GEOLOGICA CARPATHICA, 48, 1, BRATISLAVA, FEBRUARY 1997
19–26

SERPENTINES IN THE OPHIOLITE COMPLEXES OF THE VOURINOS AND KAMVOUNIA MTS. (NORTHERN GREECE)

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(Manuscript received June 20, 1996; accepted in revised form December 12, 1996)

Abstract: The Vourinos as well as the Kamvounia ophiolite complexes yielded in origin of the serpentine-group minerals of different appearance. In this stage of laboratory studies we have concentrated on: *a* — filling of shear zones occurring within ”basal serpentinites” of the Vourinos Complex (lizardite + chrysotile + splintery antigorite), *b* — the rock-forming mass of the Kamvounia massif (antigorite), *c* — slip-fiber ”asbestos” within the Kamvounia massif (chrysotile + fibrous antigorite). While the Vourinos Complex during its geological history never reached greenschist facies conditions, the Kamvounia massif underwent metamorphic recrystallization under such conditions.

Key words: Hellenides, Mesozoic, ophiolites, lizardite, chrysotile, antigorite.

Introduction

Eastern Mediterranean Mesozoic ophiolite complexes are some of the most intensively studied ones. This is a result of their economic value (chromites) and their complicated, but from several points of view instructive geological history. So, especially in recent decades numerous authors studied the complex under consideration. Available information is found in papers by Moores (1969), Rassios et al. (1983) and a review by Savvidis & Hovorka (1997). Although some published papers include micrographs of serpentinites, serpentinization as a problem has not been studied yet. So, the aim of the performed study was to: *a*) identify serpentine-group minerals in the Vourinos and the Kamvounia ophiolitic massifs, and *b*) on the basis of serpentine minerals present to compare their geological history.

Within the Vourinos Complex serpentine minerals occur especially as:

1) massive to schistose serpentinites forming the lowermost section of the complex under consideration (= ”basal serpentinites”),

2) filling of shear zones (mostly together with carbonates),

3) massive serpentines are present in the upper part of the metamorphic harzburgite section,

4) serpentines accompanying chromite accumulations both in the harzburgite tectonite as well as in the cumulate complex. There is a different situation in the Kamvounia Metaultramafite Complex.

5) The rock-mass of the Kamvounia Complex is formed by antigorite as the leading serpentine-group mineral,

6) shear zones 1–5 centimetres in thickness filled by slip-fiber asbestos of complicated mineralogy. In this communication we especially present the results of study of the serpentine-group minerals presented above under 2), 5) and 6).

Serpentine-group minerals: general problematics

Serpentine-group minerals should be classified according to several classification schemes. The most commonly used division of the serpentine-group minerals (Whittaker & Zussman 1956; Zussman & Brindley 1957) is based on their structures. According to the classification scheme of these authors, serpentines are divided into: chrysotile (ortho-, clino-, and para-), antigorite, lizardite and 6-layer orthoserpentine. The fibrous antigorite of Whittaker & Zussman (1956) has been described under the disignation picrolite in the past (Riordon 1955). 6-layers orthoserpentine is also known as unstite (Whittaker & Zussman 1956). During recent decades serpentines in the past described as ”bastite” (pseudomorphs after orthopyroxenes: Drasche 1871) have been identified as lizardite in places with chrysotile admixture. Among the latest classification schemes is that of Wicks & Whittaker (1975). According to these authors (l.c.) lizardite, chrysotile and parachrysotile are polymorphic modifications to which do not belongs antigorite.

It should be added that in the process of serpentinization of rocks with an excess of Mg-rich olivines over pyroxenes besides serpentines brucite also originates (Hostetler et al. 1966). It is present in the rock-mass, or is selectively concentrated on veinlets.

During recent decades a wealth of new experimental results on serpentinization as well as on serpentine polytypes have been published (for review see papers by Wicks & O’Hanley 1988 and Banfield et al. 1994).

Although the P-T fields of lizardite-chrysotile on one side and antigorite on the other one (Johannes 1975) partly overlap their stabilities are generally not identical (Wicks & Whittaker 1977 and others). The origin of lizardite and chrysotile is generally connected with hydration at low temperature (approx. up to 250 °C). Antigorite is stable up to higher (approx. up to 500 °C) temperatures. Taking into account the description of picrolite (splintery antigorite) given by Riordon (1955): "...common variety of fibrous material that occurs along fault planes ... It is made of bundles and sheaves of coarse fibers that lie roughly parallel to the plane of fissure. It is generally soft, and white to pale yellowish green in color, and has splintery fracture. The fibers separate with difficulty and generally break easily" we identify a part of serpentine studied with that of splintery antigorite (= picrolite).

The different P-T conditions of the origin of various serpentine minerals are reflected in differences in water content, specific gravity, chemical composition, remanent magnetization and other physical parameters of lizardite/chrysotile versus antigorite serpentinites.

