



## Spheroidal and radiating aggregates of Mn-pyroxenoids in the Olympias carbonate-hosted polymetallic sulphide ore deposit, E. Chalkidiki peninsula, N. Greece

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## Сфероидални и радиални агрегати от Mn-пироксеноиди от вместиеното в карбонатни скали полиметално сулфидно находище Олимпия, И. Халкидики, С. Гърция

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**Абстракт.** За първи път са изследвани съставът и текстурните особености на съвместно срещашите се Mn-силикати и карбонати в полиметалното сулфидно находище Олимпия, Източен Халкидики, Северна Гърция. Mn-пироксеноиди се срещат като сфероидални образувания със светлорозов до кафеникаво-розов цвят, състоящи се от радиално разположени призматични до иглести кристали в матрица от розови карбонати, калцит и кварц. Находище Олимпия е вместиено в мраморите на формацията Кердия, а рудната минерализация е свързана с терциерната хидротермалната дейност в областта. Електронно-сондови микроанализи на Mn-пироксеноиди установиха състави, попадащи в полетата на родонита и пироксмангита с молни компоненти на  $\text{MnSiO}_3$  – 82 до 90%,  $\text{CaSiO}_3$  – 2 до 9%,  $\text{FeSiO}_3$  – 3 до 12% и  $(\text{Mg}+\text{Ni})\text{SiO}_3$  – 1 до 5%. Съвместното съществуване на двата Mn-пироксеноида може да се обясни с промяната във времето на P, T и активността на компонентите в разтвора. Розовата карбонатна фаза е Mn-Mg-Fe-Ca твърд разтвор, богат на родохрозитова компонента (72–84 mol.%), значителна калцитова (9–25 mol.%) и подчинени, но променливи магнезитова (1–5 mol.%) и сидеритова (1–4 mol.%) Родохрозитът и кварцът са образувани за сметка на Mn-пироксеноиди; процесът може да бъде описан с реакцията  $\text{MnSiO}_3+\text{CO}_2=\text{MnCO}_3+\text{SiO}_2$ , която се осъществява в наситена с  $\text{CO}_2$  обстановка и понижаваща се температура.

Сфероидалните форми и радиалната структура на Mn-пироксеноиди отразяват растеж в отворено пространство (пукнатини) при постъпване на еднакъв материал от всички посоки и предпочитана ориентировка на кристалите върху сферична подложка.

**Ключови думи:** Mn-пироксеноиди, родохрозит, минерален химизъм, рудно находище Олимпия, Гърция.

**Abstract.** The composition and the textural features of coexisting Mn-silicates and carbonates in the Olympias polymetallic sulphide ore deposit, E. Chalcidiki peninsula, N. Greece are studied for the first time. Mn-pyroxenoids are locally found as spheroidal forms of light pink to brownish-pink color and consisting of radiating, prismatic to fibrous crystals within a matrix of pink-carbonates, calcite and quartz. The Olympias deposit is hosted within marbles of the Kerdylia Formation and the ore mineralization is related to the hydrothermal activity of the Tertiary magmatism in the broader area. Electron microprobe analyses on the Mn-pyroxenoids yielded compositions overlapping the fields of rhodochrosite and pyroxmangite, with molecular components  $\text{MnSiO}_3$  – 82 to 90%,  $\text{CaSiO}_3$  – 2 to 9%,  $\text{FeSiO}_3$  – 3 to 12% and  $(\text{Mg}+\text{Ni})\text{SiO}_3$  – 1 to 5%. Temporal changes in P, T and the activity of solution components can explain the coexistence of the two Mn-pyroxenoids. The pink carbonate phase is a Mn-Mg-Fe-Ca solid solution rich in rhodochrosite component (72–84 mol.%) with significant calcite (9–25 mol.%) and minor but variable magnesite (1–5 mol.%) and siderite (1–4 mol.%) end members. Rhodochrosite and quartz were formed at the expense of Mn-pyroxenoids and this process can be described by the model reaction  $\text{MnSiO}_3+\text{CO}_2=\text{MnCO}_3+\text{SiO}_2$  which took place in a  $\text{CO}_2$ -saturated environment and dropping temperature.

The spheroidal forms and radiating structure of Mn-pyroxenoids expresses a growth in open space (fissures) from a uniform supply of material to all directions and a preferred orientation of crystals to a spherical end edifice.

**Key words:** Mn-pyroxenoids, rhodochrosite, mineral chemistry, Olympias ore deposit, Greece.

## Introduction

A variety of manganese silicates of the  $RSiO_3$  type (pyroxenoids) are common constituents of the Mn silicate-carbonate rocks, metamorphosed from greenschists to the granulite facies (Roy, Purkait, 1968; Peters et al., 1978; Aikawa et al., 1979; Brown et al., 1980; Ashley, 1989; Yui et al., 1989; Abrecht, 1990; Cabella et al., 1991; Dasgupta et al., 1993; Jimémez-Millan, Velilla, 1994; Mücke et al., 2001; Mohapatra, Nayak, 2005). Besides, the manganeseiferous pyroxenoids rhodonite and its polymorph pyroxmangite occur as important and abundant primary manganese minerals in various types of ore deposits, such as hydrothermal polymetallic vein-type, skarn-type and metamorphosed manganese ores (Hodgson, 1975; Peacor et al., 1978; Winter et al., 1981; Sapountzis, Christofides, 1982; Abrecht, 1985, 1989; Damman, 1989; Dasgupta et al., 1990; Michailidis et al., 1995).

