CONDITIONS GOVERNING THE FORMATION OF OPHICALCITES AND LISTWANITES (Central Euboea, Greece)*

BY

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Abstract. Listwanites and ophicalcites are the products of hydrothermal activity both on fresh as well as on serpentinized harzburgites. While listwanitization was effected by solutions acting under high temperature (up to 400° - 500° C), ophicalcitization was accomplished under lower temperatures (below 150° C).

In the first case the solutions induced drastic mineralogical and chemical transformations in the starting materials and in particular they mobilized much MgO from the ultramafics, which became concentrated in the solutions. In the latter case, no mineralogical or chemical transformation was induced in the starting materials and therefore no MgO concentration took place in the hydrothermal solutions. In the listwanitization process both Ca and Mg - bearing carbonate phases were precipitated, while during ophicalcitization only Ca - bearing carbonates crystallized.

The two processes above are strictly correlated for they must be considered as two successive stages in the evolution of the hydrothermal activity which affected the ultramafics.

INTRODUCTION

In the central part of the Island of Euboea (Greece) and, more precisely, in the area roughly extending between Pyxaria and Kandili ranges, ophiolitic ultramafites outcrops lie on jurassic limestones.

They underwent two different low - grade transformations in two distinct periods.

a) The first transformation is serpentinization, which took place intensively yet irregularly all over the outcorps. Serpentinization is a very well known phenomenon occuring in the alpine - type peridotites and elsewhere it has been carefully investigated; therefore no further mention will be made of this process in the present paper.

b) Both fresh as well as serpentinized ultramafites were locally affected by successive hydrothermal activity, particularly in the area near Procopion and Mandouthion in correspondence of the magnesite quarries; this gave rise to listwanites and ophicalcites. Both rocks are «breccias» composed of two elements i. e. fragments of ultramafic material and carbonate cement. At first sight they appear to be very similar rocks characterized by network texture. But when studied in detail listwanites

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* The work was carried out with the financial support of the Consiglio Nazionale delle Ricerche.

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and ophicalcites exhibit peculiar differences both in their fragments as well as in their carbonate cement. In particular, listwanites of central Euboea are found to contain some carbonate phases which are absent, on the contrary, in the ophicalcites; moreover, in the first case the hydrothermal solutions induced drastic transformations both in the mineralogy as well as in the chemistry of the affected ultramafites, while in the latter case no mineralogical or chemical transformations took place.

These different features undoubtedly depend on different genetical conditions. It is the purpose of this study to investigate the hydrothermal conditions under which listwanites and ophicalcites of central Euboea were formed and, at the same time, the factors governing the precipitation of the different carbonate phases associated with them. These phenomena are considered in connection with the mineralogical and chemical transformations which the solutions induced in the affected rocks.

This may be a contribution to the ophiolite problem and although listwanites and ophicalcites have been described from all over the world, contrasting opinions exist on the formation of both rocks (ABBATE et al., 1972).

LITHOTYPES OCCURING IN THE HYDROTHERMALLY AFFECTED AREAS

In the hydrothermally affected areas four lithotypes may be recognized : a) fresh ultramafites, b) serpentinites, c) ophicalcites, d) listwanites. The first two lithotypes represent the starting materials and the latter two the products of the hydrothermal activity on a) and b). These rocks are intimately related, for the starting materials underwent gradual transformation.

a) Fresh ultramafites

They are frequently present as nodules inside the listwanites and show typical tectonite fabrics, as is normally the case in ophiolitic ultramafites. They are completely fresh as it may be deduced from their low H_2O^+ content (tab. 1). They are Harzburgites. Olivine (Fa% = 8) and orthopyroxene (enstatite with Of% =7) show variable relative percentages. Chrome spinel, green or brown colored, is a normal accessory phase. Clinopyroxene (diopside with $2V_z = 60°$, $c : Z = 36°$) is very rare as single crystals and, when present, is an accessory constituent. On the other hand, it is frequently present as exsolution lamellae in orthopyroxenes.

b) Serpentinites.

Normally they are completely serpentinized rocks consisting of serpentine minerals, magnetite and chrome spinel. Nevertheless, partially serpentinized types are present and in these cases the serpentine minerals are associated with olivine, orthopyroxene, exceptionally clinopyroxene, chrome spinel, as relic phases.

c) Listwanites.

They are widespread and derive from fresh ultramafites as well as from serpentinites.

In the first case, the more characteristic one, three concentric zones, representing successive stages of alteration, are formed around fresh ultramafic nodules (fig. 1). One may generally distinguish an inner, very thin, greenish zone at the contact with the fresh nodules, an intermediate, wide, yellowish zone, and then an outer reddish zone. This last one is normally at the contact with carbonate veins where oxidizing conditions undoubtedly existed ; its thickness is variable and seems to depend on and, particularly, to increase with the thickness of the carbonate veins.

These three concentric zones consist of fine grained rocks which are composed of secondary alteration minerals, associated with primary harzburgitic phases.

Mineralogically the greenish zone is characterized by abundant green chlorite (2V $\sim$ 40° — 60°, probably a Mg — rich chlorite). It is free or very poor in carbonates, while some quartz may be present. In the yellow zone montmorillonite is a frequent phase. Carbonates are abundant, especially as veins and veinlets, while quartz is scarce. In the reddish outer zone carbonates are abundant constituents, both as fine grained dispersed crystals as well as veinlets and veins ; hematite is associated with the carbonates which therefore assume a reddish brown color ; clay minerals may be present.

Talc and tremolite ($2V_x = 79°$, $c : Z = 18°$) are locally formed as products of the hydrothermal alteration. Talc is concentrated particulary in the inner yellowish zone, while tremolite, associated always with carbonates, occurs in the three zones as a reaction phase between orthopyroxene or talc and the Ca - bearing solutions (fig. 2).

