CONTRIBUTIONS TO STUDY OF THE MAGNESIAN MINERALS IN IUŢI-TIŞOVIŢA-PLAVIŞEVIŢA OPHIOLITIC COMPLEX FROM ALMĂJ MOUNTAINS (SOUTHERN CARPATHIANS – ROMANIA)

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ABSTRACT. The Iuţi-Tişoviţa-Plavişeviţa ophiolitic complex is composed of three major parts: gabbroid of Iuţi and gabbroid of Plavişeviţa, separated by ultrabasic massive of Tişoviţa, and is belonging to the major unit named Danubian autochthon of the Romanian Southern Carpathians = Bulgarian Prebalkans and Stara Planina. In a broader scale the Iuţi-Tişoviţa-Plavişeviţa ophiolitic complex belongs to the Tethyan-Eurasian Metallogenic Belt. He represents extension, at north from Danube, of the alignment of Paleozoic inferior basic-ultrabasic rocks from Serbia. The Tişoviţa-Plavişeviţa sector is remarkable by associations of the magnesian minerals disposed of type cross-filler and/or mass-filler in appreciable reserves. On the basis of mineralogical-petrographical investigations (optical microscopy study, diffraction RX, thermal analyses) an attempt has been made to reveal of this associations of magnesian minerals forming in the rocks from this ophiolitic complex.

ПРИНОС КЪМ ИЗУЧАВАНЕТО НА МАГНЕЗИАЛНИ МИНЕРАЛИ ОТ ОФИОЛИТОВИЯ КОМПЛЕКС ИУТИ-ТИШОВИТА ПЛАВИШЕВИТА НА ПЛАНИНИТЕ АЛМАЖ (ЮЖНИ КАРПАТИ – РУМЪНИЯ)

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РЕЗЮМЕ. Офиолитовият комплекс Иути-Тишовита-Плавишевита е съставен от три основни части: габроиди от Иути и габроиди от Плавишевита, отделени от ултрабазичния масив на Тишовита. Той се отнася към една голяма структура наречена Дунавски автохтон на румънските Южни Карпати (= българския Предбалкан и Стара планина). В по-широк аспект офиолитовият комплекс Иути-Тишовита-Плавишевита принадлежи на Тетис-Евразийския металогенен пояс. Той представлява разтягане, на север от Дунав, на поредица от палеозойски базични до ултрабазични скали от Сърбия. Секторът Тишовита-Плавишевита е забележителен с асоциация от магнезиални минерали използвани като суровина за филтри. На базата на минералого-петрографските проучвания (оптичен микроскоп, рентгенова дифракция, термичен анализ) се прави опит да се представят асоциациите от магнезиални минерали образувани в скалите на офиолитовия комплекс.

Introduction

The presents paper a complex mineralogical-petrographical investigation performed on some rock samplex from the transitional unit of the Tisoviţa ultramafic massive. These rock samples are considered representative and they have been taken from the left versant of the Danube River, more precisely, from the slope of the Orşova-Moldova Nouă road (DN57). This road follows the river, through the zone of the transition unit of the Tişoviţa serpentinite massif. The rocks of this transitional unit outcrops over a distance of approximately 3km (from the bridge over Tişoviţa valley to the Iuţi valley) being followed by the Iuţi gabbros unit. In the studied outcrops formed through the bank-sloping of the road, there are serpentinites and dunites partially serpentinized, crossed by joints which are filled white magnesian minerals (Fig. 1). The host rock has a fine granular texture and a greenish-black or reddish-brown colour.

