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Fe-CARPHOLITE IN CHLORITOID-BEARING METAPELITES-METASANDSTONES OF SKOPELOS ISLAND, N. SPORADES, GREECE

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A B S T R A C T

In Skopelos island, Panormos area, Fe-carpholite was found in chloritoid-bearing metapelites-metasandstones which belong geologically to the Mesoautochthonous Complex of the Pelagonian Zone. The mineral assemblages of the metaclastic sediments (Fe-chloritoid±Fe-carpholite-sericite-chlorite-pyrophyllite-quartz ±Cr-spinel±rutile) and those of the adjacent metabauxites (chlorite-diaspore-hematite-rutile, chloritoid-diaspore-pyrophyllite-hematite-rutile, chlorite-diaspore-rutile) suggest metamorphic conditions of blueschist facies. Fe-carpholite formed according to the reaction: pyrophyllite+chlorite+H_2O=carpholite+quartz and Fe-chloritoid by decreasing f_{H2O} with advancing metamorphic grade. Lower pressure limits of metamorphism were 4 kbar whereas upper pressure limits cannot be determined; due to lack of critical mineral parageneses. Temperatures of metamorphism ranged between 300° and 330°C (or 370°C).

Π Ε Ρ Ι Λ Η Ψ Η

Στη νήσο Σκόπελο, περιοχή Πανόρμου, σιδηρούχος καρφόλιθος βρέθηκε σε χλωριτοειδούχα μεταπηλιτικά-μεταψαμμιτικά πετρώματα τα οποία ανήκουν γεωλογικά στο Μεσοαυτόχθονο Σύμπλεγμα της Πελαγονικής ζώνης. Τα ορυκτολογικά αθροίσματα που χαρακτηρίζουν τα μετακλαστικά ιζήματα (Fe-καρφόλιθος±Fe-χλωριτοειδής-σερικίτης-χλωρίτης-πυροφυλλίτης-χαλαζίας±Cr-σπινέλιος±ρουτίλιο) καθώς και αυτά των γειτονικών μεταβωξιτών (χλωρίτης-διάσπορο-αιματίτης-ρουτίλιο, χλωριτοειδής-διάσπορο-πυροφυλλίτης-αιματίτης-ρουτίλιο, χλωρίτης-διάσπορο-ρουτίλιο) υποδεικνύουν συνθήκες μεταμόρφωσης κυανοσχιστολιθικής φάσης. Ο σιδηρούχος καρφόλιθος σχηματίστηκε σύμφωνα με την αντίδραση: πυροφυλλίτης+χλωρίτης+H_2O=καρφόλιθος+χαλαζίας και το σιδηρούχο χλωριτοειδές κατά την προϊούσα μεταμόρφωση με ελάττωση

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του f_{H_2O}. Τα κατώτερα όρια της πίεσης κατά την μεταμόρφωση ήταν της τάξεως των 4 kbar ενώ ανώτερα όρια δεν μπορούν να εκτιμηθούν λόγω έλλειψης κατάλληλων παραγενέσεων. Η θερμοκρασία κυμάνθηκε μεταξύ 300^{o}-$330^{o}C$ (ή $370^{o}C$).

INTRODUCTION

Fe-carpholite, as well as its Mg-rich equivalent, is a rather rare mineral known from a few places on earth. It develops in iron-rich metapelites of the low-grade blueschist facies (see Chopin and Schreyer, 1983 and references therein). Fe-carpholite in Greece has been described from Eastern and Central Crete (Seidel, 1978, Viswanathan and Seidel, 1979, Theye, 1988) and from Amorgos island (Minoux et al., 1981) while magnesio-carpholite is described from western Crete (Seidel, 1978, Viswanathan and Seidel, 1979, Theye, 1988), Peloponnesus (Skarpelis, 1982, Papanikolaou and Skarpelis, 1986, Varti-Mataranga and Economou, 1986) and from Samos island (Okrusch, 1981).

