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H_2O-CO_2-NaCl FLUID IMMISCIBILITY IN THE CARBONATE-HOSTED OLYMPIAS Pb-Zn(Au,Ag) SULFIDE DEPOSIT, MACEDONIA, GREECE

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ABSTRACT

Fluid inclusion data from the Olympias Pb-Zn(Au,Ag) sulfide deposit(composition, volume, temperature, pressure, density) was tested to conform to thermodynamic and chemical principles of fluid immiscibility equilibria, derived for fluid inclusions, indicating the occurrence of H_2O-CO_2-NaCl fluid unmixing. Fluid unmixing and concomitant ore-mineralization were initiated at temperatures of 350±30° C and fluctuating pressures of less than 500 bars. Unmixing is suggested to be a major mechanism of ore-sulfide deposition by causing fluid pH increase via volatile species(CO_2)separation.

ΣΥΝΟΨΗ

Τα δεδομένα ρευστών εγκλεισμάτων από το κοίτασμα σουλφιδίων Pb-Zn(Au,Ag) της Ολυμπιάδας (σύσταση, όγκος, θερμοκρασία, πίεση, πυκνότητα) εξετάστηκαν ότι είναι σε συμφωνία με θερμοδυναμικές και χημικές αρχές ισορροπίας που περιγράφουν καταστάσεις "μη συνδιαλυτότητας" ρευστών, υποδεικνύοντας έτσι την λειτουργία του φαινομένου της απόμειξης ρευστών φάσεων σε ένα ρευστό διάλυμα που περιγράφεται στο σύστημα H_2O-CO_2-NaCl. Η απόμειξη ρευστών φάσεων και η συνακόλουθη απόθεση μεταλλεύματος έλαβαν χώρα σε θερμοκρασίες 350±30° C και κυμαινόμενες πιέσεις μικρότερες από 500 bars. Το φαινόμενο της απόμειξης ρευστών φάσεων προτείνεται σαν ο κύριος μηχανισμός απόθεσης του μεταλλεύματος σουλφιδίων επειδή προκαλεί την αύξηση του pH του ρευστού διαλύματος μέσω του διαχωρισμού πτητικών συστατικών (CO_2).

ΕΙΣΑΓΩΓΗ - INTRODUCTION

Fluid immiscibility has been documented to be responsible for many spectacular petrological and geochemical phenomena in a variety of geologic environments and structural levels in the Earth's crust. Ore deposition has been extensively proposed as a result of fluid immiscibility in a wide spectrum of metallic deposits including Au(i.e. Sigma Mine, Ontario-Robert and Kelly 1987; Hollinger - McIntyre Mine, Quebec - Spooner et al. 1987), polymetallic Pb-Zn-Ag (i.e. Creed, Colorado-Woods et al. 1982; Keno Hill, Yukon-Lynch et al. 1990), W-Sn (i.e. SW England-Shepherd and Miller 1988), W-Mo (Mink Lake, Ontario -Burrows and Spooner 1987), and, porphyry Cu and Skarn (i.e., Mines Gaspe, Quebec - Shelton 1983) of various geologic habitats.

Most of the analytical evidence for fluid immiscibility in natural geologic

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processes, including ore-deposition, is derived from fluid inclusion studies. Kilias and Kalogeropoulos (1989) used fluid inclusions and arsenopyrite compositions to decipher ore-formation conditions at Olympias, considering independent fluids shown to have been trapped under similar conditions. This paper presents the results of continued study and alternative evaluation of fluid inclusion characteristics in terms of fluid

phase equilibria pertaining to unmixed('boiling') systems, which confirm the T-estimates of the earlier work, and reveal the major mechanism of ore-deposition through the occurrence of fluid-phase unmixing.

ΤΟ ΚΟΙΤΑΣΜΑ ΤΗΣ ΟΛΥΜΠΙΑΔΑΣ - OLYMPIAS DEPOSIT

The geology and genesis of the Olympias deposit are described in Nicolaou and Kokonis (1980), Kilias and Kalogeropoulos (1988) and Kalogeropoulos et al. (1989), and only a short review is given here.

