ΠΡΑΚΤΙΚΑ ΤΗΣ ΑΚΑΔΗΜΙΑΣ ΑΘΗΝΩΝ

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ΠΡΟΕΔΡΙΑ ΓΕΩΡΓΙΟΥ ΜΕΡΙΚΑ

ΓΕΩΛΟΓΙΑ.— **Lithogeochemical studies of barite mineralization in the Kilkis area, northern Greece,** by *A. E. Kelepertzis and J. Androulakis**, διὰ τοῦ 'Ακαδημαϊκοῦ κ. *Λ. Μουσούλου.*

ABSTRACT

Lithogeochemical studies have been carried out in the areas of barite mineralization at Kato Potamia and Leipsidri, of Kilkis province. The barite ore occurs in the form of veins striking NNW-SSE cutting the metamorphic rocks of the Serbo-Macedonian massif. The mineralogy of barite ore is simple: barite, galena, quartz. In terms of Sr content, the barites can be distinguished into two groups: group one from Leipsidri is characterized by Sr contents ranging between 640 and 1580 ppm while group two from Kato Potamia is characterized by Sr in the range 1310 to 2850 ppm. Pb- anomalies may be used to trace the Ba anomalies too, since the two minerals (galena and barite) are both associated with the barite veins. The barite rich samples have in a general way the lower FeO anf MgO contents, usually $\leqslant 1\%$.

INTRODUCTION

Both barite and copper mineralization occur in an area of 15 km² southeast of Kilkis town. This area is located about 50km north of Thessaloniki (Fig. 1).

The veins of barite mineralization occur within metamorphic rocks of

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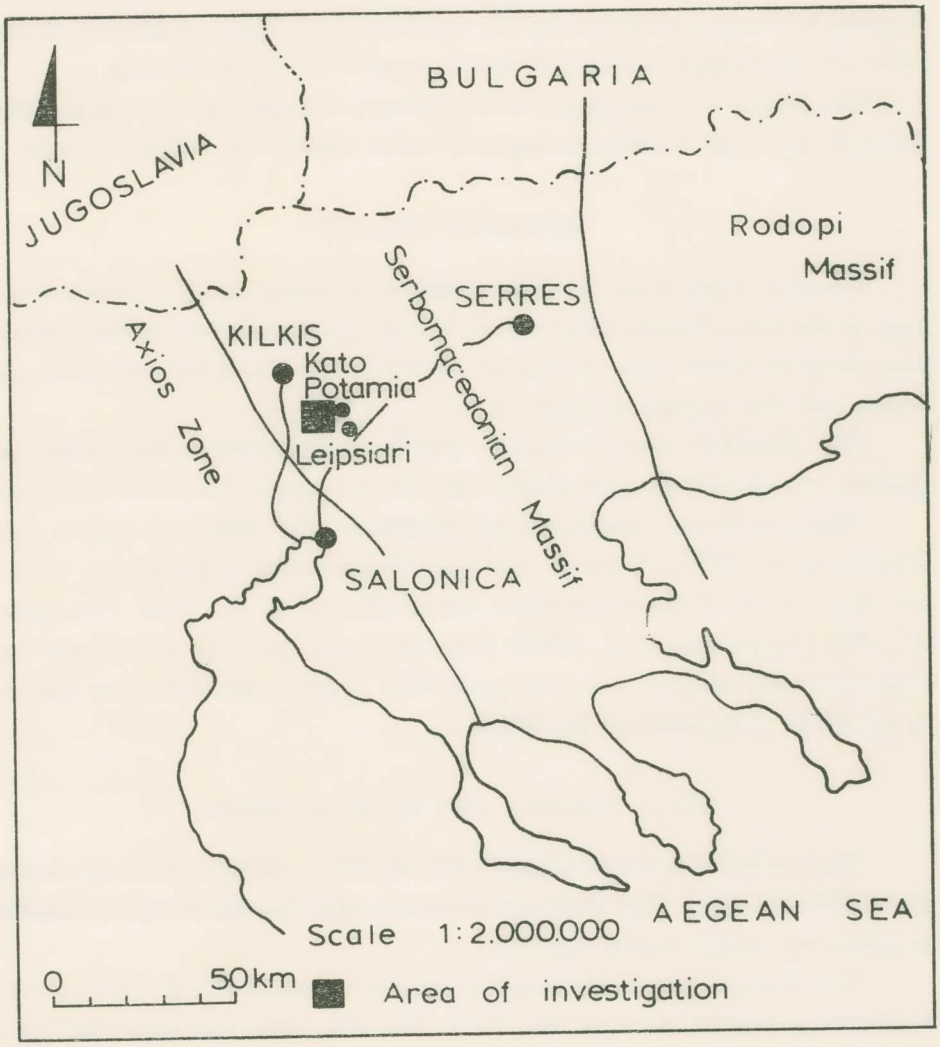