The mineralogical phases of the original fresh harzburgitic nodules tend to disappear more or less completely in the three concentric alteration zones where they are substituted by the above mentioned alteration phases. In particular, olivine is completely altered in the green zone referred above ; pyroxenes may exist, at least in part, in each of the three concentric zones. The only mineral which does not undergo alteration is chrome spinel.

In conclusion, the observed paragenesis are typical for listwanites, especially in the intermediate and in the outer zone (KASHKAI, 1964).

The alteration effects by the solutions was undoubtedly enhanced not only by the strong tectonization of the ultramafics, but also by the high total pressure fluid under which they acted on the original rocks. The solutions produced some drastic mechanical effects, as was proved by crushing the border zone of the fresh nodules, at the contact with the inner alteration zone, where a «breccia» consisting of angular fragments of strongly deformed harzburgitic primary minerals cemented by secondary silicate minerals, may be observed (fig. 3).

Listwanites may be produced also by hydrothermal alteration of serpentini-

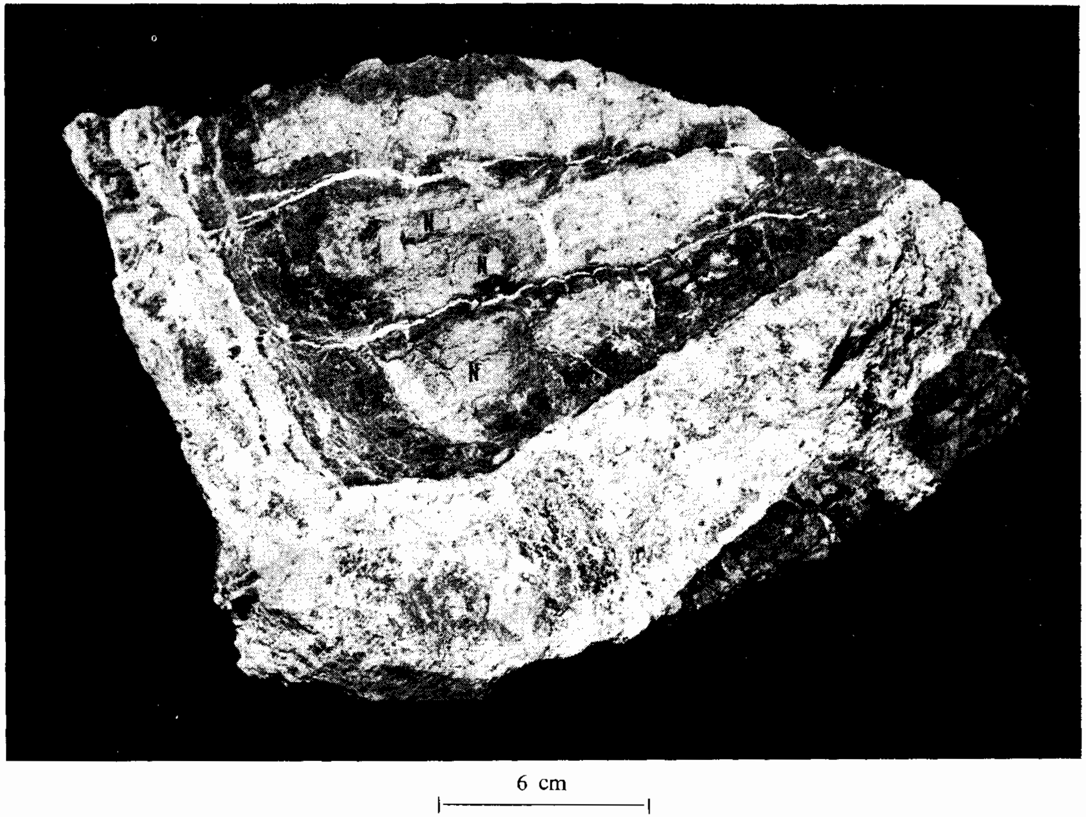

Fig. 1. Concentric alteration zones produced by the hydrothermal solutions during listwanitization of fresh harzburgitic nodules (N). Carbonate veins, white, are present.

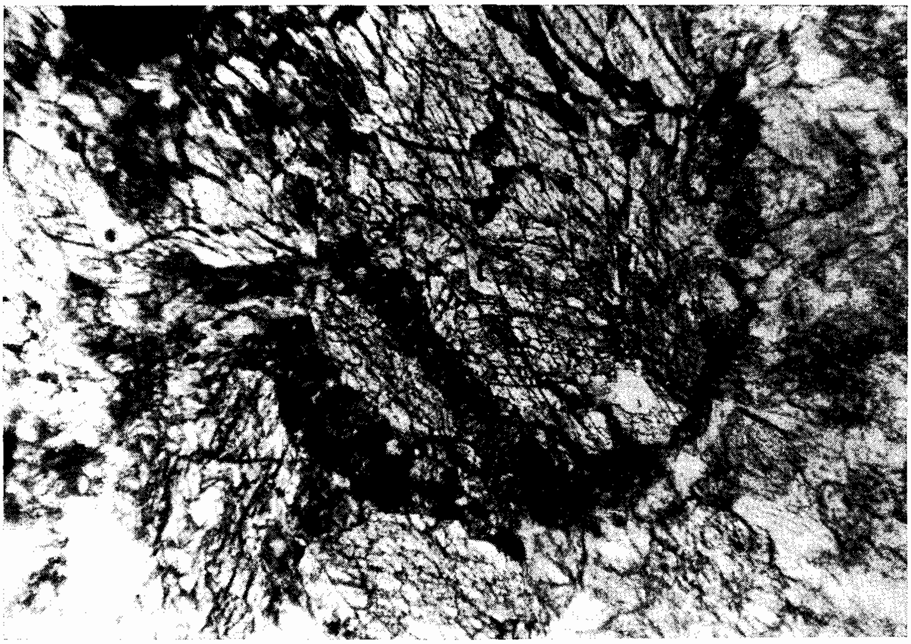

Fig. 2. Tremolite is a reaction phase between talc (t) and Ca - bearing solutions. Plane polarized light.