The present work deals with a new Fe-carpholite occurrence on Skopelos island. There, Fe-carpholite is found to be associated with Fe-chloritoid in metapelites and metasandstones.

GEOLOGICAL SETTING

Skopelos island belongs geologically to the Pelagonian zone (Aubouin, 1959) subdivided by Jacobshagen and Wellbrecher (1984) into the following tectonic units: the lowermost is the Pelagonian Nappe comprising a metaclastic unit (Skiathos unit) of Upper Permian to Lower Triassic age (see also Matarangas and Skourtsis-Coroneou, 1989) followed by Pelagonian marbles (mainly dolomitic) of Middle Triassic to Upper Jurassic age (see also Papastamatiou, 1963, Matarangas and Skourtsis-Coroneou, 1989). It is tectonically overlain by the Eohellenic Nappe consisting of a melange with ophiolites and crystalline slices followed by a series of calc-schists, platy marbles and spilites. Subsequent to the overthrust, both nappes were partly eroded, developping karsts often filled with bauxites, and were covered by the co-called Mesoautochtonous Complex consisting of M.Cretaceous to L.Tertiary metasediments. The Mesoautochthonous Complex starting with breccias, conglomerates and sandstones was followed by rudist limestones and ended with flysch.

The rocks studied in the frame of this work include metaclastic sediments and metabauxites over the dolomites in the Panormos area, Skopelos island (Fig.1) and belong to the base of the Mesoautochthonous Complex. According to Jacobshagen and Wallbrecher (1984), the Mesoautochthonous complex in S.Pelion and N. Sporades area has undergone a greenschist facies metamorphism during Tertiary times. Papastamatiou (1963) who studied in detail the metabauxites of the Panormos area reports metadiabasic rocks and metatuffs incorporated in the dolomites. According to the above author, chloritoid, glaucophane (?), albite, sericite and chlorite appear in these rocks while chloritoid, diaspore, illite and chlorite are the metamorphic minerals in the metabauxites.

Fig.1. Map showing the location of the study area on the island of Skopelos, N.Sporades.
Σχ. 1. Χάρτης της νήσου Σκοπέλου, Β.Σποράδες, όπου φαίνεται η υπό μελέτη περιοχή.

PETROGRAPHY

1. Metapelites-metasandstones

The metapelites and metasandstones are dark grey to greenish coloured fine-grained rocks. Depending on the bulk rock chemistry a great variety of modal compositionsappears. The content in clastic quartz grains ranges from a few percent up to 50% per volume. The common mineral assemblage is:

Fe-chloritoid±Fe-carpholite-sericite-chlorite-pyrophyllite-quartz±Cr-spinel±rutile

Chloritoid appears as porphyroblasts forming rosette-like aggregates in a microcrystalline matrix of sericite, pyrophyllite and chlorite (Fig. 2A). Numerous tiny inclusions of pyrophyllite, Fe-carpholite, quartz and rutile are usually observed.

Fe-carpholite appears only as a relic in form of very fine grained crystals enclosed, together with pyrophyllite and quartz, in chloritoid porphyroblasts. The association of Fe-carpholite with pyrophyllite and quartz indicates that Fe-carpholite was formed according to the water-consuming reaction:

pyrophyllite+chlorite+H_2O = carpholite+quartz (1)

Pyrophyllite appears in aggregates around resorbed quartz grains forming a reaction corona (Fig. 2B) thus indicating that it was formed according to the reaction:

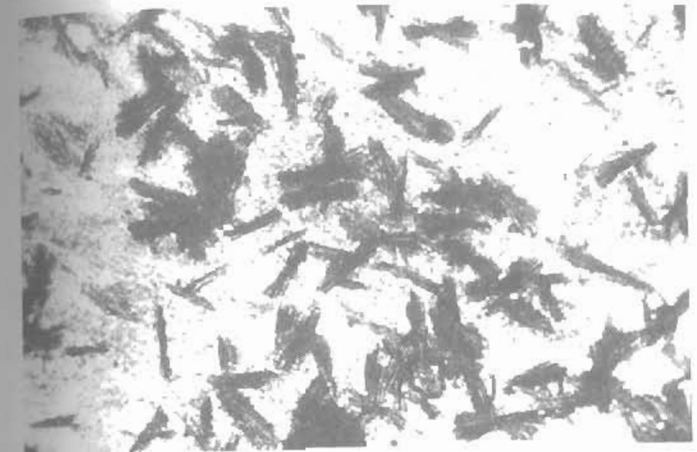
kaolinite+quartz = pyrophyllite+H_2O

It appears also as small crystals in the matrix and as inclusion in chloritoid. In some cases, pyrophyllite occurs in paragenetic association with chlorite and quartz.

Sericite appears as fine-grained mineral or in mineral aggregates in the matrix. Cr-spinel appears as clastic grains in the matrix, suggesting a source of ultramafic material during sedimentation.

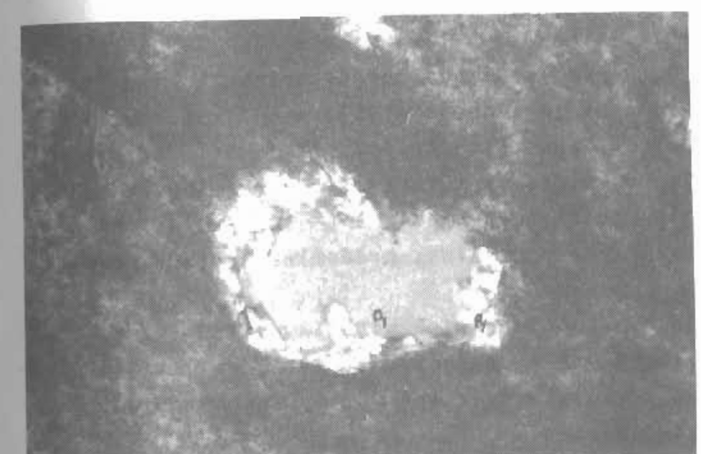
2. Metabauxites

The petrography of the metabauxites is described in detail by Papastamatiou (1963). X-ray diffraction analyses of various metabauxites from Panormos area yielded the following mineralogical compositions for these rocks:



A

0.3 mm



B

0.3 mm

Fig.2. (A) Rosette-like aggregates of chloritoid in a microcrystalline matrix of sericite, pyrophyllite and chlorite.
(B) Pyrophyllite (py) as reaction rim around quartz (q) indicating that the reaction: kaolinite+quartz = pyrophyllite+ +H_2O took place.

Σχ. 2. (Α) Συσσωματώματα χλωριτοειδούς με μορφή "βεντάλιας" σε μιά μικροκρυσταλλική κύρια μάζα από σερικίτη, πυροφυλλίτη και χλωρίτη.
(Β) Πυροφυλλίτης (py) ο οποίος περιβάλλει χαλαζία (q) σχηματίζοντας μιά άλλω αντίδρασης, υποδεικνύοντας ότι έλαβε χώρα η αντίδραση: καολινίτης+χαλαζίας = πυροφυλλίτης+H_2O.

(a) chlorite-diaspore-hematite-rutile
(b) chloritoid-diaspore-pyrophyllite-hematite-rutile
(c) chlorite-diaspore-rutile

Cr-spinel appears sometimes as clastic grains. The coexistence of pyrophyllite with diaspore in the metabauxites indicates that temperatures of metamorphism exceeded the stability curve given by the reaction:

$$\text{kaolinite} = \text{pyrophyllite} + \text{diaspore} + H_2O \qquad (2)$$

and that they were lower than those given by the reaction:

$$\text{pyrophyllite} + \text{diaspore} = \text{kyanite} + H_2O \qquad (3)$$

MINERAL CHEMISTRY

Representative microprobe analyses of the analysed minerals, as well as the bulk rock chemistry of two metapelite samples are given in Table 1.

