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A SULFUR ISOTOPE STUDY OF SULFIDES AND SULFATES FROM THE Pb-Zn (Au,Ag) SULFIDE ORE DEPOSITS OF THE E. CHALKIDIKI PENINSULA N. GREECE

S. Kalogeropoulos*, R. Both** and F. Gerouki***

ABSTRACT

The sulfur isotopic analyses of sulfide-sulfide and sulfide-sulfate pairs in ore samples frm the Pb-Zn (Au, Ag) deposits of Olympias, M. Lakkos and M. Petres, indicate that the ores were formed in a magmatic hydrothermal setting, similar to that of porphyry coppers. Deposition of sulfates most likely took place during sudden decompresssion of magma, whereas the bulk of the sulfides were deposited from fluids that have followed a reducing path, at rather constant redox conditions and at equilibrium temperatures in the range of about 200 to 600°C for the whole metallogenetic system.

ΣΥΝΟΨΗ

Ισοτοπικές αναλύσεις ζευγών θειούχων ορυκτών και θειούχων - θειϊκών ορυκτών, που βρίσκονται σε διάφορες σχέσεις επαφής, σε δείγματα από τα θειούχα κοιτάσματα της Ολυμπιάδας, Μ. Λάκκου και Μ. Πετρών, υποδηλούν ότι τα μεταλλεύματα απετέθησαν κατά τη διάρκεια της λειτουργίας ενός μαγματικού υδροθερμικού συστήματος συναφούς με εκείνο του πορφυρικού χαλκού. Η απόθεση των θειϊκών έλαβε χώρα, μάλλον κατά την αποσυμπίεση του μαγματικού συστήματος, ενώ εκείνη του κυρίου όγκου των θειούχων ορυκτών, από διαλύματα που ακολούθησαν ένα αναγωγικό περιβάλλον. Η απόθεση για εκάστη των κυρίων φάσεων απόθεσης έγινε σε σχετικά σταθερές οξειδοαναγωγικές συνθήκες και για το όλο μεταλλογενετικό σύστημα σε θερμοκρασίες που κυμαίνονται από 220~600°C.

INTRODUCTION

The Olympias, Madem Lakkos and Mavres Petres Pb-Zn (Au, Ag) sulfide deposits, are hosted primarily in marbles of the Kerdylia Formation, which together with the Vertiskos Formation, constitute the polymetamorphic terrain of early Paleozoic or older age (Fig. 1), which has been known as Servo-Macedonian Massif (SMM). (Kockel et al. 1977, Kalogeropoulos et al. 1989, Frei 1992, Sakellariou 1988, Mantzos 1991).

The SMM was deformed and regionally metamorphosed (Patras et al. 1986, Sakellariou 1988) and during Tertiary it was intruded by magmatic dykes and stocks. (Ierissos 42-52 Ma, Sithonia 38-54 Ma, Fissoka-Alatina 32 Ma, Skouries 20 Ma, J.C. Papadakis 1971, Altherr et al. 1976, Kondopoulou and Lauer 1985, Frei 1992).

Based on geological evidence, stable/radiogenic isotope data and fluid

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* Rusvar Holdings BV, 4 Nikis Str. Athens Greece
** Dept. of Geol. & Geoph. Adelaide University, Adelaide Australia
*** Dept. of Geochemistry, IGME, 70 Messoghion Str, Athens Greece.

inclusion studies on these deposits (Kalogeropoulos et al. 1989, Kilias 1991, Gilg 1993), it was concluded, that the ores formed in a Tertiary magmatic-hydrothermal setting with the sulfides being deposited along faults and replacable units (i.e. marbles).

However, despite these studies, the published sulfur isotope data base is lean. This paper presents a significant number of sulfur isotope data analyses on sulfides and sulfates and aims at the determination of 1) the sulfur isotope composition of sulfides and sulfates, 2) the equilibrium temperatures of coexisting sulfide-sulfide and sulfide-sulfate pairs and 3) the evaluation of the possible sources of sulfur.

