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THERMAL REACTION OF ANTIGORITE: A XRD, DTA-TG WORK

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ABSTRACT.- It is very important to determine the stability limits of serpentine minerals for investigation of geologic processes taking place in the oceanic lithosphere which consists of serpentinized peridotites. As a result of temperature increase in the subducting oceanic lithosphere, thermal decomposition of serpentine minerals and new mineral formations have a great effect on geologic processes related to subducting plate. In this study, serpentine minerals (antigorite) collected from the Konya-Çayırbağı region were dehydrated under constant atmospheric pressure, then mineralogical changes were determined by using X-Ray diffraction and DTA-TG analyses and finally the stability limits of antigorite was determined. Dehydration reactions on antigorite started at approximately 100-150°C, dehydroxilation reactions started at approximately 550°C and beyond this temperature forsterite started to crystallize from antigorite+brucite. Association of antigorite+forsterite continued until 650°C at which enstatite started to be formed. During all the reactions, which were carried out at the atmospheric pressure, talc was not formed but some H_2O and amorphous silica were released. Dehydroxilation reaction on antigorite occurred between 550°C and 690°C and antigorite was stable until 650°C-690°C.

Keywords: XRD, DTA-TG, Antigorite, Dehydration, Dehydroxilation

INTRODUCTION

Although several types of serpentine minerals are found in the nature, the most common ones are lizardite, chrysotile and antigorite. These minerals have the general formula of $Mg_3Si_2O_5(OH)_4$ and are described as trioctahedric (1:1) layered silicates with MgO, SiO_2 and H_2O contents between 85-95%.

Serpentine minerals are formed as a result of hydration of olivine, pyroxene and other Mg-rich silicate minerals under suitable conditions, the process so called serpentinization. Lizardite and chrysotile are formed at lower conditions of greenschist facies while antigorite mostly occurs at greenschist-amphibolite facies (Evans, 1977).

In studies conducted on serpentine minerals, minerals are generally described by petrographical methods and X-ray analyses and their formation conditions are determined and thus the rock formation processes are investigated (Gürtekin, 2001). Hydrated oceanic crust material is composed of more than 90% of serpentine minerals. During the subduction process, thermal reactions on serpentine minerals cause water release which can play an important role in subduction-related volcanic processes. Completely serpentinized peridotites contain significant amount of water (13%) which released as a result of subduction process this water can be transported to great depth which is represented by high temperature-high pressure conditions at which serpentine minerals can be stable and arc magmatism starts. Therefore, thermal reactions of serpentines and related mineralogical changes are very important for identification of some geologic processes.

The aim of this study is to describe serpentine minerals on the basis of petrographic, X-ray and DTA-TG methods, to investigate the mineralogical changes occurring during the thermal reactions and to determine the stability of antigorite under constant pressure. Samples used in the

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study were taken from the Çayırbağı ophiolite in the Çayırbağı-Hatip region in Konya (Figure 1) and serpantinites in the Hatip ophiolitic complex (Özcan et al., 1990).

THERMAL REACTION OF SERPENTINE MINERALS

Loosing of the absorbed water (H_2O) related to the increasing of heat in a mineral is described as dehydration and loss of water in its crystal structure is descbried as dehydroxilation. Process of thermal reactions in serpentine (dehydration and dehydroxilation) and forming of olivine+ pyroxene+talc+chlorite, that minerals include a few or no water is described a deserpentinization (O'Hanley, 1996). Because, lizardite is firstly formed from olivine during serpentinization, in deserpentinization olivine mostly formed from antigorite and lizardite in deserpentinization.

