ORES, EXPLORATION TOOLS AND NEW TARGET AREAS IN THE EASTERN CHALKIDIKI PENINSULA, NORTHERN GREECE

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ABSTRACT

This paper summarizes the major ore types of the eastern Chalkidiki peninsula, including the polymetallic sulphide deposits of Olympias and Madem Lakkos, the porphyry copper deposits of Fisoka and Kouries, the Pirinia sulphide skarn mineralization and the Stratoni, Piavitza, Varvara and Bazdek Lakkos supergene manganese oxide deposits. A new metallogenetic framework is proposed, in which the genetic relationship between porphyry copper intrusions and polymetallic sulphide deposits is based on mineralogy, geochemistry, lead isotopes, and P-T conditions of formation. Geochemical exploration tools are discussed, as well as the discovery of two new target areas, Papades and Pappa Choravi, that were discovered using this new metallogenetic approach.

INTRODUCTION

The Serbo-Macedonian zone in Northern Greece hosts polymetallic veins, stratiform lead-zinc sulphide ores, epithermal gold, manganese oxide deposits and skarn mineralizations, as well as a great number of hydro-thermal alterations that are the result of an interplay between large-scale tectonics, magmatic intrusions and hydrothermal episodes. The considerable potential for detecting non-outcropping economic base and precious metal ore bodies in the Chalkidiki peninsula has been the object of investigation in an international EC Research and Development project 1990-1993. This project focussed on the development of new exploration strategies by ore deposit studies and lithogeochemical modelling. The present paper describes a number of porphyry copper, carbonate, skarn, quartz vein, shear hosted and supergene mineralizat-ions, proposes a metallogenetic framework, and discusses exploration tools and two new target areas with non-outcropping mineralizations.

GEOLOGICAL SETTING

The eastern Chalkidiki peninsula, hosting the Olympias and Madem Lakkos sulphide deposits, is underlain by the southernmost extension of the Serbo-Macedonian metamorphic complex. Kockel et al. (1971, 1977) divided this complex into two formations: the Vertiskos formation in the west and the Kerdilia formation in the east. The Kerdilia formation is invaded by a variety of foliated and non-foliated intermediate to felsic intrusions of Tertiary age. It has been suggested that the Kerdilia formation represents a separate

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tectonic unit that was tectonically juxtaposed with the Vertiskos formation during the Tertiary orogeny (Dixon & Dimitriadis 1984). The contact between the Kerdilia and Vertiskos formations is a thrust fault (Neubauer 1957; Kockel et al. 1978a,b) of Tertiary age (Dixon & Dimitriadis 1984). This active fault passes through the town of Stratoni, just south of the Madem Lakkos mine. The latter deposit is situated near the southeastern closure of a major regional anticline, within the so-called "lower marble horizon" of the Kerdilia forma-



Fig. 1: Geology of the investigated area (modified from IGME maps). Legend: hatched: Kerdilia formation schists & gneisses; coarsely cross-hatched: anatectites; bricks: marbles; net: alteration halo around Stratoni diorite; v: Vertiskos schists & gneisses; finely cross-hatched: amphibolites; +: samples. tion (Kockel et al. 1977). Near the mine the anticlinal axis strikes NW-SE (Fig. 1) and plunges SE (Nebel et al. 1991). Migmatites mark the core of this anticline. Regional oxidation has affected the area up to a few hundred meters below surface. Partly oxidized polymetallic sulphides occur as relicts at the surface along the Stratoni-Varvara tectonic structure, hosted by late-stage Mn-Fe oxides. At deeper levels, non-oxidized polymetallic sulphides are being mined at the Madem Lakkos deposit.