Mode of occurrence of the studied samples

The identification of serpentine-group minerals is often complicated by their small size and the simultaneous presence of several mineral polytypes (Cressey 1979; Veblen & Buseck 1979) in the studied sample.

In this stage we have studied serpentines from the following modes of occurrences listed in the Introduction:

1) Serpentines forming a substantial part of the basal serpentinites of the Vourinos Ophiolite Complex. This rock suite crops out especially on the slopes of the Aliakmon River as well as on the new (1996) road cut between Chromio and Museum on the eastern rim of the complex under consideration. Serpentinization within this unit is mostly very intensive, although within massive to schistose serpentinite "cobbles" (blocks) of less intensively serpentinized peridotite occur. These occurrences exhibit pseudomorphic replacement of primary olivines and ortho- as well as clinopyroxenes forming lizardite pseudomorphs after orthopyroxenes on one side and a mixture of lizardite and chrysotile with characteristic mesh texture on the other. During serpentinization processes brown (Cr-rich) spinel survived. Magnetite "powder" distributed regularly or concentrated on veins and veinlets of younger generation serpentines is characteristic.

2) Within the basal serpentinites abundant shear zones occur, which rim blocks of darkgrey, greyish-black to darkgreen serpentinites with lizardites of "bastite" appearance. Shear zones are of various (mostly a few centimetres) thickness, and variable color (mostly yellowish-green, applegreen). In places within mentioned mass, light-colored carbonate vein and hair-like veinlets of hap-hazard orientation are also present.

5) The Kamvounia serpentinite massif, represented by samples from the open quarry at Zindani, have been studied. The leading rock-type is massive, darkgrey (with bluish tint) homogeneous serpentinite. Its leading rock-forming mineral is antigorite.

6) The last textural type studied is represented by slip-fiber asbestiform aggregates of light yellowish-green to silverwhite long-columnar and felty character. Being compact it behaves as hard, but easily desintegrated splintery blades and long columns. The thickness of the slip fiber serpentine filling of tectonized zones is variable — it reaches 10 cm in places. The contacts of the shear zones under consideration are sharp with no evidence of mineralogical or textural changes in orientation perpendicular to the contact planes.

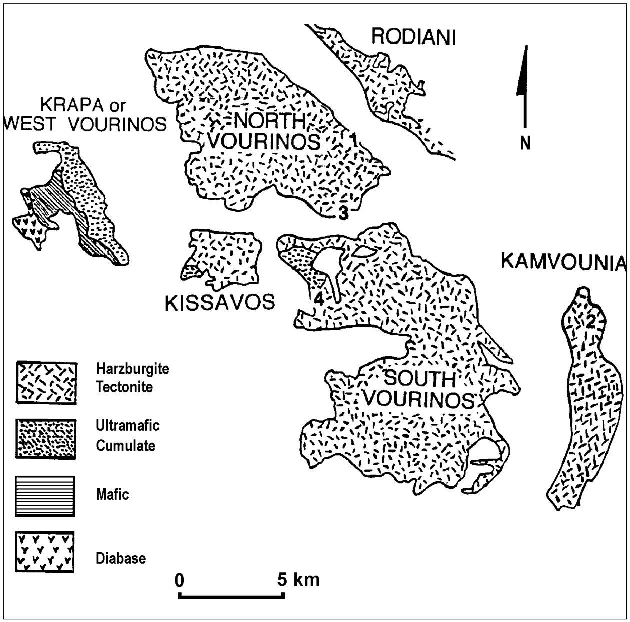

Fig. 1. Sampling localities: **1** — Museum, **2** — Zindani, **3** — Riso, **4** — Tsouka.

Methods applied

The result of study of several dozen thin sections served as the main discriminant for advanced studies. The presented micrographs represent the most common types of fabrics of studied serpentines/serpentinites.

X-ray powder diffraction

X-ray powder diffraction (XRD) patterns were obtained using DRON-3 Bragg-Brentano diffractometer with CuK radiation wavelength 0.154051 nm, step size 0.1 Θ, time per step 1 sec. The diffractometer was operated with the commercially distributed software.

The general features of the patterns recall the previous data published by Whittaker & Zussman (1956): chrysotile is characterized by reflexes at d = 0.259 nm (4) and d = 0.245 nm (8) together with a discriminant reflex at d = 0.1534 nm (9), lizardite by an intensive reflex d = 0.248 nm (9) and a less intensive doublet at d = 0.153 nm (6) and d = 0.1504 nm (4), antigorite by a strong reflex at d = 0.253 nm (9) and two reflexes at d = 0.156 nm (6) and d = 0.1536 nm (4). If antigorite is less well ordered many weak reflexes are hardly visible, and the pattern may look very similar to that of lizardite. The strong line at d = 0.156 nm in antigorite has no counterpart in the chrysotile or lizardite patterns.

