values from the current study of Tulare district are plotted on the ^{207}Pb/^{204}Pb vs ^{206}Pb/^{204}Pb diagram in Fig. 8.

In addition results of lead isotope ratios from flysch sediments from Ljig, Ugljare and Avala are given in Table 8. The comparisons of these ratios with the samples from Tulare are shown in Fig. 9. This similarity implies that the main source of lead in the examined veins was the upper continental crust, which was

Table 5. Ratios of Pb isotopes from Zletovo ore deposit (JANKOVIĆ, 1978).

	206/204	207/204	208/204
Average	18.88	15.87	39.09

Table 6. Combined data for Pb isotope measurements from Zletovo ore deposit (SERAFIMOVSKI, 1993).

	206/204	207/204	208/204
1	18.693	15.690	38.880
2	18.685	15.688	38.909
1x-350	18.685	15.674	38.890
2x-510	18.689	15.682	38.922
2x-560	18.679	15.673	38.904
3x-580	18.688	15.684	38.912
3x-580	18.686	15.675	38.887
9x-625	18.684	15.680	38.887
8x-490	18.688	15.671	38.890
Average	**18.69**	**15.68**	**38.90**

Table 7. Combined data for Pb isotope measurements from Olympias ore deposit (Chalkias & Vavelidis, 1988).

	206/204	207/204	208/204
GRL6	18.78	15.68	38.90
GRL7	18.79	15.68	38.91
GRL8	18.78	15.67	38.89
39 A-2	18.77	15.66	38.80
39E	18.77	15.66	38.82
40	18.78	15.67	38.85
40	18.76	15.66	38.82
109 B-1	18.76	15.66	38.80
Average	**18.77**	**15.67**	**38.85**

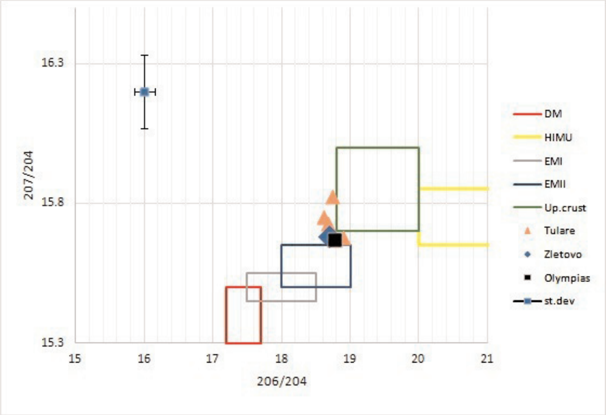

Fig. 8. Average values of isotope ratios from Tulare, Zletovo and Olympias plotted on ^{207}Pb/^{204}Pb vs ^{206}Pb/^{204}Pb. Fields for geochemical reservoirs (DM, HIMU, EMI, EMII) are taken from Zindler & Hart (1986). The standard deviation of isotope ratios measurements (1σ) from Tulare are shown in the upper left corner.

probably recycled to intermediate magma and erupted during Tertiary post-collisional magmatism. These values show good correlation with the lead isotope ratios of continental flysch sediments of Vardar Zone (Prelević et al, 2008).

Table 8. Combined data for Pb isotope measurements for flysch sediments from Ljig (06FL01, 06FL02), Ugljare (06FL03) and Avala (AV01) (Prelević et al., 2008).

Spot number	206/204	207/204	208/204
06FL01	18.687	15.706	38.922
06FL02	18.629	15.693	38.826
06FL03	19.939	15.687	39.133
AV01	18.735	15.651	38.827

Sulphur isotope analysis included a total of 8 samples: 4 sphalerite, 2 galena and 2 pyrite samples. The results of sulphur isotope measurements are presented in Table 9.

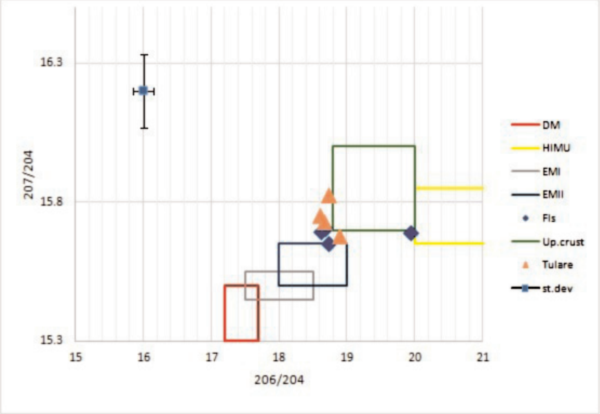

Fig. 9. Average values of isotope ratios from Tulare and flysch sediments (Fls) from SMM plotted on ^{207}Pb/^{204}Pb vs ^{206}Pb/^{204}Pb diagram. Fields for geochemical reservoirs (DM, HIMU, EMI, EMII) are taken from Zindler & Hart (1986). Standard deviation of isotope ratios measurements (1σ) from Tulare are shown in the upper left corner.

