THE OCCURRENCES OF MG-HYDROXYCARBONATES IN SERPENTINITES OF THE WESTERN SECTION OF THE SOUTH AEGEAN VOLCANIC ARC (WEST ATTICA PENINSULA-NORTHEASTERN ARGOLIS PENINSULA), GREECE

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Abstract

In the area of West Attica Peninsula, Greece, ophiolitic rocks which outcrop mainly at the Geraneia Mountains, overlie Triassic-Jurassic limestone and covered by Plio - Pleistocene sedimentary rocks. The relatively widespread ophiolite occurrences are mainly serpentinized peridotites, considered as spinel lherzolites and dunites. In the Northeastern Argolis Peninsula several small remnants of an ophiolitic nappe outcrop which consists from serpentinized and tectonically deformed peridotites, overthrusted on the Eocene flysch. Both regions are characterized by manifestations of volcanic activity. Recently, white mineral aggregates have been discovered in several places in highly altered and serpentinized ultrabasic rocks of the above regions, with the form of irregular accumulations. The identified minerals are hydromagnesite, which predominates, and also magnesite, huntite, and minerals of pyroaurite group. For the study of the Mg-hydroxycarbonate minerals assemblages and the hosting material, PXRD mineralogical analysis, SEM investigations and SEM-EDS microprobe and chemical analyses has been performed. It is suggested that the origin of the secondary Mg-rich hydroxycarbonates was controlled by the alteration of the ophiolites due to a combining actions of intense hydrothermal activity with CO_2 -rich fluids, tectonism, as well as the groundwater chemistry that is characterized by high Mg/Ca ratio and alkaline pH values.
Key words: Hydromagnesite, huntite, ultramafic, alteration, Geraneia.

Περίληψη

Στα Γεράνεια όρη (Δυτική Αττική, Ελλάδα) απαντούν οφιολιθικά πετρώματα, υπερκείμενα Τριαδικών – Ιουρασκών ασβεστολίθων και υποκείμενα Πλειοπλειστοκαινικών ιζημάτων. Οι σχετικά εκτεταμένες οφιολιθικές εμφανίσεις συνίστανται κυρίως από σερπεντινιωμένους περιδοτίτες, θεωρούμενοι ως λερζόλιθοι με σπινέλιους, καθώς και δουνίτες. Στην Βορειοανατολική Αργολίδα απαντούν αρκετές μικρές εμφανίσεις σερπεντινιτών ως υπολείμματα ενός οφιολιθικού καλύμματος, συνιστάμενες από σερπεντινιωμένους και τεκτονικά παραμορφωμένους περιδοτίτες, επωθημένους στον Ηωκαινικό φλύσχη. Και οι δυο περιοχές

χαρακτηρίζονται από εκδηλώσεις ηφαιστειακής δραστηριότητας. Πρόσφατα ανακαλύφθηκαν αρκετές ακανόνιστες συγκεντρώσεις από λευκόχρωμα ορυκτά συσσωματώματα μέσα σε έντονα εξαλλοιωμένα και σερπεντινιωμένα υπερβασικά πετρώματα των περιοχών αυτών. Προσδιορίστηκαν τα ορυκτά υδρομαγνησίτης, το οποίο επικρατεί, μαγνησίτης, χουντίτης καθώς και ορυκτά της ομάδας των πυροαυριτών. Για την μελέτη των ορυκτών αυτών, καθώς και των ξενιστών τους, χρησιμοποιήθηκαν μέθοδοι όπως, PXRD ορυκτολογικές αναλύσεις, SEM και SEM-EDS παρατηρήσεις και μικροαναλύσεις, καθώς και χημικές αναλύσεις. Υποδεικνύεται ότι ο σχηματισμός των δευτερογενών αυτών ορυκτών ελέγχεται από την εξαλλοίωση των οφιολίθων, ως συνδιασμένη δράση της έντονης υδροθερμικής δραστηριότητας πλούσιων σε CO_2 διαλυμάτων, του τεκτονισμού, καθώς και του χημισμού του εδαφικού νερού που χαρακτηρίζεται από μεγάλες τιμές του λόγου Mg/Ca και του pH.

Λέξεις κλειδιά: Υδρομαγνησίτης, χουντίτης, υπερβασικά, εξαλλοίωση, Γεράνεια.