SUMMARY OF TYPES OF MINERALIZATION AND ASSOCIATED ALTERATIONS

Porphyry copper deposits

Porphyry copper deposits occur mainly in the Vertiskos formation of the Serbo-Macedonian Zone, forming a NW trending belt extending into the former Yugoslavia. The Fisoka and Skouries deposits have been investigated by Veranis (IGME report), Eliopoulos & Economou (1991) and Frei (1992). The ore comprises stockwork veinlets and disseminations of pyrite, chalcopyrite, bornite, magnetite, minor galena and tetra-hedrite. Some enriched and oxidized zones are

developed down to a depth of 15 - 30 m. Potassic and propylitic alteration zones surround the pipe-cone mineralized subvolcanic stocks. The Skouries porphyry copper ore body is the largest known in Greece, amounting to 72 Mt of 0.5 % Cu, 0.7 ppm Au, and 2.5 ppm Ag (Kalogeropoulos 1986). Eliopoulos & Economou (1991) reported elevated PGE concentrations of mainly Pd, Pt and Ru. New geochronological datings suggest ages of 19 - 24.5 Ma for these porphyries (Frei 1992), similar to the K-Ar ages of illites of hydrothermally altered pegmatites at Madem Lakkos.

Sulphide-skarn mineralizations

Epigenetic pyrrhotite-pyrite-chalcopyrite-amphibole mineralizations occur at Pirinia, about three km NE of the Olympias deposit, in the same marble horizon that hosts the latter deposit (Diakakis et al 1986). Although the Pirinia mineralization is described as a calc-silicate occurrence, the marble

host rock shows very little calc-silicate development along the contacts with the sulphide veins. Rounded marble fragments occur in massive pyrrhotite ore without significant reaction rims. The surrounding wall rocks are transected by kaolinized pegmatites, steep fault zones containing graphite schists and silicified breccia zones with late Mn oxides. All this strongly suggest an intense but short-lived hydrothermal activity contempo-raneous with steep block faulting, brittle deformation and shearing, i.e. epigenetic hydrothermal conditions well within in the actinolite-hornblende stability field (Hellingwerf & Arvanitidis 1993).

Stratabound polymetallic sulphides

Veins and replacement polymetallic deposits containing precious metals like those at Olympias and Madem Lakkos occur throughout the metamorphosed thick carbonate units of the Serbo-Macedonian zone. Their structural emplacement is related to deep seated fractures intersecting interlayered marble-gneissamphibolite sequences of the Kerdyllia formation. Economic stratabound replacement bodies occur along the marble - biotite gneiss contacts. Undeformed ore, the most prevailing type, occurs as cavity fillings, bands, vein fillings, and disseminations. The disseminated sulphide ore is volumetrically the most important ore type. Deformed ore shows intense brecciation and shearing producing structures reminiscent of pseudo-layering. The host rock consists of calcitic to rhodochrositic marble. All marbles hosting the base metal sulphides are extremely deformed, and in some cases that much recrystallized that no relict deformation textures can be observed. There is a definite gap between the intensity of deformation recorded by the marbles and that recorded by the sulphides. The contacts between ore and host rock is usually sharp, with little reaction zones between them. The Olympias and Madem Lakkos deposits have a combined reserve of 21 Mt of ore with 8 % Pb+Zn, 120 ppm Ag and between 1.5 -5.5 ppm Au (Kalogeropoulos et al. 1989; Arvanitidis & Constantinides 1991).

There is a spatial relationship between the sulphides and abundant white "aplite" dikes and sills in the mine area. Field observations show these rocks to represent sericitized and kaolinized quartz-feldspar pegmatites, occasionally containing disseminated sulphides. It is suggested here that sericitization and kaolinization of aplite sills and dikes is due to acid attack of the low pH ore-bearing solutions along structural pathways (i.e. contact planes aplite-marble), dissolving carbonate material under production of CO₂, thereby increas-ing the solution pH as a consequence of which sulphides precipitated in newly created cavities. This mechanism implies the age of the sulphides to be slightly younger than the aplite dikes, and also explains why sulphides occur as disseminations in hydrothermally altered aplites. There is additional evidence that these polymetallic sulphide ores are of epigenetic origin (Kalogeropoulos et al 1989, Hellingwerf 1992A, Frei 1992). These arguments exclude a sedimentary-exhalative origin for the sulphides as proposed by Nebel et al (1991). Spatial and chronological relationships suggest further that the Madem Lakkos type sulphide deposits may represent the distal expressions in a Skouries type porphyry copper generated hydrothermal system.