Fig. 1. Outcrop in serpentinites and dunites partially serpentinized crossed with joints filled with white magnesian minerals (slope of the Orşova-Moldova Nouă road = DN57, near the bridge over Tişoviţa valley)

The Iuţi-Tisoviţa-Plavişeviţa (ITP) ophiolitic complex from South Banat (south-west Romania) belongs to the Balkan-Carpathian ophiolite (BCO) belt and in a broader scale to the Tethyan-Eurasian Metallogenic Belt (Jankovic, 1977). BCO extends over 250 km from north-west to south-east and includes, besides ITP ophiolitic massive, several major ophiolitic massive: Zaglavac and Deli Jovan (north-east Serbia), and Tcherni Vrach (north-west Bulgaria). The ophiolite sequence of these massive are considered as fault-block remnants of the single Late Precambrian-Earliest Cambrian (563±5Ma) ophiolite thrust sheet formed in a mid-ocean ridge setting and possibly representing a crustal fragment of large oceanic basin. It is assumed, that BCO is a part of extended South European palaeo-oceanic suture continued on southeast in Pontides and further in Arabian-Nubian Shield and representing a trace of proto-Tethys closed in early Paleozoic in relation with Cadomian orogeny (Haydoutov, Yanev, 1997; Savov et al., 2001; Zakariadze et al., 2006).

Geological and structural evidence indicates that both ITP and Deli Jovan ophiolitic complexes were parts of the same massive, located in the basement of an Upper Danubian Unit and dismembered by Oligocene dextral translations along the Cerna-Timok Fault. Because it is uncertain if the continuation of the Danubian and Getic-Supragetic Unit is developed in the western Stara Planina from the Bulgarian Balkans (Berza, 2000), it is not yet proven that all four occurrences belong to the same ophiolitic massive, as previously suggested (Haydoutov, 1989; Haydoutov, Yanev, 1997; Savov et al., 2001; Seghedi et al., 2005). If the metamorphic basement in the Stara Planina represents the continuation of the Danubian units from the South Carpathians (e.g. Săndulescu, 1984; Kräutner, 1996; Kräutner, Krstic, 2003), then the Zaglavac and Tcherni Vrah occurrences belong to the same ophiolitic massive as ITP and Deli Jovan. Alternatively, they might represent ophiolitic successions located within the Getic-Supragetic Unit complex from the Balkans (Seghedi *et al*., 2005). In the Tcherny Vrach massive cumulate, sheeted dykes and pillow lava units were recognized (Haydoutov, 1989; Haydoutov, Yanev, 1997) and the U-Pb zircon age of the Tcherny Vrach gabbro is 563±5 Ma (von Quadt et al., 1997). All geochronological data (Zakariadze et al., 2006) carried out for gabbros from Deli Jovan massive showed narrow Lower Devonian interval, the U-Pb zircon age of the Deli Jovan gabbro being 405±2.6 Ma.

The ITP ophiolitic (mafic-ultramafic) complex represents a plutonic sequence, well preserved in the Upper Danubian basement (Fig. 2), tectonically sandwiched and partly dismembered in a pre-Late Carboniferous Unit complex (Mărunţiu, 1984; Mărunţiu et al., 1997; Seghedi et al., 2005). The ITP ophiolitic complex includes two main units which show the ophiolite igneous stratigraphy: a lower unit with upper mantle lithologies and an upper association of plutonic cumulates. Plutonic and effusive rocks in the eastern, Plavişeviţa shear zone, are interpreted as the upper part of the ophiolite sequence (Mărunţiu *et al*., 1997). The mantle peridotite unit, forming the lower part of the ophiolite igneous stratigraphy, consists mainly of harzburgite with tectonite structure and subordinate dunite, hosting small podiform chromitites.