SAMPLING AND ANALYTICAL TECHNIQUES

A total of 46 ore samples were collected. The 36 samples were from the

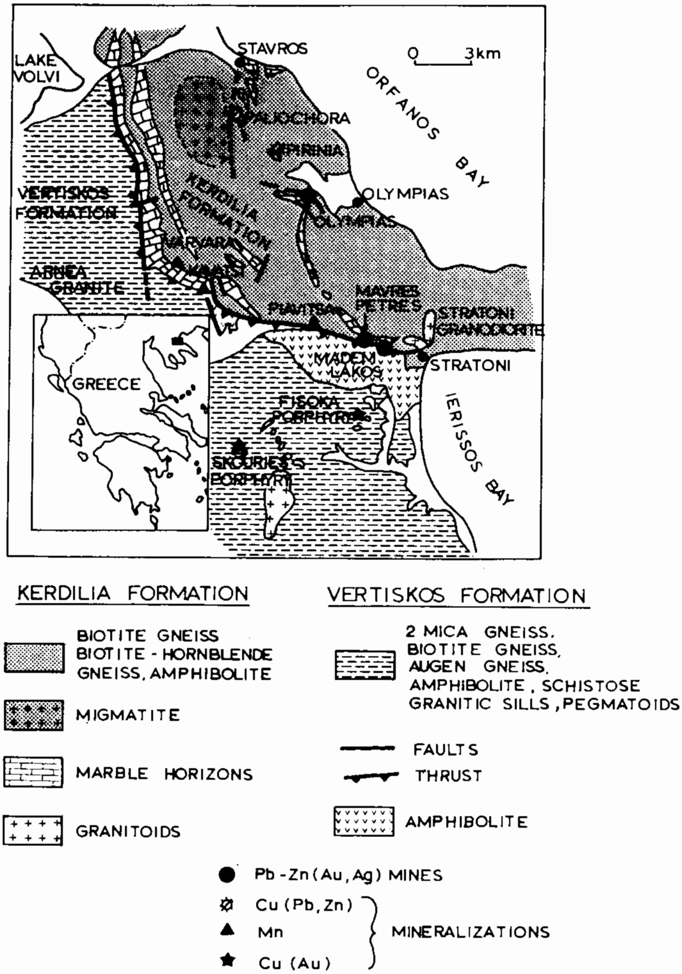

Fig. 1. Simplified geological map of E. Chalkidiki N. Greece (after Kockel et al. 1977).

Εικ.1: Απλοποιημένος γεωλογικός χάρτης της Αν. Χαλκιδικής, Β. Ελλάδα (Κατά Kockel et al. 1977).

underground workings of the Olympias, Madem Lakkos and Mavres Petres deposits and the 10 samples were from Madem Lakkos drill-holes. The minerals, at various contact relations, were hand picked from the ore specimens. The purity of the single mineral separates was better than 97 per cent.

The analyses were performed at the Department of Geology-Geophysics of Adelaide University, Australia by Prof. R.A. Both. The results are expressed in the standard δ-notation in per mil (°/oo) with respect to the Canon Diablo Troilite (CDT). Standard analytical uncertainties are ± 0.2 (°/oo) for $\delta^{34}S$ and ± 0.3 (°/oo) for $\Delta\ \delta^{34}S$. The sulphur isotope results together with the calculated equilibrium temperaturs for the galena-sphalarite pair and the anhydrite-pyrite pair are presented in Table 1 and plotted in the histograms of Figure 2.

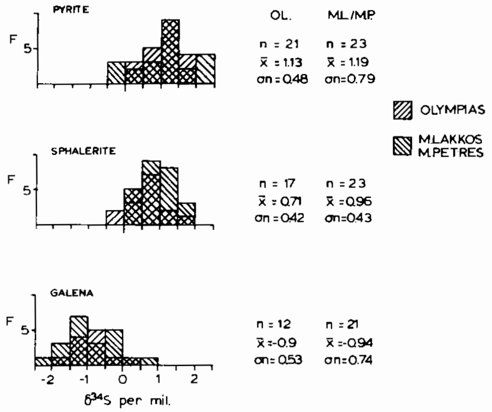

Fig. 2. Distribution of sulfur isotope composition of sulfide minerals from the Olympias - M. Lakkos (plus M. Petres) ore deposits.