The Zepkos Fe(-Pb-Zn-Mn-Au) and Vina Mn-Zn(-Pb-Fe-Au) sulphide occurrences, 5-7 km SE of Olympias, are vein- and replacement mineral-izations of the same type as Olympias and Madem Lakkos. They contain pyrite, arsenopyrite, sphalerite, galena, bournonite and semseyite in gangue material of rhodochrosite and quartz (Arvanitidis et al. 1992).

Shear-hosted sulphide-gold mineralizations

Shear-hosted quartz-sulphide-gold mineralizations occur both in carbo-nate units (Pangeon, Palea Kavala), as well as in quartz-mica schists (Stanos area). In the latter area the mineralization consists of variably deformed pyrite, arsenopyrite, chalcopyrite and minor galena, sphalerite, pyrrhotite, Co-Ni sulphides, bismuthinite, sulfosalts, gold-electrum, tellurides, molybdenite and Fe-Ti oxides. Arsenopyrite geothemometry and sphalerite geobarometry yield temperatures of 460-510 $^{\rm OC}$ and a pressure of 5.6 \pm 0.8 kb (Kalogeropoulos et al 1990). In general, the shear-hosted mineralizations are high-grade, low volume gold-bearing sulphide mineralizations (Baker et al 1992).

Oxidized sulphide and supergene manganese-gold mineralizations

Regional oxidation caused amongst others oxidation of manganiferous marbles and a coeval dissolution, transport and precipitation of manganese oxides. As a result, pyrolusitic Mn ores are common along the Stratoni-Piavitza-Varvara fault, hosted by marbles of the Kerdilia for-mation. The footwall consists of biotite gneisses of the Kerdilia for-mation, and the hanging wall by amphibolites of the Vertiskos format-ion. The contact, a thrust plane between the amphibolites and Mn mineralization, is sharp. Tectonic activity seems to have enhanced the degree of oxidation. Microcracking in grey massive marbles with veinlets filled with Mn oxides is a common phenomenon. Locally, these veinlets increase in number and size, ending up in irregular, but continuous fault zones up to 20 cm wide, in which white, secondary - non-deformed - calcite aggregates are embedded in a matrix of fine-grained, black Mn oxides. Local transportation down a geochemical gradient resulted in the concentration of this material into wider fault zones. Thus, in situ oxidation in combination with brittle/ ductile deformation of grey Mn-bearing marble produces breccias and veinlets with white calcite with black Mn oxides.

The pyrolusitic Mn oxide ores occur as massive and colloidal cavity fillings, as fine grained infiltrations accompanied by limonite in kaolinized pegmatites, and as complex aggregates with grey chalcedony and vuggy quartz in kaolinized schists. The general paragenetic sequence in order of precipitation is: Mn oxides -> Fe oxides -> Chalcedony -> Vuggy quartz. The youngest phase of silicification is pervasive throughout the entire area as it affects all older lithologies and mineralizations.

Locally, in the Mn oxide deposits of Piavitza, Varvara and Olympias, and in the Zepkos-Stratoniki mineralized zone, entirely silicified marble fragments have been observed in colloidal, non-silicified Mn oxide ore, suggesting a phase of diffuse silicification before Mn deposition. Thus, silicification occurs both before and after Mn oxide deposition.

Gold contents in the manganese-iron oxide ores from the oxidation zone are usually lower than those in the non-oxidized sulphide ores. Local secondary enrichments up to a hundred ppm do, however, occur in small manganese-limonite pockets. This is also the case in the manganese oxide deposits of the Drama region (Hellingwerf 1990, 1991).

GEOCHEMISTRY

The chemical analyses were produced by XRF, ICP and neutron activation techniques. The dataset can be supplied by N.D.A. (IGME, Thessaloniki) at request.