A number of works have addressed data concerning temperature, pressure and compositional stability limits that exist for each pyroxenoid structure (Peters, 1971; Akimoto, Syono, 1972; Ito, 1972; Abrecht, Peters, 1975; Maresch, Mottana, 1976; Ohashi, Finger, 1975; Peters et al., 1973, 1978; Brown et al., 1980; Abrecht, 1988; Pinckney, Burnham, 1988; Takahashi, Hariya, 1995). Furthermore, few reports of coexisting rhodonite and pyroxmangite in nature are available in literature (Trommsdorf et al., 1970; Oashi, Finger, 1975; Peters et al., 1978; Aikawa, 1979; Tracy et al., 1980; Winter et al., 1981; Veblen, 1985).

In this investigation the presence of spheroidal forms of Mn-pyroxenoids (rhodonite and pyroxmangite) found within the marble hosted Olympias polymetallic sulphide ore deposit, E. Chalkidiki peninsula, N. Greece, is studied for the first time.

## Geologic setting of the Olympias ore deposit

The Olympias polymetallic sulphide ore deposit is located 5 km west of the town of Olympias, in the E. Chalkidiki peninsula, northern Greece (Fig. 1). It is hosted within calcitic-rhodochrositic marbles of the Paleozoic or older Kerdylia Formation of the Serbomacedonian massif (Kockel et al., 1977). The geologic environment of the ore also comprises migmatized biotite-hornblende gneisses and amphibolites. These rocks have been regionally deformed and metamorphosed to amphibolite facies. This event in the Kerdylia Formation seems to have lasted until the early Tertiary and culminated in anatexis and calc-alkaline magmatism. These phenomena are represented by deformed and undeformed varieties of pegmatite-aplites, lamprophyre dikes, the 29.6 Ma Stratoni granodiorite, and porphyritic stocks (Papadakis, 1972; Kalogeropoulos et al., 1989).

The Olympias deposit is generally stratabound (manto) or fracture controlled and in places strati-

form; it strikes NNW for 1500 m, dips 30 to 35° SW to a depth of at least 300 m, and has an average thickness of 12 m. It develops within a lower marble horizon along the contact with an overlying unit of biotite gneiss. The ore occurs in undeformed and deformed varieties. The former predominates and is present in several forms such as cavity- and fracture-filling, banded or disseminated. The deformed ore is limited in quantity and occurs banded or in veins exhibiting shear folding and brecciation (Kalogeropoulos et al., 1989).

Most studies on the Olympias deposit are mainly concerned with the ore minerals and the origin of mineralization in the broader area. There exists a close relationship between marbles and mineralization and the ore textures confirm a successive replacement of the marbles by metallic and non metallic minerals.

The origin of the Olympias and the neighbouring Madem Lakkos ore deposits, however, are subject to controversy. Nicolaou and Kokonis (1980), Kalogeropoulos et al. (1989) and Gilg et al. (1992) supported a metasomatic replacement origin related to the hydrothermal activity of the Stratoni granodi-



Fig. 1. Location map of the Olympias and Madem Lakkos mines, Chalkidiki peninsula, Northern Greece

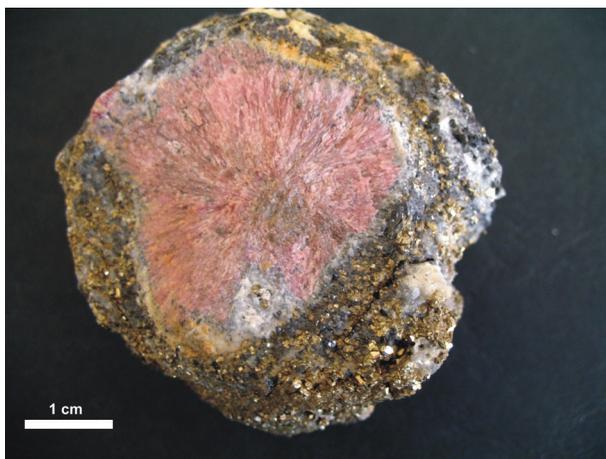
Фиг. 1. Карта на разположението на мините Олимпия и Мадем Лакос, Халкидики, Северна Гърция

orite and the associated pegmatite-aplitic formations. Nebel et al. (1991) distinguished a premetamorphic syngenetic massive ore type from a postmetamorphic, disseminated and skarn ore type. The massive ore was subsequently regionally metamorphosed and later reworked by Tertiary hydrothermal activity related to igneous rocks in the broader area. Gilg and Frei (1994) also favored an epigenetic origin of the ores and a genetic relationship to the emplacement of Tertiary porphyritic stocks in the area of Eastern Chalkidiki.

## Mineralogy

The mineralogy of the Olympias ore deposit was first described by Nicolaou and Kokonis (1980). Fe, Zn, Pb, Cu, As and Sb sulphides and sulphosalts are the paramount components including the minerals pyrite, sphalerite, galena, arsenopyrite, chalcopyrite, tetrahedrite, boulangerite, bournonite, pyrrhotite, enargite, geochronite and native gold. The principal syn-ore gangue minerals are calcite, quartz, rhodochrosite and minor Mn-pyroxenoids.