Fig. 3. Cataclastic phenomena on the border of the fresh harzburgitic nodules, induced at least in part by the hydrothermal solutions operating under high total fluid pressure. Crossed nicols.

tes ; in this case mineralogical and chemical transformations occured as well. A microgranular, homogeneous yellow - brown colored rock is formed. Mineralogically it is characterized, as must be the case, by abundant carbonates in small permeating crystals or concentrated in veins. Clay minerals are normally present in small amounts, while quartz may be very abundant ; hematite may be also well represented. Among the minerals of the starting serpentinites, magnetite may be present, while serpentine is exceptional. It is worth noting that talc and tremolite may be present, the last one as a reaction phase between talc and the Ca - bearing solutions.

d) Ophicalcites.

In central Euboea ophicalcites are «breccias» with fragments composed, completely or sometimes partially, of serpentinized ultramafites cemented by carbonate, carbonate - quartz, quartz veins. In some cases quartz is the only cementing material. The carbonates often substitute the ultramafic material and may be pseudomorphous on the minerals of the affected ultramafics.

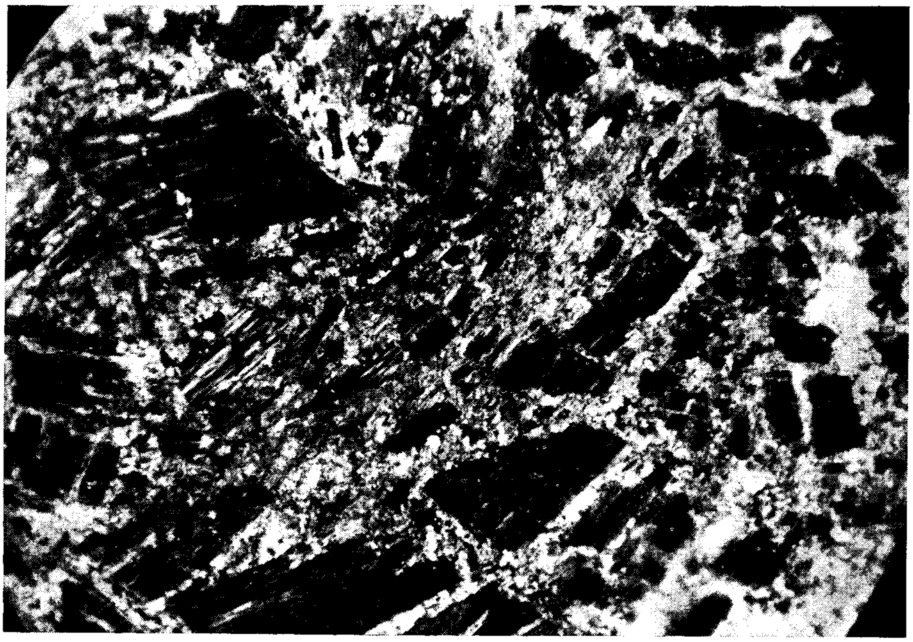

Fig. 4. Cataclastic phenomena induced by the hydrothermal solutions operating under high total fluid pressure, on serpentinite. The fragments are cemented by calcite. Crossed nicols.

No mineralogical transformation has been induced in the affected ultramafites by the hydrothermal solutions. Mineralogically, the fragments of the ophicalcites are composed of the same minerals (apart from the carbonates) observed in the serpentinites. In particular it must be stressed that no talc or tremolite have been observed. The only effect induced by the hydrothermal solutions on the starting serpentinites was the simple one of cementing the fragments of just fractured material or that of disrupting more intensively and then cementing the ultramafites by means of carbonates and quartz (fig. 4).

CHEMICAL TRANSFORMATIONS OBTAINED DURING THE HYDROTHERMAL PROCESS

a) Listwanitization.

In order to detect the chemical transformations induced in the ultramafics during listwanitization, chemical analyses were carried out on the fresh nodules and on the three surrounding concentric alteration zones, as well as on serpentinites and on listwanites thereby derived. The results are shown in Table 1.

The chemical transformations which were observed from the fresh nodules to the successive alteration zones may be summarized as follows : MgO, SiO_2, FeO and CaO (entering the silicates) decrease regularly, while Fe_2O_3 and H_2O^+ increase in the same sense.

MgO and SiO_2 are released during the alteration of olivine and orthopyroxene and the mobilized amounts represent the excess in MgO and SiO_2 with respect to the quantities required to form clay minerals. It must be noted that the highest release of MgO occurs at the first (green) alteration zone in connection with the drastic alteration of olivine : It decreases from 43.34% in the fresh nodule to 29.28% in the green zone. The successive lower mobilization of MgO may be ascribed to the increasing alteration of orthopyroxenes toward the outer zones.

CaO is released by the accessory clinopyroxenes and subordinately by orthopyroxenes and therefore the mobilized CaO is always low.

FeO, except that enters the chrome spinels which remain uneffected by the hydrothermal alteration, is gradually oxidized to the trivalent state toward the outer zone. It must be pointed out that the strongest oxidization of Fe'' «to Fe'''» occurs in the green zone, as, by passing from the fresh nodule to the green zone, FeO is reduced from 6.95 % to 1.96 % ; in the successive zones only very small quantities of «Fe''» are oxidized in the trivalent state.