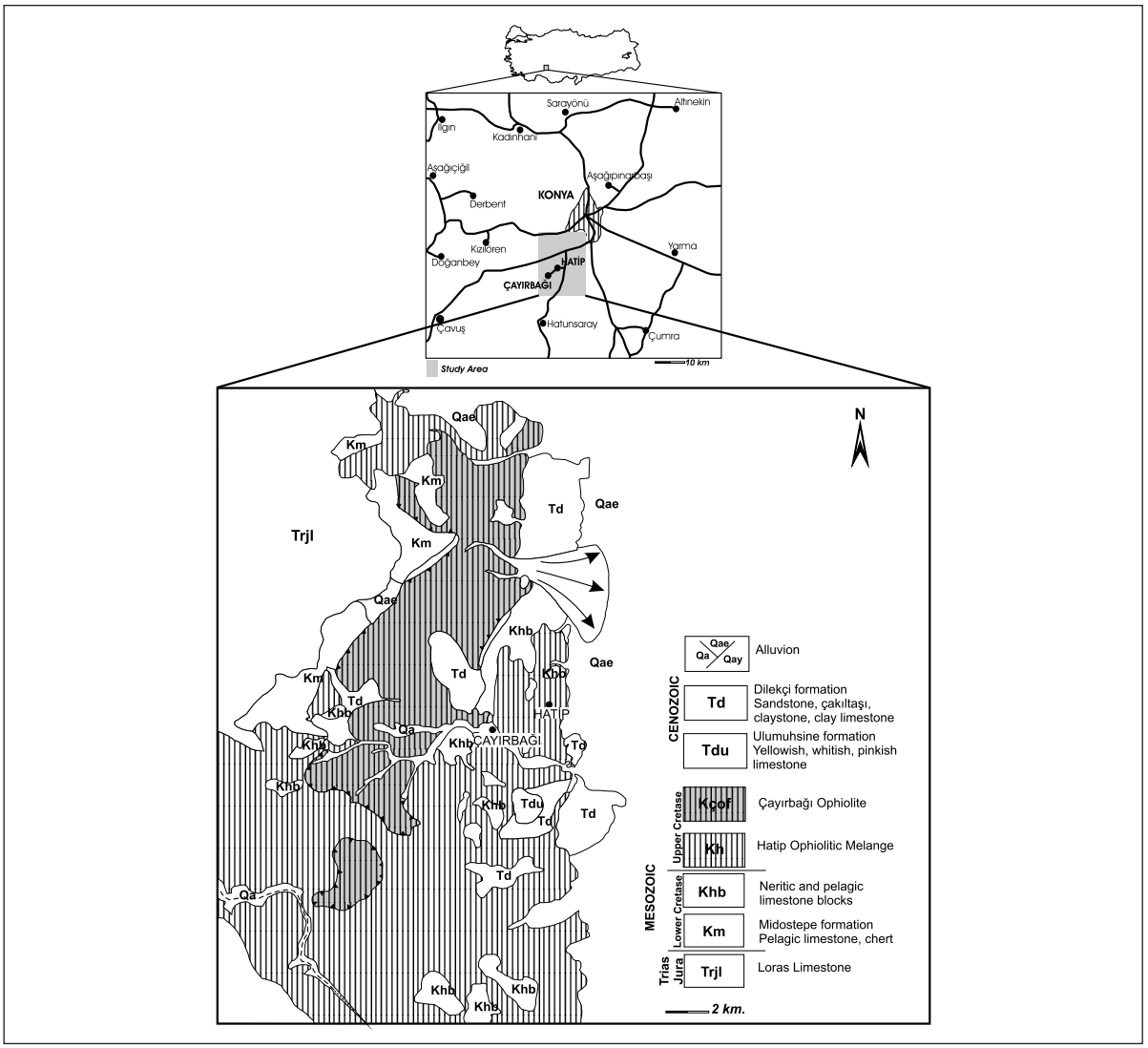

Figure 1- Geological and location maps of the study area (Revised fron Özcan et al., 1986)

In general, thermal reactions in antigorite during recessing serpentinization are in the form of antigorite + brucite ↔ olivine + H_2O orantigorite ↔ olivine ± talc + H_2O and new minerals are formed at temperatures about 500-690°C (Evans, 1977). Considering the stability boundaries of serpentine minerals (Figure 2), lizardite and chrysotile are found at lower conditions of green-schist facies while antigorite is stable over a wide range from lower green-schist to amphibolite facies.

