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ORE ELEMENT GEOCHEMISTRY OF THE PB-ZN (AU, AG)
SULFIDE DEPOSITS, EASTERN CHALKIDIKI PENINSULA, N.
GREECE

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A B S T R A C T

The ore geochemistry of the Pb-Zn (Au, Ag) sulfide ore deposits, eastern Chalkidiki Peninsula, N. Greece is utilized in an attempt to constrain their genesis. The bulk composition of these ores in terms of the Cu-Pb-Zn and the Cu-Pb+Zn-Ag $\times 10^3$ ratios shows a similarity with the skarn-replacement and sediment-hosted rather than with the volcanogenic Pb-Zn sulfide ore types. This similarity is further refined in the Pb-Ag diagram for the same ore deposit types where it is statistically indistinguishable from the skarn-replacement type; a conclusion which is further supported by the quite variable vertical distribution of the Pb/Zn ratios in the ore. This last feature is common in epigenetic and rather uncommon in syngenetic Pb-Zn sulfide ores.

ΣΥΝΟΨΗ

Η Γεωχημεία του μεταλλεύματος των θειούχων κοιτασμάτων Pb-Zn (Au, Ag) της Ανατολικής Χαλκιδικής, Β. Ελλάδα, αξιοποιείται σε μια προσπάθεια να οριοθετηθούν ορισμένοι περιορισμοί που αφορούν τη γένεσή τους. Ο χημικός αυτός των κοιτασμάτων όπως προκύπτει από τα διαγράμματα Cu-Pb-Zn και Cu-Pb+Zn-Ag $\times 10^3$ δείχνει μια ομοιότητα με το χημικό των θειούχων κοιτασμάτων Pb-Zn τύπου skarn-replacement και sediment-hosted παρά με εκείνο των αντίστοιχων ηφαιστειογενών. Η ομοιότητα αυτή διευκρινίζεται ακόμη περσιστότερο και ταυτίζεται στατιστικά με τον τύπο skarn-replacement στο διάγραμμα Pb-Ag και στηρίζεται παραπέρα από την αρκετά μεταβλητή κατακόρυφη κατανομή των μεταλλικών στοιχείων και του λόγου Pb/Zn στο μετάλλευμα. Το τελευταίο αυτό χαρακτηριστικό είναι πιο κοινό σε επιγενετικές παρά σε συγγενετικές θειούχες μεταλλοφορίες Pb-Zn.

INTRODUCTION - ΕΙΣΑΓΩΓΗ

The major constituents of the massive sulfide ore deposits are the metals Cu, Pb, Zn, Au and Ag. Plots of the relative proportions by weight of Cu-Pb-Zn and Cu-Pb+Zn-Ag $\times 10^3$ in different massive sulfide ore types are utilized for deducing an independent piece of evidence regarding possible genetic links amongst them (Sangster and Scott, 1976; Hodgson and Lydon, 1977; Franklin et al. 1981;

* Σ.Η. ΚΑΛΟΓΕΡΟΠΟΥΛΟΣ : Γεωχημεία μεταλλεύματος των θειούχων κοιτασμάτων Pb-Zn (Au, Ag) της Ανατολικής Χαλκιδικής, Β. Ελλάδα.

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Gustafson and Williams, 1981). This study utilizes the ore geochemistry of the Madem Lacos, Mavres Petres and Olympias lead-zinc sulfide ore deposits located in the eastern Chalkidiki Peninsula (Fig. 1) in an attempt to obtain genetic constraints for these ores.

ANALYTICAL METHODS - ΑΝΑΛΥΤΙΚΕΣ ΜΕΘΟΔΟΙ

The analyses for Cu, Pb, Zn and Ag were provided to us by the Hellenic Company of Chemical Products and Fertilizers S.A. They were performed by conventional AAS and the errors in percent of the reported values are : Cu=10; Pb=6; Zn=6, and Ag=6. Table I is a summary of the means and the standard deviations for each of these ore elements in the three sulfide deposits of the eastern Chalkidiki Peninsula. Tables II, III and IV, summarize details of this chemistry for the same deposits.

ASSOCIATED METALS - ΣΥΝΥΠΑΡΧΟΝΤΑ ΣΤΟΙΧΕΙΑ

Cu-Pb-Zn

Figures 2, 3 and 4 illustrate the lead-zinc character of the ores and a wide range of the lead/zinc ratios for single and a number of drill holes from the Eastern Chalkidiki sulfide deposits. In addition, Figure 5A shows the fields of metal ratios for sediment-hosted, volcanogenic together with the distribution of twelve lead-zinc (copper) skarn-type sulfide deposits as compared to the metal ratios of the Eastern Chalkidiki lead-zinc sulfide ores. The fact that the field occupied by the latter ores is closely similar with those occupied by the sediment-hosted and skarn types provides a piece of evidence for a genetic link between the studied ores and either one of the latter two ore deposit types.