Therefore one would expect Fe_2O_3 to be high in the green zone and to increase slightly from the green to the red zone. But this is not the case. «Fe'''» is low in the green zone, while it increases more and more toward the yellowish and the reddish zones; there it prevails over the theoretical Fe_2O_3 that one would expect to be formed, if all FeO measured in the fresh nodules was oxidized in the trivalent state. This may be explained only by postulating a migration of «Fe''» from the green zone toward the outer zones, where it becomes concentrated.

TABLE 1.

Chemical analyses of rocks.

	1	2	3	4	5	6	7
SiO_2	44.79	50.88	42.85	38.53	77.06	36.84	26.25
TiO_2	tr	0.15	0.07	0.12	0.25	0.09	0.11
Al_2O_3	2.10	2.64	1.84	2.23	1.02	0.34	0.45
Cr_2O_3	0.37	0.03	0.40	0,40	0.23	0.45	0.13
Fe_2O_3	0.45	3.02	9.08	10.21	7.57	6.71	4.31
FeO	6.95	1.96	1,23	1.07	0.16	0,31	0.26
NiO	0.25	0.32	0.22	0.30	0.24	0.27	0.15
MnO	0.13	0.06	0.14	0.05	0.05	0.11	0.07
CaO	1.59	1.82	7.85	6.73	3.65	1.03	11.22
MgO	43.34	29.28	20.50	23.18	4.59	36.79	30.84
Na_2O	0.05	0.05	0.06	0.05	0.02	0.07	0.07
K_2O	0.02	0.04	0.02	0.03	0.02	tr	tr
P_2O_5	0.02	0.02	0.02	0.03	0,02	0.03	0.03
CO_2	—	tr	6.18	5.23	2.15	4.22	16.64
H_2O+	0.58	6.28	5.30	7.63	2.81	11.36	8.42
H_2O-	0.16	3.75	5.14	5.24	0.40	1.81	1.57
	100.80	100.30	100.90	101.03	100.24	100.43	100.52

1.— fresh ultramafic nodule ; 2, 3, 4.— greenish, yellowish, reddish alteration zones respectively surrounding the fresh ultramafic nodule ; 5.—listwanite deriving from the serpentinite of analysis 6 ; 7.—ophicalcite with fragments of serpentinite.

The increasing amounts of H_2O^+ from the nodules toward the reddish zone clearly depend on the progressive alteration of olivine and pyroxenes into hydrated silicates.

During the listwanitization of serpentinites, chemical transformations took place which are not as clearly evidenced as in the example above. However, when the analysis of a serpentinite (analysis 6) is compared with that of a listwanite thereby derived (analysis 5), it can be seen that much MgO is released by the ultramafites during the hydrothermal process, as it is reduced from 36.76% in the serpentinite to 4.59% in the listwanite. SiO_2 is greatly concentrated in the listwanite, but under the microscope this seems to be due to many quartz veins which cut through the carbonate veins and, it is reasonable to suppose that crystallized from late hydrothermal solutions. FeO and Fe_2O_3 show no marked difference in the two analyzed samples. H_2O^+, contrary to the first case discussed above, decreased abruptly in listwanites with respect to the original serpentinites. This may be ascribed to the absence of serpentine minerals and to the scarcity of clay minerals in the listwanites.

The conclusion is that during the listwanitization the hydrothermal solutions drastically changed the composition of the starting materials ; in particular, great quantities of MgO and, in the case of listwanitization of fresh ultramafites, considerable quantities of SiO_2 have been mobilized from the ultramafic material and were reasonably concentrated in the hydrothermal solutions. «Fe′′′», although intensively mobilized during the alteration process, becomes concentrated in the listwanites and not in the hydrothermal solutions.

b) Ophicalcitization

The analysis 7 shown in table 1 refers to an ophicalcite consisting of serpentinite fragments and carbonate veins. When compared to the analysis of a serpentinite (analysis 6), it exhibits lower SiO_2, Fe_2O_3, MgO_3, H_2O^+ contents and of course much higher CO_2 and CaO contents. Anyway, these differences are due to the masking effects produced by the abundant carbonate veins in the ophicalcite. In effect, if the two analyses above are recalculated on a CO_2 free base, they appear almost identical. In particular, in the ophicalcite the four oxides above assume the following values : $SiO_2 = 31.34$, $Fe_2O_3 = 5.15$, $MgO = 36.82$, $H_2O^+ = 10.05$; and in the serpentinite they become : $SiO_2 = 38.39$, $Fe_2O_3 = 6.99$, $MgO = 38.33$, $H_2O^+ = 11.83$. This means that during the ophicalcitization process, the hydrothermal solutions produced no chemical transformations in the starting materials.

THE CARBONATE PHASES

As it has just been said, both listwanites as well as ophicalcites contain carbonates, which may be present as fine grained crystals permeating the ultramafic material or, more evidently, are concentrated in anastomizing veins.

The following carbonate phases were recognized in the veins both under the microscope and by the diffractometer and by staining techniques : dolomite, calcite, aragonite and siderite. The veins may be monomineralic or may be filled with different carbonate phases. Quartz may be associated.

Magnesite

Normally it forms fine grained monomineralic concentrations in the form of sills and veins, or in the form of subspherical bodies. The sills are very variable in size, but they are generally the thickest among those formed by the above mentioned carbonates and are very abundant. The sills are normally strongly fractured. The subspherical bodies are very variable in size, ranging from a few cm^3 to 300 m^3. These magnesite concentration constitute the well known magnesite quarries of Euboea ; in later times they might have been crossed by the other carbonates.

Dolomite

Like magnesite, dolomite is fine grained. It forms veins which are normally thicker than the ones formed by aragonite and calcite, but generally thinner than those formed by magnesite. It may be associated with calcite : in this case dolomite builds up the outer bands of the veins, while calcite is concentrated at the centre or may form clusters of radiating crystals which substitute dolomite.

Dolomite veins may be traversed by calcite and aragonite veins.