Fig. 1. Map showing the area under study.

the Serbo-Macedonian massif. At the same area veins of pyrite + chalcopyrite mineralization have been studied before (Kelepertzis et al., 1987). Most of the barite veins have been mined in the past on a small scale. Recently, a research program has been undertaken by the Institute of Geology and Mineral Exploration in an attempt to find new barite deposits in the above area.

The purpose of this paper is to evaluate lithogeochemical exploration methods as an aid for discovering new barite deposits in Kilkis province.

REGIONAL GEOLOGY

The area under study is at the western boundary of the Vertiskos subzone of the Serbo-Macedonian massif. The Serbo-Macedonian massif extends from Beograd south across the Greek border to the Chalkidiki peninsula and thence into the Aegean sea (Fig. 1).

The Vertiskos subzone consists mainly of muscovite-biotite schists and gneisses of high metamorphic grade, with minor amphibolites as intercalations.

These rocks are interrupted by pegmatites and numerous quartz veins (Kockel et al., 1977). Volcanic and subvolcanic rocks, occur in the western boundary of the Serbo-Macedonian massif (Kockel et al., 1975; Panagos et al., 1978; Kelepertzis et al., 1985). Some of the subvolcanic rocks have been hydrothermally altered and associated with copper mineralization (Kockel et al., 1975; Kelepertzis et al., 1986).

LOCAL GEOLOGY AND MINERALIZATION

The studied area is one of gently sloping hills sparsely covered by shrubs, and cultivated land. The drainage system is well developed and is marked in places by deeply incised systems.

The local geology of the Leipsidri area is shown in Fig. 2. There are not available geological data for the Kato Potamia area. The main rock types encountered are muscovite-biotite gneisses, schists and amphibolites as intercalations. The schistosity trends approximately N-S. Both large scale folding and microfolding are common, and the rocks are crushed and mylonitized along fold axes. The metamorphic rocks are cut by numerous quartz and aplitic pegmatite veins. In the western part of the area a quartzite unit marks a stratigraphically lower horizon of the metamorphic suite.

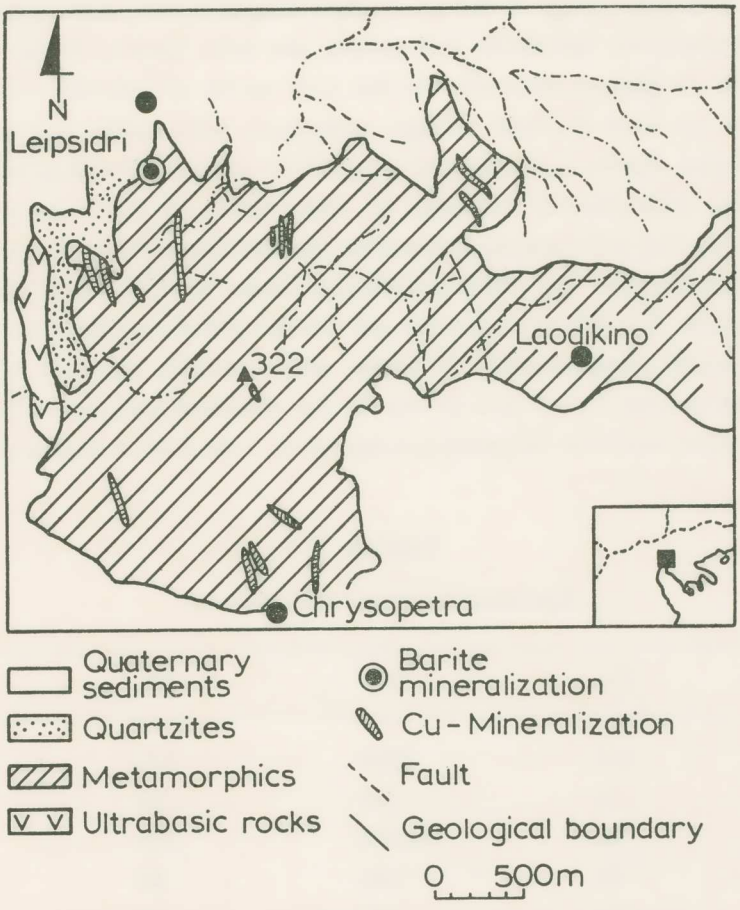

Fig. 2. Map showing the local geology of the Leipsidri area.