Differential thermal analysis

Differential thermal analysis (DTA) also offer discrimination between lizardite-chrysotile serpentines on one side and that of antigorite on the other. In combination with thermal gravimetric analysis (TGA), this method has been used in the past for determination (Faust & Fahey 1962; Ivanova et al. 1974) of serpentines in rock-mass or vein filling. Thermic analyses were operated on the MOM (Budapest) derivatograph (system Paulik - Paulik - Erdey). The treatment (of 1200 mg of powdered samples) was performed under air conditions. Speed of heating: 10 °C/min^{-1}.

Generally DTA patterns show shallow endothermic reactions under low temperatures mostly below 150 °C. Broad and shallow endothermic peaks are the consequence of the gradual release of mechanically adsorbed (surface) water in studied samples. The loss of the weight from this endothermic reaction is in range 0.8–3.0 per cent.

The DTA patterns of serpentine-group minerals, especially those of lizardite and chryzotile are characterized by large endothermic peak adequate to the temperature range 600–820 °C. Within this temperature range processes of dehydration took place caused by the breakdown of serpentine structure. On the DTA records of serpentine minerals with ideal structure a third very weak endothermic peak is observable at temperature 830 °C.

Another characteristic exothermic peak corresponds to the temperature of 820 °C and represents the formation of forsterite on the expense of lizardite and chrysotile. In the case of serpentine minerals with imperfect structure only the first two endotherms are expressed. With the decrease of the order of the crystal structures the increase of the intensity of this exothermic peak is visible. Simultaneously the beginning of the endothermic effect is shifted to higher temperatures.

Other methods

To obtain information on the morphology of some of the serpentines studied we present selected TEM and scanning electron microscope micrographs. The index of refraction have been determined on several samples.

Results

1 — Serpentines forming the column of ”basal serpentinites” are represented by lizardite and chrysotile mixture of variable quantitative proportions of these serpentine polytypes. Beside serpentines also relic ortho- and especially clinopyroxenes are present in variable amounts.

Lizardite pseudomorphs after orthopyroxene crystals and mesh texture are characteristic for this type of studied samples. The serpentinites under consideration correspond to the 3rd type described by Wicks & Whittaker (1977) which originate under falling or constant temperature, the absence of substantial shearing and no antigorite nucleation.

2 — The filling of shear zones within the basal serpentinite of the Vourinos Complex is of variable thickness, composition, fabric and general appearance.

Chrysotile and lizardite are the most abundant polymorphs of these samples, while antigorite except the sample ”C” (Fig. 2c) is the least common and simultaneously belongs to the less ordered one. Carbonates forming net-like veinlets belong to calcite and dolomite (Pl. I: Figs. a–d).

X-ray powder diffractometre traces (Fig. 2) were used to compare different proportions of serpentine minerals present in the samples examined. In sample ”A” (Fig. 2a) chrysotile is strongly predominant while sample ”B” (Fig. 2b) represents chrysotile-lizardite mixture, which is the most common situation in the samples of this group. For all samples of this genetic group presence of white, or whitish carbonates is characteristic. In one sample (a) except of chrysotile and antigorite also chlorite has been determined (Fig. 3).

Serpentine-group minerals studied belonging to this category are characterized by weak low-temperature endotherm with maximum 115 °C and intensive endothermic peak at maximum at 695 °C and 712 °C. According to the intensity of the exotherm with its maximum usually at 820 °C, which

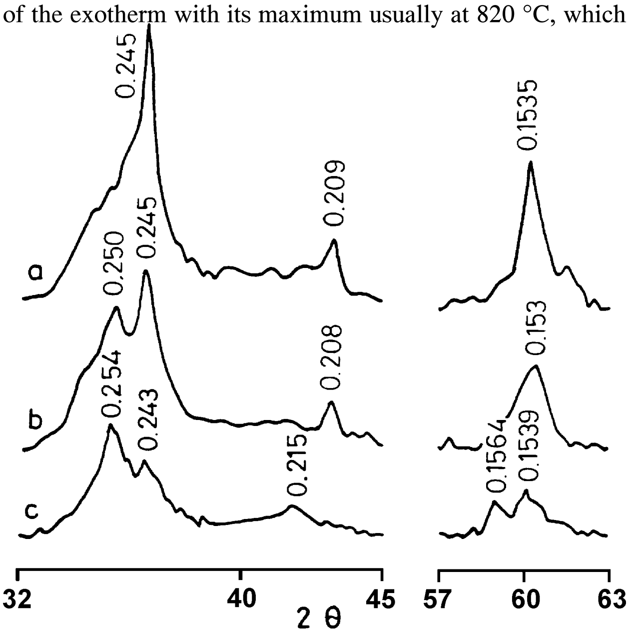

Fig. 2. X-ray diffraction patterns of: a — predominant chrysotile; b — chrysotile-lizardite mixture; c — less ordered antigorite.