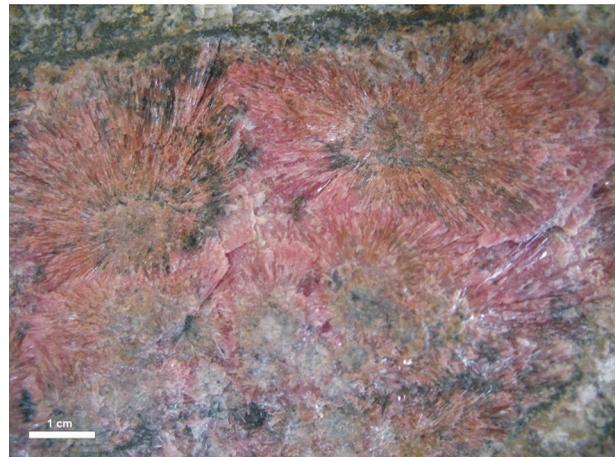
Characteristic spheroidal forms of light-pink to brownish-pink color were locally found in the Olympias deposit within either metallic or gangue mineral assemblages (Fig. 2). The size of the spherules varies between 1 and 5 cm across. They occur as isolated or in three-dimensional clusters of many spherules (Fig. 3). Macroscopically, as well as under the optical microscope or the electron microscope the spherules are consisting of an intimate intergrowth of radiating long prismatic to fibrous crystals of Mn-pyroxenoids in a matrix of pink carbonates (rhodo-



**Fig. 2.** Hand specimen from the Olympias ore deposit with an isolated spheroid consisting of radiating aggregates of Mn-pyroxenoids

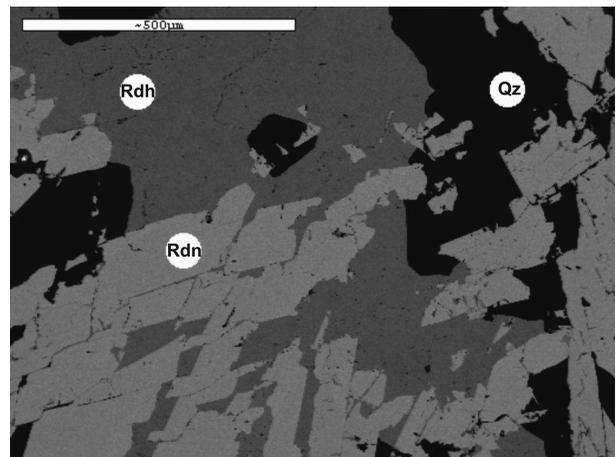
**Фиг. 2.** Образец със сфероиди от радиално-лъчести агрегати от Мп-пироксеноиди от рудно находище Олимпия

chrosite), calcite and quartz. Rhodochrosite forms complex intergrowths with quartz at the expense of Mn-pyroxenoids (Fig. 4). A decomposition of Mn-pyroxenoids is indicated by the corrosion of prism end faces that produces teethlike forms. Traces of ore minerals in minute crystals are also found dispersed



**Fig. 3.** Hand specimen from the Olympias ore deposit with clusters of spheroidal and radiating aggregates of Mn-pyroxenoids

**Фиг. 3.** Образец с натрупвания от сфероидални и радиално-лъчести агрегати от Мп-пироксеноиди от рудно находище Олимпия



**Fig. 4.** Backscattered electron micrograph of Mn-pyroxenoids crystals (Rdn) associated with rhodochrosite (Rdh) and quartz (Qz)

Note the replacement textures between rhodochrosite and the Mn-pyroxenoids

**Фиг. 4.** Снимка в обратно-отразени електрони на кристали от Мп-пироксеноиди (Rdn), асоцииращи с родохрозит (Rdh) и кварц (Qz)

Обърнете внимание на структурите на заместване между родохрозит и Мп-пироксеноиди

within the spheroidal forms. Sometimes, the color of the Mn-pyroxenoids is covered with brown or black oxidation products. Secondary oxidation products are also present on joint and cracks of manganese silicate and carbonate minerals.

A manganese oxide mineralization covers the upper parts of the Olympias deposit constituting probably the product of supergene oxidation of rhodochrosite, which is an important component in the primary sulphide ore at deeper levels. Supergene-derivative manganese deposits were mined at several locations, though these mines are all closed now.

The Olympias deposit was considered as one of the greatest polymetallic sulphide deposits in Europe. The ore reserves were calculated to be about 10 million tons with average grades of 3.6 wt.% Pb, 4.5 wt.% Zn, 17 wt.% S, 2.4 wt.% As, 0.19 wt.% Cu, 0.15 wt.% Sb, 130g/t Ag and 7g/t Au. The concession now belongs to the "Hellenic Gold" mining company.

However, this mine has gradually closed down for economical and environmental reasons.