Several silicified veins, 300-500m long and 5-10m wide, with a NW-SE and or /N-S strike occur within the metamorphic rocks. These veins are associated with sulphide mineralization, mainly copper sulphides (Kelepertzis et al., 1987). The mineralogy of the ore is quite simple: pyrite, chalcopyrite, with minor arsenopyrite. Sphalerite and galena are rare. Quartz, barite and silicates occur as gangue minerals. In the area south of Leipsidri village and north-west of Kato-Potamia village, exposures with barite mineralization are also found. Barite is common as a veinstone associated with galena, depositing from hydrothermal solutions or from solutions which have leached barium from the surrounding Palaeozoic metamorphic rocks. It seems that barite mineralization has filled preexisting faults of NW-SE strike in the metamorphics. The mineralized veins are characterized by simple mineralogy, which consists predominantly of barite with variable amounts of pyrite, galena and quartz. This is also shown by the chemical analyses of barite ore from two sites, one from Leipsidri and the other from Kato Potamia (Table 1).

TABLE 1.

Chemical analyses of barite ore

	Cu	Pb	Zn	Sr
L-1	100	3900	210	1580
L-2	70	720	90	640
L-3	80	61000	190	810
L-4	60	520	60	660
P-1	190	300	70	2070
P-2	220	840	70	1310
P-3	100	640	70	2250
P-4*	50	620	90	310
P-5	50	1360	30	2850
P-6	60	360	30	2070

*P-4 is a gneiss

SAMPLING AND ANALYTICAL PROCEDURES

Ore samples (10) were collected from two barite exposures, four samples from the barite mineralization of Leipsidri and six from the barite veins of Kato Potamia (Fig. 3). For the lithogeochemical research core samples have been collected from bore holes at Leipsidri area. The samples were taken from the mineralized zone and from the unmineralized rocks above and below the barite veins. All the samples were analysed by atomic absorption spectroscopy at the Chemical Lab. of I.G.M.E., Xanthi Branch. The first 10 ore samples were analysed for Cu, Pb, Zn, and Sr (Table 1). The samples from drillings were analysed for Pb, Sr, Ba, FeO, MgO and SiO_2 (Table 2). Polished sections were also examined under the ore microscope for mineral texture determination.

GEOCHEMICAL RESULTS-DISCUSSION

Ore chemistry

From Table 1 it is obvious that apart from barite, the other metallic mineral present in the mineralization is galena. The Pb level in the ore samples analysed varies between 61000 and 360 ppm, showing that the Pb distribution in barites is not uniform. On the other hand, the concentrations of Cu and Zn are very low, suggesting that individual minerals are insignificant in the barite ore, although Cu—bearing quartz veins are encountered in the surrounding area.

The Sr levels of barites range between 640 and 2850ppm. Table 1 shows that the samples from Leipsidri have Sr contents ranging between 640 and 1580 ppm with an average of 922 ppm, while the barites from Kato Potamia have Sr contents ranging between 1310 and 2850 ppm with an average of 2110 ppm. This Sr variation depends on the $m_{Sr^{2+}}/m_{Ba^{2+}}$ ratio in the solution and on the mixing properties of the $BaSO_4$-$SrSO_4$ solid solution, according to equation*:

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* $(BaSO_4)_{solid} + (Sr^{2+})_{soln} \leftrightarrows (SrSO_4)_{solid} + (Ba^{2+})_{soln}$

$$K_{(P,T)} = \frac{(SrSO_4)_{bar}\,(Ba^{2+})_{soln}}{(BaSO_4)_{bar}\,(Sr^{2+})_{soln}}$$