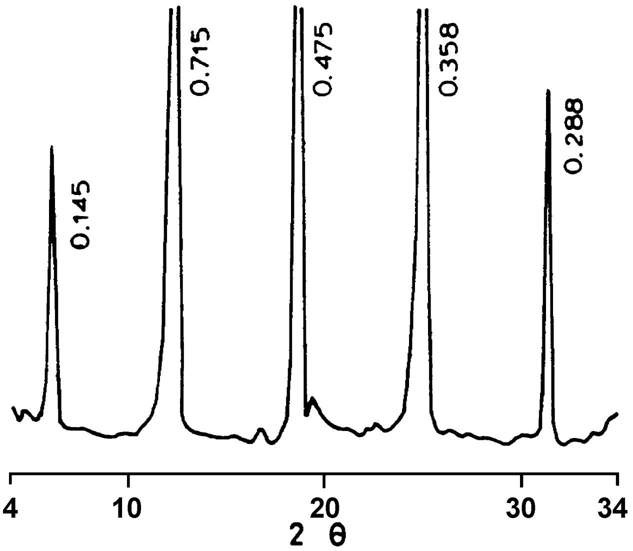

Fig. 3. X-ray diffraction pattern of chlorite occurring in sample ”A”.

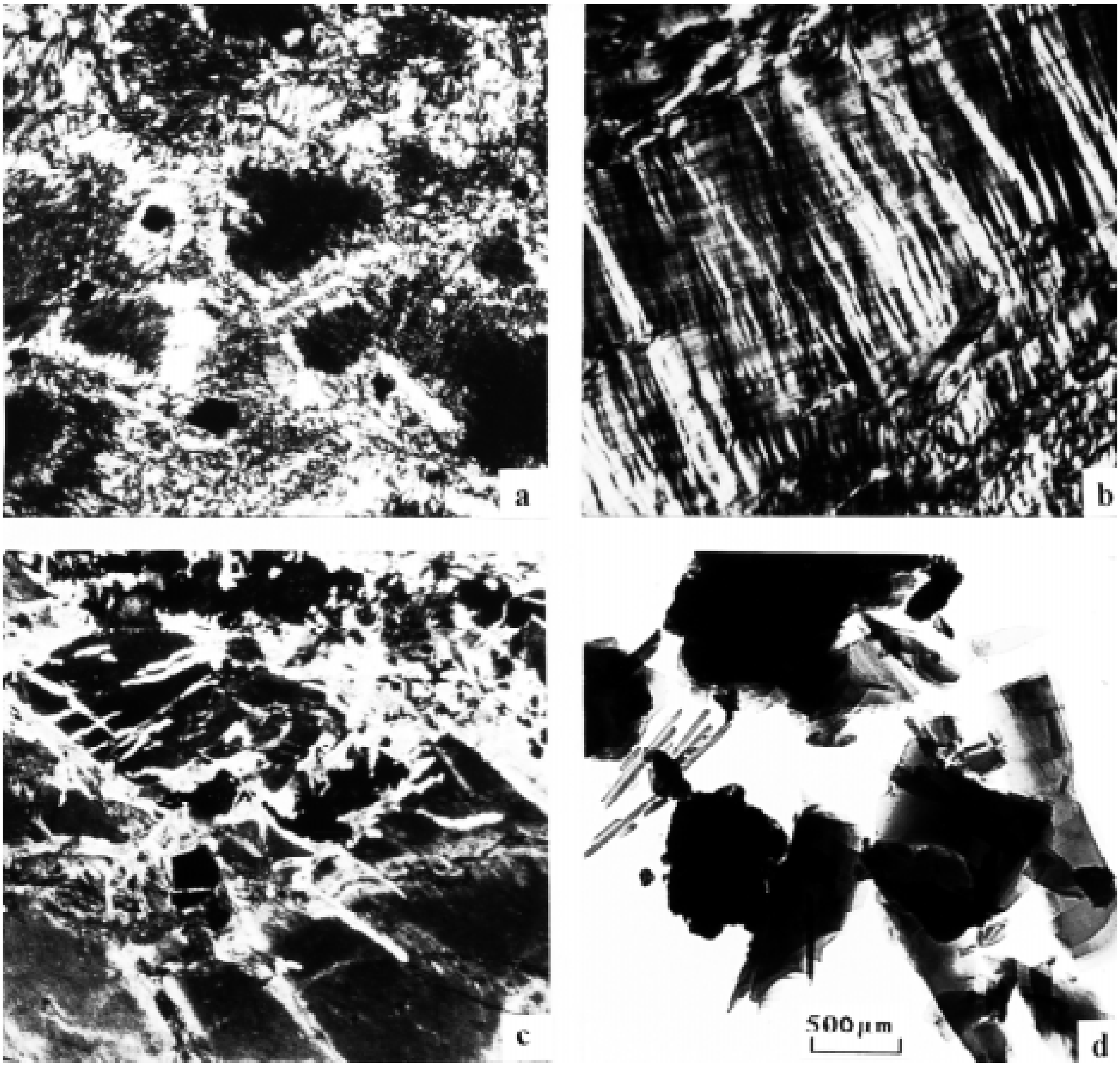

Plate I: Fig. a. Tectonically crushed and recrystallized lizardite-chrysotile serpentinite from the shear zone (type 2). Serp I = serpentine of the 1st generation (dark), serp. II = serpentine of the 2nd generation (light). Enlarg. 27×, crossed nicols. **Fig. b.** Cross fiber chrysotile from the shear zone within lizardite-chrysotile serpentinite (type 2). Enlarg. 46×, crossed nicols. **Fig. c.** Net-like veinlets of carbonates from the shear zone within lizardite-chrysotile serpentinite (type 2). Enlarg. 26×, crossed nicols. **Fig. d.** Plates of antigorite and fibers of chrysotile from the shear zone within lizardite-chrysotile serpentinite (electron microscope, suspension). All micrographs are from the shear zone of the Vourinos Complex.

in some cases gradually pass into a very weak endotherm, it is possible to conclude, that minerals with various degrees of structural order are present (Figs. 4a, 4b). The weight loss observed by thermogravimetry (TG) in the majority of samples studied is over 13 weight per cent which is the consequence of the calcite and dolomite present (Fig. 4c). The content of carbonate minerals in this sample ranges up to 55 weight per cent (manometric determination).