Fe-carpholite : Fe-carpholite composition is characterized by X_{Mg} between 0.10 and 0.18 thus corresponding to the iron carpholite in the sense of dè Roever (1951) who first described this mineral from Celebes area (Indonesia). It is of great importance that carpholite develops in metapelitic rocks involved in metamorphism where low geothermal gradient ($\approx 10^{o}C/km$), similar to that of blueschist facies terrains, predominates (see Chopin and Schreyer, 1983).

Chloritoid is also iron-rich with X_{Mg} values ranging between 0.08 and 0.15. It is a characteristic mineral of high alumina metapelites and is stable over the whole range of blueschist and greenschist facies fields.

Chlorite has Fe/Fe+Mg values around 0.55 and is characterised as ripidolite (according to the nomenclature of Hey, 1954).

PHASE RELATIONS AND PT-CONDITIONS

As already mentioned, Fe-carpholite generally develops in iron-rich pelitic rocks of the blueschist facies. With rising metamorphic grade it reacts continuously toward more magnesian carpholite and the ferrous component breaks down in favour of Fe-rich chloritoid (Chopin and Schreyer, 1983, E.W.F. de Roever,1977). According to Seidel (1978), the following paragenetic relation-

Table 1: Representative microprobe analyses of minerals and bulk rock chemistry of two metapelites from the Panormos area. Skopelos island.

	Fe-carpholite		Fe-chloritoid		chlorite	
	SK30-1	SK31-1	SK30-6	SK31-4		SK30-8
SiO_2	35.9	36.4	24.2	24.6		26.0
TiO_2	0.16	0.47	0.37	-		
Al_2O_3	31.1	30.4	40.9	41.3		23.8
FeO*	19.2	17.6	26.7	24.8		25.7
MgO	1.26	2.10	1.32	2.45		12.2
MnO	-	-	.34	.28		.14
	-----	------	-----	-----		-----
	87.62	86.97	93.83	93.15		87.84
	8(O)		12(O)			28(O)
Si	1.989	2.031	1.999	2.009	Si	5.433
					Al^{iv}	2.567
Al	2.051	2.001	3.989	3.980		-----
Fe*	.891	.823	1.846	1.695		8.000
Mg	.104	.175	.163	.298		
Mn	-	-	.024	.019		
Ti	.007	.020	.023	-	Al^{vi}	3.305
					Fe*	4.490
X_{Mg}	10.4	17.5	8.1	15.0	Mg	3.801
					Mn	.026

						11.622

	SK-30	SK-31
SiO_2	42.5	49.1
TiO_2	1.25	1.00
Al_2O_3	32.3	29.8
FeO*	12.3	10.8
MgO	2.70	2.16
MnO	.08	.06
CaO	.09	.07
K_2O	1.99	1.60
Na_2O	.76	.61
L.O.I.	5.83	4.66
	-----	-----
	99.80	99.86

ships appear with advancing metamorphic grade, in blueschist terrains:

Fe-carpholite-pyrophyllite-chlorite → Fe-chloritoid-Fe/Mg carpholite-pyrophyllite (or chlorite)

The presence of Fe-carpholite and pyrophyllite as inclusions in chloritoid in the rocks of Panormos area indicates that metamorphic conditions exceeded the field defined by the paragenesis Fe-carpholite-pyrophyllite-chlorite and that high water activity conditions prevailed at that stage of metamorphism (see reaction 1). With advancing metamorphism, f_{H2O} decreased prohibiting further formation of carpholite and favouring instead that of chloritoid, according to the reaction:

chlorite+pyrophyllite = chloritoid+quartz+H_2O

An analogous case is described by Theye (1988) from metapelitic rocks of Crete.