Εικ. 2: Κατανομή ισοτοπικής σύστασης θείου, από θειούχα ορυκτά, από τα κοιτάσματα Ολυμπιάδας - Μ. Λάκκου (και Μ. Πετρών)

SULFUR ISOTOPE DATA

The $\delta^{34}S$ (°/oo) values (mean ± 1sd) for pyrite, sphalerite and galena are 1.14±0.66, 0.84±0.45, -1.14±1.28 respectively, whereas for anhydrite is 13.9±0.9. Thermodynamic considerations (Sakai, 1968) and experimental data (Kajiwara and Krouse, 1971) indicate, that under isotopic equilibrium conditions, the $\delta^{34}S$ values of the coexisting sulfides should decrease in the order pyrite > sphalerite > galena. The majority of the examined samples follow this trend (Table 1), indicating thus equilibrium. It is known (Ohmoto and Rye, 1979) that under sulfur isotopic equilibrium conditions, the fractionation factor between coexisting sulfide mineral pairs varies, as a function of their formation temperature, if no post-crystallazation isotope exchange took place. The small difference in $\delta^{34}S$ values between the pyrite-sphalerite and pyrite-galena pairs makes them unreliable geothermometers. The sphalerite-galena pair, is the most reliable and widely used sulfur isotope geothermometer, due to its tendency to equilibrate faster, than the other two mineral pairs (Kajiwara and Krouse, 1979) and it is therefore used for the temperature estimates.

The temperature range of 200-600°C obtained from the sulfur isotopes, is in good agreement with the temperatures obtained from fluid inclusions (Kalogeropoulos et al., 1989, Gilg, 1993), indicating that sulfur isotopes have attained equilibrium.

Sulfur isotope exchange between sulfate and sulfide in solution, is kinetically inhibited because of the large valence difference between oxidized and reduced sulfur species. Sulfur isotope equilibrium between aqueous sulfur species is obtained only at intergration time and temperatures in magmatic environments (Rye et al., 1992). The experimental work of Ohmoto and Lasaga (1982) indicates, that the time to obtain sulfur isotope equilibrium between aqueous sulfate and sulfide in acid solutions, ranges from days at 200°C to minutes at

Table 1: Sulfur isotope data ($\delta^{34}S^{o}/_{oo}$) from the Olympias and M.Lakkos/M. Petres Pb-Zn (Au, Ag) sulfide ore-bodies , Chlakidiki Peninsula, N. Greece and Delta (Δ) values of coexisting sphalerite-galena and anhydrite-pyrite pairs with isotopic temperature (°C) estimates in parentheses (after data of Ohmoto) and Rye, 1972).

Πίν. 1: Ισοτοπικά δεδομένα ($\delta^{34}S^{o}/_{oo}$) από τα θειούχα κοιτάσματα Pb - Zn (Au, Ag) της Ολυμπιάδας, Μ. Λάκκου / Μ. Πετρών της Χαλκιδικής, Β. Ελλάδα καθώς και τιμές Δέλτα (Δ) από συνυπάρχοντα ζεύγη σφαλερίτη - γαληνίτη και ανυδρίτη - πυρίτη με αντίστοιχες υπολογισθείσες θερμοκρασίες (°C) (σύμφωνα με δεδομένα από Ohmoto and Rye, 1979).