Regional element variations

 sio_2 in marbles reaches up to 26.1 wt% (Fig. 2A), and is related to a process of widespread silicification, especially in the Olympias, Varvara and Stratoni



Fig. 2: Regional element variations in the area. A) SiO₂, max value 27.3 wt%, 160 samples; B) MnO, max value 2.07 wt%, 129 samples; C) MgO, max value 22.6 wt%, 179 samples; D) Na₂O max value 0.96 wt%, 171 samples; E) K₂O, max value 0.72 wt%, 171 samples; F) Cr, max value 15 ppm, 92 samples; G) Cu, max value 300 ppm, 124 samples; H) Sr, max value 580 ppm, 103 samples

domains (Hellingwerf et al. 1993). Obviously, the vuggy quartz in the sulphide assemblages at Stratoni and Olympias suggests late stage silica deposition associated with sulphide mineralization (as is the case at Pirinia, Stanos, etc.), but the major phase of silicification is related to the supergene Mn oxide precipitation. The spatial distribution of Fe_2O_3 parallels that of SiO₂. Thus, in a regional context, silicification and iron enrichment of the marbles reflect the presence of Mn oxides nearby.

MnO in unmineralized marbles from the Piavitza, Olympias and Varvara domains (up to 1.7 wt%), all spatially associated with Mn oxide deposits (Fig. 2B) show elevated Mn concentrations as a result of primary rhodochrosite components and secondary dispersion processes. Thus, irrespective whether Mn is primary or secondary, the presence of nearby Mn oxides is reflected. The Pappa Choravi area reveals a single anomaly that has been checked with follow-up fieldwork, showing Mn oxides at the surface.

 Fe_2O_3 (not illustrated; max value 2.34 wt%; 146 samples) mirrors essentially the distribution pattern of SiO₂.

MgO is highest (22.6 wt%) in unaltered marbles away from the structural zones (Fig. 2C), i.e. dedolomitization - secondary, clean calcite development - rather than dolomitization is associated with the manganese mineralizing processes. This conclusion complies with microscopical observations (Hellingwerf et al 1993).

 Na_2O shows maximum values in marble containing Mn oxides and relict base metal sulphides (Fig. 2D). It is not clear whether Na_2O is associated with the older sulphide or with the younger Mn oxide supergene system. However, the fact that Na_2O increases towards only those Mn mineralizations that do contain relict sulphide mineralizations, suggests that sodium metasomatism is related to the older, sulphide mineralizing system. The same phenomenon has been observed in Swedish Proterozoic marble hosted polymetallic sulphide deposits (e.g. Hellingwerf 1992B).

 $\mathbf{K}_2\mathbf{O}$ shows maximum values in marbles of the Olympias, Pirinia, Piavitza and Varvara domains (Fig. 2E). At these localities also **Rb** displays maximum values. Each one of the anomalies is associated with base metal sulphides or Mn oxide mineralizations. In the western part of the project area, north of Varvara, only minor anomalies are associated with Mn oxide mineralizations. Thus, it seems that the major anomalies are related to sulphide mineralizations.

Cr concentrations in marbles are relatively low. However, the distribution pattern (Fig. 2F) does reveal significant anomalies around the entire Pirinia-Olympias-Stratoni sulphide belt, around the Mn oxide mineralizations at Varvara, whereas anomalous values occur in the Pappa Choravi area.

Cu shows maximum values in marbles of the Stavros domain, not far from a pyrite-chalcopyrite mineralization, as well as in the Papades prospect (Hellingwerf 1992), around Stratoni and north of Varvara (Fig. 2G). Since Cu in most cases reflects the presence of base metal sulphides, the Pappa Choravi area, north of Varvara, seems an interesting target on the basis of Cu and other elements described above.

Zn (not illustrated; max value 1400 ppm; 102 samples), **As** (not illustrated; max value 3000 ppm; 53 samples) and **Pb** (not illustrated; max value 800 ppm; 97 samples) display a distribution pattern similar to that of Cu, with the same conclusion.

Sr shows a variable behaviour towards the Stratoni-Varvara structural zone (Fig. 2H). Generally Sr decreases towards this zone, but there is a slight increase towards the western part with a maximum of 580 ppm in the Pappa Choravi area, north of Varvara.