Table 9. Results of S isotope analysis, expressed in permil in the typical delta notation compared to the standard VCDT (Vienna Canyon Diablo Troilite).

Sample number	**Mineral analyzed**	**δ^{34}S (‰)**
47918 Sp	sphalerite	+2.89
47918 PyD	pyrite	+2.97
50026 SpD	sphalerite	+1.84
50030 SpD	sphalerite	+2.06
50030 GD	galena	+0.38
50033 GD	galena	+0.90
50033 SpD	sphalerite	+2.93
50032 Py	pyrite	+2.47

In general, all sulphides exhibit a slight enrichment of heavy isotope in comparison with the standard. No negative δ^{34}S values were measured. All the analyzed samples have δ^{34}S values in the range of 0.4‰ to 3‰, which indicates that the sulphur has a mantle origin (Rollinson, 2014) and that sulphates from meteoric water did not have an influence in the formation of the deposit. This is in accordance with the previously analyzed samples from other similar deposits of the Serbo-Macedonian Metallogenic Province which also contain sulphur that has a mantle origin.: Zletovo ore field (Serafimovski, 1990), Olympias in Greece (Kalogeropoulos et al., 1989), Trepča (Palinkaš et al., 2013) and Veliki Majdan (Schirra, 2015) Serafimovski et al. (2006) presented data of sulphur isotopes from several ore deposits of the Serbo-Macedonian Mass (Bučim, Borov Dol, Plavica, Toranica, Sasa, Zletovo and Olympias). The results are shown in Table 10. Most of these values are similar with measured values from Lece (between –3‰ and +3‰) indicating that the main source of sulphur in this metallogenic belt is the mantle.

Table 10. Results of S isotope analysis (‰) from different ore deposits in the Serbo-Macedonian Metallogenic Province (SERAFIMOVSKI et al., 2006).

Ore deposit	Range (from)	Range (to)
Bučim	0	2.53
Borov Dol	-7.52	0.72
Plavica	0.41	1.42
Toranica	-7.52	2.18
Sasa	-1.22	6.94
Zletovo	-3.12	3.4
Olympias	-0.3	2.7
Sb-As mineral deposits	-5.6	3.7

Furthermore, the average values of ratios of lead isotopes shown on Fig. 8 and Tables 5, 6 and 7, from three distant deposits in Lece–Chalkidiki zone are relatively similar implying that upper continental crust was the major source of lead and probably other ore metals. This is in agreement with the opinion of SERAFIMOVSKI (1990) and other authors who consider that the ore deposits in this metallogenic zone were all formed under the same geodynamic condition (post-collisional magmatism). However there is still a question whether a magma derived by partial melting of lower continental crust could be sustained because the lead isotope ratios show that it is more likely the upper crust to be the main source of these metals (SERAFIMOVSKI & JANKOVIĆ, 2000).

In cases where different sulphide minerals were measured for the same sample (e.g. 47918, D50030, D50033), the values follow the trend pyrite > sphalerite > galena. Experimental data by KAJIWARA & KROUSE (1971) show that this should be the trend under isotopic equilibrium of sulphides, so it can be assumed (along with textural characteristics from ore microscopy examinations) that these sulphides were deposited in equilibrium.

Since the textural relations between galena and sphalerite in carbonate veins imply that these minerals were deposited in the same phase (Fig. 10) and that there is a trend of decreasing $\delta^{34}S$ values from pyrite, to sphalerite and to galena, it can be assumed that galena and sphalerite were formed in isotopic equilibrium and that their relations can be used to calculate the temperature of deposition.

The temperatures were calculated using the formula of OHMOTO & RYE (1979):

$$\Delta ZnS\text{-}PbS = (0.73/T^2)*10^6$$

The precision of the calculated temperature is ±20° C at 300° C. The temperatures of deposition for samples D50030 and D50033 are shown in Table 11. Both of these samples come from the same type of veins, brown carbonate veins which contain galena, sphalerite and chalcopyrite. They probably belong to the most important generation of veins in this metallogenic zone. Considering the stated precision of this method, it is assumed that the real temperature of formation is the mean between these two values - around 350° C.

