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WOLLASTONITE AND ASSOCIATED COPPER MINERALIZATION IN THE CONTACT METAMORPHIC AUREOLE OF KIMMERIA, XANTHI, N. GREECE

N. Skarpelis* and A. Liati**

ABSTRACT

Wollastonite, usually associated with copper minerals, appears in the contact metamorphic aureole of Kimmeria, near Xanthi, and is genetically related to the Xanthi plutonite. The mineral assemblages: (a) wollastonite±garnet±clinopyroxene±scheelite±chalcopyrite±bornite±chalcocite±aikinite and (b) wollastonite±garnet±clinopyroxene±calcite±quartz±epidote±hematite (specularite) were found. Coexistence of chalcopyrite-bornite with wollastonite-andradite indicates moderate relative fO_2 - fS_2 conditions. Hematite and epidote which form in a late stage of retrogression indicate increasing oxidation conditions. A zonal pattern characterized by a depletion of Fe and decrease in fO_2 from the granodiorite toward the surrounding marbles is recognised in the contact metamorphic aureole of Kimmeria.

ΣΥΝΟΨΗ

Βολλαστονίτης, που συνοδεύεται συνήθως από χαλκούχα ορυκτά, αναπτύσσεται στη ζώνη μεταμόρφωσης επαφής των Κιμμερίων και συνδέεται γενετικά με τον πλουτωνίτη της Ξάνθης. Διαπιστώθηκαν τα ακόλουθα ορυκτολογικά αθροίσματα (α) βολλαστονίτης±γρανάτης± κλινοπυρόξενος±σεελίτης±χαλκοπυρίτης±βορνίτης±χαλκοσίνης± αϊκινίτης και (β) βολλαστονίτης±γρανάτης±κλινοπυρόξενος±ασβεστίτης±χαλαζίας±επίδοτο±αιματίτης(σπεκουλαρίτης). Η συνύπαρξη χαλκοπυρίτη-βορνίτη με βολλαστονίτη-ανδραδίτη υποδηλώνουν σχετικά ενδιάμεσες συνθήκες fO_2 - fS_2. Η παρουσία αιματίτη και επιδότου που σχηματίζονται στην ανάδρομη φάση του skarn υποδηλώνουν υψηλότερες οξειδωτικές συνθήκες. Στη ζώνη μεταμόρφωσης επαφής των Κιμμερίων διαπιστώνεται μία ελάττωση του Fe και μείωση της fO_2 από τον γρανοδιορίτη προς τα περιβάλλοντα μάρμαρα.

Ν. ΣΚΑΡΠΕΛΗΣ & Α. ΛΙΑΤΗ. Βολλαστονίτης και η συνδεόμενη με αυτόν χαλκούχος μεταλλοφορία στην άλω μεταμόρφωσης επαφής των Κιμμερίων, Ξάνθη, Β. Ελλάδα.

*University of Athens, Department of Geology, Section of Economic Geology and Geochemistry, Panepistimioupoli, 157 84 Athens.

**Section of Geological Sciences, National Technical University, Patission 42, 106 82 Athens.

ΕΙΣΑΓΩΓΗ-INTRODUCTION

In the area of Xanthi, which belongs qeologically to the Rhodope Zone, an extended plutonic body of 10.5 km in lenght and 4.5 km maximum width is exposed (Fig. 1). The surrounding metamorphic rocks are mainly quartzofeldspathic and pelitic gneisses, eclogitic amphibolites, marbles, and minor calcsilicate rocks, meta-ultramafics and mica schists. The Xanthi plutonite is a composite plutonic body, its composition changing eastwards to more mafic (Christofides, 1977). The prevailing rock type is granodiorite (≈75% of exposed area) while monzonite, quartz monzonite, monzogabbro, gabbro and quartz monzonite porphyry are subordinate. In the studied area the plutonite is of granodioritic composition. The geochemical and mineralogical characteristics of the granodiorite, in conjunction with its magnetic susceptibility indicate that it belongs to the magnetite-series granitoids (Skarpelis, 1989).

A contact metamorphic aureole, formed by interaction of the Xanthi plutonite with the surrounding metamorphic rocks, mainly with the marbles, is exposed north of Kimmeria village and north of Xanthi (Fig. 1). In both contact metamorphic aureoles extended wollastonite bodies, occasionally with copper mineralization, occur at the immediate contact with the marbles.

This paper deals with the petrography of the wollastonite bodies and the physicochemical conditions prevailing during deposition of the associated copper mineralization.