The Olympias Pb-Zn (Au,Ag) sulfide deposit is hosted by marbles of the amphibolite facies metamorphic Kerdilia Formation (Servo-Macedonian Massif, N. Greece). Both deformed and undeformed ore varieties were formed during the same Tertiary skarn-replacement metallogenetic event, in an uplifting and cooling but tectonically still active crystalline basement, from fluids of primarily magmatic derivation through reaction with the host marble. Conditions of ore deposition at low pressures (300-800 bars) and high temperatures (300-400° C) were primarily based on fluid inclusion intersecting isochore method.

ΡΕΥΣΤΑ ΕΓΚΛΕΙΣΜΑΤΑ - FLUID INCLUSIONS

The following description follows the classification of Kilias and Kalogeropoulos (1988) including additional new data (Kilias 1991). Petrographic and microthermometric studies on primary and pseudosecondary (Roedder 1984) fluid inclusions in gangue quartz from undeformed and deformed ore samples have revealed the presence of three types of inclusions:

Type 1 represents aqueous two-phase liquid- plus vapor-H_2O inclusions. The vapor bubble occupies 20 to 60 vol. % of the inclusions. A content of less than 2.2 molal CO_2 deduced from clathrate formation upon cooling (Hedenquist and Henley 1985) is suggested for a substantial number of type 1 inclusions, classified as 1a.

Type 2 refers to CO_2-rich three-phase inclusions containing an aqueous liquid and CO_2-liquid and vapor phases. The liquid CO_2 always forms a very thin film around the gaseous CO_2 and homogenizes to the vapor phase at temperatures up to 31° C, the critical temperature of CO_2. The carbonic phase occupies 50 to 90 % of the inclusion volume.

Type 3 refers to rare inclusions consisting less than 5% of the total inclusion population and was only found in the undeformed ore. These are aqueous three-phase high-salinity inclusions containing liquid-H_2O, vapor-H_2O and a cubic halite Crystal. Vapor and halite phases occupy 20-30 and 20-50% of the inclusion volume. The halite crystals show a consistency in their dissolution temperatures upon heating and always dissolve before disappearance of the vapor bubble indicating the trapping of an unsaturated solution.

Tables 1 and 2 present the summary of the microthermometric data and calculated properties of the inclusion types. Microthermometric measurements are symbolized as follows :

$Tm,_{CO2}$: Final melting temperature of frozen CO_2.
$Tm,_{CLAT}$: Clathrate hydrate melting temperature.
$Tm,_{ICE}$: Melting temperature of ice.

Th,$_{CO2}$: Homogenization temperature of CO_2-liquid and vapor phases.
Tm,$_{HAL}$: Temperature of halite dissolution.
Th,$_{TOTAL}$: Total homogenization temperature.

Salinities were calculated from Tm,ICE (Potter et al. 1977) for type 1 inclusions, Tm,CLAT for type 1a and 2 inclusions (Collins 1979), and Tm,HAL (Haas 1976) for type 3 inclusions. Figure 1 is a plot of salinity versus total homogenization temperatures in an attempt to depict variation patterns and relationships existing among inclusion types 1, 1a, and 3 as will be discussed later in the paper.