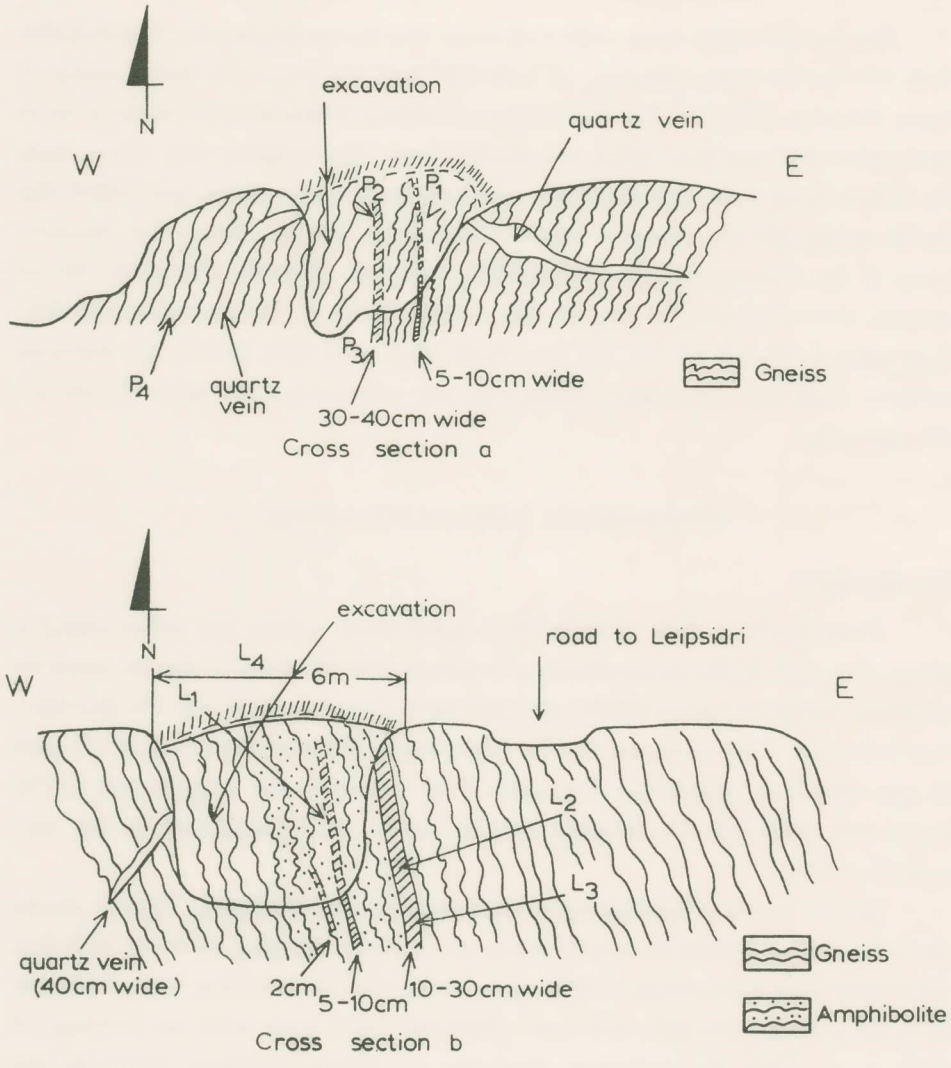

Fig. 3. Schematic cross section showing barite veins of the two excavations a and b Kato Potamia and Leipsirdi reprectively.

TABLE 2.

Chemical analyses of core samples (%)

Bore hole	Sample number	Pb*	Sr*	Ba	FeO	MgO	SiO2
6/6	1	6200	31	0.06	1.43	1.96	61
	2	2760	20	0.26	0.57	1.11	71
	3	52	7	0.04	10.20	7.3	50
	4	34	10	0.08	10.34	6.3	50
	5	124	24	0.06	5.74	7.13	48
	6	5360	33	1.76	3.01	2.99	58
6/1	7	7280	18	3.10	0.43	0.81	65
	8	6240	14	1.22	0.71	0.94	62
	9	3440	37	20.6	0.00	0.50	53
	10	60	8	0.24	4.16	5.81	49
	11	40	23	0.20	3.87	5.81	48
	12	2600	29	2.7	0.57	1.11	65
	13	300	11	0.66	1.14	1.19	68
	14	660	18	0.44	0.86	1.31	68
6/10	15	34	18	4.0	0.14	0.33	73
	16	92	16	0.48	0.14	0.33	78
	17	36	3	0.12	0.28	0.35	78
	18	30	2	0.10	0.14	0.73	77
	19	140	20	1.06	0.28	0.21	78
	20	12	4	0.12	0.28	0.50	76
	21	50	3	0.12	0.28	1.19	69
6/2	22	2280	5	0.36	4.02	2.32	55
	23	9920	16	1.80	0.57	1.16	61
	24	8	11	0.14	4.02	2.65	61
	25	450	40	0.26	1.00	1.52	58
	26	14	5	0.12	5.60	2.65	54
	27	96	6	0.18	2.44	1.79	70
	28	2400	6	0.62	0.43	0.91	77