ΠΑΡΑΤΗΡΗΣΕΙΣ ΥΠΑΙΘΡΟΥ-FIELD RELATIONS

The contact metamorphic aureole of Kimmeria appears two kilometers north of Kimmeria village and extends about 300 m from the contact with the granodiorite. It is developed mainly at the expense of marbles. The skarns generally follow the bedding of the marbles (stratiform) but irregular forms also occur. Metasomatism affected also the marginal parts of the granodiorite giving rise to the so-called endoskarns. Approaching the contact with the country rocks the granodiorite becomes bleached due to the disappearance of ferromagnesian minerals. Both calcic and magnesian skarns occur; they formed at the expense of calcitic and dolomitic marbles, respectively. The calcic skarns are the predominant type. Garnet (grossular to andradite), clinopyroxene (diopside to hedenbergite) and epidote are the main minerals of the calcic skarns whereas olivine, spinel and phlogopite appear in the magnesian skarns. Orthopyroxene and cordierite occur in the contact metamoprhic biotite-gneisses (see Liati, 1986 for details). An important magnetite mineralization as well as scheelite-powellite, molybdenite, and sulfide mineralizations are found. According to Liati (1986), maximum temperatures during contact metamorphism should have been around 750^{o} C,

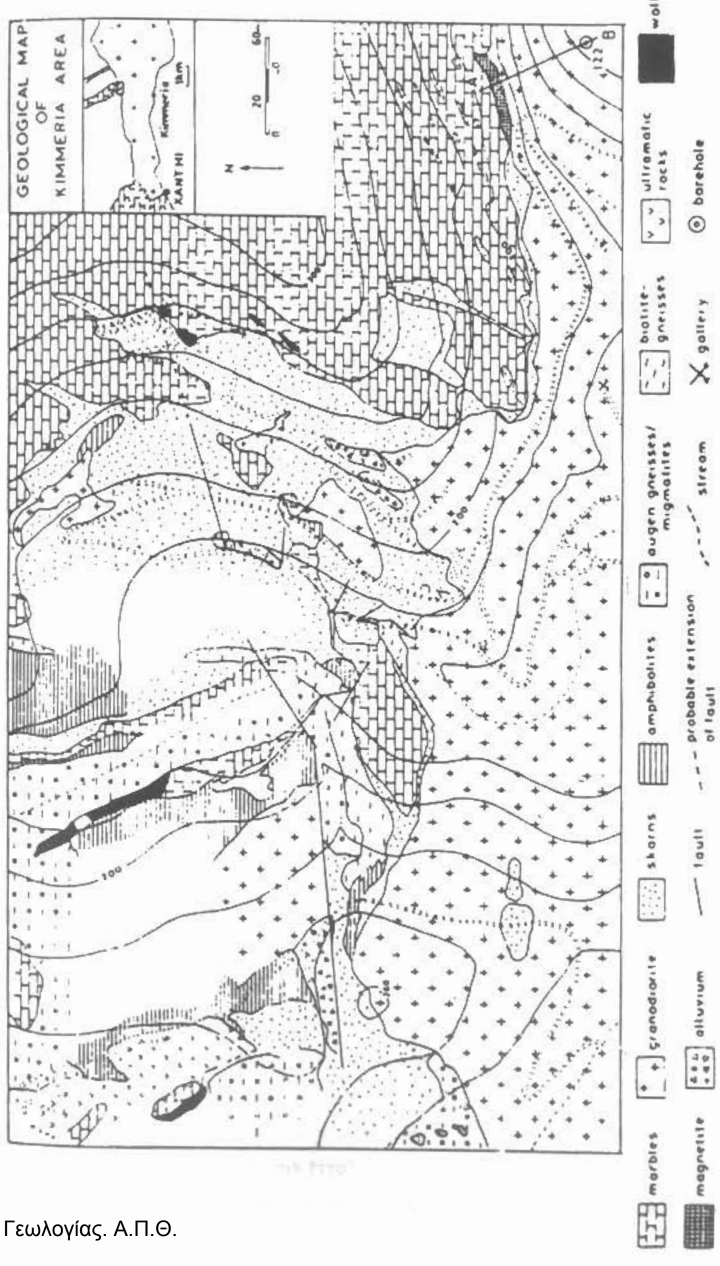

Fig. 1. Geological map of the contact metamorphic aureole of Kimmeria with the wollastonite outcrops (from Liati, 1986).
Εικ. 2. Γεωλογικός χάρτης της ζώνης μεταμόρφωσης επαφής των Κιμμερίων με τις εμφανίσεις βολλαστονίτη (από Liati, 1986).

as was determined for rocks lying at the immediate vicinity with the granodiorite. Pressures should not have exceeded 3 Kbar.