Cu-Pb+Zn-Ag x 10³

Figures 2, 3 and 4 are plots of the bulk composition of the eastern Chalkidiki Peninsula sulfide ore deposits in terms of their silver-lead+zinc-copper contents by weight percent for single and a number of drill holes from the three ore deposits. Figure 5B is a ternary plot similar to that shown in Figure 4. Eventhough, the distribution of the ore components referred to above shows a statistically valid similarity with those of the sediment-hosted and skarn lead-zinc ore deposit types no conclusive evidence can however be deduced as to their genetic links due to the broad overlapping in their fields.

Pb-Ag RELATIONS

The composition of both the ore-forming fluid and a base (precious)

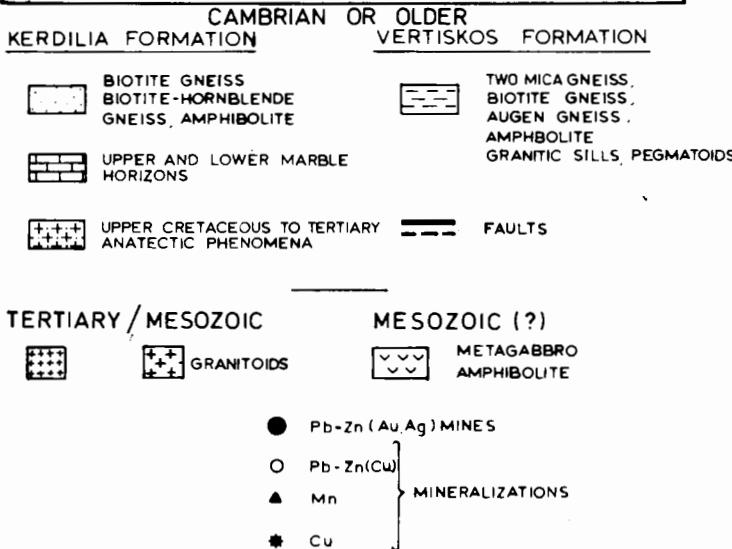
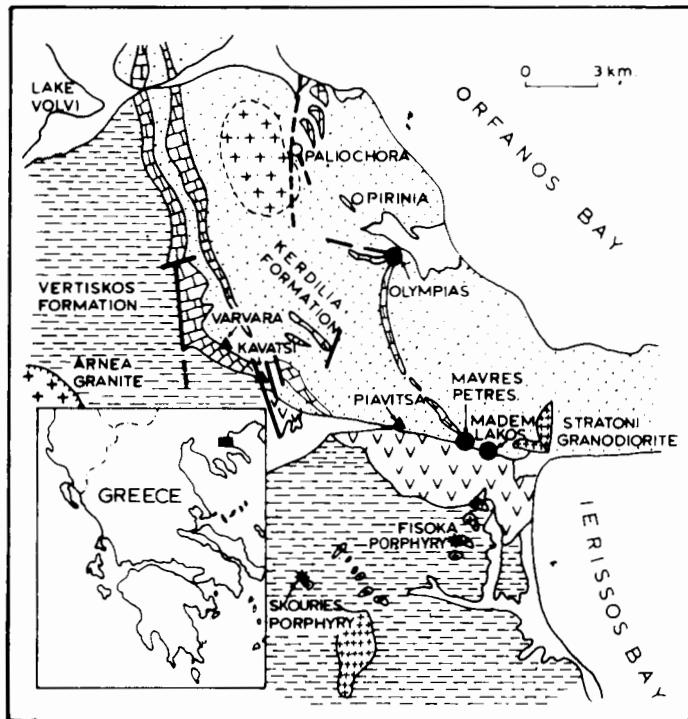


Fig. 1. Location map of the Pb-Zn (Au, Ag) sulfide ore deposits in the eastern Chalkidiki Peninsula (Kockel et al., 1977).
 Εικ. 1. Θέση των θειούχων κοιτασμάτων Pb-Zn (Au, Ag) της Ανατολικής Χαλκιδικής (Kockel et al., 1977).

Table 1. Mean (standard deviation; number of analyses) concentrations for Pb, Zn, Cu and Ag in the three Pb-Zn (Au, Ag) sulfide ore deposits of the eastern Chalkidiki Peninsula, N. Greece.

Πίν. 1. Μέσες τιμές (σταθερή απόκλιση* αριθμός αναλύσεων) συγκεντρώσεων Pb, Zn, Cu και Ag στα τρία θειούχα κοιτάσματα Pb-Zn (Au, Ag) της Ανατολικής Χαλκιδικής, Β. Ελλάδα.

NAME OF ORE DEPOSITS	Pb	Zn	Cu	Ag
		Wt%		ppm
MADEM LACOS	13.69 (16.7;13)	7.49 (6.08;13)	0.05 (0.05;13)	323 (415;13)
MAVRES PETRES	7.04 (4.08;21)	8.4 (4.07;21)	0.15 (0.15;20)	170 (99 ;18)
OLYMPIAS	3.98 (4.2;22)	5.79 (5.6;22)	0.12 (0.20;20)	114 (125;22)

Table 2. Ore chemistry form drill hole data of the Madem Lacos sulfide deposit, eastern Chalkidiki Peninsula, N. Greece.