Ba (not illustrated; max value 400 ppm; 34 samples) mirrors the distribution of MnO and Cu, with maximum values around Olympias and Pappa Choravi.

Sb (not illustrated; max value 700 ppm; 28 samples) and **Li** (not illustrated; max value 10 ppm; 41 samples) displays a distribution pattern similar to that of K_2O , Ba and Cu, with maximum values around Olympias, Varvara and the Papades prospect.

Local element variations

Two profiles, one at Stratoni and one at Varvara, were sampled across the Stratoni-Varvara tectonic zone containing major marble-hosted Mn oxides. Since the element behaviour at Varvara is similar to that at Stratoni, only the latter profile is presented. Fig. 3 displays this profile with unaltered marbles in the north, and the tectonic zone in the south containing supergene Mn oxides, limonitic pockets and relict base metal sulphide mineralizations.

 sio_2 contents are generally low in unaltered marbles, but within the Mn oxide mineralization, it is clearly enriched and displays a distribution curve parallel to that of MnO (therefore not illustrated in Fig. 3). Silicification coupled to supergene Mn mineralization has also been observed in Mn oxide mineralizations of the Drama area (Hellingwerf 1990, 1991).

MnO is low in unaltered marbles and yet being depleted approaching the tectonic zone (Fig. 3). Locally, minor quantities of Mn oxides are precipitated in limonitic pockets.

Zn contents clearly reflect the presence of oxidized and relict polymetallic sulphide mineralizations hosted by Mn oxides (Fig. 3).

Sr is progressively depleted towards the tectonic zone, which complies well with its regional behaviour (Fig. 5D).

 K_2O , **Rb** (following the behaviour of K_2O) and **Li** (Fig. 3) have been mobilized from the marbles and co-precipited with the Mn oxides along the tectonic zone. Thus, increasing concentrations of these elements reflect the proximity of supergene Mn oxides.



Fig. 3: Cross section, sample profile and element distribu-tion patterns across the Stratoni-Varvara fault zone, N of Stratoni village.

MANGANIFEROUS MARBLE AS PROTORE FOR MN OX-IDES ?

The mechanism observed in outcrops and thin sections, involving crackling, brecciation, shearing and in situ oxidation of grey marbles, producing Mn oxides plus secondary, white calcite suggests that the manganiferous and rhodochrositic marbles may represent the protore for the Mn oxides. A back-of-the-envelope calculation, based on average marble compositions as presented in Table I, leads to an estimated deposit of 1 to 2 Mt with 75 wt% MnO, with the present outcrop configuration. Considering the effect of weathering and erosion of the overlying marble-bearing sequences, this calculation is a conservative one. Thus, in terms of volume only, the marbles could very well be the source rock for the supergene Mn oxides in the Olympias-Varvara-Stratoni area. The field observations and textures described above provide further support for this.

METALLOGENETIC FRAMEWORK

The temperature conditions for the various types of mineralizations, based on mineral parageneses, fluid inclusions and isotopic studies are summarized by Hellingwerf &

Arvanitidis (1993), clearly illustrating the grouping of the various ore types into hypothermal (porphyry copper deposits), mesothermal (Cu-Fe sulphide skarn and polymetallic sul-phides), epithermal (polymetallic sulphides) and supergene (Mn oxide deposits). The porphyry copper intrusions are very likely genetically related to the polymetallic sulphide deposits of Olympias and Madem Lakkos, since the Pb isotopes from the Olympias and Madem Lakkos sulphide deposits 1) are identical, 2) argue against the Stratoni diorite as a source of the mineralizing fluids, and 3) suggest a close relationship between Pb in the porphyries and Pb in the sulphide deposits (Frei 1992). The metallogenetic framework (Fig. 4) illustrates the various ore types arranged according to the temperature of formation, structural control and regional **Table I:**