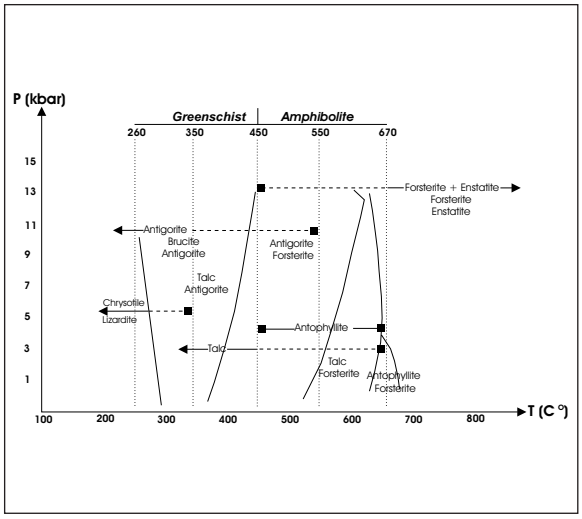

Figure 2- Stability limits of serpentine minerals (Bucker and Frey, 1994)

MATERIAL AND METHOD

This work was conducted as two stages: X-ray analyses and DTA-TG analyses. However, prior to X-ray and DTA-TG analyses, petrographical studies were carried out to determine textural characteristics, mineral paragenesis and source rock types of serpentinites. In petrographical studies, mineral paragenesis and textural properties of rocks were described and classifications of Wicks and Whittaker (1977) which were later developed by O'Hanley (1991, 1996) were used.

X-ray analyses of 5 samples from the study area were made with Rigaku Geigerflex brand X-ray diffractometer at the MTA General Directorate. Samples were thermally treated at constant pressure at the laboratory and the resulting mineralogical changes were determined with the X-ray analyses. Since the main peaks have very close values, secondary peaks are very important for evaluation of serpentine minerals and therefore, analyses were conducted at 2θ=0-70º. Following the routine analyses performed at ambient conditions, powdered samples were first mixed with pure water and taken into suspension then they were dried on glass lamellas. Before the X-ray analyses, dried samples were left in furnace for about one hour at temperatures of 200°C, 400°C, 500°C, 550°C, 600°C, 650°C, 700°C, 800°C, 900°C, 1000°C and 1100°C. In order to prevent melting of glass lamellas, porcelain containers were used for heating processes at 900°C, 1000°C and 1100°C.

DTA-TG analyses, which give information on phase transformations in parallel to temperature increase and the amount of mass loss, were performed with Rigaku Thermoflex TG 8110 brand device at the MTA General Directorate. During the analyses which were conducted at temperatures between 18.7°C and 1100°C, temperature increasement were selected as 20°C/minute and 100 mg sample was used for the analyses.

Petrography

In petrographical studies, source rock of serpentines was found as harzburgite. In completely serpentinized rocks with pseudomorphic texture, serpentine±talc±magnetite mineral paragenesis is observed but olivine (forsterite) and orthopyroxene (enstatite) minerals are absent and serpentinized (bastitized) orthopyroxene relicts showing plastic deformation signs were also detected. According to classification of Wicks and Whittaker (1977) and O'Hanley (1991, 1996) on the basis of textural features under microscope, antigorite±lizardite and vein-type chrysotile were found in samples of pseudomorphic texture.

X-Ray Analyses (XRD)

In order to determine mineralogical changes as a result of thermal reactions, samples that were heated at certain temperature were subjected to X-ray analyses. For easily determination of mineralogical changes, block diagrams prepared using the Jade program that show the results of analyses at various temperatures were presented in figures 3, 4, 5, 6 and 7.

Results of routine analyses are conformable with those of petrographic studies and antigorite was the main mineral observed. However, due to its lower abundance (2-3%), chrysotile could not be detected in X-ray analyses. There was no mineralogical change in analyses of all samples conducted at 200°C, 400°C and 500°C while only a little decrease was observed in the antigorite abundance with temperature increase. It was observed that the antigorite abundance was continued to decrease at 550°C and olivine (forsterite) started to crystallize. At 600°C, antigorite abundance was significantly decreased and forsterite continued to crystallize and its abundance was increased. At 650°C, antigorite was mostly disappeared and forsterite continued to crystallize and enstatite was started to appear. In analyses performed at temperatures higher than 700°C, forsterite and enstatite continued to crystallize and their abundances were increased. Considering the analyses conducted at 550°C, 600°C and 650°C, a significant amorphousization was detected in samples 11S and 29A (Figure 8).

DTA-TG Analyses

According to results of DTA analyses, samples 1 and 29A yielded endothermic and exothermic peaks at 695°C and 810°C, respectively. Samples 6, 11B and 11S also showed similar features with three endothermic peaks at 210°C, 380°C and 690°C and, one exothermic peak at 810°C (Figures 9, 10, 11, 12 and 13).