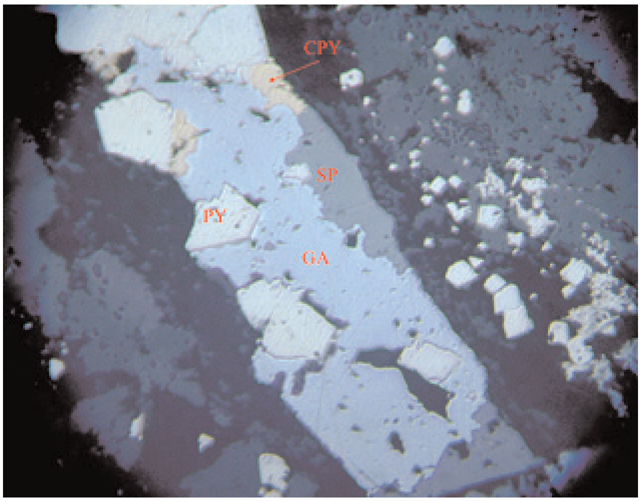

Fig. 10. Photomicrograph of polished thin section from sample D50033: pyrite (PY), chalcopyrite (CPY) and sphalerite (SP) inside an elongated galena (GA) grain indicating they were formed in a common phase. Picture length: 2 mm

However, these values should be taken with caution, since according to BORTNIKOV et al. (1995) the mineral precipitation in epithermal base metal and gold deposits occurs at relatively high oxygen fugacity. In addition small changes in pH and oxygen fugacity may result in large changes in $\delta^{34}S$ values of deposited minerals and especially when deposition occurs in the presence of fluids rich in H_2S and SO_4^{2-}. In the same paper, the authors suggest that sulphur isotope thermometer values which haven't been compared with other methods should not be accepted as valid without doubt.

Table 11. Results of calculations of temperature based on S isotopes in galena and sphalerite.

Sample number	ΔZnS-PbS (‰)	T (K)	t (°C)
D50030	1.68	659.40	386.2
D50033	2.03	599.76	26.6

According to mineral and textural composition of veins, this mineralization can be classified as "Carbonate base-metal gold system". CORBETT & LEACH (1997) state that in such systems, the deposition of galena and sphalerite occurs at temperatures below 200° C.

Considering all the above, the calculated temperature values by sulphur isotope ratios of around 350° C should be accepted with caution and other methods should be employed for verifying this result (e.g. fluid inclusion analysis, analysis of microelements in galena and sphalerite, etc.).

Conclusions

All the analyzed samples from the Tulare ore field (both from high and low sulphidation zones) present similar average ratios of Pb isotopes which imply that all the minerals originated from a same or similar source.

The mineralization is related to magmatism dericed from upper mantle that was contaminated by material from upper crust, probably during post-collisional recycling processes. Considering the fact that high values of ^{207}Pb indicate an old geochemical reservoir, there is a possibility that the high values of ^{207}Pb/^{204}Pb in some samples from Tulare might indicate that the recycled continental crust contained Precambrian - Paleozoic rocks from Serbo-Macedonian massif.

The main source of lead in the examined veins was the upper continental crust, which was probably recycled to intermediate magma and erupted during Tertiary post-collisional magmatism.

The analyzed samples present δ^{34}S values in the range of 0.4‰ to 3‰, indicating that the sulphur has a mantle origin and that none sulphate interference from meteoric water took place in the formation of Tulare ore deposit.

The textural relations between galena and sphalerite imply that these minerals were deposited in the same phase but they were not formed in isotopic equilibrium. The temperature of their deposition was calculated around 350° C.

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Резиме

Порекло олова и сумпора у рудном пољу Туларе, магматски комплекс Леце, Југоисточна Србија

Појаве олова и цинка Бакрењача и Губавце, које се изучавају у овом раду, налазе се у рудном пољу Туларе, односно рудном рејону Леце у склопу металогенетске зоне Леце–Халкидики. Терцијарна магматска активност која је довела до настанка сложеног вулканског комплекса Леце била је испољена у периоду од олигоцена до касног палеогена; геотектонски је везана за пост-колизионе процесе након затварања дела Тетиског океана дуж зоне Вардар–Измир–Централна Анатолија. Узорци у којима су анализирани изотопи олова и сумпора потичу из истражних бушотина са локалитета Бакрењача и Губавце у јужном делу овог комплекса. Просечне вредности односа изотопа олова указују да анализирани галенити имају релативно висок однос $^{207}Pb/^{204}Pb$ (виши од 15.65), што је карактеристично за горње делове континенталне коре. Слична мерења односа изотопа олова су вршена у другим лежиштима олова и цинка у Леце–Халкидики зони, као што су Злетово у Македонији. Просечне вредности односа изотопа из три удаљена лежишта у зони Леце–Халкидики су релативно слична и указују да је горњи део континенталне коре био основни извор олова и вероватно других рудних метала, што је у сагласности са мишљењем да су сва рудна лежишта у овој зони формирана у истим геодинамичким условима (пост-колизиони магматизам). Сви анализирани узорци имају вредности $\delta^{34}S$ у распону 0.4‰ – 3‰, што указује да сумпор у лежиштима има порекло из омотача, као и да сулфати из воде метеорског порекла нису имали значајнији утицај на формирање лежишта. Преко односа изотопа сумпора у сулфидима (галениту, сфалериту и пириту), одређена је температура депоновања минерала од 300–400° C. Међутим, ова температура је превисока за епитермална лежишта, што вероватно указује да ови сулфиди нису депоновани у изотопском еквилибријуму.

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