Composition \ Oxide	sio ₂	Fe ₂ 0 ₃	MnO	MgO	CaO
Unaltered marble (n=55) MnO between 0.03 and 0.2 wt%	2.30	0.28	0.06	2.67	51.42
Oxidized &leached marble (n=34) MnO < 0.03 wt%	1.98	0.24	0.02	2.71	51.58
Oxidized & mineralized marble (n=19) MnO between 0.2 and 40.0 wt%	12.44	3.78	3.92	3.52	38.37

distribution. Apparently, their distribution shows a consistent behaviour with respect to temperature of formation versus stratigraphical depth. Most, if not all deposits were formed syn-magmatic (porphyry copper), syn-shearing (Stanos, Pirinia) to slightly later post-shearing syn-block faulting (Zepkos) and late, supergene (Varvara, Piavitza).

The observed regional and local element distributions are closely related to the proposed metallogenetic framework. The mesothermal Pirinia-type sulphide mineralizations, for example, are surrounded by narrow geochemical haloes with anomalous K, Rb, Cr, Cu and Zn. The restricted lateral extent of these haloes complies well with the earlier conclusion that this type of mineralization was developed during a short-lived hydrothermal period. The supergene Mn oxide mineralizations, in contrast, are accompanied by much wider alteration haloes with Mn, Fe and Si, extending several hundreds of meters away from the mineralizations (Hellingwerf 1991).

NEW EXPLORATION TARGETS

Two new target areas, one for epithermal, polymetallic sulphides and one for Mn oxides, were discovered applying the above metallogenetic model. The "Papades" sulphide prospect (Hellingwerf 1992A) is situated along the Zepkos-



Fig. 4: Proposed metallogenetic framework after Hellingwerf (1992A), based on information from Arvanitidis, Constantinides, Diakakis, Galanopoulos, Kalogeropoulos, Kougoulis, Stephanides, Theodoroudis, Veranis (all IGME), and Nebel et al (1991)

Stratoniki structural zone (Fig. 1). Rhodochrosite, bluish-white chalcedony, pyrite disseminations and sphalerite occur only in 0.2 - 2 m wide fault and shear zones in the NE part of this zone, whereas Mn oxides predominate in the SW parts. The Papades prospect contains silicification zones with pyrite disseminations, chalcedony, vuggy quartz and colloidal Mn oxides cut by thin quartz veins in 0.2 to 1 m wide zones. The host rock schists, aplites and pegmatites are commonly strongly kaolinized.

The Mn oxide target has been outlined in an early stage by remote sensing and digital mapping carried out by GEOREM AB (Nyborg et al 1992; Hellingwerf 1992A; Hellingwerf & Arvanitidis 1993), and in a later stage by a regional geochemical survey. A detailed field check revealed the presence of finegrained to earthy Mn oxides in cleavages and along foliations of (shear-) banded marble, with simultaneous generation of white, secondary calcite. This type of Mn mineralization is identical to that occurring in the Mn deposits of Varvara, Piavitza and Stratoniki.

CONCLUSIONS

- There is good evidence that the polymetallic sulphide ores of Olympias and Madem Lakkos are of epigenetic origin, coeval with kaolinization of pegmatites and aplites.

- In Mn oxide mineralizations the carbonate fabric is commonly replaced by contemporaneous silica and Mn oxides in a kaolinized environment. Thus, there seems to be a genetic link between regional kaolinization, liberation of surplus silica, epithermal-supergene silicification, and supergene Mn oxide deposition.

- On a regional scale elevated Mn concentrations reflect the proximity of Mn oxide deposits, while haloes of dedolomitization surround the marble-hosted mineralizations.

- On a local scale K₂O, Rb and Li are enriched whereas Mn and Sr are depleted approaching supergene Mn oxide mineralizations.

- The Papades prospect along the Zepkos-Stratoniki structural zone should be investigated more closely.

- A number of regional distribution patterns - those of SiO_2 , MnO, K_2O , Cr, Cu, Zn, Pb, Ba and Sr - suggest that the Pappa Choravi domain, north of Varvara, is an interesting target area for base metal sulphides at depth.

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