## Mineral chemistry

### Analytical methods

Chemical compositions of co-existing Mn-pyroxenoids and carbonates in the Olympias ore deposit were determined by a CAMECA-CAMEBAX electron microprobe at the Department of Geology, University of Manchester, U.K. This instrument is fitted with two wavelength dispersive spectrometers (WDS) and a Link Systems 860-500 Energy dispersive spectrometer (EDS). Operating conditions were 15 kV accelerating potential and 3 nA beam current. Natural minerals or pure metals were used as standards. Element concentrations were calculated with ZAF-4FL software provided by LINK systems. Scanning electron microscope (SEM) studies were performed on a JEOL JSM-840A at the University of Thessaloniki. Representative analyses of the minerals, the cation proportions on the basis of 6 oxygens (pyroxenoids) and 3 oxygens (carbonates) and the molecular percentages are presented

Table 1

Representative electron probe microanalyses of Mn-pyroxenoids from Olympias ore deposit (wt.%)

Таблица 1

Представителни микросондови анализи на Mn-пироксеноиди от находище Олимпия (wt.%)

Sample	1	2	3	4	5	6	7	8	9	10	11	12
SiO <sub>2</sub>	46.66	46.10	46.32	46.21	46.38	46.22	46.64	46.21	46.37	46.53	46.47	46.13
Al <sub>2</sub> O <sub>3</sub>	0.07	0.00	0.07	0.02	0.11	0.07	0.00	0.12	0.00	0.01	0.00	0.00
FeO*	2.99	2.40	2.64	3.32	2.42	2.94	2.67	2.49	2.88	6.06	3.71	5.98
MnO*	47.59	47.97	47.83	47.77	48.03	48.50	49.33	48.21	48.46	45.69	47.97	44.52
MgO	1.09	0.50	0.74	0.83	1.38	0.36	0.41	1.40	1.24	1.12	1.19	1.09
NiO	0.00	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.18	0.04	0.00
CaO	2.07	2.36	2.34	1.99	1.80	1.83	1.71	1.26	1.22	0.90	1.30	1.59
Na <sub>2</sub> O	0.22	0.00	0.00	0.00	0.00	0.20	0.03	0.00	0.00	0.00	0.00	0.00
Total	100.69	99.41	99.94	100.14	100.12	100.12	100.79	99.69	100.17	100.49	100.68	99.31
Number of ions on the basis of 6 oxygens												
Si	1.995	2.001	1.994	1.994	1.992	1.998	1.999	1.994	1.994	1.999	1.993	1.998
Al	0.003	0.000	0.003	0.001	0.006	0.003	0.000	0.006	0.000	0.001	0.000	0.000
Fe <sup>2+</sup>	0.107	0.087	0.095	0.120	0.087	0.106	0.096	0.090	0.103	0.218	0.133	0.217
Mn	1.724	1.764	1.746	1.746	1.747	1.776	1.790	1.762	1.765	1.663	1.743	1.633
Mg	0.069	0.033	0.048	0.054	0.088	0.023	0.026	0.090	0.080	0.072	0.076	0.070
Ni	0.000	0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.006	0.001	0.000
Ca	0.095	0.110	0.108	0.092	0.082	0.085	0.078	0.058	0.056	0.041	0.060	0.074
Na	0.018	0.000	0.000	0.000	0.000	0.017	0.000	0.000	0.000	0.000	0.000	0.000
Sum	4.011	3.998	3.997	4.007	4.002	4.008	3.989	4.000	3.998	4.000	4.006	3.992
Molecular ratio												
FeSiO <sub>3</sub>	5.36	4.36	4.76	5.96	4.34	5.33	4.82	4.50	5.14	10.90	6.61	10.88
MnSiO <sub>3</sub>	86.42	88.33	87.43	86.78	87.18	89.25	89.95	88.10	88.07	83.15	86.59	81.90
(Mg,Ni)SiO <sub>3</sub>	3.46	1.80	2.40	2.68	4.39	1.16	1.31	4.50	3.99	3.90	3.83	3.51
CaSiO <sub>3</sub>	4.76	5.51	5.41	4.57	4.09	4.27	3.92	2.90	2.79	2.05	2.98	3.71
X <sub>Ca</sub>	0.048	0.055	0.054	0.046	0.041	0.043	0.039	0.029	0.028	0.021	0.030	0.037

\* Total iron and manganese as FeO and MnO respectively

Table 2

Representative electron probe microanalyses of rhodochrosites from Olympias ore deposit (wt.%)

Таблица 2

Представителни микросондови анализи на родохрозит от находище Олимпия (wt.%)