1. Introduction

There are several references for hydromagnesite (and similar minerals, as huntite, pyroaurite group minerals, as well as magnesite, hereinafter referred as Mg-hydroxycarbonates) related with ultramafic rocks (Hostetler et al., 1966, Barnes and O'Neil, 1969, Okamoto et al., 2006, Teir et al., 2009, Wilson et al., 2009). However, these reports, as well as the related occurrences and their extent are very limited on the spread of the ultramafic rocks. The occurrence of Mg-hydroxycarbonates (such as hydromagnesite and huntite etc) is mainly referred from sedimentary deposits in lacustrine basins of Tertiary to recent age (Calvo et al., 1995, Stamatakis, 1995, Russell et al., 1999, Zedef et al., 2000). However, many of the large magnesite deposits of commercial grade are hosted in ultrabasic rocks in the form of vein and stockwork (Dabitzias, 1980, Pohl, 1990, Zachmann and Johannes, 1989). Sometimes, concretionary magnesites occur in soil weathered ultramafics (Schroll, 2002).

The aim of this paper is the presentation for first time some occurrences of Mg-hydroxycarbonates in ultramafic rocks of Greece, mostly in Geraneia Mountain, as well their description and the mineralogical and geochemical constrains; their relationship with specific geotectonic environment such as the South Aegean Active Volcanic Arc also investigated.

2. Geologic-Tectonic and Geothermal Features

In areas in West Attica Peninsula, Greece (S in Figure 1), ophiolitic rocks which occur on the surface mainly at the Geraneia Mountains, are overlying Triassic-Jurassic limestone and covered by Plio-Pleistocene sedimentary rocks (Mettos et al., 1982, Vakondios, 1996). The ophiolites are consisting mainly from peridotites were considered as spinel lerzolites -Western Mediterranean type, which include dunite bodies (Vakondios, 1996). The wide South section (Crommyonia) is characterized by the presence of manifestations of volcanic/geothermal activity, which has finally resulted in the alteration of ultramafic rocks mainly in the Soussaki and Agia Marina regions. The alteration observed is represented by extensive silicification of the ultramafic rocks (opal and chalcedony formation), as well as by clays formation (smectite and halloysite), which are often Cr-bearing (Mitsis et al., 2009). The Crommyonia region constituted the NW end of the Aegean volcanic arc, characterized by the existence of geothermal field, as well as intense tectonic and seismic activity. The sparse outcrops of dacitic rocks are the remnants of the volcanic activity 4.0-2.3 Ma, late-Pliocene (Fytikas et al., 1986, Pe-Piper and Hatzipanagiotou, 1997). In places, a weak mineralization of vein-type magnesite was located and also some mineralization of authigenic minerals (mainly sulphates) formed from volcanic emanations has been studied (Kyriakopoulos et al., 1990, D'Alessandro et al., 2009). The peninsula of Methana, located in the Northeastern Argolis (M in fiure 1), is mostly formed of volcanic product consisting mainly from basaltic andesites

to dacites of Pleistocene age (0.9 Ma to historical time]). In the Northeastern Argolis Peninsula several small remnants of an ophiolitic nappe outcrop which consists from serpentinized and tectonically deformed peridotites, as well as ophiolitic mélange (Gaitanakis and Photiades, 1989, Hatzipanagiotou et al., 1988). The nappe is overthrusted on the Eocene flysch. These ophiolite rocks are generally serpentinized, altered, tectonized and mylonitized. The volcanic system of Soussaki is a recent but, extinct volcano, with the post volcanic activity manifestations restricted now to argillification processes, hydrothermal alteration-mineralization, acid leaching, fumaroles and thermal waters (Dotsika et al., 2009). Gas escape displays typical geothermal gas composition, with CO_2 as the main component (>950 mmol/mol), and CH_4 and H_2S as minor components (D'Alessandro et al., 2006). However, the volcanic/geothermal system of Methana shows much lower activity, which confirmed by the very low CO_2 output (D'Alessandro et al., 2008).
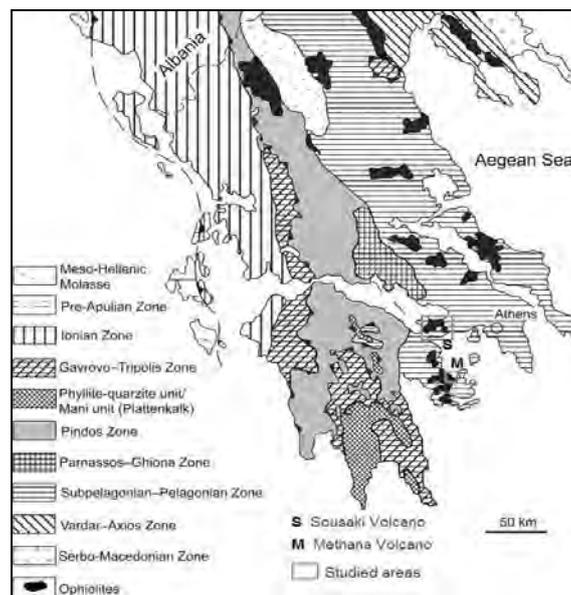