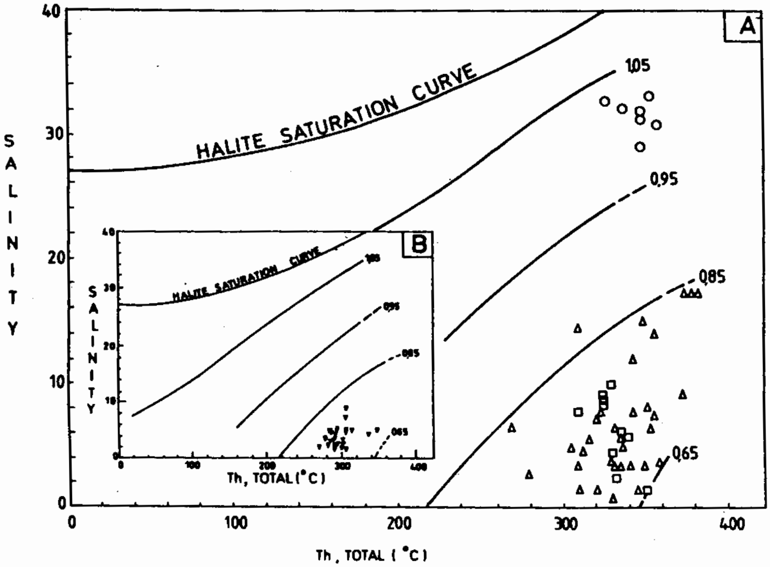

Fig. 1: Salinity (wt% NaCl equiv.) Vs. total homogenizationtemperature (° C) for inclusion types 1( ),1a( ),and 3( )in Undeformed ore (A) and inclusion type 1 ( ) in Deformed ore (B). NaCl saturation curve (halite + liquid + vapor curve) and selected isodensity curves are also shown (Data from Sourirajan and Kennedy 1962; Urusova 1975; and Haas 1976).

Εικ. 1: Σχέση αλατοτητας(% κ.β. ισοδύναμο NaCl) προς θερμοκρασία ολικής ομογενοποίησης(°C) για εγκλείσματα τύπου 1( ),1α( ), και 3( ) από μη παραμορφωμένη μεταλλοφορία(A), και τύπου 1( ) από παραμορφωμένη μεταλλοφορία(B). Φαίνονται ακόμη η καμπύλη κορεσμού σε NaCl (καμπύλη αλίτης + υγρό + αέριο) και επιλεγμένες καμπύλες ίσων πυκνοτήτων (Δεδομένα από Sourirajan and Kennedy 1962, Urusova 1975, Haas 1976).

Primary and pseudosecondary type 1(1a) and 2 inclusions coexist in three-dimensional clusters or intragranular planar arrays, or they are isolated. Typically clusters or planar arrays are dominated by one inclusion type (1 or 2) whereas a small number of inclusions of the other type (<10 vol.%) may be present. The admittedly very few halite-bearing type 3 inclusions occur mainly isolated and rarely in clusters dominated by type 1(1a) inclusions.

"ΜΗ ΣΥΝΔΙΑΛΥΤΟΤΗΤΑ" ΡΕΥΣΤΩΝ ΦΑΣΕΩΝ - FLUID IMMISCIBILITY

The association of fluid types 1(1a) and 2 in both undeformed and the deformed ores may be interpreted in several ways including unmixing, independent

Table 1: Microthermometry data[1] and properties of type 1(1a) and 3inclusions.
Πίν. 1: Μικροθερμομετρικά δεδομένα[1] και ιδιότητες εγκλεισμάτων τύπου 1(1α) και 3.

INCLUSION TYPE	FREEZING AND MELTING TEMPERATURES (°C)			APPARENT SALINITY (EQUIV. WT% NaCl)	HOMOGENIZATION TEMPERATURE (°C)	BULK DENSITY (g/cm^3)[2]
	$Tm,_{ICE}$	$Tm,_{CLAT}$	$Tm,_{HAL}$		$Th,_{TOTAL}$	
1	U(n=37) R:-13.2 - -0.5 X:-4.19±3.4 M:-2			U(n=36) R:0.87-17.19 X:6.43± 4.49 M:3.37	U(n=41) R:270.0-382.20 X:338.9± 26.20 M:350	U(n=36) R:0.61-0.85 X:0.70±0.06 M:0.69
	D(n=33) R:-5.70 - -0.7 X:-2.6±1.2 M:-3			D(n=33) R:1.22-8.81 X:4.28±1.91 M:4.94	D(n=26) R:251.0-349.00 X:297.1± 19.32 M:295.0	D(n=26) R:0.69-0.86 X:0. 74±0.03 M:0.75
1a		U(n=18) R:4.2-9.4 X:6.7±1.7 M:6.0		U(n=18) R:0.70-10.00 X:5.67± 3.24 M:5.77	U(n=21) R:240.0-350.0 X:324.9± 29.5 M:350.0	U(n=18) R:0.66-0.84 X:0.72±0.06 M:0.77
3			U(n=7) R:120.0-210.0 X:182.8 ± 32.5 M:210.0	U(n=7) R:28.61-32.4 X:31.3± 1.4 M:32.40	U(n=7) R:325.0-356.0 X:349.0 ± 11.0 M:356.0	U(n=7) R:0.96-1.01 X:0.98±0.01 M:0.99