Πίν. 2. Χημισμός του θειούχου κοιτάσματος Μ. Λάκκου από γεωτρήσεις, Ανατολική Χαλκιδική, Β. Ελλάδα.

Drill hole Depth in meters	Cu	Pb	Zn	Ag
		Wt %		ppm
<u>Σ 63</u>				
220,5 - 222,7	0,008	0,20	0,13	13
231 - 232,5	0,006	0,06	0,03	6
237,5 - 242,2	0,022	0,32	0,09	27
244,8	0,022	0,57	0,36	30
248,2	0,17	37,52	7,68	828
255 - 255,8	0,03	0,17	9,13	13
290,2 - 291,4	0,08	6,45	6,68	102
295,4 - 295,6	0,18	12,23	8,62	306
300,3 - 306	0,05	54,45	14,63	1400
<u>Λ 21</u>				
184 - 187,5	0,03	11,8	7,9	269
188 - 189	0,03	8,8	9,0	174
191,2 - 194,5	0,03	27,1	18,4	660
197 - 199,3	0,09	16,5	14,7	364

Table 3. Ore chemistry from drill hole data of the M. Petres sulfide deposit, eastern Chalkidiki Peninsula, N. Greece.
 Πίν. 3. Χημειούς του θελούκου κατόπινος Μ. Πέτρες, από γεωδρήσεις, Ανατολική Χαλκιδική, Β. Ελλάδα.

Drill Hole	Depth in meters	Cu			Pb			Zn			Ag		
		Wt %			ppm			ppm			ppm		ppm
0 148													
503	- 503,8	0,005	0,4	0,14	16			0,11	8,8	10,6		187	
	- 504,8	0,01	2,3	1,16	51			0,14	3,1	16,4		132	
	- 506,2	0,005	0,8	0,4	17			0,60	10,8	5,7		236	
	- 508,5	0,009	3,4	11,8	87			0,32	5,0	12,8		199	
	- 509,5	TRACES	1,6	1,7	43			0,20	9,3	6,3		286	
	- 510,5	0,03	4,9	6,6	107			0,07	1,1	6,3		43	
	- 511,5	TRACES	0,3	0,3	10			0,07	1,0	9,7		40	
	- 512	0,2	9,6	14,2	159								
	- 512,2	0,005	0,09	8									
0 130													
613,5	- 614,5	0,17	3,0	12,4	94			0,13	9,2	11,5		235	
	- 615,5	0,14	3,9	5,3	95			0,13	17,0	10,0		238	
	- 616,2	0,17	5,6	9,6	218								
	- 618,2	0,10	4,0	6,9	106								
0 134													
473,5	- 474,7	0,05	5,4	5,3	188			0,08	5,9	3,6		110	
475,2	- 478	0,02	1,7	3,0	52			0,01	11,4	5,7		25	
478,4	- 481,2	0,02	0,6	0,7	19			0,02	11,2	15,7		190	
481,55	- 482,8	0,01	0,7	1,3	26			0,02	2,5	2,5		44	
0 138													
638,5	- 640	0,18	8,1	14,5	302								
645,2	- 645,4	0,02	0,6	1,2	21								
0 175													
568,3	- 570,3	0,3	4,7	10,2	144								
575,3	- 576,5	0,9	18,6	18,3	549								
576,5	- 578	0,18	6,5	2,4	184								

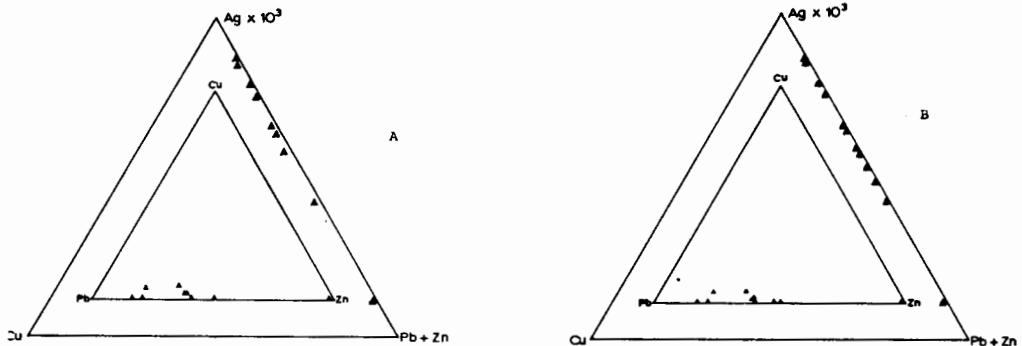


Fig. 2. Ternary diagrams of the ratios of Cu-Pb-Zn (weight percent; inside) and Cu-Pb+Zn-Ag $\times 10^3$ (weight percent) in ore from single drill holes (A) and a number of drill holes (B) of the Madem Laccos sulfide deposit. Data from Hellenic Company of Chemical Products and Fertilizers S.A., Greece.

Εικ. 2. Τριαδικά διαγράμματα των αναλογιών Cu-Pb-Zn (κ.β. % ; εσωτερικό) και των Cu-Pb+Zn-Ag $\times 10^3$ (κ.β.%) από μία γεώτρηση (Α) και αριθμό γεωτρήσεων (Β) στο κοίτασμα Μ. Λάκκο. Στοιχεία από την ΑΕΕΧΠ & Λ.