Sample	1	2	3	4	5	6	7	8	9	10	11	12
MnO*	52.73	49.57	46.61	47.19	51.38	45.98	49.09	45.91	48.92	45.47	51.80	50.54
CaO	4.45	9.42	11.92	11.43	5.38	12.83	6.92	9.67	6.82	9.45	4.64	4.64
MgO	1.35	0.47	0.49	0.43	1.09	0.29	1.91	1.52	1.52	1.64	1.51	1.66
FeO*	2.06	0.77	1.27	0.79	2.49	1.25	2.28	1.82	2.86	2.72	2.40	2.56
ZnO	0.00	0.03	0.01	0.26	0.35	0.18	0.28	0.11	0.23	0.37	0.08	0.50
CuO	0.00	0.00	0.03	0.11	0.16	0.00	0.01	0.26	0.27	0.14	0.36	0.46
NiO	0.00	0.00	0.00	0.00	0.00	0.04	0.09	0.22	0.08	0.37	0.13	0.00
CO <sub>2</sub>	38.89	39.09	39.61	39.41	39.08	39.82	39.59	40.08	39.43	39.59	39.22	38.95
Total	99.48	99.35	99.94	99.62	99.93	100.39	100.17	99.60	100.13	99.75	100.14	99.31
Number of ions on the basis of 3 oxygens												
Mn	0.840	0.786	0.730	0.743	0.815	0.716	0.770	0.727	0.770	0.713	0.819	0.806
Ca	0.090	0.189	0.236	0.228	0.108	0.253	0.137	0.194	0.136	0.188	0.093	0.094
Mg	0.037	0.013	0.014	0.012	0.031	0.008	0.053	0.042	0.042	0.045	0.042	0.047
Fe	0.033	0.012	0.020	0.012	0.039	0.020	0.035	0.029	0.044	0.042	0.038	0.040
Zn	0.000	0.000	0.000	0.004	0.005	0.002	0.004	0.001	0.003	0.005	0.001	0.007
Cu	0.000	0.000	0.000	0.002	0.002	0.000	0.000	0.004	0.004	0.002	0.005	0.006
Ni	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.003	0.001	0.005	0.002	0.000
Sum	1.000	1.000	1.000	1.001	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Molecular ratio												
MnCO <sub>3</sub>	84.03	78.64	73.01	74.68	82.14	71.78	77.29	73.03	77.51	71.78	82.44	81.69
CaCO <sub>3</sub>	8.97	18.91	23.61	22.89	10.88	25.34	13.77	19.48	13.66	18.89	9.34	9.49
(Mg,Ni)CO <sub>3</sub>	3.73	1.28	1.40	1.19	3.07	0.92	5.40	4.57	4.36	5.09	4.44	4.73
FeCO <sub>3</sub>	3.27	1.17	1.98	1.24	3.91	1.95	3.53	2.86	4.46	4.25	3.77	4.09
X <sub>Ca</sub>	0.048	0.055	0.054	0.046	0.041	0.043	0.039	0.029	0.028	0.021	0.030	0.037

\* Total iron and manganese as FeO and MnO respectively

in Tables 1 and 2. Total Fe and Mn were calculated as Fe<sup>2+</sup> and Mn<sup>2+</sup> respectively, because ferric iron and trivalent manganese contents are usually low for Mn-pyroxenoids and carbonates. Carbon dioxide (CO<sub>2</sub>) was calculated according to the formula of the respective carbonate mineral.

X-ray powder diffraction (XRPD) was performed using an X-ray diffractometer (Philips PW 1710) with CuK $\alpha$  radiation ( $\lambda=0.154\text{nm}$ ) and 35 kV, 25 mA.

## Mn-pyroxenoids

Rhodonite and pyroxmangite constitute polymorphs of MnSiO<sub>3</sub> with varying amounts of Ca<sup>2+</sup>, Fe<sup>2+</sup> and Mg<sup>2+</sup> substituting for Mn<sup>2+</sup> and they were found to occur in intimate intergrowth in specimens from Broken Hill, Australia (Burell, 1942; in Deer et al., 1963).

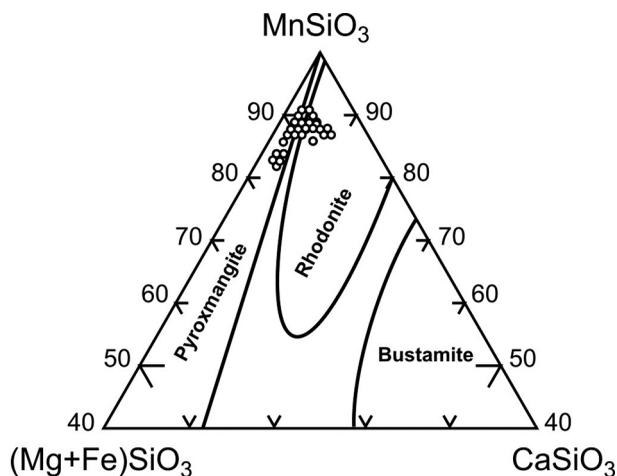
Among the natural rhodonites the maximum contents of Ca<sup>2+</sup>, Fe<sup>2+</sup> and Mg<sup>2+</sup> are about 20 mol.% as CaSiO<sub>3</sub>, about 26 mol.% as FeSiO<sub>3</sub> and about 15 mol.% as MgSiO<sub>3</sub>, respectively (Momoi, 1964).

The chemical data of the studied Mn-pyroxenoids were plotted on the ternary MnSiO<sub>3</sub>-CaSiO<sub>3</sub>-(Mg, Fe)SiO<sub>3</sub> diagram (Fig. 5). From this diagram results that the analyzed Mn-pyroxenoids span the rhodonite-pyroxmangite fields, which were well defined by plotting natural rhodonite and pyroxmangite compositions on the ternary diagram (Ohashi et al., 1975).

Because of the close similarity in composition most of the strong peaks of the studied rhodonite and pyroxmangite overlap to some extent (Fig. 6) and thus the distinction between them in the X-ray diffraction pattern is difficult. High-resolution transmission electron microscopy (HRTEM) and electron diffraction studies of the Mn-pyroxenoids described in this paper are in progress to determine their structures and probable replacement mechanisms.