Table 2: Microthermometry data[1] and properties of type 2 inclusions
Πίν. 2: Μικροθερμομετρικά δεδομένα και ιδιότητες εγκλεισμάτων τύπου 2.

FREEZING TEMPERATURES (°C)		APPARENT SALINITY (EQ. WT% NaCl)	HOMOGENIZATION TEMPERATURES (°C)			DENSITY (g/cm^3)[3]	
$Tm,_{CO2}$	$Tm,_{ICE}$		$Th,_{CO2}$	$Th,_{TOTAL}$	CO_2-PHASE	H_2O-PHASE	BULK
U&D(n=17) R:-56.5- -56.0 X:-56.5±0.24 M:-56.6	U(n=27) R:7.80-9.40 X:8.55±0.52 M:8.30	U(n=27) R:1.43-3.94 X:2.52±0.83 M:2.03	U(n=18) R:17.6-25.0 X:20.9±1.93 M:20.9	U(n=20) R:320-382 X:344± 22 M:320	U(n=20) R:0.17-0.24 X:0.19±0.02 M:0.20	U(n=18) R:1.00-1.02 X:1.00±0.06 M:1.00	U(n=18) R:0.35-0.38 X:0.07±0.14 M:0.37
	D(n=22) R:8.90 X:9.44±0.27 M:9.50	D(n=22) R:0.41-2.30 X:1.10±0.63 M:0.41	D(n=18) R:19.2-30.8 X:26.0±3.41 M:26.8	D(n=22) R:306-368 X:340±19 M:333	D(n=22) R:0.18-0.37 X:0.26±0.05 M:0.25	D(n=22) R:0.99-1.03 X:1.00±0.01 M:1.00	D(n=18) R:0.31-0.47 X:0.35±0.04 M:0.36

[1] U:undeformed,D:deformed,R:range,X:average,M:mode,±standard deviation,n:No. of measurements

[2] Density calculations are based on tables of interpolating constants by Potter and Brown(1977)

[3] Densities: CO_2-phase is derived from Angus et al. (1976); H_2O-phase from Potter and Brown (1977)

co-trapped fluids (Kilias and Kalogeropoulos 1989), or trapping of different generations of fluids at different T-P conditions.

On the basis of the fundamental work of Ramboz et al. (1982) on thermodynamic and chemical principles of phase equilibrium applied to isochoric-isoplethic systems, such as fluid inclusions, several lines of evidence have been provided that inclusion types 1(1a) and 2 may constitute stable immiscible phases generated by fluid unmixing("boiling") under fixed T-P conditions.

1. The two types of inclusions coexist in the same in the same regions of individual quartz crystals in primary or pseudosecondary assemblages and thus they are closely related in space. This in turn may also suggest contemporeneity (i.e., Robert and Kelly 1987)(i.e., close relation in trapping time) of the two inclusion types.

2. The contrasting densities of the two inclusion types (Tables 1 and 2) lead to total homogenization via opposite phase transition to liquid and vapor phases respectively. All type 1(1a) inclusions homogenize to liquid whereas surrounding or coexisting type 2 inclusions with CO_2/H_2O volumetric proportions of 70 to 90% homogenize to vapor, at overlapping temperatures between 320° and 382° C(Tables 1 and 2).