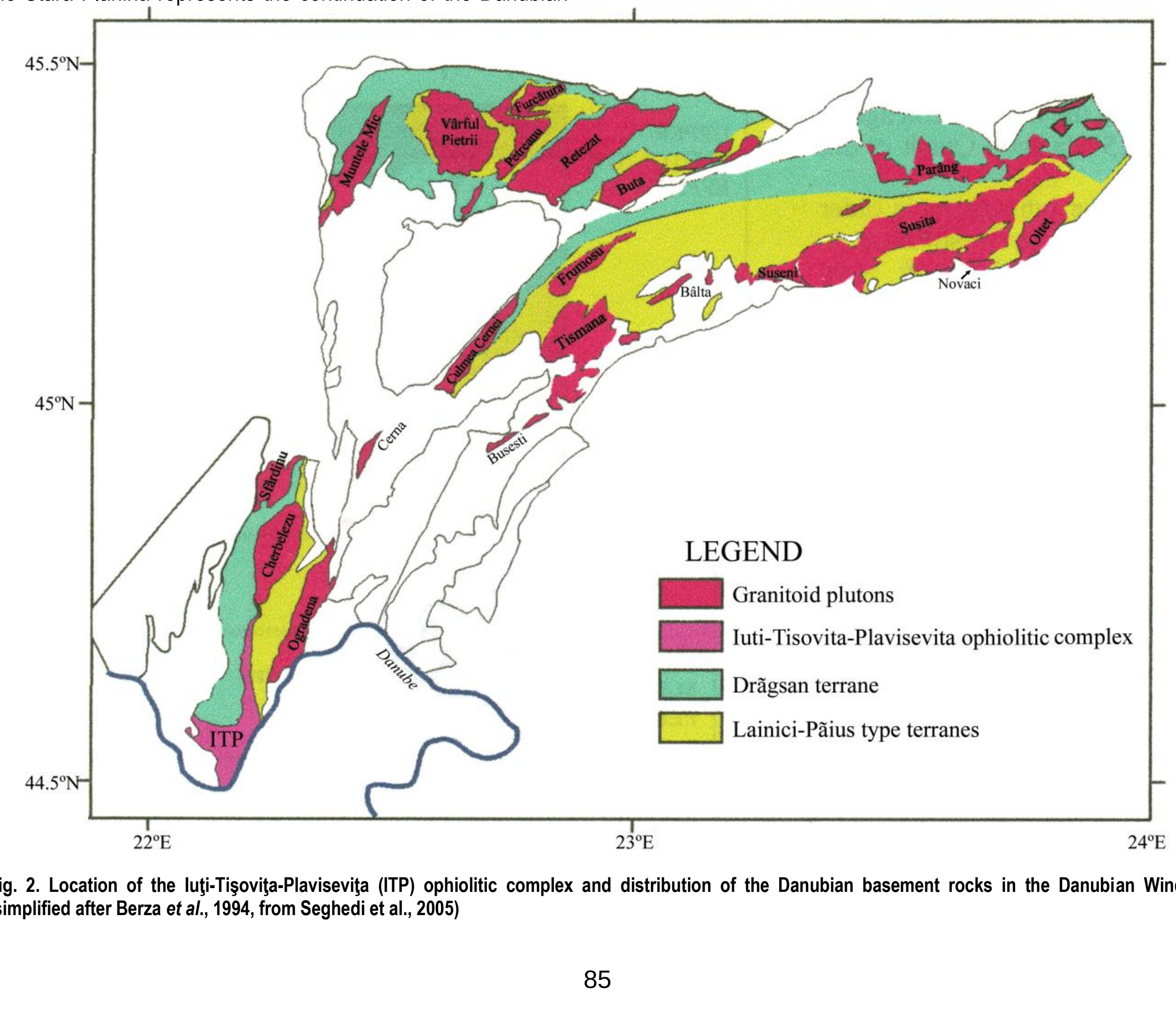

Fig. 2. Location of the Iuţi-Tişoviţa-Plaviseviţa (ITP) ophiolitic complex and distribution of the Danubian basement rocks in the Danubian Window (simplified after Berza *et al*., 1994, from Seghedi et al., 2005)

The cumulate sequence includes an ultramafic unit (dominated by layered dunites, which show lens-shaped bodies of plagioclase-bearing dunite, troctolite, olivine gabbro and gabbro), a transitional zone (consists of alternating cumulates, mafic = troctolite, olivine gabbro, gabbro, and ultramafic = dunite, plagioclase dunite, wehrlite, clinopyroxenite) and a layered mafic unit (include gabbro, olivine gabbro and troctolite, forming a rhythmic layered sequence which is cross-cut by isotropic olivine gabbro). The entire cumulate pile is characterized by rhythmical layering, marked by alternation of isomodal, modally graded and grain-size graded layers. The adcumulus texture is most widespread, with mesocumulus texture shown only by some mafic cumulates (Mărunţiu et al., 1997).