Aragonite

It normally forms veinlets, thin to very thin, where it may be the only carbonate phase present; more frequently, however it is associated with calcite. The aragonite crystals, medium to coarse grained, grew normally to the walls of the veins. When aragonite is associated with calcite, the last phase crystallized first at the contact of the walls, while aragonite separated later in the inner part of the vein (fig. 5).

Aragonite and aragonite - calcite veins may be cut by later veins of calcite.

Aragonite is normally deformed ; fine lamellar secondary twinning on (110) is conspicuous in most aragonite grains cut approximately perpendicular to the acute bisectrix, but it is not observed on other orientations.

Distinction between aragonite and calcite is possible at a glance in thin section, as the aragonite can always be turned to a position of low relief in plane polarized light where it is almost perfectly clear. Calcite, due to its different refractive index and the presence of well developed twinning and rhombohedral cleavage, shows more prominent relief and generally appears somewhat turbid. Between crossed nicols the interference colors of aragonite remain smooth and uniform when rotated to extin-

Fig. 5. Portion of a vein with calcite$_1$ turbid, highly deformed (C), separated on the outer zone of the vein, and aragonite (A) separated at the centre. Plane polarized light.

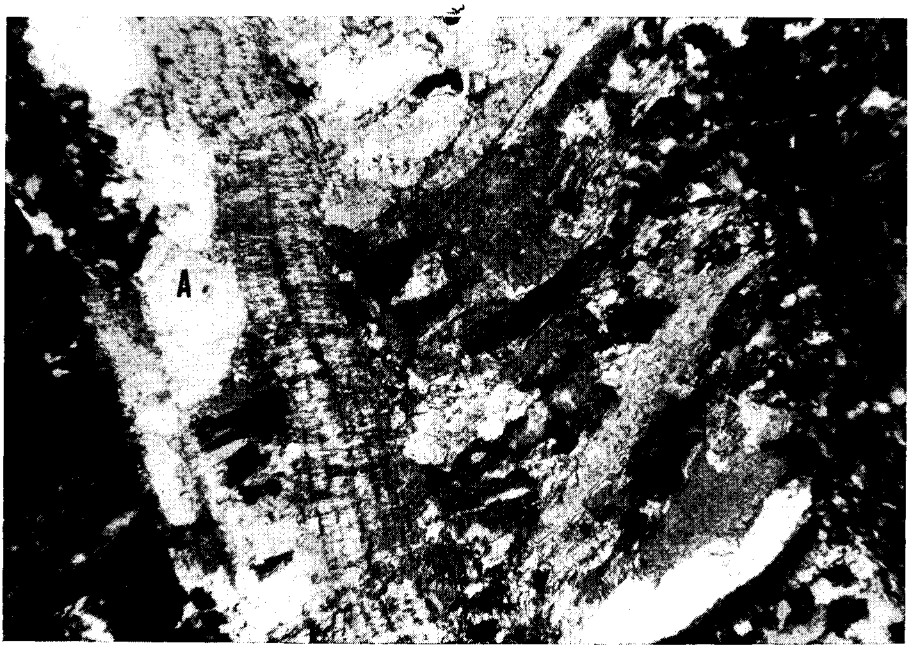

Fig. 6. Calcite$_2$ vein cutting an aragonite vein (A). Crossed nicols.

ction upon the microscope stage and do not give the «twinning» effect shown by calcite.

All the aragonite crystals observed show no degree of inversion to calcite.

Calcite

As stated before, calcite may be associated with aragonite, or may form monomineralic veins. The first will be referred to as calcite$_1$, and the second as calcite$_2$. In each case it is medium to coarse grained. When associated with aragonite, it is strongly deformed and normally shows polysynthetic twins (fig. 5). The monomineralic veins which cut aragonite veins, may consist of strongly deformed calcite crystals, or completely undeformed euhedral crystals (fig. 6). The last veins are generally undisturbed.

Fig. 7. Calcite$_3$ generation separated in the core of quartz vein. Plane pol. light.

Calcite$_2$ may be associated with quartz : this last mineral postdates calcite$_2$ separation as it forms the centre of the veins.

A third calcite (calcite$_3$) generation may occur, especially in ophicalcites ; it postdates quartz vein separation, as it builds up the centre of the quartz-veins (fig. 7) or forms clusters of radiating crystals which grow inside the quartz-veins.

Siderite

It is the rarest among the carbonate phases encountered so far. It does not form veins by itself, but is associated, although not frequently, with calcite$_2$. In cases where the calcite$_2$ crystals are strongly deformed the associated siderite crystals seem to be euhedral and undeformed (fig. 8). They are easily recognized as they are of deep brown color.

Dolomite, aragonite and calcite$_1$, are often associated with euhedral tremolite crystals formed by the reaction of talc or orthopyroxene with the Ca-bearing solutions. Aragonite and calcite$_1$ veins may contain, although very rarely, small euhedral magnetite crystals ; on the contrary, magnetite has not been found in the calcite$_2$, calcite$_3$ and siderite veins.

Fig. 8. Euhedral undeformed siderite growing on a highly deformed calcite$_2$ generation. Crossed nicols.

From the description above it may be concluded that the carbonates did not crystallize together, but separately according to the following order :
magnesite, dolomite, calcite$_1$, aragonite, calcite$_2$, siderite and calcite$_3$.

With respect to the distribution of the carbonate phases between listwanites and ophicalcites it is of utmost importance to note that while in the former all the above carbonate phases were observed, in the latter only calcite$_2$ and calcite$_3$ were detected.

GENETIC CONSIDERATIONS

The hydrothermal solutions which affected the ultramafics must have been rich in Ca ions, as they precipitated abundant Ca - bearing carbonate phases ; they reasonably assumed Ca while traversing the limestone formations including the ultramafics.