3. Calculated internal pressures $Ph,_{TOTAL}$, at $Th,_{TOTAL}$, of inclusion types 1 and 2 are partly overlapping (Figs. 2A and 2B). This is in apparent contradiction with an important prerequisite of fluid phase equilibria that the pressures of the immiscible inclusion fluids should reach the same values (trapping pressures) at homogenization, as a consequence of compatibility of the bulk molar volumes of the liquid(type 1) and vapor(type 2) inclusions with equilibrium coexistence at a unique value of $Ph,_{TOTAL}$. This is shown on Figure 2 that superimposes $Th,_{TOTAL}$ and $Ph,_{TOTAL}$ of inclusion types 1 and 2 for undeformed(Fig. 2A) and deformed (Fig. 2B) ores in P-T space. Internal pressures were calculated for type 1 inclusions using the equations given by Haas (1976, eqs. 3-6), and for type 2 inclusions using Redlich-Kwong equation of state modified by Bowers and Helgeson (1983) using the computer program of Nichols and Crawford (1985).

The partly overlapping areas of Figure 2 indicate that indeed some type 1 and 2 inclusions were trapped at identical pressures. The discrepancy for the rest of the inclusions may be due to errors in inclusion-phases' volume visual estimation or trapping under different T-P conditions. However, considering that fluid unmixing is not an isothermal (hence the range of homogenization temperatures (Tables 1 and 2)-isobaric process, a time delay between entrapment of type 1 and 2 inclusions in a fluid system undergoing simultaneous unmixing and P-T evolution in a tectonically active environment, could produce the observed pressure difference of 300-400 bars (Ramboz et al. 1982; Diamond 1990). The difference in pressure shown in Fig. 2 by approximately a factor of two to three geologically may be interpreted to indicate fluctuating pressure conditions between lithostatic and hydrostatic (Lynch 1990).

4. Inclusion compositions conform fairly well to chemical equilibrium fractionation at $Th,_{TOTAL}$ AND $Ph,_{TOTAL}$. Any chemical species should be distributed between two immiscible fluid phases L(type 1) and V(type 2) according to:

$K_{D,i}^{LV} = (X_i^V/X_i^L)_{P,T}$ where:

K_D: distribution coefficient and X: composition of species i

The distribution coefficients, calculated from bulk molar compositions of pairs of selected type 1 and type 2 inclusions, as best representing the equilibrium coexisting immiscible phases (Table 3), display the distribution trend:

$K_D(NaCl)<K_D(H_2O)<K_D(CO_2)$ (Ellis 1979) (Table 4)

which may qualitatively be used to show immiscible phases (Diamond 1990). Bulk fluid inclusion compositions were calculated in the system H_2O-CO_2-NaCl assuming that type 1(1a) inclusions contain CO_2 between <0.85 and 2.2 *molal* as evidenced by clathrate formation on freezing using the computer program of Nicholls and Crawford (1985).

Table 3: Calculated molar compositions and properties of selected type 1(1a) and 2 inclusions considered to represent immiscible phases in the system H_2O - CO_2 - NaCl (see text for discussion).

Πίν. 3: Υπολογισμός της γραμμομοριακής σύστασης και ιδιοτήτων επιλεγμένων εγκλεισμάτων τύπου 1(1α) και 2 τα οποία θεωρούνται ότι αντιπροσωπεύουν "μη συνδιαλύτες" φάσεις στο σύστημα H_2O - CO_2 - NaCl (βλ. συζήτηση στο κείμενο).

	UNDEFORMED				DEFORMED			
	TYPE 1(1A)		TYPE 2		TYPE 1(1A)		TYPE 2	
	PAIR 1	PAIR 2	PAIR 1	PAIR 2	PAIR 1	PAIR 2	PAIR 1	PAIR 2
H_2O	90.4-92.6	93.4-95.6	76.2	80.2	94.8-97.0	93.6-95.8	68.8	56.6
CO_2	1.4 TO	3.6	23.3	18.8	1.4 TO	3.6	31.0	43.0
NaCl	6.0	3.0	0.5	1.0	1.6	2.8	0.2	0.4
SALINITY	17.20	9.20	2.00	3.90	4.95	8.81	1.20	1.8
DENSITY (g/cm^3)	0.79	0.69	0.35	0.47	0.67	0.79	0.32	0.5
MOLAR VOLUME (cm^3)	25.7	27.70	69.10	48.80	27.50	23.90	81.80	68.4

Table 4: Chemical distribution coefficients (K_D), calculated from data in Table 3 showing the relative trend $K_D(NaCl)<K_D(H_2O)<K_D(CO_2)$ (see text for discussion).