Figure 1 - Simplified geological map with the main tectonostratigraphic zones of the Hellenides and ophiolites also. The studied areas are: S (Sousaki-Geraneia) and M (Kaloni-Methana).

3. Materials and Methods

3.1. Studied Areas and Sampling

Recently, in highly altered, often earthy, serpentinite masses, white nodules and cotton-balls, fissure fillings and crusts, as well as veins (Figure 2) composed of Mg-rich hydroxycarbonates were identified mostly in Geraneia Mountain. The main development of the Mg-hydroxycarbonates was found to occur in the highly altered ultrabasic rocks; these rocks occur close to tectonic contact with limestones and close to regions with apparent signs of volcanic/geothermal activity. Away from such areas, the ultramafics are not intensely altered do not contain hydromagnesite, pyroaurite or huntite, but only locally vein-stockwork magnesite. In the South Geraneia Mt (Sousaki area) the ultrabasic rocks are very intensely altered due to volcanic and hydrothermal activity as well as tectonic activity. The Mg-hydroxycarbonate minerals (with the hydromagesite prevails) are well developed and include a variety of forms. Hydromagnesite with the form of cotton balls up to 4cm in diameter and as fissure fillings are located in several places within the highly altered serpentinite masses. Magnesite occurs mainly as small layers of white nodular accumulations, crusts or cauliflower forms with colloform texture. Also, boudinaged layers of huntite up to 2cm thick as well as nodules up to 2cm in diameter occur,

scattered near surface in totally weathered/altered ultrabasic rocks. The mineralogical analysis has shown that hydromagnesite systematically coexists with pyroaurite (Table 1). In the northern part of Geraneia Mt. (near Schinos area) hydromagnesite cotton balls occur also in totally altered ultrabasic rocks that appears as an earthy, clayey matrix of greenish or yellowish-brown color. The maximum visible thickness of the hydromagnesite horizon development exceeds 10 meters. The hydromagnesite cotton-balls range in size from few mm up to 5-7cm in diameter (Figure 2); the content of irregularly developed hydromagnesite in the host earthy-serpentinite can be close to 30%. In addition, rarely hard magnesite in the form of cauliflower or lettuce-leave assemblages is developed near the present-day surfaces, above hydromagnesite accumulations. In the east-southern Geraneia Mt at Ag Theodoroi area white nodular, botryoidal to nephroid and cauliflower accumulations of hard magnesite and rarely disseminated soft huntite nodules have been located in the intensely altered ultrabasic rocks.

In the Northeastern Argolis, at the Kaloni area, near Methana, white nodules, crusts and fissure fillings of hydromagnesite with pyroaurite (Table 1) occurred also in highly altered serpentinite masses. However, these occurrences are clearly quite limited (both in extent and frequency of occurrences) compared with those of Geraneia Mt.

Figure 2 - Hydromagnesite white nodules, fissure fillings and crusts, as well as veins in altered serpentinite in Geraneia Mt.