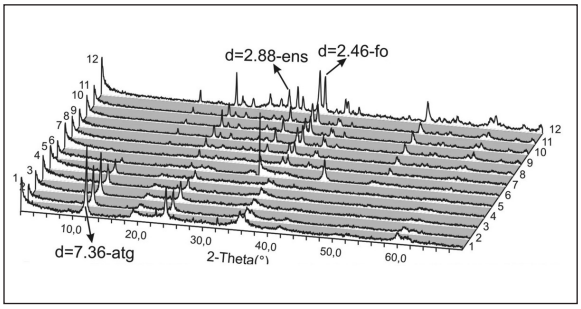

Figure 3- XRD block diagram of sample 1. The numbers 1: Dried, 2:200°C, 3:400 °C, 4:500°C, 5:550°C, 6:600°C, 7:650°C, 8:700°C, 9:800°C, 10:900°C, 11:1000°C, 12:1100°C show the XRD analyses at that temperatures. (atg: antigorite, fo: forsterite, ens:enstatite)

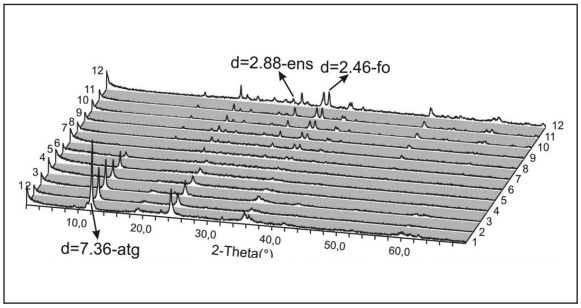

Figure 4- XRD block diagram of sample 6. The numbers 1: Dried, 2:200°C, 3:400 °C, 4:500°C, 5:550°C, 6:600°C, 7:650°C, 8:700°C, 9:800°C, 10:900°C, 11:1000°C, 12:1100°C show the XRD analyses at that temperatures. (atg: antigorite, fo: forsterite, ens:enstatite)

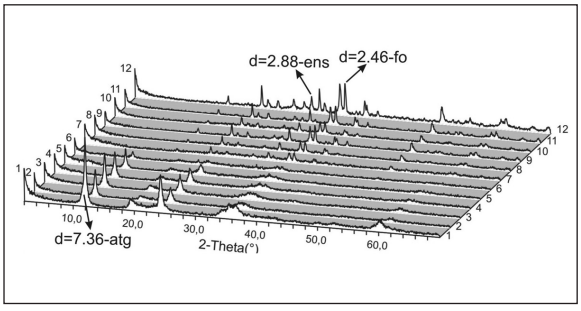

Figure 5- XRD block diagram of sample 11B. The numbers 1: Dried, 2:200°C, 3:400 °C, 4:500°C, 5:550°C, 6:600°C, 7:650°C, 8:700°C, 9:800°C, 10:900°C, 11:1000°C, 12:1100°C show the XRD analyses at that temperatures. (atg: antigorite, fo: forsterite, ens:enstatite)

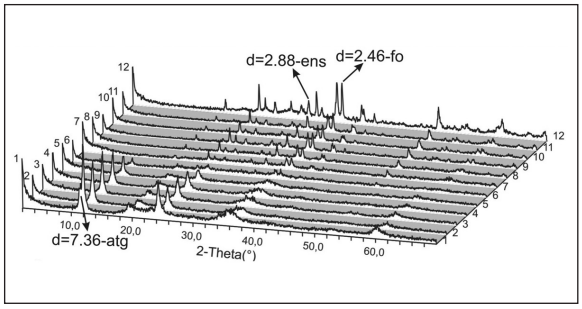

Figure 6- XRD block diagram of sample 11S. The numbers 1: Dried, 2:200°C, 3:400 °C, 4:500°C, 5:550°C, 6:600°C, 7:650°C, 8:700°C, 9:800°C, 10:900°C, 11:1000°C, 12:1100°C show the XRD analyses at that temperatures. (atg: antigorite, fo: forsterite, ens:enstatite)