Πίν. 4: Συντελεστές χημικής κλασματοποίησης (K_D), που υπολογίστηκαν με βάση τα δεδομένα του Πίνακα 3 και δείχνουν την σχετική τάση $K_D(NaCl)<K_D(H_2O)<K_D(CO_2)$ (βλ. συζήτηση στο κείμενο).

	UNDEFORMED		DEFORMED	
INCLUSION PAIR	1	2	1	2
K_DNaCl	0.08	0.33	0.12	0.14
K_DH_2O	0.82- 0.84	0.84- 0.86	0.70- 0.72	0.58- 0.60
K_DCO_2	6.50-16-70	5.30-13.40	8.60-22.10	11.90-30.70

Figure 3 shows the bulk molar compositions of Table 3 plotted on a ternary H_2O-CO_2-NaCl isobaric-isothermal diagram exhibiting the limits of immiscibility at temperatures of 350-400°C and pressures of 400-500 bars based on experimental data of Gehrig (1980). As it can be seen bulk compositions compare favorably with the experimental data thus strongly indicating the actual occurrence of immiscibility at the temperatures and pressures of this diagram.

Based on the combination of all the above lines of evidence it is strongly suggested that the higher-temperature type 1 and type 2 inclusions constitute stable immiscible phases, generated by unmixing of a single homogeneous aqueous CO_2-bearing parent fluid of moderate salinity as its P-T path crossed a solvus surface at temperatures of 300° to 400°C and pressures of 400-500 bars.

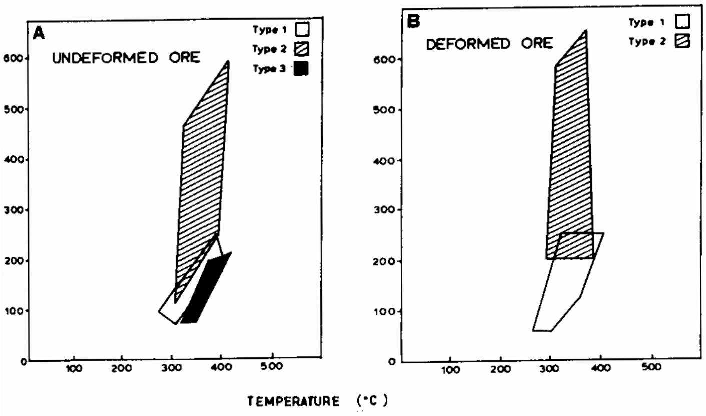

Fig. 2: Comparison of homogenization conditions (Ph,$_{TOTAL}$ vs.Th,$_{TOTAL}$) of inclusion types 1(1a), 2 and 3 for Undeformed (A) and Deformed (B) ores.

Εικ. 2: Σύγκριση των συνθηκών ομογενοποίησης (Ph,$_{TOTAL}$ προς Th,$_{TOTAL}$) των εγκλεισμάτων τύπου 1 (1a), 2 και 3 για Μη Παραμορφωμένη (A) και Παραμορφωμένη (B) μεταλλοφορία.

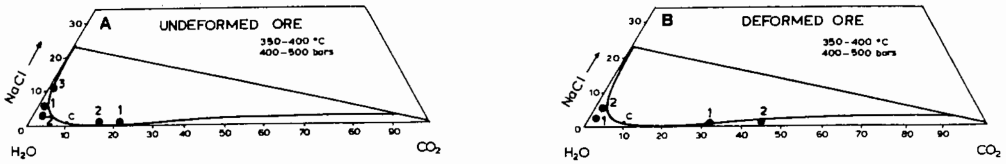

Fig. 3: Isobaric-isothermal plot of pairs (1,2) of calculated bulk molar type 1 and 2 inclusion compositions(Data from Table 3) at temperatures of 350°-400°C and pressures of 400-500 bars, for Undeformed (A) and Deformed (B) ores. The experimental limits of immiscibility in the system H_2O - CO_2 - NaCl at the above P-T conditions are shown (Gehrig 1980). The dot along the immiscibility boundary (c) indicates the position of the consolute point at which "liquid" (Type 1) and "vapor" (Type 2) become indistinguishable. -3- in (A) designates the area where calculated bulk molar compositions of type 3 inclusions are plotted.