When natural pyroxenoids are found in the system (Mn, Ca, Mg, Fe)SiO<sub>3</sub>, the coexisting pyroxmangite and rhodonite pairs represent the mutual solubility limit of elements in the two phases.

In the studied Mn-pyroxenoids the variation in the molecular components are as follows (in mol.%):



**Fig. 5. Plot of the Olympias deposit Mn-pyroxenoid chemical compositions on the ternary diagram of the  $MnSiO_3$ – $(Mg+Fe)SiO_3$ – $CaSiO_3$  system**

Compositional fields for respective minerals are from Ohashi et al. (1975)

**Фиг. 5. Химичен състав на Mn-пироксеноиди от находище Олимпия в тройната диаграма на системата  $MnSiO_3$ – $(Mg+Fe)SiO_3$ – $CaSiO_3$**

Полето на съставите на съответните минерали са по Ohashi et al. (1975)

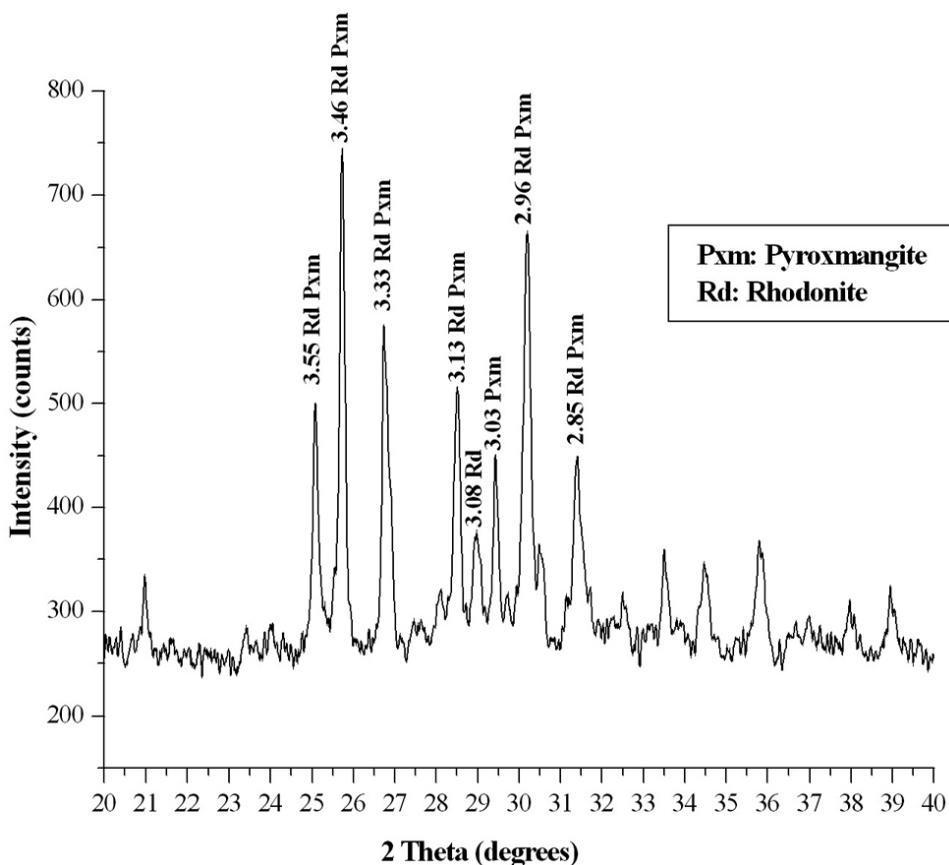
rhodonite – 85.01–89.95  $MnSiO_3$ , 3.61–8.55  $CaSiO_3$ , 3.24–5.96  $FeSiO_3$ , 1.00–4.79  $(Mg, Ni)SiO_3$ , 0.036–0.085 XCa; pyroxmangite – 81.54–89.54  $MnSiO_3$ , 2.05–3.71  $CaSiO_3$ , 4.24–11.56  $FeSiO_3$ , 2.68–5.15  $(Mg, Ni)SiO_3$ , 0.021–0.037 XCa.

The wollastonite component ( $CaSiO_3$ ) is on average higher in the rhodonite, while the ferrosilite ( $FeSiO_3$ ) and enstatite ( $(Mg, Ni)SiO_3$ ) components are higher in pyroxmangite. Besides, the enstatite component is smaller than the ferrosilite in both minerals.

In his important mineralogical study of rhodonites and pyroxmangites from Japan, Momoi (1964), discussed their chemical characteristics with special reference to the Ca contents, because this element plays an important role in their structure. The plot of the chemical data obtained from the studied Mn-pyroxenoids on the Momoi's  $CaSiO_3$ – $MnSiO_3$ ,  $CaSiO_3$ – $FeSiO_3$  and  $CaSiO_3$ – $MgSiO_3$  diagrams (Fig. 7 a–c) showed that:

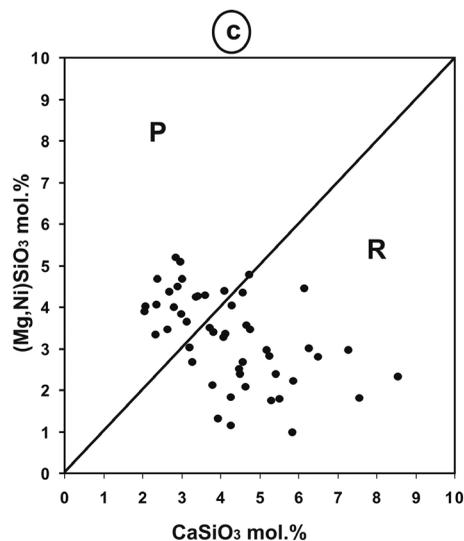
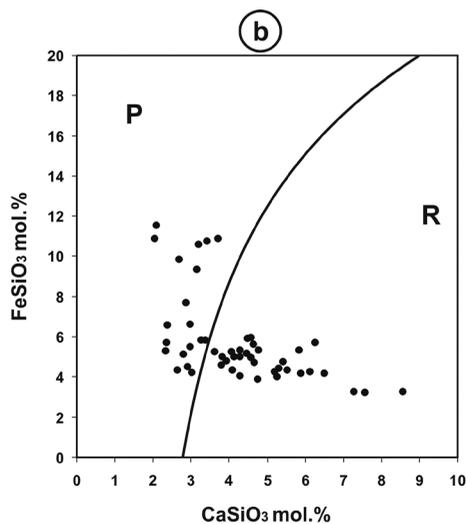
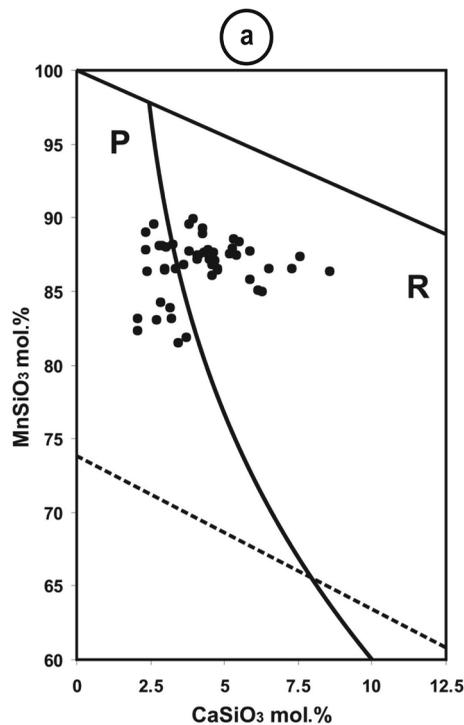
a. The variation of manganese component is more remarkable in pyroxmangite than in rhodonite. The decrease of Mn content with increasing of Ca is more remarkable in pyroxmangite than in rhodonite (Fig. 7a).

b. Iron contents remarkably vary in pyroxmangite than in rhodonite. Besides, pyroxmangite contains more iron and rhodonite more calcium (Fig. 7b).



**Fig. 6. X-ray diffraction pattern of Mn-pyroxenoids from the Olympias ore deposit**

**Фиг. 6. Дифрактограма на Mn-пироксеноиди от находище Олимпия**



**Fig. 7. Relations between: a)  $\text{MnSiO}_3$  and  $\text{CaSiO}_3$ , b)  $\text{FeSiO}_3$  and  $\text{CaSiO}_3$ , and c)  $\text{MgSiO}_3$  and  $\text{CaSiO}_3$  in the studied Mn-pyroxenoids from the Olympias ore deposit**

The compositional boundaries between rhodonite (R) and pyroxmangite (P) are after Momoi (1964)

**Фиг. 7. Връзка между: а)  $\text{MnSiO}_3$  и  $\text{CaSiO}_3$ , б)  $\text{FeSiO}_3$  и  $\text{CaSiO}_3$ , и в)  $\text{MgSiO}_3$  и  $\text{CaSiO}_3$  в изследваните Мн-пироксеноиди от находище Олимпия**

Границите в състава между родонита и пироксмангита са по Momoi (1964)

c. Magnesium slightly decreases with increasing of calcium content in both minerals. However, pyroxmangite contains more magnesium and rhodonite more calcium (Fig. 7c).

The variation in calcium content of the studied Mn-pyroxenoids is well expressed by the  $X_{\text{Ca}}$  (where  $X_{\text{Ca}} = \text{Ca}/(\text{Ca} + \text{Mn} + \text{Mg} + \text{Fe} + \text{Ni})$ ) values, which were found within the range 0.04 to 0.09 and 0.02 to 0.04 for rhodonite and pyroxmangite, respectively.

## Carbonates

The pink carbonate phase in the Olympias ore deposit is a Mn-Ca-Mg-Fe solid solution rich in rhodochrosite component (71.78–84.03 mol.%) with significant calcite (8.97–25.34 mol.%) and siderite (0.58–4.46 mol.%) end members. The  $X_{\text{Ca}}$  varies within the range 0.09 to 0.25.

## Discussion

Two main problems arise for the genesis of the studied Mn-pyroxenoids, namely the formation of spheroids with radiating texture and the physicochemical conditions prevailing during mineral assemblages formation.