3.2. Analytical Methods and Techniques

All analytical procedures were performed at the laboratories of Faculty of Geology and Geoenvironment, UoA, with the following facilities:

X-ray diffraction measurements were carried out on a Bruker Model 5005 X-ray diffractometer in combination with the DIFFRACplus software package. The diffractometer was operated using Cu Ka radiation at 40 kV and 40 mA, with graphite monochromator, and employing the following scanning parameters: 0.020° step size and 1.0 sec. step time. The raw files were evaluated for mineralogical identifications by use of the EVA 10.0 program of the Bruker DIFFRACplus- software package. Electron probe microanalyses and SEM studies were carried out on a Scanning Electron Microscopy (SEM) JEOL JSM-5600, combined with microanalyzer energy dispersive system OXFORD LINK ISIS 300, with software ZAF correction quantitative analysis. The system was operating at 20KV, 0.5nA and 50sec dead time. Wet chemical analyses were performed with AAS spectrophotometer Perkin Elmer, model 1100b and with colorimetric method, using a HACH DR/4000 spectrophotometer.

4. Results

4.1. XRD Mineralogical Analyses

As it was resulted from the Powder XRD analyses (Table 1) the major Mg-hydroxycarbonates are: hydromagnesite, pyroaurite, magnesite and huntite. However, several cotton-balls, nodular or crust/fissure filling aggregates revealed that an Mg-Fe-(Ni-rich) hydroxyl-carbonate mineral of the pyroaurite group (Table 1, 2) occur, along with hydromagnesite and serpentine mineral.

Table 1 – PXRD Mineralogical analyses.

SAMPLE	SERP	HUN	HYM	MG	PAU
AT1	TR	MD		MJ	
AT2				MJ	
AD2	TR		MJ		MD
S7a	TR	MJ			
S7b	TR			MJ	
S7c	TR		MD	MJ	TR
S7nd	TR		MJ		MD
S7v	TR			MJ	
AT4	TR		MJ		MIN
AT11	TR		MJ		MIN
AM1	MJ		MIN		MD
AMcb	TR		MJ		MD
AMg	TR		MJ		MIN
AL2	TR		MJ		MIN
AL7	MD		MJ		TR
MPa2	MD		TR		MJ
MPb1	TR		MJ		TR
BPb	TR		MD		MJ
MPb2	TR		TR		MJ
MPb	TR				MJ
BPf	MD		TR		MJ
BPf1	MD		MJ		MD
F2b	TR		MJ		TR
F2f	MJ		MJ		MD
PNc	TR		MJ		TR
PN5	TR		MJ		MD
K2a			MJ		MIN
K2	MIN		MJ		MD
K3	TR		MJ		MD
K20	TR		MJ		MIN

Explanatory notes - SERP=serpentine, HUN =huntite, HYM=hydromagnesite, MG=magnesite, PAU=pyroaurite group. MJ=major constituent, MD=medium constituent, MIN= minor constituent, TR= trace constituent. (AD, S)=Sousaki area, (AM, AL)=Ag. Marina area, (PN,F)=Moni Panagia area, (AT)=Ag. Theodoroi area, (BP,MP)=Sxinos area, (K)=Kaloni area.

4.2. EPMA Analyses - SEM Micrographs and Study

SEM study on Mg-hydroxycarbonate phases and varieties of occurrences, shown that all these minerals are authigenic, as forms well developed microcrystals. Hydromagnesite forms euhedral crystals, as well large aggregations with pyroaurite and serpentine (Figure 3).

EPMA analyses, as well SEM semi qualitative analyses on free surface of Mg-carbonate phases and varieties of occurrences shown that: hydromagmesite is a pure phase, pyroaurite contains about 2.0 % NiO and Magnesite contains about 2.5 % CaO (Table 2).
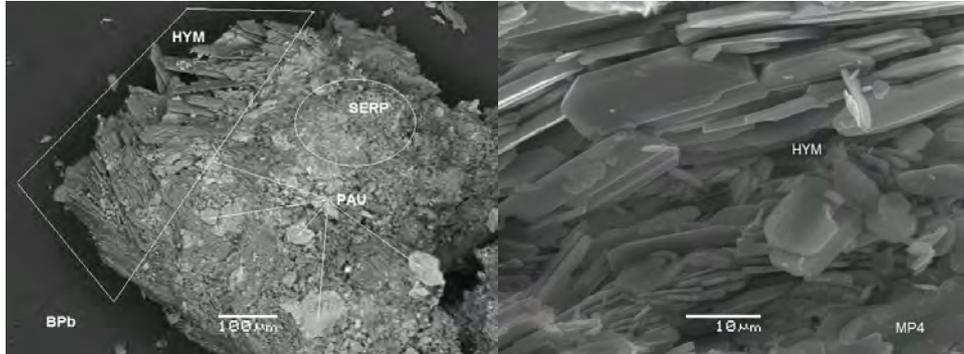

Figure 3 – SEM micrographs of Hydromagnesite (HYM) crystals (euhedral blades), in an aggregation with pyroaurite (PAU) and serpentine (SERP).