Εικ.3. Ισοβαρομετρική - ισοθερμική προβολή ζευγών (1,2)υπολογισμένων συνολικών γραμμομοριακών συστάσεων, από εγκλείσματα τύπου 1 και 2 (Δεδομένα του Πίνακα 3), σε θερμοκρασίες 350°-400° C και πιέσεις 400-500 bars, από Μη Παραμορφωμένη (A) και Παραμορφωμένη (B)μεταλλοφορία. Φαίνονται επίσης τα πειραματικά όρια της "μη συνδιαλυτότητας" στο σύστημα H_2O - CO_2 - NaCl στις παραπάνω συνθήκες P-T (Gehrig 1980). Η τελεία (c) κατά μήκος του ορίου "μη συνδιαλυτότητας" υποδεικνύει τη θέση του σημείου στο οποίο "υγρό" (Τύπος 1) και "αέριο" (Τύπος 2) γίνονται δυσδιάκριτα. Το σύμβολο 3 στο (A)δείχνει την περιοχή προβολής της υπολογισμένης συνολικής γραμμομοριακής σύστασης των εγκλεισμάτων τύπου 3.

The latter is in full accordance with experimental solubility data in the system H_2O-CO_2-NaCl (Gehrig 1980; Bowers and Helgeson 1983). The cause of unmixing may be induced pressure-temperature evolution of the parent fluid as a consequence of reaction progress with the host marble when the evolving fluid intersected its miscibility boundary at the inferred conditions.

Since inclusion types 1(1a) and 2 are unmixing products homogenization T-P conditions are, in principle, equal to trapping T-P conditions (Pichavant et al. 1982; Ramboz et al. 1982). Therefore, by inference it may be concluded that the Olympias ores were deposited from an ore-bearing fluid undergoing unmixing at temperatures of 350±30°C and fluctuating pressures of less than 500 bars. The striking overall similarity in fluid composition and P-T conditions of the deformed and udeformed ores supports the conclusion that both ore varieties are integral parts of the same Tertiary metallogenetic system.

ΣΧΕΣΕΙΣ ΑΛΑΤΟΤΗΤΑΣ ΠΡΟΣ ΘΕΡΜΟΚΡΑΣΙΑ - SALINITY VS. TEMPERATURE RELATIONS

Two features shown in Figure 1 demand explanation taking into account the presented fluid inclusion evidence:

1. Type 1 inclusions display a wide range of salinities from 0.9 to 17.2 wt% NaCl equiv. over a relatively narrow range of temperatures.
2. A complete gap exists between the salinities of type 1 inclusions, and those of type 3 inclusions (undeformed ore) which cluster within a narrow range of 28.6-32.5 wt% NaCl equiv.

The salinity range of type 1 inclusions is probably the result of a complex overlapping between a near vertical salinity enrichment trend with decreasing temperature, caused by unmixing, due to decreasing volatile(CO_2) content during adiabatic cooling (Drummond and Ohmoto 1985), and a positive correlation trend between decreasing salinity and temperature due to mixing(dilution) of the high-temperature moderate- salinity unmixed fluid with cooler low-salinity meteoric waters (Reed and Spycher 1985; Shepherd et al. 1985). The involvement of meteoric waters in the Olympias system is supported by recorded salinities well below that of sea water (3.2 wt% NaCl equiv.), final melting temperatures very close to that of pure water (0.0°C)(Table 1), and oxygen isotopes (Kalogeropoulos and Kilias 1989).