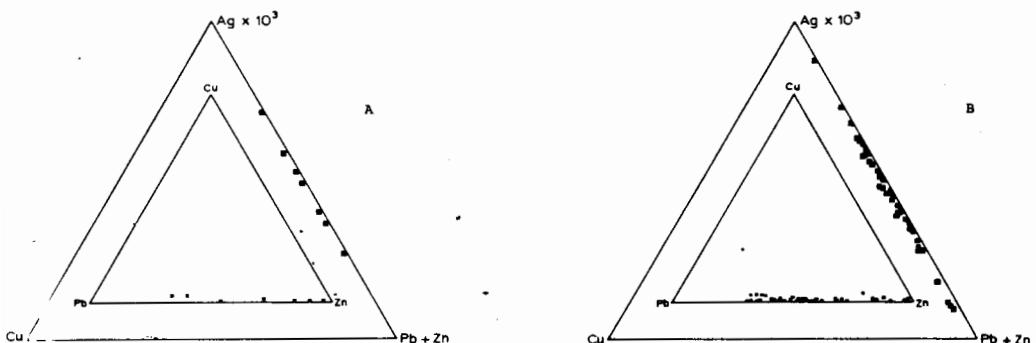


Fig. 3. Ternary diagrams of the ratios of Cu-Pb-Zn (weight percent; inside) and Cu-Pb+Zn-Ag $\times 10^3$ (weight percent) in ore from single drill holes (A) and a number of drill holes (B) of the Mavres Petres sulfide deposit. Data from Hellenic Company of Chemical Products and Fertilizers S.A., Greece.

Εικ. 3. Τριαδικά διαγράμματα των αναλογιών Cu-Pb-Zn (κ.β.%; εσωτερικό) και των Cu-Pb+Zn-Ag $\times 10^3$ (κ.β. %) από μία γεώτρηση (Α) και αριθμό γεωτρήσεων (Β) στο κοίτασμα Μ. Πέτρες. Στοιχεία από την ΑΕΕΧΠ & Λ.

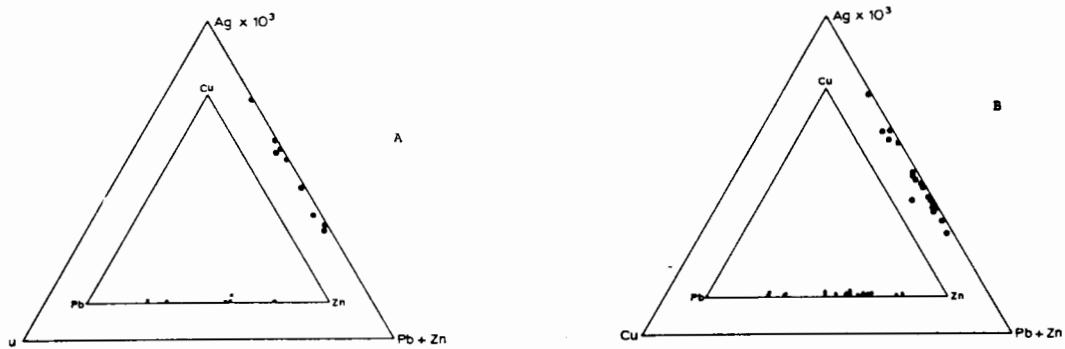


Fig. 4. Ternary diagrams of the ratios of Cu-Pb-Zn (weight percent; inside) and of Cu-Pb+Zn-Ag $\times 10^3$ (weight percent) in ore from single drill holes (A) and a number of drill holes (B) of the Olympias sulfide deposit. Data from Hellenic Company of Chemical Products and Fertilizers S.A., Greece.

Εικ. 4. Τριάδικα διαγράμματα των αναλογιών Cu-Pb-Zn (κ.β.% ; εσωτερικό) και των Cu-Pb+Zn-Ag $\times 10^3$ (κ.β.%) από μια γεώτρηση (A) και αριθμό γεωτρήσεων (B) στο κοίτασμα Ολυμπίας. Στοιχεία από ΑΕΕΧΠ & Λ.