* Chemical analyses in ppm (partial analyses)

Geochemical correlations

From Table 2 it is obvious that the borehole 6/1 shows the Pb/Ba association very clearly; to some extent this is apparent in 6/2 also but not in the other two. Since no galena mineralization of economic significance was found and galena is associated with barite in the veins, Pb anomalies could be used to trace the Ba anomalies in this area (Leipsidri). On the other hand, there is a general association between Pb and Ba in the soils of Kato Potamia as mentioned in a previous paper (Reeves et al., 1986) where both elements were considerably raised above «normal» levels and above levels of other sulphide soils, even though the detailed correlation of Pb/Ba within the Kato Potamia area was not strong.

The correlation between FeO and MgO is high (Fig. 4) suggesting that FeO and MgO are both associated with mafic minerals in amphibolites ($r = 0.89$). There is no correlation between Ba and FeO/or MgO contents in all the samples analysed, but inspection of Table 2 shows that the barite rich-samples (7, 8, 9, 12, 13, 14, 15, 16, 19, 23, 28) have in a general way the lower FeO and MgO contents, usually $\leq 1\%$. The barite richer sample (6/9) has the lowest FeO and MgO content. The rest of the samples have variable FeO and MgO contents.

The SiO_2 contents range between 48 and 78%. Some of the samples have SiO_2 levels which are higher than the SiO_2 contents even of acidic magmatic rocks (Brownlow, 1979). This means that the rocks studied have been subjected to intense silicification.

CONCLUSIONS

The lithogeochemical studies for barite mineralization of Kato Potamia and Leipsidri of Kilkis province lead to the following conclusions:

(a) The mineralogy of the barite ore is simple: barite, galena, quartz. The chemistry of the ore showed that any other sulphide minerals are insignificant.

(b) In terms of Sr content, the barites can be distinguished into two groups: group one from Leipsidri is characterized by an average Sr content of 922 ppm, while group two from Kato Potamia is characterized by an average Sr content of 2110 ppm.

(c) A Pb/Ba association is apparent in samples from borehole 6/1 and to some extent in borehole 6/2, but not in the other two. In general, Pb-