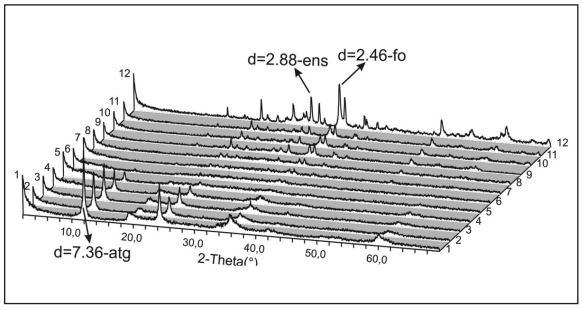

Figure 7- XRD block diagram of sample 29A. The numbers 1: Dried, 2:200°C, 3:400 °C, 4:500°C, 5:550°C, 6:600°C, 7:650°C, 8:700°C, 9:800°C, 10:900°C, 11:1000°C, 12:1100°C show the XRD analyses at that temperatures. (atg: antigorite, fo: forsterite, ens:enstatite)

Thermal reactions in antigorite are developed in parallel to temperature increase and at a temperature of 100°C, free water in samples and absorbed water on the surface are lost due to dehydration. Examination of DTA and TG curves reveals that there is such a change in all samples at 100°C. Endothermic peaks at 210°C and 380°C for samples 6, 11B and 11S are attributed to clay minerals and brucite within the serpentine minerals that could not be detected in X-ray analyses due to their lower abundance. According to McKenzie (1970), montmorillonite group clay minerals give two endothermic peaks at 125-260°C and 625-750°C temperature range while brucite gives only one endothermic peak at 356-455°C temperature range. Examination of DTA diagrams yields endothermic peaks of clay minerals at about 210°C and of brucite at 380°C. The endothermic peak expected for the clay minerals at temperatures between 625°C and 750°C coincides with that of antigorite.

Antigorite peaks in all samples are observed as endothermic at 690°C and exothermic at 810°C. As shown in DTA curves, dehydroxilation was occurred at about 550°C to 690°C. As determined by the X-ray analyses, reactions associated with dehydroxilation resulted in formation of forsterite from antigorite ($Mg_3Si_2O_5(OH)_4$) at temperatures above 550°C and enstatite ($MgSiO_3$) at temperatures above 650°C. In XRD analyses, antigorite was lastly found at 650°C and considering the results of both DTA and XRD analyses reveal that antigorite can be stable at temperatures mostly 650°C-690°C. At temperatures higher than 690°C which defines the upper stability limit of antigorite, forsterite and enstatite continued to crystallize and this new mineral formation was recorded on DTA diagrams as two exothermic peaks at around 810°C. As a result, all these mineralogical changes determined with the XRD studies are found to be conformable with DTA analyses.

According to results of TG analyses, 11% mass decrease was found in all samples (Figures 9, 10, 11, 12 and 13).

RESULTS AND DISCUSSION

Water plays an important role in formation of various geological processes. Serpentinized oceanic lithosphere is believed to be the source of water that is effective in development of subduction-related calc-alkaline arc volcanism (Ulmer and Trommsdorf, 1995). In this respect, stabilities of serpentine minerals are very important for determination of mode of occurrence and depth of these processes. Therefore, thermal reactions of serpentine minerals and mineralogi-