Table 2 – EPMA analyses (%).

Sample	PN5	F2f		BPb					AT2	
Mineral	PAU	HY	HY	PAU	HY	HY	PAU	SER	MG	MG
SiO$_2$	0.1	0.3	0.2	0.1	0.1	0.1	0.2	42.2	0.1	0.2
TiO$_2$	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Al$_2$O$_3$	0.0	0.3	0.2	0.2	0.1	0.1	0.2	0.2	bdl	bdl
Fe$_2$O$_3$	24.8	0.1	0.1	24.2	0.1	0.1	23.9	3.7	0.1	0.1
MnO	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.1	0.2
MgO	34.3	41.6	42.5	33.7	41.6	42.2	33.4	41.8	43.2	42.7
CaO	bdl	bdl	bdl	0.2	0.1	0.1	0.2	0.1	2.6	2.8
Na$_2$O	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
K$_2$O	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Cr$_2$O$_3$	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.2	bdl	bdl
NiO	1.9	bdl	bdl	2.2	bdl	bdl	2.3	0.3	bdl	bdl
Total	61.1	42.3	43.0	60.6	42.0	42.6	60.2	88.5	46.1	46.0

Explanatory notes - PAU: Pyroaurite, HYM: Hydromagnesite, SERP: Serpentine,   bdl: below detection limits

4.3. Water Analyses

The water chemical analyses of all samples analyzed indicate waters of Mg-OH type (Table 3). Moreover, the high pH values, high magnesium and bicarbonates content, low calcium content and therefore high Mg/Ca ratio are characteristic of waters emanated from ultrabasic rocks (Papastamataki, 1977).

5. Discussion – Conclusions

It has been emphasized the presence of brucite in partially serpentinized dunites or in olivine rich peridotites (Hostetler et al., 1966, Mposkos and Perdikatsis, 1986). It is generally regarded that hydromagnesite and/or pyroaurite formed at the expense of brucite during weathering of ultrabasic rocks. In New Idria serpentinites the content of brucite in the partial serpentinized averages 7-8 per cent and its origin took place during the initial serpentinization of the olivine rich parent. However, it is almost absent from the surface weathering zone (Mumpton and Thompson, 1966). Instead in this zone pyroaurite and hydromagnesite are presented. The latter is localized above the water table often as pea-size concretions. These minerals are considered as alteration products of the brucite: the former in situ, while the hydromagnesite precipitated from ground waters if they

are in excess (Hostetler et al., 1966, Mumpton and Tompson, 1966). Also, been studied thoroughly the formation of pyroaurite at the expense of brucite during weahtering in dunitic serpentenite in Vourinos, Greece (Mposkos and Perdikatsis, 1986).

Table 3 - Spring waters chemical analyses.

	units	AL Wf	MA Wf	BP Sp	SN Fn
Conductivity	$\mu S\ cm^{-1}$	1098	1020	680	680
TDS	$mg\ L^{-1}$	605	520	340	341
pH		8.6	8.6	9.3	9
Eh	mV	-109.8	-103.3	-142.1	-124.1
T	^{o}C	21.4	20.2	19.4	20.0
NO_3^-	$mg\ L^{-1}$	3.5	3.5	3	4.4
HCO_3^-	$mg\ L^{-1}$	558	578	354	371
Ca	$mg\ L^{-1}$	3	2.8	0.8	1.2
Mg	$mg\ L^{-1}$	120	154	89	87
SO_4^{2-}	$mg\ L^{-1}$	15	15.6	2.1	0.3
Mg/Ca ratio		40	55	100	80