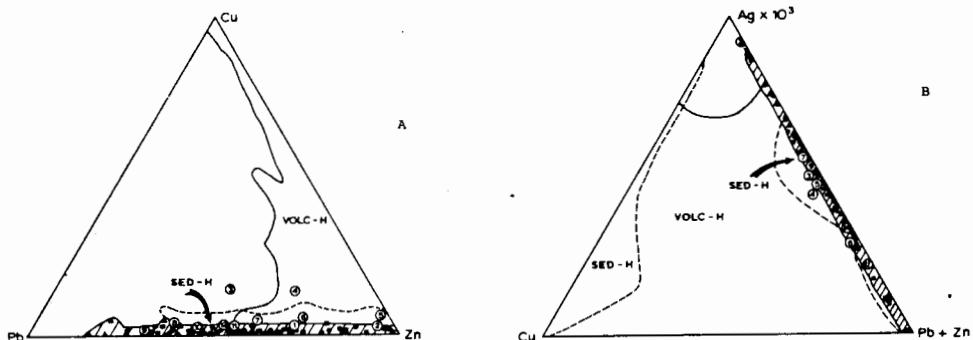


Fig. 5. Comparison of the bulk Cu-Pb-Zn (A) and Cu-Pb+Zn-Ag $\times 10^3$ (B) compositions of the sediment-hosted, (SED-H) volcanogenic (VOLC-H) and skarn-replacement Pb-Zn massive sulfide ore types with the Eastern Chalkidiki Peninsula Pb-Zn sulfide ores (hatched area). Data for the former two types in (A) are from Lydon (1983) and in (B) are from Gustafson and Williams (1981). Data from skarn-replacement type Pb-Zn sulfide ores shown in circled numbers are from Einaudi et al. (1981) : 1=Ulchin, Korea; 2=Yeonbwa II, Korea; 3=Henpaoshan-Sikarg Province, China; 4=Washington Camp, Arizona; 5=Hanover area N. Mexico; 6=Groundhog, N. Mexico; 7=Frisco, Mexico; 8=Hildago, Mexico; 9=Stri Trg, Trepca, Yugoslavia; 10=Ara-vaipa, Arizona; 11=Bluebell, Canada; 12=Uchucchacwa, Peru. Data for the latter ores are from the Hellenic Company of Chemical Product and Fertilizers S.A., Greece. Symbols are as in Figures 2, 3 and 4.

Εικ. 5. Σύγκριση στα διαγράμματα Cu-Pb-Zn (A) και Cu-Pb+Zn-Ag $\times 10^3$ (B) της σύστασης θειούχων κοιτασμάτων βασικών μετάλλων με ξενιστή ίζημα (SED-H), ηφαιστειογενών (VOLC-H), και σκαρν-μετασωματικά σε σχέση με εκείνα της Ανατολικής Χαλκιδικής (διαγραμμισμένη περιοχή). Τα στοιχεία για τους δύο πρώτους τύπους στο (A) είναι από τον Lydon (1983) και στο (B) από τους Gustafson and Williams (1981). Στοιχεία για τον σκαρν-μετασωματικό τύπο (αριθμοί σε κύκλους) είναι από τους Einaudi et al. (1981) : 1=Ulchin, Korea; 2=Yeonbwa II, Korea; 3=Henpaoshan-Sikarg Province, China; 4=Washington Camp, Arizona; 5=Hanover area N. Mexico; 6=Groundhog, N. Mexico; 7=Frisco, Mexico; 8=Hildago, Mexico; 9=Stri Trg, Trepca, Yugoslavia; 10=Ara-vaipa, Arizona; 11=Bluebell, Canada; 12=Uchucchacwa, Peru. Στοιχεία για τα τελευταία κοιτάσματα είναι από την ΑΕΕΧΠ & Λ. Φημιακή Βιβλιοθηκή Θεόφραστος - Τμήμα Τεωλογίας. Α.Π.Θ.

metal sulfide ore deposit resulting from the operation of a magmatic-hydrothermal system depends largely on the rock composition, the temperature and chemistry of the hydrothermal reservoir and the temperature at deposition. Therefore, different Pb-Zn (Ag) sulfide ore deposit types in different geologic settings are expected to exhibit differences in their metal-ratios. A comparison of the Pb/Ag ratio populations between the Eastern Chalkidiki ores on one hand and each one of the sediment-hosted, volcanogenic and skarn ore types on the other hand, respectively shows a statistically significant difference (t-test; 95% level of significance) between the populations in the former two pairs and a similarity in the latter. Figure 6 presents an evidence that the Eastern Chalkidiki ores are distinctly different from the sediment-hosted and volcanogenic ore types, whereas they bear similarity with the skarn type. This conclusion is further strengthened by the quite different slopes of the best-fit lines (Fig. 6B) for the ore types referred to above.

VERTICAL DISTRIBUTION OF METALS AND OF METAL RATIOS IN THE SULFIDE ORES.- ΚΑΤΑΚΟΡΥΦΗ ΚΑΤΑΝΟΜΗ ΜΕΤΑΛΛΩΝ ΚΑΙ ΛΟΓΩΝ ΜΕΤΑΛΛΩΝ ΣΤΑ ΘΕΙΟΥΧΑ ΚΟΙΤΑΣΜΑΤΑ.

The vertical distribution of copper, lead+zinc and of the lead/zinc and of the lead/zinc ratios have been studied in eight drill holes; two from the Madem Lacos, three from the Mavres Petres and three from the Olympias sulfide ore deposits (Figs. 7, 8 and 9).

Copper and lead+zinc variations by weight percent exhibit both negative and positive correlations. The negative correlation may be attributed to the replacement of sphalerite by chalcopyrite as it is suggested by the "chalcopyrite disease" texture (Kalogeropoulos, 1984; Kalogeropoulos and Economou, 1987), whereas the positive correlation reflects a common evolution of the three major ore metals.