The mylonitic gabbro in the eastern shear zone (Plavişeviţa zone) represents a highly tectonized mixture of various lithologies (Bercia and Bercia, 1975; Mărunţiu, 1984). This mylonite zone is characterized by association of cumulate and isotrope gabbro, cross-cut by high level intrusives (dykes of dolerite and porphyritic basalt with preserved chilled margins, along with dykes of plagiogranite). The association suggests remnants of the upper part of the plutonic complex (Seghedi et al., 2005).

From structurally point of view in the ultrabasic massive of Tişoviţa have been distinguished two types of serpentines: cellular serpentines (chrysotilic) corresponding to compact serpentines present in Tişoviţa-Baia Nouă zone, and lamellar serpentines (antigoritic) that correspond to serpentines varieties forming predominantly formed of antigorite in association with chlorites, carbonates and chromite, localized especially in narrow zone between Tişoviţa and Ciucaru Mare. Serpentinites are crossed, especially in the south part, by numerous veins of gabbros and plagioclasites, rarely by veins of trachite and lenses of the plagioclasic gneisses (Bercia and Bercia, 1962).

According to mineralogical composition and ultrabasic rocks (host-rocks) from which serpentinites have resulted, we can distinguish (Bercia, Bercia, 1962): 1 – dunitic-type serpentines, partially or totally serpentinized; 2 – harzburgitic serpentines; 3 – wehrlitic serpentines (at border with Iuţi gabbros).

Mineralogical-petrographical investigations

The joint-host rock system

The joint mineral content is heterogeneous. Macroscopically a friable, easily soluble white matrix can be observed, and it contains dark coloured fragments with a contrasting composition. These fragments have submillimetric to centimetric sizes.

The microscopic study made on thin sections revealed that this matrix is predominantly composed of a colourless mineral, with fibrous habit, negative relief and moderate to strong birefringence in longitudinal sections (second or third order birefringence colors). These fibrous crystals have maximum 50 μm thickness and lengths ranging from 0.1 mm to 0.5 mm. They form small groups with radial orientation (Fig. 3).

Besides the fibrous and colourless mineral the matrix contain rare crystals of carbonate (magnesite) (Fig. 4) and in some regions iron hydroxide which imprints locally a reddish brown colour.

Also microscopically it has been found that the dark coloured fragments are serpentinite fragments. These rock fragments have also a heterogeneous structure: small eyes of serpentine are bordered with thin walls of iron hidroxide (Fig. 5). Smalll crystals of unaltered magnetite resulted by the desagregation of the mentioned serpentinites can also as fragments be found.

Macroscopically in the host-rocks for these joints, we can observe zonings at a centimetric scale given by the alternation of some lenticular and tabular domains with different colors: light green next to the joints which passes with distance to black and brown. The microscopic study has also allowed the determination of the mineralogical composition for each of these zones.

The light green domains near the joints are composed of colourless magnesian chlorite and magnesite (Fig. 6). The black and brown domains are dunitic domains in which the olivine partially altered to serpentine group minerals. There are present two members of serpentine group: a serpentine with relatively low Fe content and an iron serpentine (greenalite) which is found only near the olivine relicts (Fig. 7). In these dunitic domains the magnetite is also present and it remained unaltered. Where the iron from the serpentine group minerals is in bivalent form the color of the dunitic domains is black and where the iron from the serpentine group minerals is in trivalent form the color is reddish brown (Fig. 8).

X-ray diffraction analyses

X-ray diffraction analyses on a sample from joints filling formed in ultrabasic massive from Tişoviţa were performed using an HZG 4/A diffractometer with following parameters: CuKα radiation, Ni filter, l=1,54Å, 25kV/15mA, measuring speed 1º/min. On diffractogram (Fig. 9) of analyzed sample were identified peaks that may be attributed serpentine, greenalite, minnesotaite and nesquehonite.

The serpentine was identified by diffractogram by its characteristic reflections of the higher intensities (006), (0.0.12), (204) and (2.0.24), in a lower quantity. Greenalite was evidenced by the peak of higher intensity from 2.57Å followed by a series of peaks of lower intensities from 7.12Å, 2.198Å and 1.55Å. In a significant proportion comparatively with greenalite, minnesotaite was identified by characteristic reflections of the higher intensities (002) from 9.62Å and (006) from 3.18Å.