These solutions, as has been shown in the preceding paragraphs, produced both listwanitization as well as ophicalcitization ; but while the latter process was accomplished without any chemical change of the ultramafics, during listwanitization the affected rocks suffered drastic chemical transformations, and in particular were depleted in Mg which concentrated in the hydrothermal solutions.

The carbonate phases mentioned above, therefore, crystallized from chemically different solutions, only for the reason that some were only Ca - rich while others were Ca as well as Mg - rich. These solutions must be considered as successive stages in the evolution of the same hydrothermal cycle, whose last stages may actually be represented by the hot springs present on the island.

It is worth investigating the temperature conditions under which the hydrothermal solutions operated.

Some information may be deduced from the observed reaction of talc with the Ca - bearing solutions to give tremolite.

Experimental data show that in hydrothermal conditions (KALININ, 1967) tremolite may be synthesized at temperatures not below the range 400° - 450° C, when operating at 500 atm and under low CO_2 pressure. On the other hand, METZ et al. (1968) have shown that the temperature at which tremolite is stable in the reaction :
5 talc$+$6 calcite $+$4 quartz$\rightarrow$3 tremolite $+$ $6CO_2$ $+$ $2H_2O$ is strongly influenced by the mole fraction X_{CO_2}, and in particular increases with it. When operating under total gas pressure of 1000 bars, tremolite may crystallize from the reaction above at a temperature near 500° C.

Furthermore, the presence, although exceptional, of magnetite in the calcite$_1$ and aragonite veins is of particular importance. From the experimental data on hydrothermal solutions given by JOHANNES (1968), it appears that under a pressure of 1000 bars from Ca^{++}, Mg^{++} - bearing solutions with $Ca^{++} / (Ca^{++} + Mg^{++}) \sim 0.77$, magnetite may precipitate only at temperatures above 400° C (fig. 9), while at lower temperatures, siderite is the stable phase.

In order to check these supposed T values, it has been determined the $MgCO_3$ content of calcite$_1$ in a listwanite by measuring the shift of the $(10\bar{1}4)$ reflection with respect to the (100), (101), (110) reflections of quartz. It is well known that the $MgCO_3$ content of calcite is a function of T (HARKER et al., 1955), when other ions as Fe, Mn, Sr, Ba are absent or present in very low amounts (CAPEDRI et al., in press). A $MgCO_3$ content of 3.7% and a T of 458° C have been determined for calcite$_1$.

As tremolite is associated either with dolomite or calcite$_1$ or aragonite, and moreover, magnetite is associated with calcite$_1$ and aragonite, it may be stated that these carbonate phases crystallized all under rather high temperatures (400 - 500°C).

As no tremolite and no magnetite has been discovered associated with calcite$_2$, siderite and calcite$_3$, a lower temperature of crystallization may be postulated for these carbonate phases.

No precise value for the fluid pressure (P_f) may be deduced in the present case ; however, it may be reasonably assumed that P_f must have been higher than the load pressure and therefore it could not have been lower with respect to the pressure of the experiments refered to above.

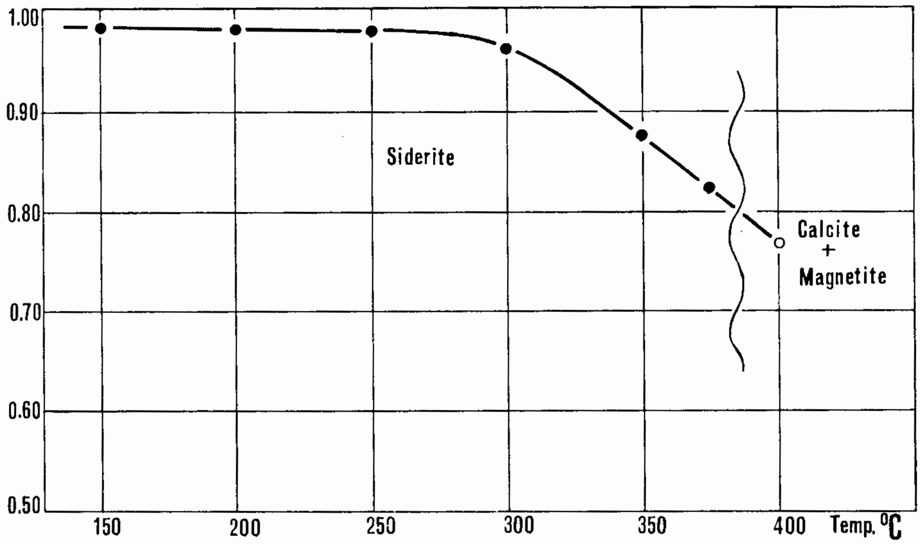

Fig. 9. Stability fields for calcite, siderite, magnetite in relation to Ca/(Ca+Fe'') (ordinate) and temperature (abscissa). (JOHANNES, 1968, pag. 161)

In particular the $MgCO_3$ content of calcite$_2$ in ophicalcites reaches 1% and a temperature of crystallization of 130° C may be deduced.

It is well known that the crystallization of magnesite, dolomite and calcite from Ca^{++}, Mg^{++}—bearing solutions depends primarily on T and on Ca^{++} and Mg^{++} concentrations (JOHANNES, 1970). In the present case, as T did not vary greatly untill calcite$_2$ separation, the determining factor governing the crystallization of magnesite, dolomite and calcite must be principally the Ca^{++} and Mg^{++} relative concentrations. For temperatures between 400° - 500° C, the stability field for magnesite is wider than that of dolomite and calcite, as it covers a wide range of variation for Ca^{++} / (Ca^{++} + Mg^{++}) ratio (fig. 10). On the contrary, the stability fields for dolomite and calcite cover narrow ranges of variation for the ratio above.