If the gap between the salinity trends of inclusion types 1 and 3 from 17.2 to 28.6 wt% NaCl equiv. is real, unmixing as major mechanism for generation of the high-salinity type 3 inclusions may be precluded, because in both cases fluid inclusions with the missing salinities should have been present. Consequently, inclusion type 3 fluids may have either a different source than type 1 or have been generated by a different mechanism. In either case a probably early high-temperature high-salinity fluid recorded in type 3 inclusions should be invoked. However, if this salinity gap is an artifact due to metastability in the region near halite saturation (Roedder 1984, p. 447-448), then two explanations may be used :

1. The range in salinities may be explained by mixing of an early high-temperature, high-salinity fluid recorded in type 3 inclusions with a moderate-salinity high-temperature fluid (type 1) at temperatures higher than those inferred for unmixing.
2. The unmixing process that produced the inclusion types 1(1a) and 2 may have almost isothermally driven the residual liquid towards halite saturation, as it is shown in Fig. 1, during occasional "opening" of the system and concomitant complete vapor(CO_2) loss. Vapor loss as a mechanism for fluid saturation in salt components has been indicated by Trommsdorf and Skippen (1986) in metasomatic phenomena in the Suiss Alps. Under the constrained of the artificial salinity gap the latter interpretation is supported by overlapping calculated $Ph,_{TOTAL}$ of inclusion types 1 and 3 (Fig. 2A), and the satisfactory

fit of calculated type 3 bulk molar compositions to chemical equilibrium fractionation at the conditions inferred for umnixing (Fig. 3A), allowing for the possibility that type 3 inclusions formed undetected clathrates(content max. 2.2 *molal* CO_2). Calculated bulk molar compositions of type 3 inclusions may range: H_2O: 85.6 to 83.8 - CO_2: 3.4 to 3.3 - NaCl: 11 to 12.9 for salinities of 28.6 to 32.5 wt% NaCl equiv. (CO_2 values are maximum).

ΑΠΟΘΕΣΗ ΣΟΥΛΦΙΔΙΩΝ - SULFIDE DEPOSITION

CO_2 plays an important role in constraining fluid pH changes during fluid phase separation (Hedenquist and Henley 1985) and therefore indirectly affects mineral solubilities. When unmixing occurs in an H_2O-CO_2-NaCl fluid as in the case of a reaction progress shown here, the reacting fluid responds first to the preferential separation and loss of the volatile gases CO_2 and H_2S to the vapor phase resulting in a pH increase, and progressive oxidation of the fluid. Separation of CO_2 may lead to an increase in pH by disturbing the preexisting equilibrium state of the following reaction:

$$HCO_3^- + H^+ = CO_{2(g)} + H_2O$$

The reaction proceeds to the right on CO_2 loss thus to H^+ concentration decreases and hence to pH increase (Hedenquist and Henley 1985; Bowers 1991). The loss of CO_2 from the fluid is accommodated almost quantitatively by an increase in pH; 90% loss of CO_2 results in a pH increase of about one unit. Type 1 fluid inclusion compositions in this study indicate dramatic CO_2 volumetric separation.

At temperatures >200° C base metals such as Pb, Zn, and Ag are transported dominantly as chloride complexes (Seward 1984). An increase in pH value can be a very effective mechanism of sulfide precipitation through the solubility reactions :

$MCl_2 + H_2S = MS + 2H^+ + 2Cl^-$ where M : Pb and Zn

The loss of CO_2 and the associated decrease in the activity of H^+(pH increase) moves this reaction to the right resulting in the precipitation of sulfides. In the case of PbS a pH increase results in a solubility decrease on the order of 100 (Henley et al. 1984) around 300° C. In high-temperature geothermal systems most heat is lost by unmixing("boiling") or dilution with cooler waters whereas cooling by conduction is minimal(Truesdell et al. 1977). Conductive cooling would decrease the solubility of galena six times(Hedenquist and Henley 1985) compared to 100-fold solubility decreases due to "boiling". Therefore "boiling" is clearly an important kinetically favorable process leading to the deposition of base metals. A similar mechanism has been strongly indicated to have been responsible for base metal ore-sulfide deposition at the Olympias deposit.

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