Inedited is the presence in a big quantity of nesquehonite identified by the peak of maximum intensity (110) from 6.56Å, followed by the peaks of lower and lower intensities (200), (121), (220), (041), (310), (241), (400), etc.

Thermal analyses

Thermal analyses that consist in thermodifferential analyses (DTA) and thermogravimetric analyses (TG) were performed using an DERIVATOGRAF MOM type apparatus, on the same sample taken from joints filling in ultrabasic massive from Tişoviţa, in an oven of 1000ºC having a heating rate of 10ºC/min.

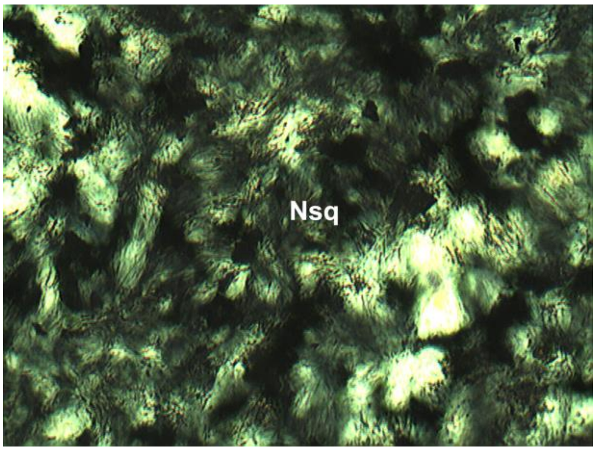

Fig. 3. The fibrous habit of the nesquehonite (Nsq) crystals and the radiar structure of the aggregate (N|| 250x)

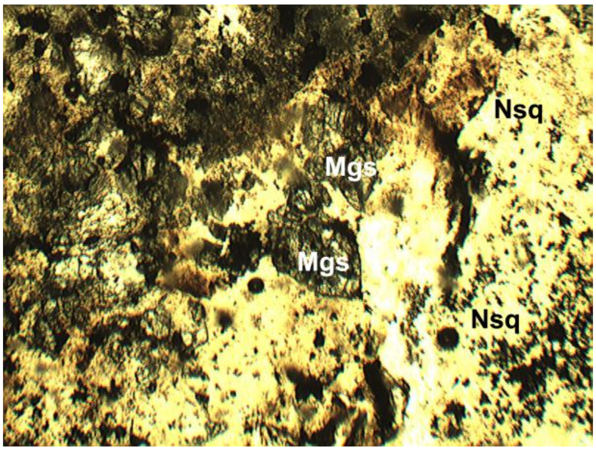

Fig. 4. Rare magnesite (Mgs) crystals and iron hydroxide in the joints filled prevalent with nesquehonite (N|| 40x)

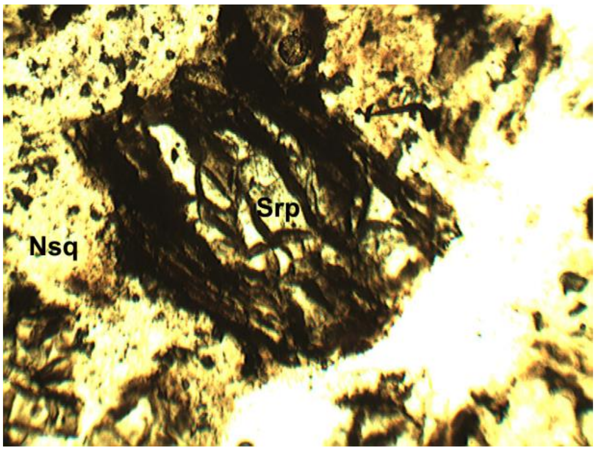

Fig. 5. Serpentine (Srp) relics in the matrix prevalently composed of nesquehonite (N|| 40x)