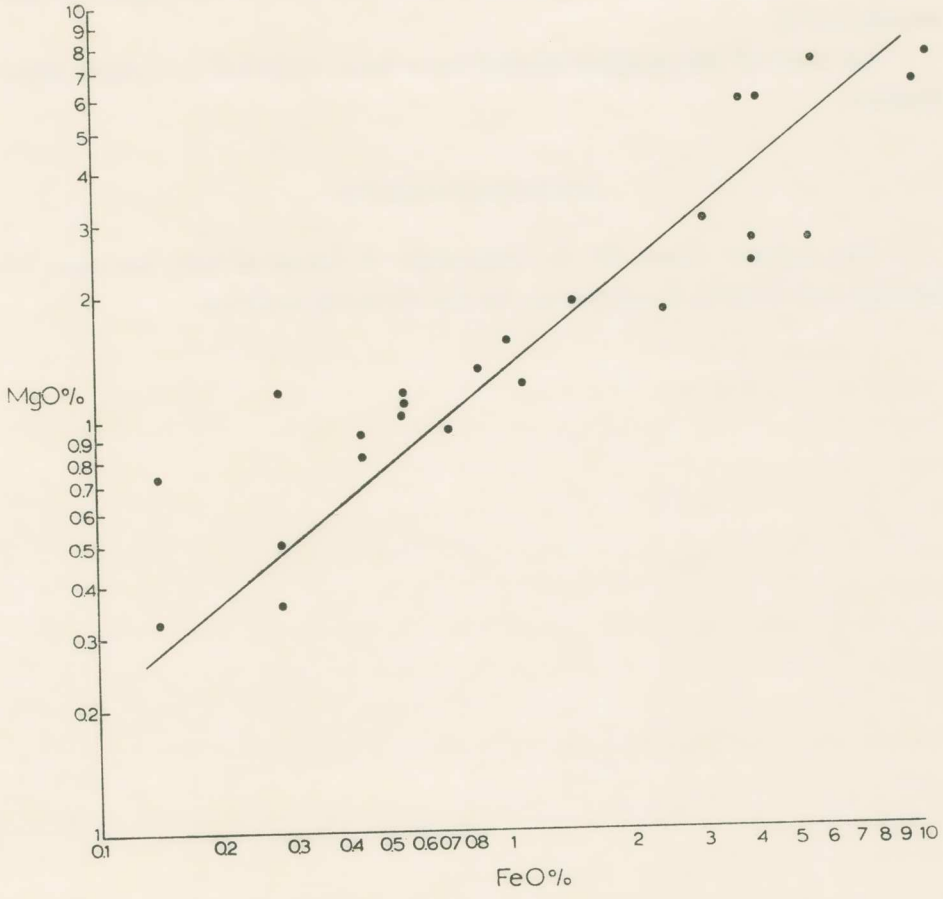

Fig. 4. Relationship between FeO and MgO contents.

anomalies may be used to trace the Ba anomalies too, since the two minerals (galena and barite) are both associated within the barite veins.

(d) There is a positive correlation between FeO and MgO contents. The barite rich samples have in a general way the lower FeO and MgO contents usually $\leq 1\%$.

(e) Most of the samples studied have been subjected to intense silicification.

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ΠΕΡΙΛΗΨΗ

Λιθογεωχημικὲς μελέτες μεταλλοφορίας βαρύτη στὴν περιοχὴ τοῦ νομοῦ Κιλκίς. Βόρεια Ἑλλάδα.

Ὁ σκοπὸς τῆς μελέτης αὐτῆς εἶναι ἡ ἐκτίμηση τῆς δυνατότητας ἐφαρμογῆς τῶν συμπερασμάτων λιθογεωχημικῶν ἐρευνῶν στὶς περιοχὲς Λειψυδρίου-Κάτω Ποταμιᾶς μὲ σκοπὸ τὸν ἐντοπισμὸ νέων φλεβῶν βαρύτη στὴν εὐρεῖα περιοχὴ τοῦ νομοῦ Κιλκίς.

Στὶς περιοχὲς νότια τοῦ χωριοῦ Λειψύδρι καὶ βορειοδυτικὰ τοῦ χωριοῦ Κάτω Ποταμιᾶ τοῦ νομοῦ Κιλκὶς ἁπαντᾶ μεταλλοφορία βαρύτη μέσα στὰ μεταμορφωμένα πετρώματα τῆς Σερβομακεδονικῆς ζώνης.

Ὁ βαρύτης συναντᾶται ὑπὸ μορφὴ φλεβῶν καὶ ἀποτέθηκε ἀπὸ ὑδροθερμικὰ διαλύματα ἐμπλουτισμένα σὲ βάριο μέσα σὲ προϋπάρχοντα ρήγματα τῶν μεταμορφικῶν πετρωμάτων. Τὰ πετρώματα αὐτὰ εἶναι μοσχοβιτικοὶ-βιοτικοὶ γνεύσιοι, σχιστόλιθοι καὶ ἀμφιβολίτες μὲ τὴ μορφὴ παρεμβολῶν.

Ἡ ὀρυκτολογικὴ σύσταση τῆς μεταλλοφορίας εἶναι ἁπλὴ καὶ περιλαμβάνει κυρίως βαρύτη, μὲ μικρότερα ποσὰ σιδηροπυρίτη, γαληνίτη καὶ χαλαζία. Ἡ χημικὴ ἀνάλυση 10 δειγμάτων μεταλλεύματος βαρύτη (Πίνακας 1) ἔδειξε ὅτι εἶναι παρόντα ποικίλλα ποσὰ μολύβδου καὶ στροντίου. Τὰ στοιχεῖα ψευδάργυρος καὶ χαλκὸς ἁπαντοῦν σὲ μικρὲς περιεκτικότητες.