Massive wollastonite occurs either at the immediate contact of the granodiorite with the marbles, or within the marbles, as isolated bodies. Its colour varies from nearly white to pink or light brown while its crystal aggregates reach 15 cm in length. The wollastonite bodies have mainly a lenticular shape and are either monomineralic or associated with garnet and/or clinopyroxene. In some cases, green-coloured garnet forms almost pure garnetite bands and/or small pods in the wollastonite bodies. Cu-Fe sulfides and hematite (specularite) are often observed either in form of small pods and veinlets or as disseminated minerals in the matrix, while some wollastonite occurrences are selectively enriched in Cu-Fe sulfides.

ΠΕΤΡΟΓΡΑΦΙΑ-PETROGRAPHY

The following mineral assemblages were observed in the wollastonite bodies:

(a) wollastonite±garnet±clinopyroxene±scheelite±chalcopyrite±bornite±chalcocite±aikinite.

(b) wollastonite±garnet±clinopyroxene±calcite±quartz±epidote±hematite (specularite).

The paragenesis: calcite+ quartz+ epidote+ specular hematite was not observed in association with the sulfides.

Garnet is euhedral to subhedral and in most cases is strongly birefringent with or without sector twinning. It is often in textural equilibrium with wollastonite and clinopyroxene while more rarely it occurs as inclusion in wollastonite.

Clinopyroxene forms fine-grained aggregates. It occurs either in form of inclusions in wollastonite indicating early formation during the initial stages of contact metamorphism or in the matrix, together with garnet, as a later mineral formed during the main skarn stage.

The Cu-Fe mineralization comprises chalcopyrite, bornite and chalcocite. Aikinite is found as disseminated grains between the former minerals. Massive aggregates of these ore minerals are dispersed into the wollastonite-garnet masses. Chalcopyrite is commonly developed interstitially between wollastonite and garnet grains. Chalcopyrite lamellae in the shape of very thin plates parallel to the (001) plane occur commonly within bornite grains. Chalcopyrite and bornite grains are surrounded by a rim consisting of chalcocite. Specular hematite occurs as a retrograde phase in form of coarse-bladed sheafs, usually associated with quartz and/or epidote.

ΧΗΜΙΣΜΟΣ ΟΡΥΚΤΩΝ-MINERAL CHEMISTRY

Microprobe analyses of silicate and ore minerals are given in Table 1. Garnet is almost pure andradite and clinopyroxene is enriched in diopside relative to hedenbergite (= 75% diopside). Epidote is rich in pistacite end-member. Chalcopyrite and bornite are very close to the ideal formula. Concentrates of Cu minerals, commercially analyzed for Au by the Fire Assay method, yielded Au contents ranging from 0.5 - 1 gr/tn.Native gold is reported from the Kimmeria metamorphic aureole, where it occurs in retrograde pyrite and chalcopyrite within massive magnetite (average content: 3.2 gr/tn; Michailides et al., 1989).

ΣΥΝΘΗΚΕΣ ΓΕΝΕΣΗΣ-GENESIS

Wollastonite is formed at the earliest stages of contact metamorphism by the interaction of carbonate material with a plutonic intrusion, according to the reaction:

$$\text{calcite+ quartz} = \text{wollastonite} + CO_2$$

usually at relatively high temperatures depending on the XCO_2 of the fluid phase (Tanner et al., 1985). Its formation is usually isochemical unless, the carbonates are pure calcitic. In that case, Si can be supplied from the intruding pluton. The widespread occurrence of andradite associated with the wollastonite of Kimmeria area indicates that oxidizing metasomatic fluids (transporting Fe^{3+}) infiltrated the zone of wollastonite. The Ca required for the formation of andradite was supplied either from the wollastonite or from the adjacent marbles.Textural features indicate that more than one generation of andradite exist, therefore implying oxidizing conditions throughout several stages of the contact metamorphic processes. The highly oxidizing conditions of the fluid phase are incompatible with the formation of hedenbergite-rich clinopyroxene which is missing from the mineral assemblage of the wollastonite-skarns.