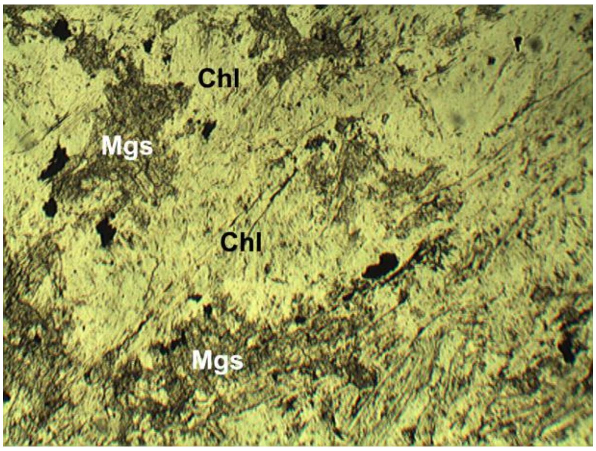

Fig. 6. The domains composed of colorless magnesian chlorite (Chl) and magnesite (N|| 40x)

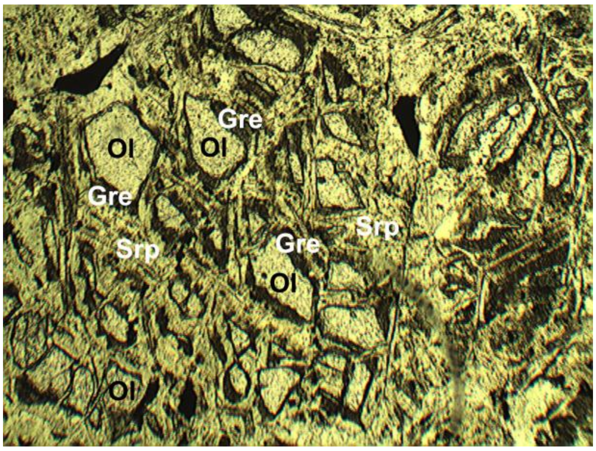

Fig. 7. The structure of the dunitic domains in which olivine relics are surrounded by minerals of the serpentine group. The greenalite (Gre) is located exclusively near the olivine (Ol) relics. Here the iron from the serpentine group mineral is in the bivalent form (N|| 40x)

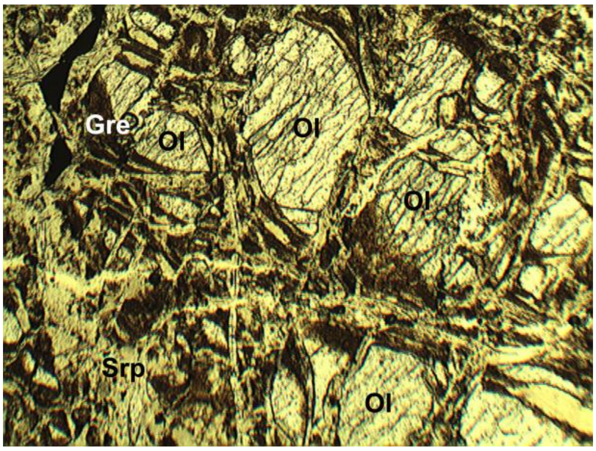

Fig. 8. Detail on the olivine relics surrounded by greenalite. Here the iron is in the trivalent form (N|| 100x)