The distribution of the lead/zinc ratios in the ore of single drill holes, drill holes of the same deposit and of different deposits is quite variable and ranges from 0.1 to 4.9. Similar mode of variation is also seen in the zinc/lead+zinc ratios which range from 0.17 to 0.98. This distribution does not bear any statistically valid tendency towards vertical zonation; a feature which is uncommon in epigenetic and common in syngenetic sulfide ores.

CONCLUSIONS - ΣΥΜΠΕΡΑΣΜΑΤΑ

The chemistry of the Eastern Chalkidiki Pb-Zn sulfide ores (Figs. 2,3, 4 and 5) and the Pb/Ag ratio (Fig. 6) indicate a statistically valid similarity

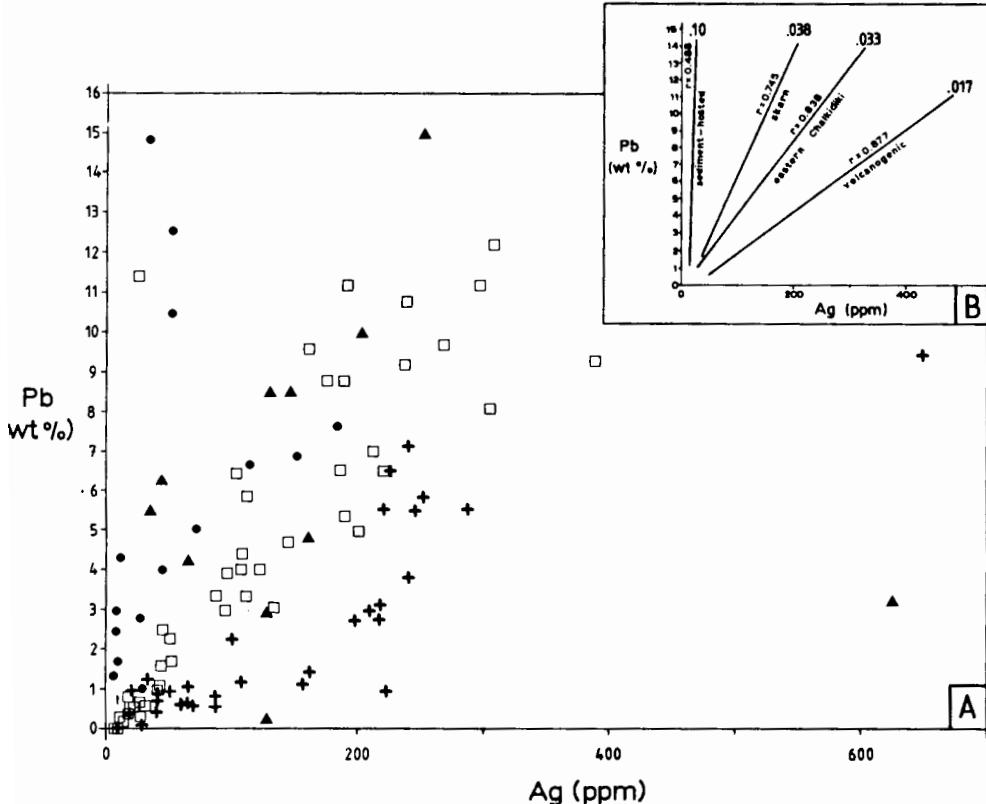


Fig. 6. A.: Pb-Ag plot for worldwide distributed sediment-hosted (●), volcanogenic (+) and skarn-replacement (▲) Pb-Zn (Au,Ag) massive sulfide ore types as compared with the Eastern Chalkidiki Peninsula Pb-Zn (Au,Ag) ores (■). Note the separation of the Chalkidiki ores from the former two ore types and a significant overlapping with the third. Data are from : Short course in sediment-hosted stratiform lead-zinc deposits (1983); Geology of the Kuroko deposits (1974); Skarn deposits, in Einaudi et al. (1981); Hellenic Company of Chemical Products and Fertilizers S.A.

B.: Best-fit lines, correlation coefficients (r) and slopes (upper end of line) resulted from data of Figure 6A. Two outliers (Ag-rich/Pb-poor samples) from the skarn-replacement and three from the sediment-hosted ore types were excluded from the calculations.

Εικ. 6. A.: Διάγραμμα Pb-Ag για θειούχα κοιτάσματα Pb-Zn(Au, Ag) που φιλοξενούνται σε ιζήματα (●), ηφαιστειογενή (+) και σκαρν-αντικατάστασης (▲) σε σύγκριση με εκείνα της Ανατολικής Χαλκιδικής (■). Σημειώστε τη διαφορά των θειούχων κοιτασμάτων της Ανατολικής Χαλκιδικής με τους δύο πρώτους τύπους και την επικάλυψη με τον τρίτο. Τα στοιχεία είναι: Short course in sediment-hosted lead-zinc deposits (1983); Geology of the Kuroko deposits (1974); Skarn deposits in Einaudi et al.(1981); ΕΕΕΧΠ & Λ.