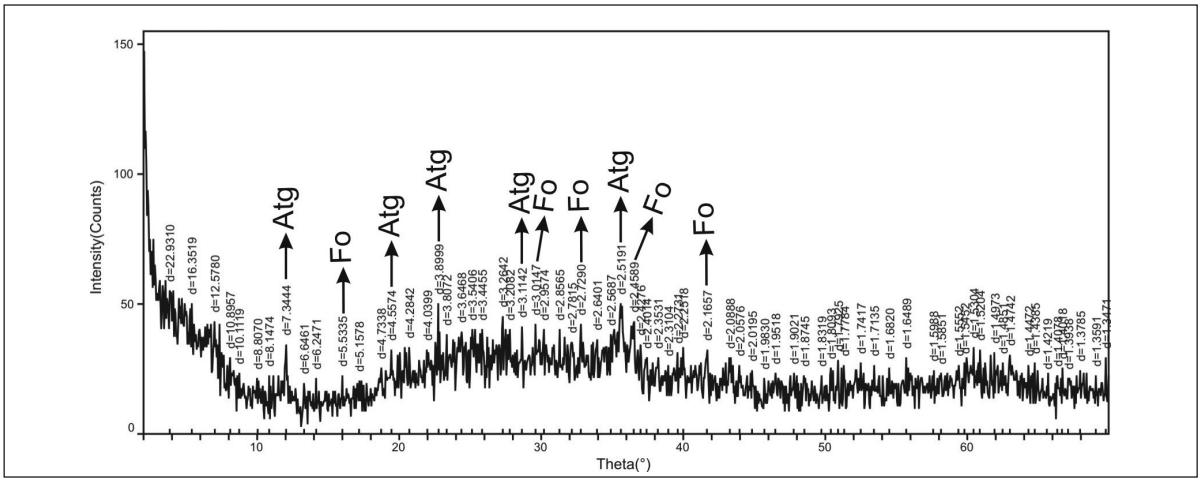

Figure 8- The amorphousization at 600°C (Sample 29A, Atg: antigorite, Fo: Forsterite)

cal changes occurring during these events are primarily important.

A number of experimental works were conducted for determination of stabilities of serpentine minerals (Wunder and Schreyer, 1997) (Figure 14). In this study, serpentine minerals were subjected to thermal treatment to investigate the upper stability limits of these minerals and resulting new mineral paragenesis. In this study antigorite was used which is more stable in comparison to other serpentine minerals and, it was determined that different mineral paragenesis were obtained under various pressure and temperature conditions. Wunder and Schreyer (1997) compiled results of previous works (Figure 14) and determined the stability limits of antigorite and following reactions were stated to be taken place during dehydroxilation of antigorite:

Antigorite ↔ talc + forsterite + H_2O
(15 kbar, 640 °C) (1)

Antigorite ↔ forsterite + clinoenstatite + H_2O
(77 kbar, 680 °C) (2)

Antigorite ↔ clinoenstatite + brucite + H_20
(>77 kbar, >680 °C) (3)

According to Ulmer and Trommsdorf (1995), forsterite is formed by the reaction between antigorite and brucite (if available) at low temperatures (antigorite + brucite ↔ forsterite + H_2O) and about 3.5% H_2O is released. With further increase of pressure and temperature, brucite is completely removed and as shown in reactions 4 and 5, different minerals are formed. Diagram showing the stability limits of antigorite is shown in figure 15.

Antigorite ↔ forsterite + talc + H_2O
(low pressure) (4)

Antigorite ↔ forsterite + enstatite + H_2O
(high pressure) (5)

In this study, antigorite minerals were subjected to thermal treatment under constant pressure (laboratory conditions). Mineralogical changes occurred during this process were determined with XRD and DTA-TG analyses and stability limits of antigorite were determined under constant atmosphere pressure.

All the samples are mostly composed of antigorite. However, on the basis of DTA analyses results, little amount of montmorillonite and brucite were also found in samples 6,11B and 11S.