Sample	Py	Sph	Gal	Anhd	Δsph-gal (°C)	Δanhd-py (°C)
OLYMPIAS	^{34}S	^{34}S	^{34}S			
OL-160 $B\Delta_1$	1.2	0.3	-1.3		1.6(400°)	
OL-160 Δ_2	1.0	0.4	-1.6		2.0(330°)	
OL-160 Δ_3	1.6	0.6	-0.9		1.5(424°)	
OL-160 Δ_4	1.3	1.0		-		
OL-160 Δ_5	1.5	1.0	-1.1		2.1(313°)	
OL-160 Δ_6	1.1	0.5	-		-	
OL-174 Δ_7	1.3	1.1	-0.6		1.7(381°)	
OL-160 Δ_9	0.4	0.8	-0.9		1.7(381°)	
OL-184.5 Δ_{10}	1.1	1.3	-		-	
OL-184.5 Δ_{11}	2.0	0.9	-		-	
OL-184.5 Δ_{11A}	2.0	1.6	-0.4		2.0(330°)	
OL-184.5 Δ_{12}	1.1	0.4	-0.8		1.2(503°)	
OL-195 Δ_{13}	1.8	1.0	-1.0		2.0(330°)	
OL-40*	1.3	0.7	-		-	
OL*	0.8		0.5		-	
OL-68.1*	1.0	0.0	-1.3		1.3(472°)	
OL-68.2*	0.7	0.0		-		
OL-76.2*	0.1		-1.4		-	
OL-76.2 B*	1.0	0.5		-		
OL-76.8*	0.4		-			
OL-84.2*	1.1			-		
MADEM LAKKOS						
ML 120 Δ_1	2.2	1.6	-0.4		2.0(330°)	
ML 120 Δ_2	-0.3	0.1	-1.8		1.9(34°)	
ML 120 Δ_3	2.4	1.4	-0.1		1.5(424°)	
ML 120 Δ_3		1.8				
ML 108 Δ_4		0.7	-1.3		2.0(330°C)	
ML 105 Δ_5	0.8	1.2	-0.2		1.4(447°)	
ML 93 Δ_6		1.1				
ML 78 Δ_7	1.5	1.3	-0.6		0.9(624°)	
ML66S10 A						
ML66S10 C	1.5	1.3	-1.6		2.9(227°)	
ML66S11		0.6	-1.4		2.0(330°)	
ML66S12		0.4	-0.6		1.0(577°)	
ML66S13		0.9	-0.6		1.5(422°)	
ML66S14		1.1	-0.4		1.5(422°)	

ML66S15		1.1	-1.3		2.4(275°)	
ML66S16 A		0.2	-1.1		0.9(473°)	
ML66S16 B	-0.4	0.7	-1.3		2.0(330°)	
ML66S17	0.1	0.7	-1.4		2.1(314°)	
ML66S18	1.5					
ML66S19	0.8	-1.8				
ML66S20	1.3	1.0	-1.5		2.6(255°)	
ML 78.1*	0.9		0.7		2.5(265°)	
DRILL HOLES (M.LAKKOS)						
KOYL 8K39						
KOYL 8K53				13.5		14.1(462°)
KOYL 8K57						
KOYL 8K58	1.5					
KOYL 8K60	0.3			14.1		13.8(469°)
AGNIC5K42	1.3					
MOR 18K17	0.5			14.1		13.6(475°)
17 OP6540	0.7					
17 OP6541	2.0					
17 OP6549	2.5					
MAVRES PETRES						
MP S21	1.3	1.1	-0.7		1.8(360°)	
MP S22	1.1	1.2	-0.4		1.6(401°)	
MP 247*		1.0				
MP 160*		0.5				

* Note: Samples with asterisk (8) are from Kalogeropoulos et al. (1989). Uncertainties of temperatures are 25°C at 200°C and ±80° at 600°C.

400°C. Temperatures obtained from our sulfide-sulfate pairs range from 460-475°C indicating that on the basis of the above mentioned experimental result the sulfide-sulfate species must have attained equilibrium. Our calculated equilibrium temperatures are also corraborated from fluid inclussion data (Gilg, 1993).

ORIGIN OF SULFUR

The Madem Lakkos anhydrite sulfur isotope ratios range from 13.5 to 14. 1 $^{\circ}$/oo (Table 1). This range when plotted on the sulfur isotope age curve for marine sulfates of Claypool et al (1980) (Fig. 3), indicates that if our sulfates were of marine origin and thus, syngenetic, their age, as depicted from Figure 3, would be either late Paleozoic or early Mesozoic. However, based on an early Paleozoic or older age that has been assigned to the Kerdylia rocks (Kockel et al. 1977, Sakellariou 1988, Mantzos 1991, Frei 1992, Gilg 1993), it can be concluded that our sulfates are not of syngenetic but rather of epigenetic origin.

The sulfur isotope data on sulfides and sulfates of the present study are plotted on Figure 4, for comparative purposes, with similar data from porphyry copper systems of the American Cordilleran (Ohmoto and Rye, 1979). This comparison indicates the similarity of the sulfur isotope characteristics of the studied sulfide ores with those of the porphyry copper systems. Moreover, the narrow range of sulfur isotope ratios of all the sulfides and their proximity to 0°/oo, combined with the rather limited occurrence of the sulfates at Madem Lakkos, suggest the combined effects of high reduced/oxidized sulfur species ratios, relatively high temperatures and sulfur mineral isotopic composition close to that of the original fluid (Ohmoto 1972, Rye and Ohmoto, 1974). Therefore the approximated $\delta^{34}S$ values of the ore fluids during sulfide mineralization would be near 0°/oo . This value is within the range of $\delta^{34}S$ fluid derived from granitic magmas (-3 to 7°/oo) (Ohmoto and Rye 1979) and the $\delta^{34}S$ fluid values of an intergrated crustal average attained by circulating hot fluids that mobilize sulfides from deep seated crustal rocks (Rye 1993).