Radial structures and concentric banding are common features in most colloform minerals and the dominant factor controlling their formation is a relatively high degree of supersaturation, resulting in relatively high rates of nucleation and crystallization (Roedder, 1968). Ramdohr (1969), however, stated that radial growth of crystals, particularly in an open space, derives from a more or less uniform supply of material from all directions, acting in conjunction with a preferred growth direction in the crystal to promote a spherical or globular growth. The radial growth structures in the studied Mn-pyroxenoids rather suggest infiltration along discrete pathways (fissures), with rhodonite nucleation along these paths and subsequent growth in all direction by grain boundary diffusion (Abrecht, 1985).

The predominant aspect for the origin of the Olympias deposit ore mineralization is the infiltration

of hydrothermal fluids related to the emplacement of magmatic rocks into the host marbles. Manganese is one of the metals that are strongly concentrated in the aqueous phases derived from acid magmas (Holland, 1972). The observed replacement phenomena in marble host rocks as well as cavity- and fracture-filling forms are clearly indicative of a hydrothermal activity. Besides, the scatter of  $X_{Ca}$  in rhodochrosite suggests a changing T and/or  $X_{CO_2}$  environment during ore deposition (Abrecht, 1989) and further supports a hydrothermal origin.

The magmatic origin of the Olympias deposit is supported by oxygen isotope evidence (Kalogeropoulos, Kiliyas, 1989) as well as by the similarity of the Olympias mineralizing fluids, in terms of salinity-temperature gradients, with other Pb-Zn mineralizing fluid gradients formed in "granite"-related environments (Kiliyas et al., 1995).

Fluid inclusion systematics on syn-ore gangue quartz of the Olympias deposit (Kiliyas et al., 1996) may be explained by trapping during unmixing of an aqueous, high-temperature,  $CO_2$ -bearing fluid of low salinity. Fluid unmixing, and concomitant ore-mineralization, took place at temperatures of  $350 \pm 30$  °C and fluctuating pressures of less than 500 bar.

Natural assemblages and experimental data (Abrecht, 1988; Takahashi, Hariya, 1995; Mohapatra, Nayak, 2005), suggest that the relative stability of Mn-pyroxenoids is a function of pressure and temperature as well as of the chemistry, especially of the Ca/Ca+Mn ratio and the  $CO_2$  content of the fluid phase. Thus, rhodonite structure is stabilized with respect to pyroxmangite by Ca, whereas Fe and Mg increase the stability of pyroxmangite with respect to rhodonite. Experimental work by Maresch and Mottana (1976) on the phase relations in the system  $MnSiO_3$ - $MgSiO_3$ - $SiO_2$ - $H_2O$  showed that polymorphism between the two pyroxenoids may exist. Besides, pyroxmanganite of  $MnSiO_3$  composition was shown to be the high-P, low-T polymorph with respect to rhodonite of the same composition, and it was the stable phase at atmospheric pressure, below 350–405 °C. Although the possibility of applying the experimental results to natural systems is very limited, because of the great extent and variety of cationic substitutions possible in natural Mn-pyroxenoids the conditions of formation estimated by the fluid inclusion systematics (Kiliyas et al., 1996) of the Olympias deposit are consistent with the experimental work of Maresch and Mottana (1976).

Thus, temporal changes in the activity of solution components can explain the coexistence of the two Mn-pyroxenoids in the Olympias ore deposit.

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Mineral reactions in Mn silicate and carbonate associations were interpreted to be of decarbonation type (Dasgupta et al., 1993) depending on the  $CO_2$  activity and the bulk element composition of the mineralizing fluids.

Mutual boundaries of the associated minerals show that rhodochrosite and quartz were formed as younger phases and include corroded crystals of Mn-pyroxenoids in teethlike forms. These replacement textures can be expressed by the reverse reaction to that proposed by Abrecht (1988), i.e.  $MnSiO_3 + CO_2 = MnCO_3 + SiO_2$ , in a  $CO_2$ -saturated environment and dropping temperature.

Therefore, the following scenario was proposed for the explanation of the Mn silicate and carbonate associations. Rhodonite was first formed, followed by pyroxmanganite during dropping temperature and relative increasing concentration of Fe and Mg in the mineralizing fluids. Rhodochrosite and quartz originated by a "carbonatization" process in  $CO_2$ -saturated environment and further dropping temperature.

## Conclusions

The presence of characteristic spheroidal and radiating aggregates of Mn-pyroxenoids in the carbonate-hosted Olympias ore deposit (Chalkidiki peninsula, N. Greece) was studied. They are locally found as isolated or in three-dimensional clusters of many spherules, within either metallic or gangue mineral assemblages. Textural features showed that rhodochrosite and quartz were formed at the expense of Mn-pyroxenoids. Mn-pyroxenoids compositions overlap the field of rhodonite and pyroxmangite on the ternary diagram of the  $MnSiO_3$ -(Mg,Fe) $SiO_3$ - $CaSiO_3$  system. The spheroidal forms and radiating structure of Mn-pyroxenoids denote a growth in open space, a uniform supply of material and a preferred orientation of the crystals. Temporal change in P, T, and the activity of solution components can explain the coexistence of the two Mn-pyroxenoids.

Rhodonite was first formed followed by pyroxmanganite as temperature dropped and the concentration of Fe and Mg in the mineralizing fluids increased. Rhodochrosite and quartz associated with Mn-pyroxenoids originated by a "carbonatization" process in  $CO_2$ -saturated environment and further dropping temperature.

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