Explanatory notes : (MA, AL)=Ag. Marina area, (BP,SN)=Sxinos area

The typical occurrences of hydromagnesite, situated in the areas under investigation, are localized in highly weathered serpentinites. Typical also is the systematic involvement of the pyroaurite group minerals (Table 1, Figure 3); the intimately growth of the hydromagnesite with pyroaurite and serpentine in cotton balls is obvious. The coexistence of the two former minerals in almost all occurrences is remarkable (Table 1, 2). Has been suggested that brucite is converted to hydromagnesite if the partial pressure of CO_2 (P_{CO2}) is at least 10-6 atm., whereas probably even smaller P_{CO2} values are required for conversion of brucite to pyroaurite group (Hostetler, 1960, Hostetler et al., 1966). The coexistence of hydromagnesite with pyroaurite may indicate intermediate P_{CO2} values. However, the predominance of hydromagnesite is also related with the arrangement of the relevant supply of Mg and Fe (and Ni also). Note that the studied hydromagmesite is pure, while pyroaurite contains about 2.0% NiO (Table 2). If the concentration of Mg and the P_{CO2} are both high, magnesite forms, whereas low P_{CO2} favors the formation of hydromagnesite for a constant Mg/Ca ratio (Carpenter, 1962, Stamatakis, 1995). As the P_{H2O} approaches the vapor pressure of liquid water brucite or hydromagnesite are stable phases (White, 1997). Besides Mg^{2+} release from the original Mg-silicate minerals during serpentinization, some Fe^{2+}, as well some Ni^{2+} is also liberated, and it may be incorporated in precipitated brucite. Fe-bearing brucite, under small P_{CO2} values, is converted to pyroaurite (Hostetler, 1960, Hostetler et al., 1966). In addition, a partial oxidation of the soluble Fe^{2+} when exposed to mixing zone Eh-pH conditions to Fe^{3+} in the Mg^{2+} rich environment at pH around 8.5 leads to the precipitation of pyroaurite (Hansen and Taylor, 1990, Taylor et al., 1991). Pyroaurite has been formed in a zone beneath the water table and its formation appeared to be restricted to depths near and below the presumed zone of mixing of two different water layers of different composition (Taylor et al., 1991). These are in consistence with two main features of almost all studied occurrences: the weathering and hydrological regimes. The earthy (highly weathered) serpentinite outcrops in the studied areas containing several cotton-balls and veinlets hydromagnesite - pyroaurite occurrences (e.g. near Schinos, Ag. Dimitrios, Kaloni etc) are often wet, due to the present day circulation of surface and ground-water. Obviously, here do not expected to have retained brucite.The secondary Mg-hydroxycarbonates are constantly associated with these "foliated- friable -earthy" serpen-tinites, usually in areas of tectonic discontinuities and contacts, indicating that the fluid flow was controlled by reactions occurred in these easily accessible masses. Chemical analysis of spring water derived from the altered serpentinite, close to the contact with the limestone has high pH values, high magnesium and bicarbonates content, low calcium content and therefore high Mg/Ca