From the discussion above, magnesite is expected to be the most abundant carbonate phase precipitating from Ca^{++}, Mg^{++}-bearing solutions at temperatures near 400° - 500° C. Magnesite is also expected to be the first carbonate phase to precipitate from Mg-rich solutions, followed, by lowering the Ca^{++}/(Ca^{++} + Mg^{++}) ratio, by dolomite and then calcite. These deductions tally perfectly with the observations made on the reciprocal relationships between the carbonate phases in the ultramafics of central Euboea.

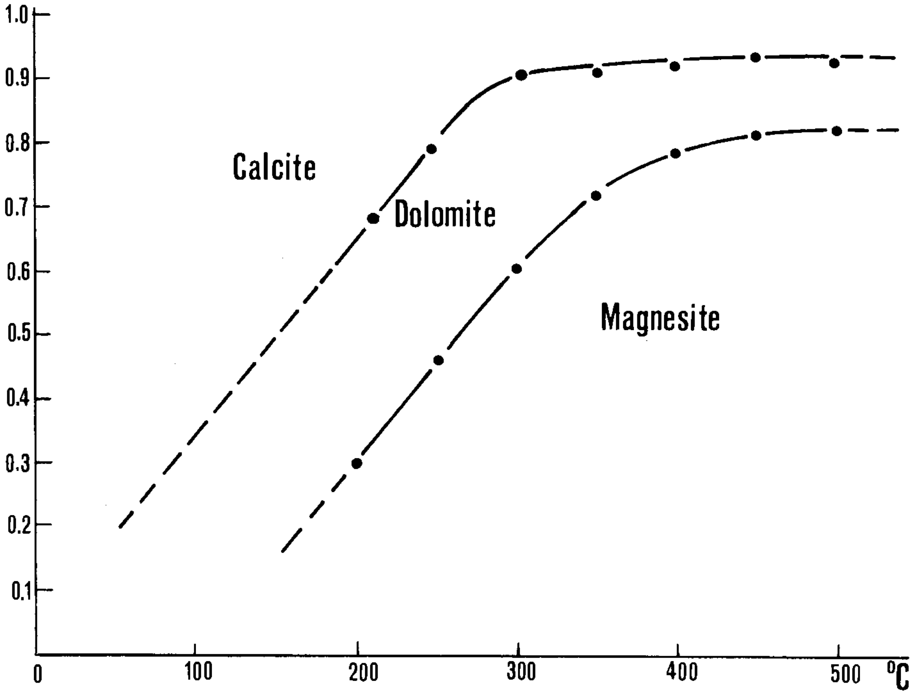

Fig. 10. Stability fields for calcite, dolomite, magnesite in relation to Ca/(Ca + Mg) (abscissa) and the temperature of the solutions (ordinate). (JOHANNES, 1970, pag. 308)

It is well known that aragonite is stable at higher pressures with respect to calcite. It is of importance to remember that the calcite - aragonite transition boundary most probably represents the lowest pressure boundary at which aragonite can be stable at any given temperature (JOHANNES et al., 1971) : addition of $MgCO_3$ to the pure system CaO - CO_2 moves the calcite - aragonite boundary to higher pressures (GOLDSMITH et al., 1969). This implies that from a Mg - bearing solution calcite may separate instead of aragonite at pressures above those given for calcite precipitating from pure system CaO - CO_2. When the

Mg content in the solution is lowered on entering the calcite structure, aragonite may crystallize in turn.

Calcite$_1$, as stated before, predates the aragonite separation, and it has been shown that it contains considerable amounts of $MgCO_3$.

It is possible that the whole system, between magnesite and calcite$_1$ separation, developed under relatively high fluid pressures, exceeding those expected on the basis of the calcite-aragonite transition boundary, for the deduced temperatures, in the pure system $CaO - CO_2$.

Aragonite does not show any relation suggesting inversion from calcite$_1$, a phenomenon which may happen at very low pressures from strained calcites (NEWTON et al., 1969).

It is well known, on the contrary, that aragonite is a metastable phase and tends to be converted into calcite. The experimental data on the transition of aragonite to calcite under hydrothermal conditions (METZGER et al., 1968) suggest that aragonite conversion to calcite depends largely on T : no calcite is formed below 150° C, while the conversion is drastic at temperatures higher than 200° C. In dry environments, on the contrary, the above transformation is very difficult : the laboratory experiments by DAVIS et al. (1965) on the kinetics of the aragonite - calcite indicate that at low pressures (below 4 kb), 2×10^9 years would be required for 99 percent inversion to calcite at temperatures as high as 250° C.

Therefore the persistence of aragonite in the present case may be due : i) either to the fact that T of the late hydrothermal solutions was low (the experimental data suggest that aragonite could exist for million of years at temperatures between 100° - 150° C : METZGER et al., 1968) ; ii) or to the fact that the veins were impermeable to the liquid solutions so that water could not exert its catalytic influence in the aragonite - calcite transformation.

Microscopic observations reveal that many aragonite veins have been traversed by calcite$_2$ veins ; nevertheless aragonite, also at the contact with calcite$_2$, shows no transformation to calcite. This may be due to the fact that the late hydrothermal solutions, precipitating calcite$_2$ and, locally, siderite, had a temperature below 150° C.

With respect to siderite, it must be remembered that it is formed locally from calcite$_2$. It has been shown by experimental studies (JOHANNES, 1968) that siderite may be formed instead of calcite or that calcite may be transformed into siderite if the hydrothermal solutions contain some Fe^{++}. In particular, at temperatures below 250° C the mole proportion $Ca^{++} / (Ca^{++} + Fe^{++})$ in the fluid phase coexisting with calcite and siderite, exceeds the value 0.98 when the fluid pressure is of 1000 bars (fig. 9). At temperatures above 400° C, magnetite is formed instead of siderite.