In Fig.3, the phase relations indicate a stepwise metamorphic evolution in the metaclastic sediments of the Panormos area, expressed in AFM diagrams.

The mineral assemblages of the metapelites-metasandstones and metabauxites of the Panormos area allow estimation of the metamorphic conditions of the Tertiary metamorphic event (connected with the Neohellenic tectonism according to Jacobshagen and Wallbrecher, 1984). In the diagram of Fig.4, the most relevent metamorphic reactions are shown. The presence of pyrophyllite+diaspore and the lack of kyanite in the metabauxites restricts the prevailing temperatures between the curves:

kaolinite = pyrophyllite+diaspore+H_2O (2) and
pyrophillite+diaspore = kyanite+H_2O (3)

Regarding pressures, the presence of Fe-carpholite (with $X_{Mg} \approx 0.2$)+quartz, as inclusions in chloritoid indicates that during prograde metamorphism, pressures exceeded those defined by the reaction:

chlorite+pyrophyllite+H_2O = Fe-carpholite+quartz

which, for the temperature range defined by the curves (2) and (3), are in the order of 4 kbar (Goffe, 1982, Goffe and Velde, 1984, Goffe 1985) (Fig.4). Upper pressure limits cannot be deter-

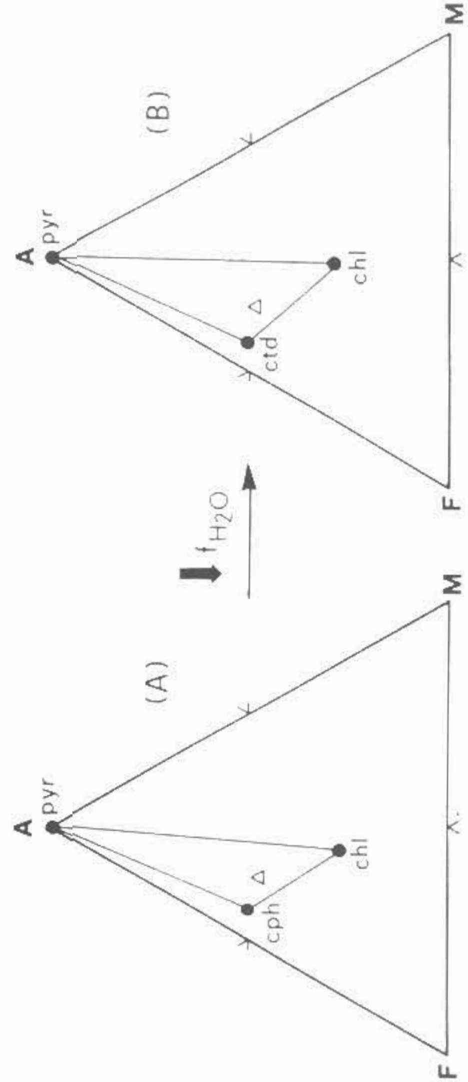


Fig.3. Schematic presentation of the metamorphic evolution assumed for the metapelites-metasandstones of Skopelos island, Panormos area, in AFM diagrams. See text for discussion.

Σχ. 3. Σχηματική απεικόνιση της μεταμορφικής εξέλιξης που υπέστησαν οι μεταπηλίτες-μεταψαμμίτες της ν.Σκοπέλου, περιοχή Πανόρμου, σε AFM διαγράμματα. Βλ.κείμενο για συζήτηση.