B.: Συσχετίσεις, συντελεστές συσχέτισης (r) και κλίσεις (ανώτερο τμήμα των γραμμών συσχέτισης) όπως έχει προκύψει από τα δεδομένα που προβάλλονται στην Εικ. 6A. Δύο ακραίες τιμές (Ag-πλούσιοι/Pb-πτωχά δείγματα) από τον τύπο σκαρν-αντικατάστασης και τρεις από εκείνον τον ξενιστή ιζήματα δεν συμπεριελήφθησαν στους υπολογισμούς.

L 21

110m



Σ 63

320m

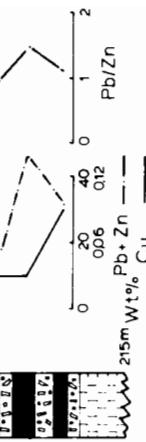
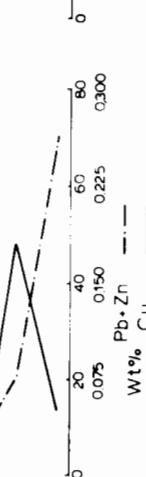


Fig. 7. Variation of Cu, Pb/Zn and Pb+Zn ratio in ore from the drill holes 563 and L21 of the Madem Laccos deposit. The legend applies also to Figures 8 and 9. Drill hole data are from the Hellenic Company of Chemical products and Fertilizers S.A., Greece.

ΕΙΚ. 7. Μεταδοτικός Cu, Pb+Zn και Pb/Zn από μεταλλεύμα από το λευκό καλαβρύτης στα ζεύγη 563 και L 21 του Kolindiaouc M. Λάκκου. Η ίδια λέξη γάντια λογίευτη και είναι η παραγωγή της εταιρείας ALEXΠΗ & Λ.

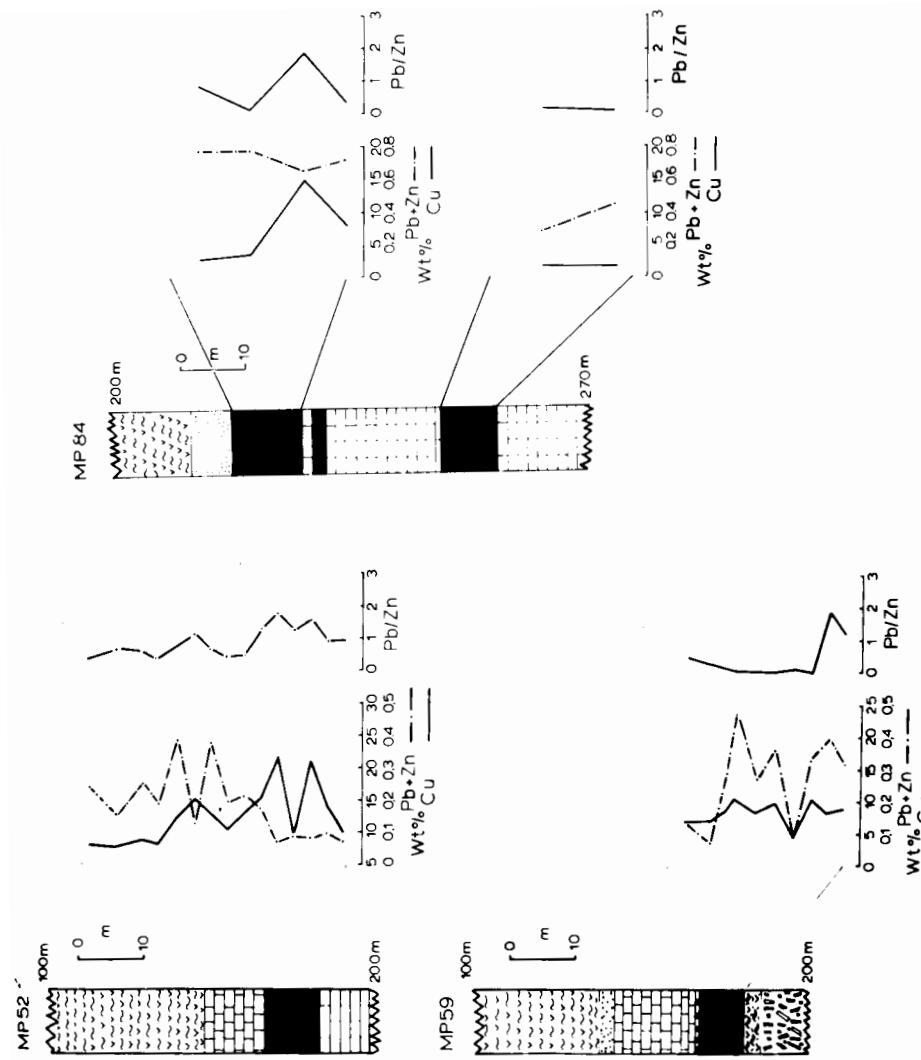


Fig. 8. Variation of Cu, Pb+Zn and Pb/Zn ratio in ore from the drill holes MP52, MP59, and MP84 of the Mavres Petres deposit. The legend for the rock types is as in Figure 7. Drill hole data from Hellenic Company of Chemical Products and Fertilizers S.A., Greece.