Wollastonite as an early-forming mineral tends to react with solutions depositing iron-rich ore minerals, such as chalcopyrite, to produce andradite plus iron-poor ore minerals, such as bornite, according to the reaction (Burt, 1972):

$$\underset{Cp}{5CuFeS_2} + \underset{Wol}{6CaSiO_3} + 3O_2 \rightleftharpoons \underset{Bn}{Cu_5FeS_4} + \underset{And}{2Ca_3Fe_2Si_3O_{12}} + 3S_2 \qquad (1)$$

It is apparent that under relatively oxidizing or low sulfur conditions, chalcopyrite is incompatible with wollastonite. The formation of andradite implies depletion of the fluid phase in Fe thus favouring the deposition of bornite rather than chalcopyrite. Andradite is stable with Fe-sulfides only at low to intermediate fS_2 and fO_2 conditions, but its stability is enhanced by high temperatures (>400° C) or by low μCO_2. At high fS_2 values andradite is

Table 1. Representative microprobe analyses of silicate and ore minerals

	cpx	gt	wol
SiO_2	53.1	35.3	50.3
Al_2O_3	0.18	0.37	0.37
Fe_2O_3	0.64	30.0	0.29
FeO	6.47	-	-
MnO	1.57	-	0.38
MgO	12.0	-	-
CaO	25.6	33.8	48.4
Na_2O	0.3	-	-
	99.86	99.47	99.74
	(4) cations	(8) cations	(3) oxygens
Si	1.998	2.985	0.981
Al IV	0.002	0.015	0.009
Al VI	0.006	0.021	-
Fe^{3+}	0.018	1.912	0.004
Fe^{2+}	0.203	-	
Mn	0.050	-	0.006
Mg	0.669	-	-
Ca	1.031	3.066	1.012
Na	0.022	-	
	3.999	7.999	

	cp		bn	
Cu	34.8	35.4	62.4	62.2
Fe	30.1	29.3	11.2	11.6
S	34.9	35.0	26.1	26.1
	99.8	99.7	99.7	99.9
	2(S)		4(S)	
Cu	1.01	1.02	4.82	4.81
Fe	0.99	0.96	0.99	1.02

cpx: clinopyroxene
gt: garnet
wol: wollastonite
cp: chalcopyrite
bn: bornite

unstable regardless of other constraints (Burt, 1972; Einaudi et al., 1981; Einaudi, 1982) whereas high fS_2 can produce an assemblage containing an Fe^{2+} bearing calcsilicate and an Fe-rich Cu sulfide (Einaudi, 1982), such as hedenbergite plus chalcopyrite, respectively.

In the case of Kimmeria area, oxidizing conditions were deduced for the skarn-forming stage. It seems that during later formation of the Cu-mineralization in wollastonite, oxidation conditions have been reduced, as indicated by the coexistence of wollastonite with chalcopyrite (reaction (1)). High fS_2 conditions are also precluded by the coexistence of bornite with andradite, according to the same reaction. It seems therefore that moderate fS_2-fO_2 conditions prevailed during the formation of the Cu-mineralization associated with the wollastonite which probably took place after the main skarn stage characterized by high oxidation conditions. Chalcocite rims around chalcopyrite and bornite crystals can be explained by lower temperatures or by decreasing sulfidation of the fluid. The presence of pistacite-rich epidote as a late forming retrograde mineral suggests that late stage fluids, which followed the formation of Cu-mineralization was H2O-rich and oxidizing, since this variety of epidote is stable only under relatively high oxygen fugacities (Liou, 1973). The association of epidote with specular hematite is an additional evidence for the high oxidation state of the late (retrograde) fluid phase.

ΣΥΜΠΕΡΑΣΜΑΤΑ-CONCLUSIONS

The mineral parageneses appearing in the wollastonite bodies of Kimmeria reflect continuous cooling and evolution of the chemistry and oxidation state of the metasomatic fluids. Andradite is the dominant metasomatic mineral formed in the main skarn stage. Cu-Fe rich fluids reacted with wollastonite to form andradite+ bornite at a later phase when fO_2 became moderate relative to fS_2. The Cu-minerals coexisting with wollastonite + andradite are potentially valuable indicators of relative oxygen and sulfur fugacities in hydrothermal ore depositing solutions. Fig 2 is a schematic fS_2-fO_2 diagram based on natural assemblages of the system: $CaSiO_3$-Fe-Cu-O-S, as compiled by Burt (1972) for temperatures slightly greater than about 330° C. In the case of the skarns of Kimmeria, the coexistence of wollastonite, chalcopyrite, bornite and andradite suggests conditions along the univariant line (1). As temperature dropped, during retrograde processes, fO_2 increased and stability conditions entered the field of hematite (line 2). This is also evident by the formation of epidote as a retrograde mineral, usually along with quartz and specular hematite. The presence of a hydrous retrograde phase such as epidote suggests that H_2O-rich fluids dominated throughout the retrograde stage (compare Kerrick, 1974). However, in some cases