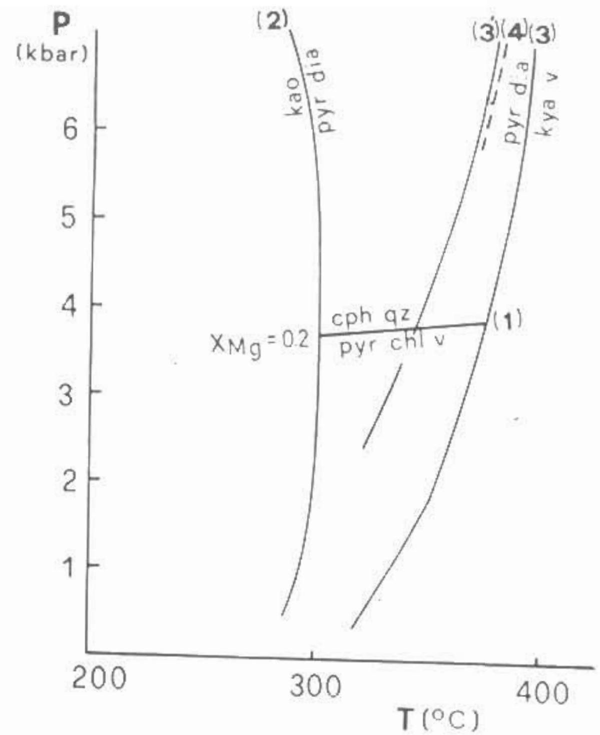


Fig.4. PT diagram showing the metamorphic conditions on Skopelos island, Panormos area. Curve (1) stability limit of Fe/Mg carpholite with 20 mol% Mg end-member (from Goffé, 1985). Curves (2) and (3) after Hemley et al. (1980), curve (3') same as curve (3), after Chatterjee et al. (1984), curve (4) hypothetical upper stability limit of Fe-carpholite (Chopin and Schreyer, 1983).
kao:kaolinite, pyr:pyrophyllite, dia:diaspore, qz:quartz, kya:kyanite, cph:carpholite, chl:chlorite.

Σχ. 4. PT διάγραμμα που απεικονίζει τις συνθήκες μεταμόρφωσης στην περιοχή Πανόρμου της ν.Σκοπέλου. Η καμπύλη (1) παριστά το όριο σταθερότητας του Fe/Mg-καρφόλιθου με σύσταση 20% σε μαγνησιούχο ακραίο μέλος (από Goffee, 1985). Οι καμπύλες (2) και (3) κατά Hemley et al. (1980). Η καμπύλη (3') είναι ίδια με την καμπύλη (3) αλλά κατά Chatterjee et al.(1984). Η καμπύλη (4) παριστά το υποθετικό ανώτερο όριο σταθερότητας του σιδηρούχου καρφόλιθου (Chopin and Schreyer, 1983).

mined with certainty on the basis of the recognised assemblages. The paragenesis:chloritoid+pyrophyllite+chlorite is stable within a wide pressure range (greenschist and blueschist facies).

REFERENCES

AUBOUIN, J. (1959). Contribution à l'étude géologique de la Grèce septentrionale:les confins de l'Epire et de la Thessalie.- *Ann.Geol.Pays Hell., 10, 1-484.*

CHATTERJEE, N.D., JOHANNES, W. and LEISTNER, H. (1984). The system $CaO-Al_2O_3-SiO_2-H_2O$: new phase equilibria data, some calculated phase relations and their petrologic applications.- *Contrib.Mineral.Petrol., 88, 1-13.*

CHOPIN, Ch. and SCHREYER, W. (1983). Magnesiocarpholite and Magnesiochloritoid:two index minerals of pelitic blueschists and their preliminary phase relations in the model system $MgO-Al_2O_3-SiO_2-H_2O$.- *Amer.J.Sci., 283A, 72-96.*

GOFFÉ, B. (1982). Definition du facies a Fe/Mg-carpholite-chloritoid, un marqueur de métamorphisme de HP-LT dans les métasédiments alumineux.- *Thèse d'Etat, Univ.P. et M.Curie, Paris, 232 pp.*

GOFFÉ, B. (1985). Le facies à carpholite-chloritoid dans la couverture Briançonnaise des Alpes Ligures: un temoin de l'histoire tectono-métamorphique régionale.- *Mémoire Soc.Geol.Ital., "Convegno sulla Geologia delle Alpi Liguri, 1984".*