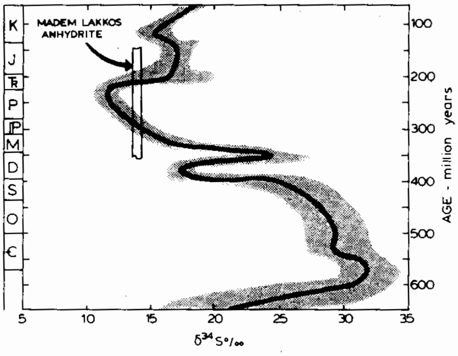

Fig. 3. Sulfur isotope data for M. Lakkos anhydrite relative to sulfur isotope age curve for marine sulfates. (after Claypool et al. 1980). The shaded area is an estimate of the uncertainty of this curve.

Εικ. 3: Ισοτοπικά δεδομένα θείου από ανυδρίτες του Μ. Λάκκου σε σχέση με την ισοτοπική καμπύλη ηλικίας του θείου από εβαπορίτες (κατά Claypool et al. 1980). Η γραμμοσκιασμένη περιοχή υποδεικνύει τα όρια αβεβαιότητας της συγκεκριμένης καμπύλης.

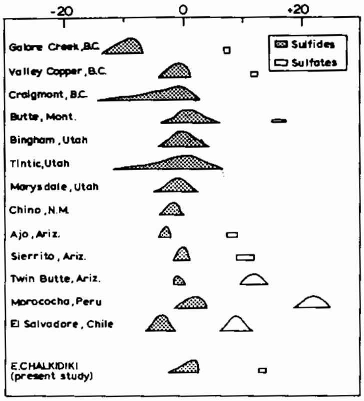

Fig. 4. Schematic presentation of sulfur isotopic data of E. Chalkidiki sulfide ores as compared to those of porphyry copper systems (after Ohmoto and Rye, 1979).

Εικ. 4: Σχηματική παρουσίαση ισοτοπικών δεδομένων θείου από τα θειούχα κοιτάσματα της Αν. Χαλκιδικής σε σχέση με τα αντίστοιχα των συστημάτων πορφυρικού χαλκού (κατά Ohmoto and Rye 1979).

Within a magmatic hydrothermal context as indicated above, the sulfates (i.e. anhydrite) are deposited from fluids leaving the magma upon a sudden decompression where they become SO_2-rich (Gerlach 1993). Subsequently, the ore forming system follows a reducing path (Rye 1993) depositing the main bulk of the sulfides.

CONCLUSIONS

According to our study the following conclusions can be deduced :

1) Sulfur isotope temperatures obtained from coexisting sphalerite-galena pairs and anhydrite-pyrite pairs, when compared with known homogenization temperatures from fluid inclusions indicate that the sulfur isotope system

attained equilibrium.

2) The small variation of the $\delta^{34}S$ value within and between the coexisting sulfide minerals, suggests a homogeneous sulfur source and rather constant redox conditions at their deposition.

3) The $\delta^{34}S$ value of the ore forming fluids during the main sulfide deposition falls within the respective range of fluids derived from granitic magmas and/or the range of $\delta^{34}S$ fluid values attained by circulating hot fluids that mobilize sulfides from deep seated rocks.

4) The $\delta^{34}S$ values of our sulfates cannot be related to sulfates of sedimentary origin (i.e. evaporites) of early Paleozoic or older age, as is the age assigned to the rocks of the Kerdylia Formation. On the cotrary it falls within the $\delta^{34}S$ value of sulfates formed in magmatic hydrothermal systems (i.e. porphyry copper systems). In the latter systems the sulfates are envisaged to have precipitated early from fluids leaving the magma during sudden decompression, whereas the bulk of the sulfides have precipitated from fluids that subsequently followed a reducing path.

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