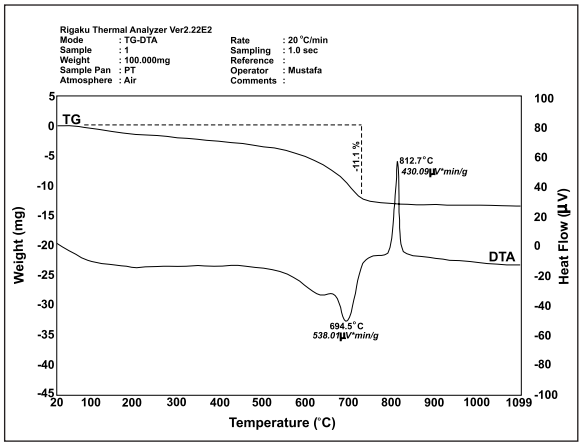

Figure 9- DTA-TG curves of sample 1

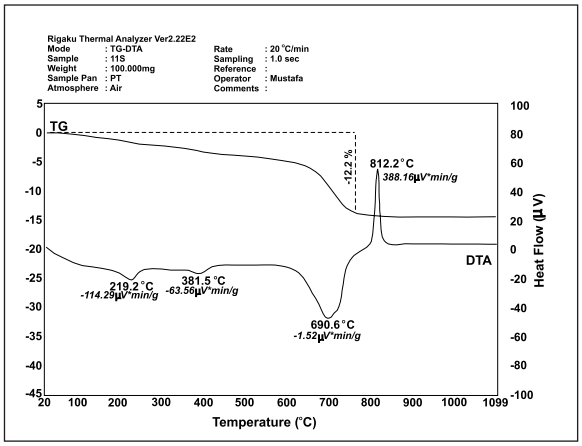

Figure 12- DTA-TG curves of sample 11S

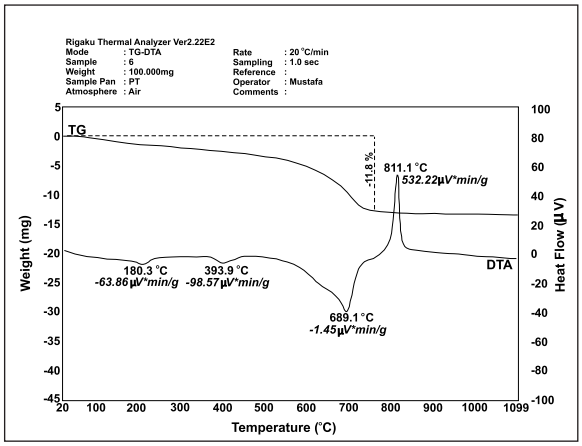

Figure 10- DTA-TG curves of sample 6

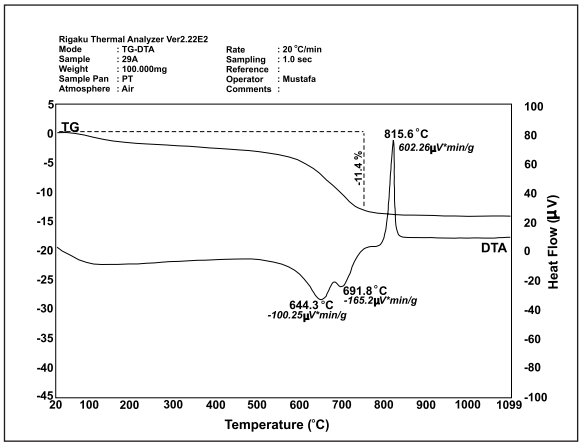

Figure 13- DTA-TG curves of sample 29A

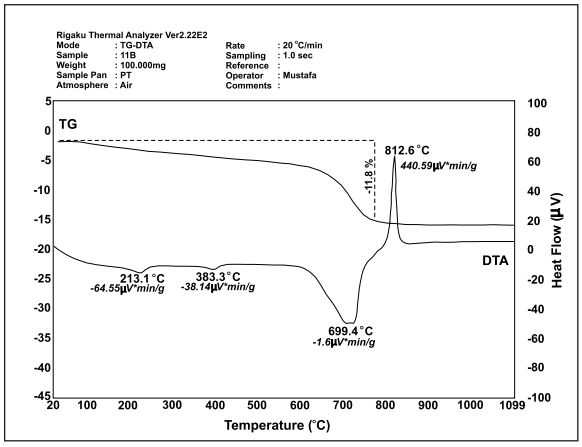

Figure 11- DTA-TG curves of sample 11B

Considering the results of XRD analyses, antigorite can be stable until a temperature range of 650°C-690°C but its abundance decreases depending on reactions associated with temperature increase. Increase in antigorite abundance was determined from peak intensities on XRD charts. In analyses at temperatures above 550°C, the amount of antigorite was further decreased and forsterite started to be formed. Antigorit+forsterite association at temperatures above 550°C was continued until 650-690°C and antigorite was removed at higher temperatures. Results of DTA analyses which were conformable with X-ray determinations indicated that