Optical studies of powder samples brought evidence that the studied samples represent inhomogeneous material composed of chrysotile, lizardite and antigorite in variable proportions. Antigorite is present in substantial amounts only in samples E, G, but its presence is evident for all the samples studied.

3 — The Kamvounia massif is composed of antigorite serpentinites. Total serpentinization of the primary mineral association is characteristic. Lathy antigorite has haphazard orientation and is pigmented by tiny magnetites (Pl. II: Fig. a). The presented X-ray diffraction pattern of the rock-forming antigorite (Fig. 5) is in good agreement with the data of Whittaker & Zussman (1956). The presented DTA pattern prove this optical thin sections determination (Fig. 4d). It is

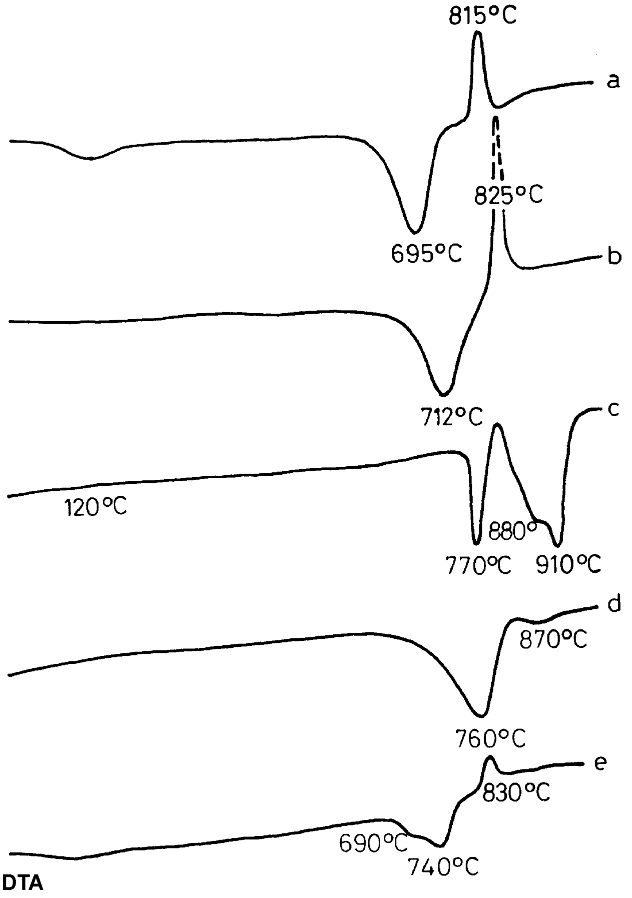

Fig. 4a. Derivatogram of chrysotile-lizardite mixture. **Fig. 4b.** Derivatogram of chysotile-lizardite mixture with less ordered structure. **Fig. 4c.** Derivatogram of carbonate minerals from shear zone. **Fig. 4d.** Derivatogram of rock-forming antigorite. **Fig. 4e.** Derivatogram of the mixture of antigorite + lizardite/chrysotile + carbonates.

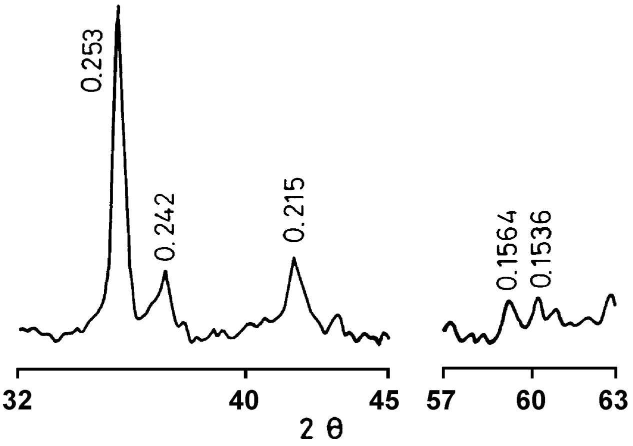

Fig. 5. X-ray diffraction pattern of rock-forming antigorite.