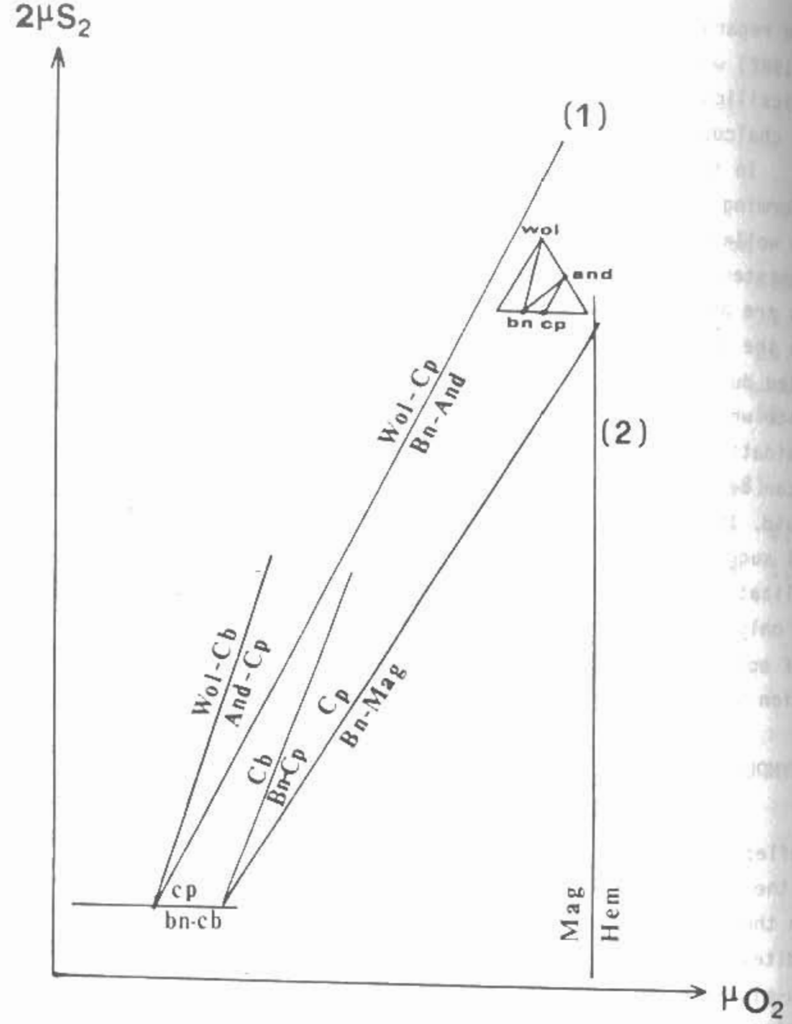

Fig. 2. Part of the schematic $2\mu S_2$-μO_2 diagram of the system $CaSiO_3$-Fe-Cu-O-S, at temperatures slightly above 330°C (Burt, 1972), with the most relevant reactions. See text for discussion.
Wol:wollastonite, Cp:chalcopyrite, Bn:bornite, And:andradite, Cb:cubanite, Mag:magnetite, Hem:hematite.

Εικ.2. Τμήμα του σχηματικού διαγράμματος $2\mu S_2$-μO_2 του συστήματος $CaSiO_3$-Fe-Cu-O-S, σε θερμοκρασίες λίγο υψηλότερες από 330°C (Burt, 1972), που περιλαμβάνει τις σχετικές αντιδράσεις. Επεξήγηση στο κείμενο.
Wol: βολλαστονίτης, Cp:χαλκοπυρίτης, Bn:βορνίτης, And:ανδραδίτης, Cb:κουβανίτης, Mag:μαγνητίτης, Hem:αιματίτης.

μCO_2 increased locally resulting in the formation of secondary calcite.

The association of andradite-rich skarns with magnetite-pyrrhotite-chalcopyrite±Fe-rich sphalerite ore at the immediate contact with the intrusive in the area of Kimmeria, and the presence of chalcopyrite-bornite in the wollastonite zone reflect a decrease in total iron in the contact metamorphic zone, outwards. A zonal pattern is therefore recognized in the calcic skarns, whereby total iron was depleted and fO_2 decreased from the granodiorite to the marble contact.

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