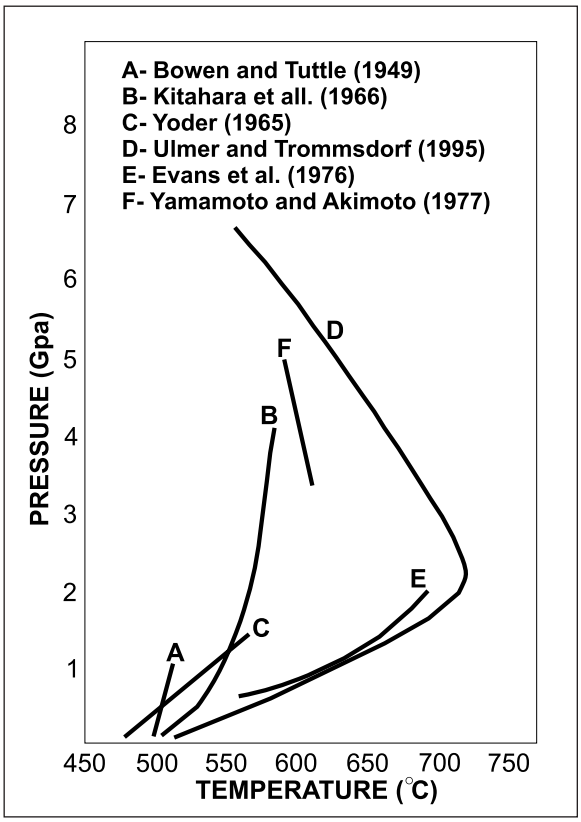

Figure 14- Previous experimental study of stability limit of serpentine minerals (Wunder ve Schreyer, 1997)

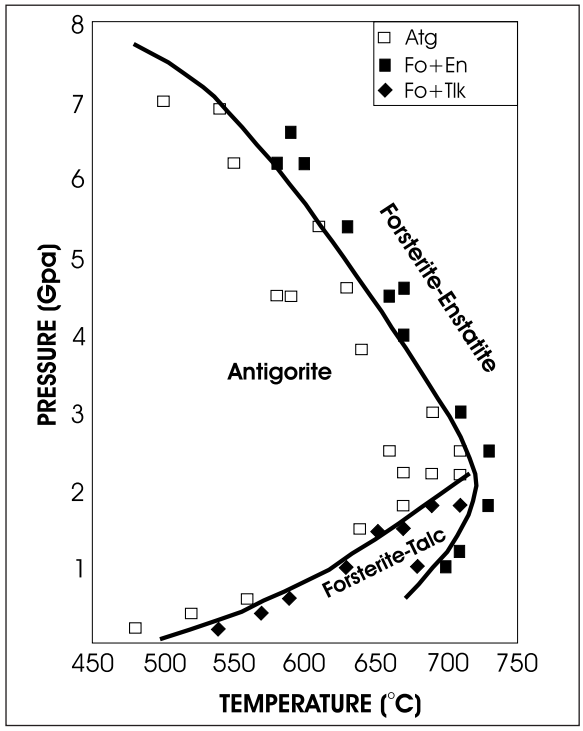

Figure 15- Stability limit of antigorite (Ulmer ve Trommsdorf, 1995)

antigorite dehydroxilation reactions were started at 550°C and continued until 690°C.

X-ray analyses conducted at temperatures above 650°C reveal that in addition to forsterite, enstatite also occurs and abundance of both minerals increases with temperature increase. According to results of DTA analyses , endothermic peak shown at 810°C following the dehydroxilation at 690°C correspond to formation of forsterite and enstatite. However, XRD results imply that enstatite forms in a later stage than forsterite (after 650°C).

In samples 6, 11B and 11S, antigorite is accompanied by little amount of brucite and, as a result of their reaction forsterite is formed and some amount of water is released. In brucite-free samples (e.g., 1 and 29A), forsterite is formed from antigorite and similarly some amount of water is released. Examination of XRD analyses conducted at 550°C, 600°C and 650°C reveal the presence of amorphousization that is observed in all samples but particularly significant in samples nos. 1 and 29A. The amorphousization is thought to be derived from silica that is released during the thermal reactions. Considering this, following reactions were first occurred during thermal reaction of antigorite:

Antigorite + brucite $\leftrightarrow$ forsterite + H_2O + SiO_2 (550°C-650°C) (6)

Antigorite $\leftrightarrow$ forsterite + H_2O + SiO_2 (550°C-650°C) (7)

According to results of XRD analyses, during thermal reaction of antigorite enstatite is formed

following the forsterite (650°C) and following reactions took place during the formation of enstatite:

Antigorite ↔ forsterite + enstatite + H_2O (650°C-690°C) (8)

Forsterite + SiO_2 ↔ enstatite (>650°C) (9)

As a result of dehydroxilation reactions occurring between 550-690°C it was found that first forsterite forms antigorite. The amorphousization that was determined by XRD analyses and observed in between dehydration and crystallization reactions may indicate that in addition to water some amount of silica was also released during these reactions. At temperature above 650°C forsterite is accompanied by enstatite.

Considering all these data, antigorite was found to be stable up to temperatures about 650 to 690°C. During dehydroxilation, antigorite-forsterite association was observed at temperatures above 550°C and enstatite starts to crystallize above 650°C. Forsterite+enstatite association is dominant by 690°C.

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