ratio (Table 3). The extremely low Eh values also revealed that the spring waters are derived from deep levels and environments isolated from the atmosphere (Garrels and Christ, 1965, Appelo and Postma, 2007). The Mg/Ca ratio is ranging between 40 and 100 and it is high enough to start the precipitation of metastable magnesium carbonate minerals such as hydromagnesite and huntite (Stamatakis, 1995, Konigsberger et al., 1999). Brucite formed during initial serpentinization must be regarded as a prime candidate for reaction with CO_2 solutions to form magnesite either hydromagnesite either pyroaurite (or coalingite or artinite). In natural environments at surface temperatures hydromagnesite (and/or nesquehonite) can precipitate directly from solutions (Hostleter, 1964); also hydromagnesite (and dipyngite) can precipitate at subsurface directly from solution (Wilson et al., 2009). Magnesite may form by dehydration of hydromagnesite, which forms more rapidly under aqueous conditions (Möller, 1989, Guthrie et al., 2001). The vein type magnesite deposit at Malentrata (Tuscany, Italy) considered as a result of interaction of fluids derived from the active Larderello-Travale high enthalpy geothermal field and the Ligurian serpentinites (Boschi et al., 2009). The serpentinite host rock were hydrothermally completely altered by Si- and CO_2 –rich geothermal fluids to a friable rock consisting mainly of opal, chalcedony, Al-Mg-Cr phyllosilicates and accompanied by the formation of a network of magnesite and dolomite veinlets. These researchers regard that the formation of magnesite may be the result of dehydration of a hydrated precursor (e.g. hydromagnesite). The presence of cauliflower or botryoidal-nodular magnesite with colloform texture at or near surface outcrops above hydromagnesite – pyroaurite occurrences, favoured for such an origin (dehydration of hydromagnesite) of these specific type magnesite aggregates in the studied areas of Geraneia ophiolites. In situ test for CO_2 fixation in serpentinite rock mass in the Iwanaidake ultramafic rocks, northern Japan, showed that the groundwater acidified by injected CO_2 dissolves brucite and serpentine minerals in the host serpentinite to increase its Mg content. It is possible that Mg- hydroxycarbonates precipitate from the highly alkaline groundwater by reaction between CO_2 and excess Mg component; hydromagnesite precipitate in the case of the dunitic serpentinite and pyroaurite or coalingite also formed (Okamoto et al., 2006). Also, serpentinite material from Finland has been acid leaching and then the products magnesium-rich solutions were carbonated by bubbling CO_2 and with raising the alkalinity to pH 9, hydromagnesite precipitated (Teir et al., 2009). Most of the required CO_2 for the formation of Mg-hydroxycarbonates of the studied areas is more likely to derive from the relevant geothermal system. The CO_2 needed for the Mg-hydroxycarbonates formation may derive from meteoric water, but especially in areas of the volcanic manifestations (e.g. gas emanations, fumes and vents in Soussaki area) the geothermal system should virtually be the only source of CO_2. Indeed the large amount of CO_2 discharged as diffuse and focused in Sousaki area, which estimated for an area of $0.015\ Km^2$ and for two small caves to be more than 50 tons/day (D'Alessandro et al., 2006). Obviously it is not necessary volcanic activity for the formation of Mg-hydroxycarbonates, but the high output CO_2 in Sousaki volcanic/geothermal area should be correlated with the relatively large and frequent their occurrences. The study of the carbon and oxygen isotopic compositions of the Mg-hydroxycarbonates would help to clarify the source of CO_2 as well the conditions of their deposition. The research on this topic is in progress and will be the subject of a forthcoming paper. However, the isotopic composition of carbon and helium of geothermal fluids at Sousaki suggest a prevalent origin from decarbonation reaction of subducted carbonates with only a minor contribution of mantle degassing (D'Alessandro et al., 2005, Dotsika et al., 2009). Obviously the limited occurrences of Mg-hydroxycarbonates at Kaloni area could be correlated with the very low activity of the volcanic/geothermal system of Methana and the very low CO_2 output (D'Alessandro et al., 2008).

Therefore, we attribute the relatively widespread Mg-hydroxycarbonate occurrences in Geraneia ophiolites, compared with other regions, in the combination of the following factors:

- The ultrabasic character of Geraneia ophiolites: spinel peridotites whith dunite bodies.
- The active and intense tectonic regime of this region.

- The great activity of the geothermal fluids and the high CO_2 output of Sousaki volcanic/geothermal system.

We conclude that there existed several phases of the evolution of the weathering and the hydrothermal alteration due to geothermal system and tectonic regime of the ultrabasic rocks. Hence, at early periods vein-type magnesite may formed, suggesting that P_{CO2} would be was quite high. At later stages, when the P_{CO2} and the temperature were lower, as well as the P_{H2O} approaches the vapor pressure of liquid water, as represents a geothermal system in their waning stage, hydromagnesite and pyroaurite are formed in highly altered, serpentinized masses irregularly developed in the ultrabasic rocks of the studied area. Part of the hydromagnesite then can be dehydrated to the cauliflower or botryoidal-nodular type magnesite with colloform texture, occurred at near surface outcrops, especially near to areas with volcanic/geothermal manifestations. Also, indicated that the Mg-hydroxycarbonate in Argolida may have limited extent due to the very low CO_2 output of the Methana volcanic system, in contrast to the case of the region of Sousaki volcano.

6. Acknowledgments

7. References

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