The very late solutions from which calcite$_3$ precipitated must have been characterized by a low temperature, in any case lower than 150° C. It must be mentioned here that these calcite weins frequently occur as «cementing» material in ophicalcites.

CONCLUSIONS

The ultramafites which outcrop in central Euboea (Greece), both fresh as well as serpentinized, underwent intense hydrothermal activity, which transformed the original rocks and gave listwanites and ophicalcites.

In these carbonate - rich rocks, different carbonate phases have been detected which have crystallized in the following order :
magnesite - dolomite - calcite$_1$ - aragonite - calcite$_2$ - siderite - calcite$_3$.

On the basis of the existing experimental data for the mineralogical reactions and paragenesis observed in the present case, a temperature up to 400° - 500° C may be deduced for magnesite, dolomite, calcite$_1$, and aragonite. On the contrary, a lower temperature of crystallization, at any rate below 150° C, may be inferred for calcite$_2$, siderite and calcite$_3$.

Since all the carbonate phases above have been found in listwanites, it must be concluded that the hydrothermal solutions acted under a wide range of temperatures. On the other hand, as magnesite, dolomite, calcite$_1$, and aragonite appear to be by far the most abundant carbonate phases in listwanites, it must be concluded that these rocks were formed, fundamentally, at temperatures in the order of 400°-500° C. The other carbonate phases present in listwanites may be due to the successive ophicalcitization process.

Ophicalcites are found to contain only calcite, and in particular calcite$_2$ and calcite$_3$ crystallizations : therefore they must have been formed at temperatures below 150° C.

The hydrothermal solutions operated at high total fluid pressure as it is proved by the disrupting effects which they produced both in listwanites and in ophicalcites : the fracturing may be safely attributed to tectonization, but the effects of the hydrothermal solutions must have been of some importance.

In the case of listwanites it may be supposed that the whole system developed, up to aragonite separation, subject to pressures exceeding those expected on the basis of the calcite-aragonite transition boundary, at the temperatures reffered to in the pure system $CaO - CO_2$.

The listwanitization process which took place under high temperatures, led to complete mineralogical and chemical transformations of the starting ultramafites : in particular, great quantities of MgO concentrated in the solutions from which both Ca and Mg - bearing carbonate phases could precipitate.

On the contrary, the solutions which led to ophicalcitization acted at lower temperatures and therefore could not produce any mineralogical and chemical transformations in the affected ultramafites. In particular, no Mg concentration occured in the solution from which only Ca - bearing carbonate phases could precipitate.

In the scheme proposed above, listwanites and ophicalcites must not be regarded as petrogenetically unrelated rocks, but as products representing different stages in the evolution of the hydrothermal transformation of the ultramafites.

ΠΕΡΙΛΗΨΙΣ

Οἱ ὀφιτοασβεστίτες καὶ οἱ λιστβενίτες (Listwanites) ποὺ συνυπάρχουν μετὰ τῶν ὑπερβασικῶν πετρωμάτων τῆς Κεντρικῆς Εὐβοίας, ἀποτελοῦν τὸ προϊόν τῆς ὑδροθερμικῆς δράσεως ἡ ὁποία ἐνήργησε τόσον ἐπὶ τῶν ὑγειῶν χαρτσβουργιτῶν ὅσον καὶ ἐπὶ τῶν σερπεντινιωμένων τοιούτων. Ἐνῷ ἡ δημιουργία λιστβενίτου (Listwanite) προῆλθε ἐξ ὑδροθερμικῶν διαλυμάτων ὑψηλῆς θερμοκρασίας (ἕως 400^0 - 500^0C), ἡ δημιουργία ὀφιτοασβεστίτου ὀφείλεται εἰς διαλύματα χαμηλοτέρων θερμοκρασιῶν (κάτω τῶν 150^0 C).

Εἰς τὴν πρώτην περίπτωσιν τὰ ὑδροθερμικὰ διαλύματα ἐπέφερον ἐντόνους χημικοὺς καὶ ὀρυκτολογικοὺς μετασχηματισμοὺς ἐπὶ τῶν ἀρχικῶν ὑλικῶν καὶ ἰδιαιτέρως συνετέλεσαν εἰς τὴν κινητοποίησιν μεγάλων ποσοτήτων MgO τὸ ὁποῖον συγκεντροῦται εἰς τὰ διαλύματα. Εἰς τὴν δευτέραν περίπτωσιν, ἀντιθέτως, δὲν διεπιστώθησαν χημικοὶ ἢ ὀρυκτολογικοὶ μετασχηματισμοὶ τῶν ἀρχικῶν ὑλικῶν καὶ δι' αὐτὸ δὲν ἐγένετο οὐδεμία συγκέντρωσις MgO εἰς τὰ διαλύματα.

Κατὰ τὴν διαδικασίαν τῆς δημιουργίας λιστβενίτου σχηματίζονται ἀνθρακικὰ τόσον τοῦ Ca ὅσον καὶ τοῦ Mg, ἐνῷ ἐκ τῶν διαλυμάτων τὰ ὁποῖα ἐπέδρασαν εἰς τὴν δημιουργίαν ὀφιτοασβεστίτου κατεκριμνήσθησαν μόνον ἀνθρακικὰ τοῦ Ca.

Αἱ δύο διαδικασίαι εἶναι στενῶς συνδεδεμέναι καθ' ὅσον θεωροῦνται ὡς δύο διαδοχικαὶ φάσεις εἰς τὴν ἐξέλιξιν τῆς ὑδροθερμικῆς δράσεως ἡ ὁποία ἐπέδρασε ἐπὶ τῶν ὑπερβασικῶν πετρωμάτων.

Aknowledgements: Dr J. Kanaris, of N.I.G.M.R. Athens, is greatfully aknowledged for his help and kind assistance.

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