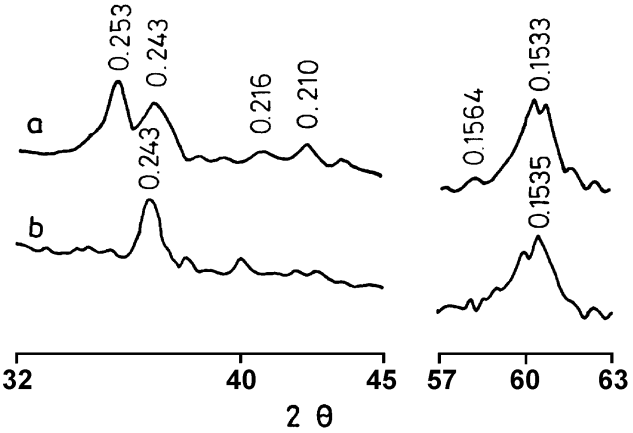

Fig. 6. X-ray diffraction patterns of: **a** — splintery-shape particles being mixture of antigorite (picrolite) and chrysotile; **b** — long fibers with the predominence of chrysotile. Included Figs. 2, 3, 5 and 6 are parts of diffractograms used for distinction of serpentine-group minerals present.

characterized by absence of the first (low-temperature) serpentine-group endotherm (Ivanova et al. 1974). The maximum of the second intensive endotherm is shifted to the temperature of 760 °C and the consequent exothermic peak, which is characteristic for chrysotile, is missing. At 870 °C a very weak endothermic peak is expressed, which together with the above mentioned features of DTA curve determine antigorite. This is also in accordance with published results.

4 — Slip fiber asbestos from the Kamvounia massif. The thickness of the splintery and fibrous serpentine (Pl. III) filling of shear zones within the Kamvounia Complex is variable — it reaches 10 centimetres on places. The contacts of the shear zones under consideration are sharp with no evidence of mineralogical as well as textural changes in orientation perpendicular to contact planes. Two main substances make up the shear zones in the antigorite serpentinites of Kamvounia: serpentines of fibrous and splintery character as well as pale carbonates. Mutual proportions of serpentines and carbonates varies. Within the fibrous filling of the shear zones we have picked up two main types of material: *a*) silver-white to yellowish-white long-fibrous asbestos of the textile type quality and several centimetres in length. They have been determined as chrysotile (Fig. 6b), *b*) light-green, splintery, in the case of natural occurrence hard aggregates, which have X-ray patterns of a mixture of antigorite ("picrolite") and chrysotile (Fig. 6a). On the DTA records (Fig. 4e) of the set of samples of this group, a low temperature endothermic peak (by 100 °C) together with a broad endothermic peak, or two endotherms with maxima at 690 °C and at 740 °C are observable. Endothermic reactions are expressed by the loss of weight in the range 1.5 to 15.5 per cents. Such high loss of weight is caused by the presence of carbonates. The exothermic peak with its maximum at 830 °C is connected with a very low (0.4 %) loss of weight.

This DTA pattern is typical for a mixture of fibrous antigorite, chrysotile or lizardite. Measured indexes of refraction (N = 1.55 and N = 1.53 or N = 1.457 and N = 1.535) and high birefringence (0.012) prove the presence of chrysotile in this mineral mixture forming the slip-fiber asbestos occurring in shear zones.

Discussion and conclusion

Within the whole Vourinos ophiolite mass lizardite and chrysotile are the dominant serpentine-group minerals present. The degree of serpentinization of harzburgite tecto-