Γιὰ τὴ λιθογεωχημικὴ ἔρευνα ἐλήφθησαν 28 δείγματα ἀπὸ πυρῆνες γεωτρήσεων ποὺ εἶχαν γίνει στὴν περιοχὴ Λειψυδρίου. Τὰ δείγματα αὐτά, ποὺ παριστοῦν μεταλλοφόρα καὶ μὴ πετρώματα ὑπερκάνω καὶ κάτω τῶν ζωνῶν βαρύτη, ἀναλύθηκαν μὲ τὴ μέθοδο τῆς ἀτομικῆς ἀπορρόφησης γιὰ τὰ στοιχεῖα Pb, Sr, Ba, FeO, MgO καὶ SiO2.

Στὴ γεώτρηση 6/1 φαίνεται μία σαφὴς θετικὴ συσχέτιση μεταξὺ Pb καὶ Ba. Αὐτὸ εἶναι ἐπίσης καταφανὲς στὴ γεώτρηση 6/2, ἀλλὰ ὄχι στὶς δύο ἄλλες. Ἐπειδὴ δὲν συναντήθηκε μεταλλοφορία μολύβδου οἰκονομικῆς σημασίας στὴν εὐρεῖα περιοχὴ Κιλκίς, οἱ ἀνωμαλίες Pb μποροῦν νὰ χρησιμοποιηθοῦν γιὰ τὴν ἀνίχνευση ἀνωμαλιῶν Ba. Τέτοια συσχέτιση μεταξὺ Pb καὶ Ba βρέθηκε ἐπίσης σὲ ἐδάφη ἀποσάθρωσης πάνω ἀπὸ φλέβες βαρύτη στὶς πιὸ πάνω περιοχὲς (Reeves καὶ Κελεπερτζῆς 1986).

Ἡ συσχέτιση μεταξὺ FeO καὶ MgO εἶναι πολὺ ὑψηλὴ ($r=0.89$) καὶ αὐτὸ δηλώνει τὴ συμμετοχή των σὲ φεμικὰ ὀρυκτὰ ἀμφιβολιτῶν.

Ἀπὸ τὸν Πίνακα 2 φαίνεται ἐπίσης ὅτι τὰ δείγματα ποὺ εἶναι ἐμπλουτισμένα

σὲ Ba(7, 8, 9, 12, 13, 14, 15, 16, 19, 23, 28) ἔχουν τὰ μικρότερα περιεχόμενα FeO καὶ MgO, συνήθως $1 \leq \%$ τὸ δὲ πλουσιότερο σὲ βάριο δεῖγμα (6/9) ἔχει τὸ μικρότερο περιεχόμενο FeO καὶ MgO.

Τὰ συμπεράσματα ἀπὸ τὴν παρούσα μελέτη τῆς γεωχημικῆς ἔρευνας δειγμάτων ἀπὸ πυρῆνες γεωτρήσεων εἶναι:

(α) Οἱ γεωχημικὲς ἀνωμαλίες Pb μπορεῖ νὰ χρησιμοποιηθοῦν γιὰ τὴν ἀνίχνευση ἀνωμαλιῶν βαρύτη, ἀφοῦ ὁ γαληνίτης σὰν παραγενετικὸ ὀρυκτὸ εἶναι παρὸν στὸ μετάλλευμα βαρύτη.

(β) ὑπάρχει ἀρνητικὴ συσχέτιση μεταξὺ τοῦ Ba καὶ τῶν ὀξειδίων FeO καὶ MgO, δηλαδὴ οἱ ζῶνες γεωχημικῶν ἀνωμαλιῶν Ba χαρακτηρίζονται ἀπὸ χαμηλὰ περιεχόμενα FeO καὶ MgO.

(γ) τὰ περισσότερα ἀπὸ τὰ δείγματα ποὺ μελετήθηκαν ἔχουν ὑψηλὸ περιεχόμενο SiO_2 ποὺ ὀφείλεται στὴν ἔντονη πυριτίωση.

(δ) Τὰ συμπεράσματα (α), (β) καὶ (γ) μπορεῖ νὰ ἐφαρμοσθοῦν στὴ γεωχημικὴ μελέτη τῆς εὐρείας περιοχῆς τῆς ὑποζώνης Βερτίσκου τῆς Σερβομακεδονικῆς ζώνης μὲ σκοπὸ τὸν ἐντοπισμὸ νέων συγκεντρώσεων βαρύτη.