GOFFÉ, B. and VELDE, B. (1984). Contrasted metamorphic evolution in thrusted cover units of the Briançonnais zone (French Alps): a model for the conservation of HP-LT metamorphic mineral assemblages.- *Earth Planet. Sci.Lett., 68, 351-360.*

HEMLEY, J.F., MONTOYA, J.W., MARINENKO, J.W. and LUCE, R.W.(1980). Equilibria in the system $Al_2O_3-SiO_2-H_2O$ and some general implications for alteration/mineralization processes.- *Econ. Geol., 75, 210-228.*

HEY, M.H. (1954). A new review of the chlorites.- *Min.Mag., 30, p.227.*

JACOBSHAGEN, V. and WALLBRECHER, E. (1984). Pre-Neogene Nappe structure and metamorphism of the North Sporades and the south Pelion peninsula.- *In "The geological evolution of Eastern Mediterranean", Dixon and Robertson eds., Geological Society Special Publ., No 17, p.591-602.*

MATARANGAS, D. and SKOURTSIS-CORONEOU, V. (1989). Stratigraphical data from a metamorphic sequence of the North Sporades (Pelagonian zone, Greece) .- *N.Jb.Geol.Palaeont. Mh., H3, 182-192.*

MINOUX, L., BONNEAU, M. and KIENAST, J.R. (1981). L'ile d' Amorgos, une fenêtre des zones externes au coeur de l'Egee (Grece) métamorphisée dans le facies schistes blues.- *Acad.Sci. Paris Comptes rendus, 291 D, 745-748.*

OKRUSCH, M. (1981). Chloritoid-führende Paragenesen in Hochdruckgesteinen von Samos: *Fortschr.Mineralogie, v.59, Bh. 1, 145-146.*

PAPANIKOLAOU, D.J. and Skarpelis, N. (1986). The blueschists in the external metamorphic belts of the Hellenides: composition, structure and geotectonic significance of the Arna Unit.- *Ann.Geol.Pays Hell., 33/II, 47-68.*

PAPASTAMATIOU, J. (1963). Les bauxites de l'ile de Skopelos (Sporades du Nord).- *Bull.Geol.Soc.Greece, 5, 52-74 (in Greek*

with french summary).
ROEVER, E.W.F. de (1977). Chloritoid-bearing metapelites associated with glaucophane rocks in western Crete. Some remarks.- *Contrib.Mineral.Petrol., 60, 317-319.*
ROEVER, W.P. de (1951). Ferrocarpholite, the hitherto unknown ferrous iron analogue of carpholite proper.- *Amer.Mineral., 36, 736-745.*
SEIDEL, E. (1978). Zur Petrologie der Phyllit-Quartzit-Serie Kretas.- *Habilitationsschr., TU Braunschweig, 145pp.*
SKARPELIS, N. (1982). Metallogeny of massive sulfides and petrology of the external metamorphic belt of the Hellenides (SE Peloponnesus).- *Unpubl.PhD.Thesis, Univ. of Athens, 149pp (in Greek with English summary).*
THEYE, Th. (1988). Aufsteigende Hochdruckmetamorphose in Sedimenten der Phyllit-Quarzit-Einheit Kretas und des Peloponnes.- *Unpubl.Dissertation, TU Braunschweig, 224pp.*
VARTI-MATARANGA, M. and Economou, G. (1986). Présence de carpholite ferro-magnesienne dans des métapelites de la region de Taygetos-Lakonia (Peloponnese du Sud).- *Geol.Geoph.Res., special issue, IGME, Athens, p.15-23 (in Greek with french summary).*
VISWANATHAN, K. and SEIDEL, E. (1979). Crystal-chemistry of Fe-Mg carpholites.- *Contrib.Mineral.Petrol., 40, 41-47.*