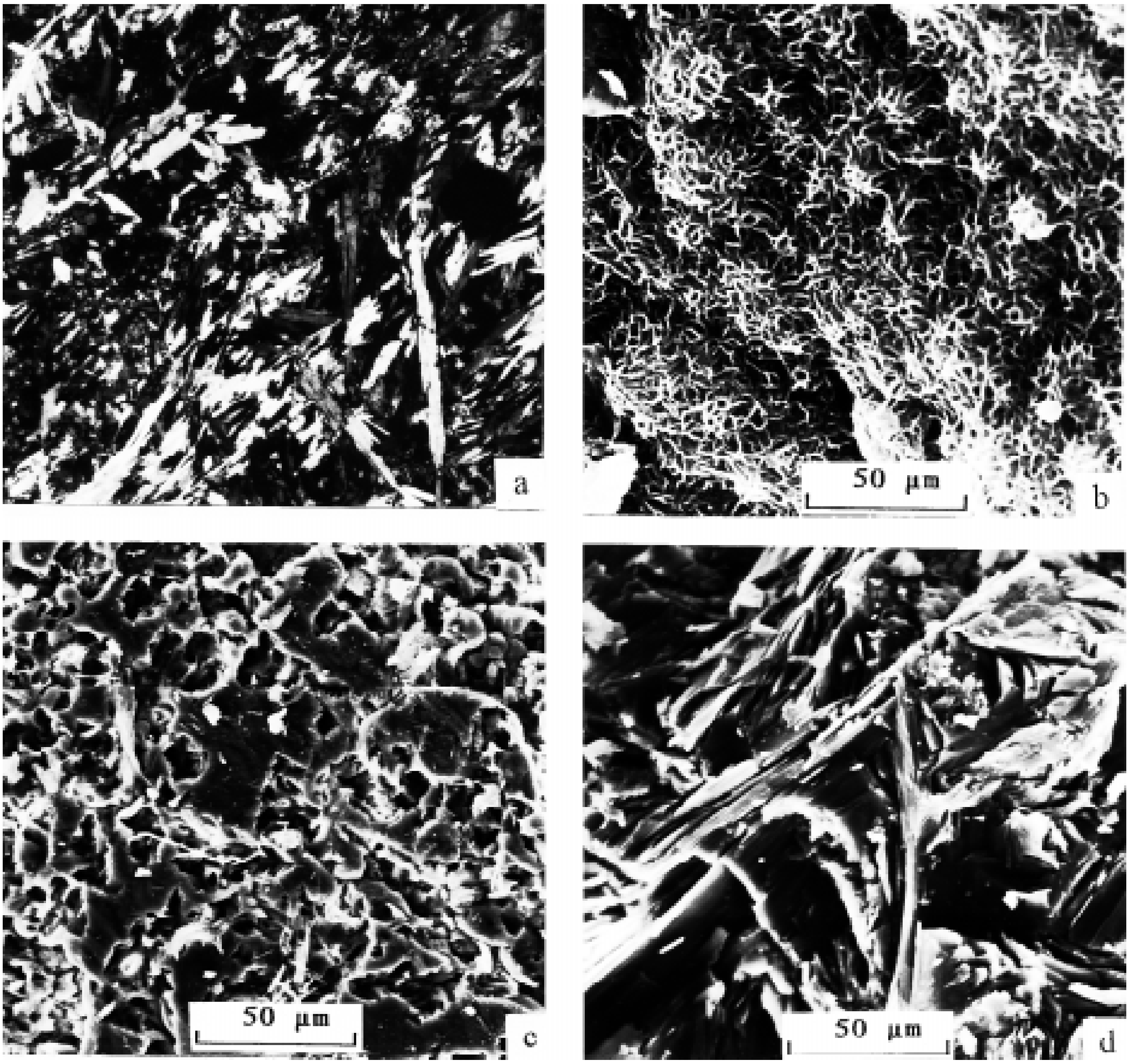

Plate II: Fig. a. Thin section of antigorite serpentinite — the Kamvounia massif. Enlarg. 45×, crossed nicols. **Fig. b–d.** Natural surfaces of antigorite serpentinite of the Kamvounia massif. Scanning electron microscope.

nites generally increases in the direction of its basal plane. Within the column of ”basal serpentinites” there are numerous shear zones of several generation filled by younger generation serpentines + carbonates.

The dominant phases of shear zones within the basal serpentinites are chrysotile ± lizardite. In several samples antigorite — mostly of fibrous character — has been identified together with the prevailing chrysotile. Therefore an elevated temperature, in comparison to that responsible for serpentinization of the rock-mass of the basal part of the ophiolite complex under consideration, is supposed. The fluids needed for the origin of serpentines of the younger generation (together with carbonates) used the shear zones and fractures as communication paths. The heat responsible for the antigorite-chrysotile (± lizardite) filling of the shear zones could be friction heat generated precisely within those zones.

In contrast to Vourinos, the Kamvounia Complex is formed by antigorite serpentinites. Thus metamorphic recrystallization under greenschist facies conditions is responsible for the origin of antigorite.

The filling of shear zones (chrysotile and fibous antigorite of slip-fiber character + carbonates) within the Kamvounia massif indicate the activities of fluids under lower temperature conditions (indicative is the presence of chrysotile) in comparison with the processes responsible for rock-forming antigorite (± chlorite) formation.

Taking into account the lower water contents in antigorite in comparison with chrysotile, fluids (with CO_2 content) influx into mechanically weakened zones during mentioned tectonic events have been responsible for slip-fiber serpentines (chrysotile and antigorite) + carbonates origin.