ΕΙΚ. 8. Μεταρυθμός Cu, Pb+Zn και τον λόγο Pb/Zn στο μετάλλευμα από τις γεωτρήσεις MP 52, MP 59 και MP 84 του κοιλανταράς Μ. Πέτρες. Η λεύκωση για τα πετρώματα είναι εκείνη της Ελκόνα 7. Τα στοιχεία είναι από την ΑΕΕΧΠ & Λ.

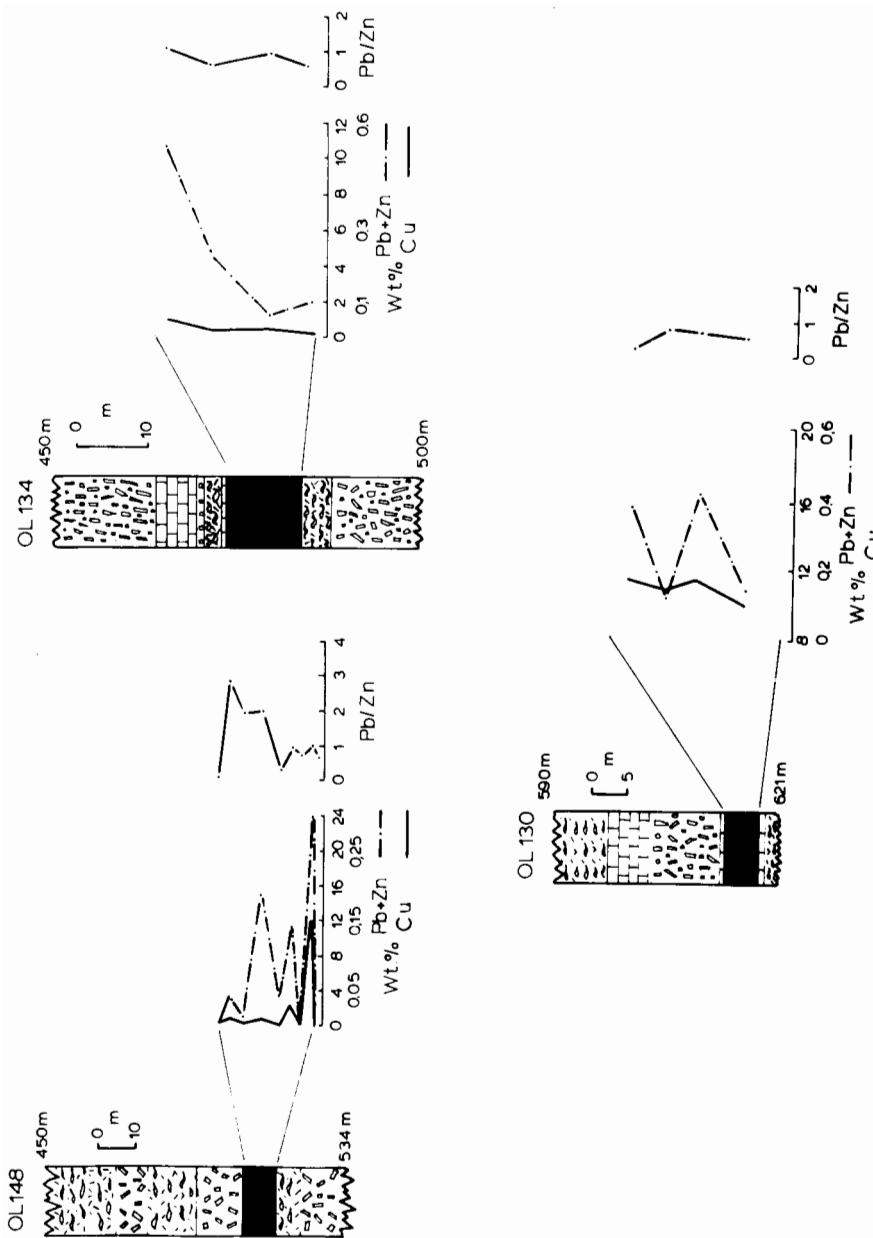


Fig. 9. Variation of Cu, Pb+Zn and Pb/Zn ratio in ore from the drill holes OL148, OL130 and OL134 of the Olympias deposit. The legend for the rock types is as in Figure 7. Drill hole data from Hellenic Company of Chemical Products and Fertilizers S.A., Greece.

Εικ. 9. Μεταβολής Cu, Pb+Zn και Pb/Zn στο μετάλλευμα από της υεωθοίσις OL148, OL130 και OL134 του κορδόνας Θλυπιάς. Η λεζάντα για τα περιώδεια είναι σκέψιν της Στρόβας 7. Τα στοχεύει είναι από την ΑΕΕΧΠ & Λ.

with the skarn-replacement and difference from the sediment-hosted and the volcanogenic Pb-Zn sulfide ore types. In addition, the vertical variation of the lead/zinc ratio in the ore from drill holes (Figs. 7, 8 and 9) is quite variable; a feature that is common in epigenetic and rather uncommon in syngenetic sulfide ores.

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