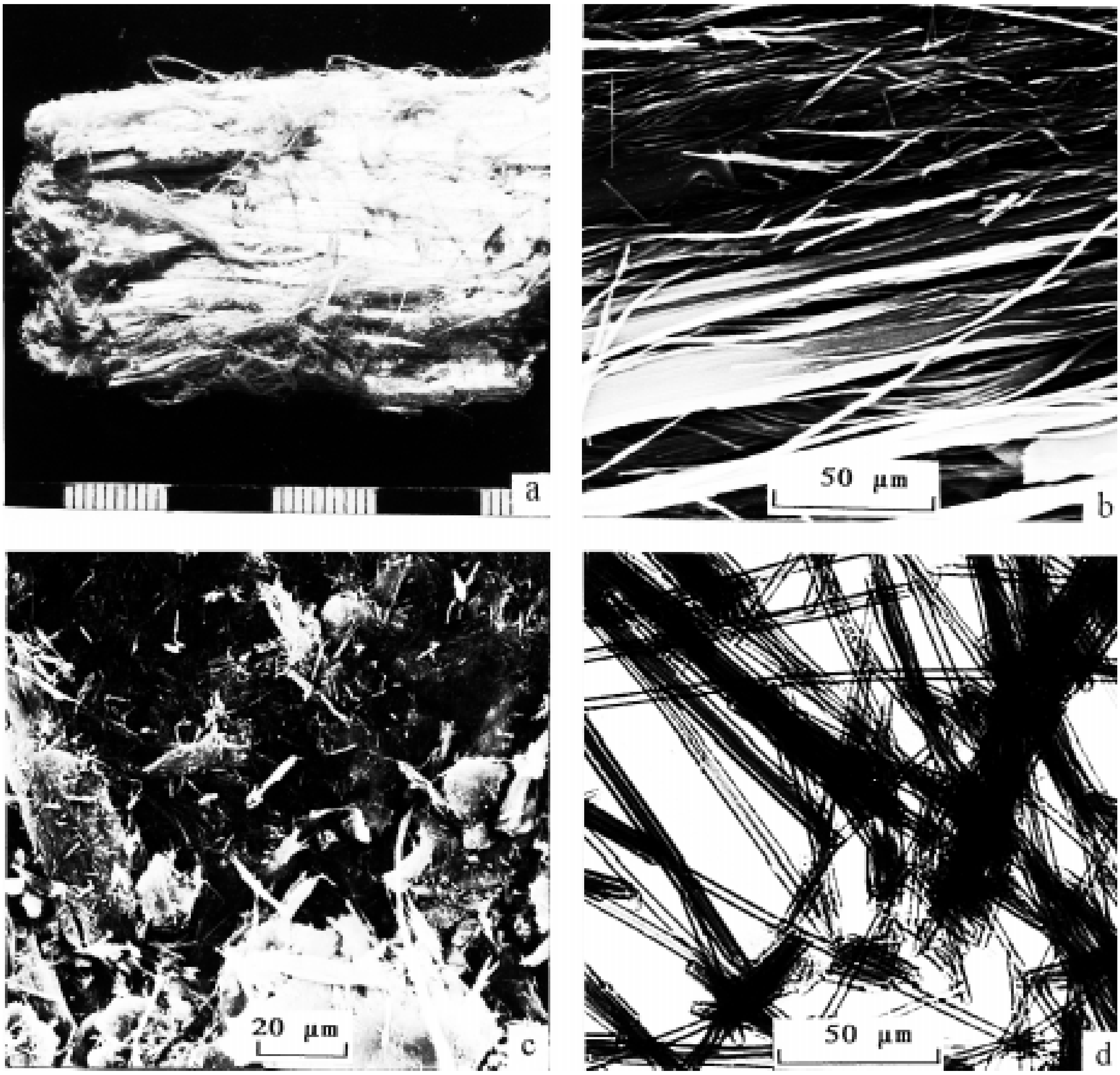

Plate III: Fig. a. Mixture of splintery antigorite and fibrous chrysotile from shear zone — Kamvounia massif. **Fig. b.** Splintery antigorite from shear zone Kamvounia massif. **Fig. c.** Natural surface of the mineral aggregate filling shear zone — Kamvounia massif, Micrographs b and c = scanning electron microscope. **Fig. d.** Chrysotile fibers from the shear zone — Kamvounia massif. Transmission electron microscope.

In accordance with results of Prichard's (1979) studies (and studies of numerous authors' cited here) we consider that serpentinization process which resulted in the origin of the rock-forming lizardite and chrysotile in both the massifs studied occurred in an oceanic environment (= ocean floor serpentinization). On the basis of the different serpentine minerals present in these massifs we suppose their different subsequent history. The Kamvounia massif was subsequently recrystallized under the greenschist facies P-T conditions, while Vourinos Complex never underwent recrystallization under such P-T conditions. During the meso- and probably neoalpine geological events both massifs were involved in more-or-less identical P-T conditions. They are documented by the common appearance of chrysotile (+ lizardite) and antigorite (mostly of "fibrous antigorite" character) in shear zones within both massifs under consideration.

From the petrological point of view the formation of chrysotile at the expense of antigorite should be classified (from the temperature point of view) as a retrogressive and simultaneously hydration process.

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