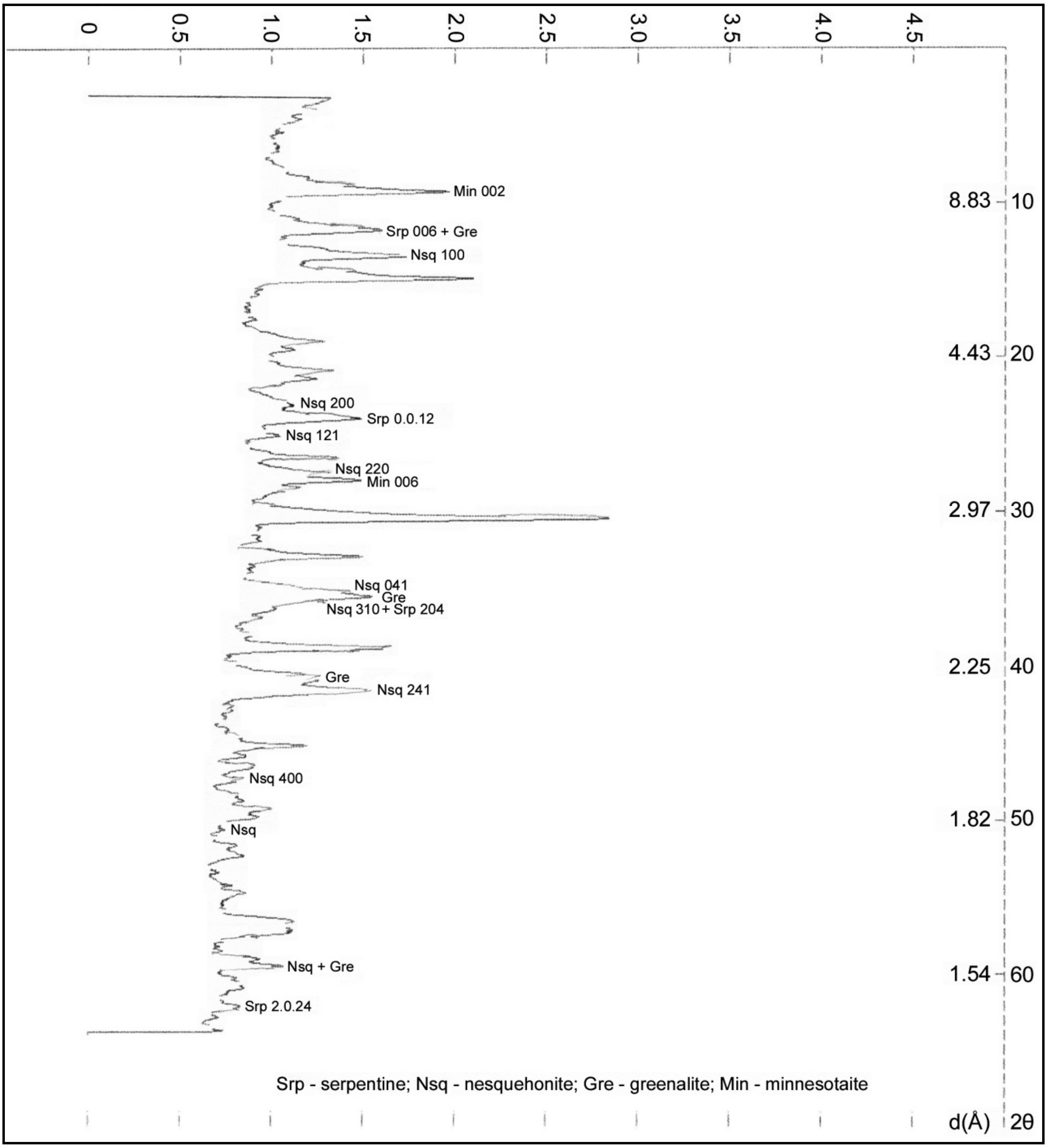

Fig. 9. Diffractogram of the sample from joints filling developed in ultrabasic massive from Tişoviţa

Weight loss marked on the thermogravimetric curve (TG) correspond to enthalpy variations registered on DTA curve by endothermic and exothermic effects (Fig. 10) which characterize a sample of nesquehonite ($MgCO_3 \cdot 3H_2O$), contamined with calcite, clinochlore and serpentine.

An endothermic effect from 300ºC and 390ºC, pointed, with double shape and maximum development at 300ºC, is marked by two steps of weight loss on the TG curve (Fig. 10) and corresponds to elimination of the crystallized water from nesquehonite. The exothermic effect from 460ºC corresponds to structural reorganization and elimination of a molecule of CO_2 from nesquehonite structure. Endothermic effect from 500ºC, pointed by third step of weight loss with steep slope on the TG curve was attributed to dehydroxylation and losing of a molecule of CO_2 from magnesian carbonate. The endothermic effects from 625ºC and 700ºC correspond to decomposition of $MgCO_3$ and $CaCO_3$ by elimination CO_2 from nesquehonite and calcite structures. Exothermic effect pointed at 780ºC indicates the presence of chlorite (clinochlore) and serpentine having endothermic effects from 640ºC and 700ºC masqued by elimination of CO_2.

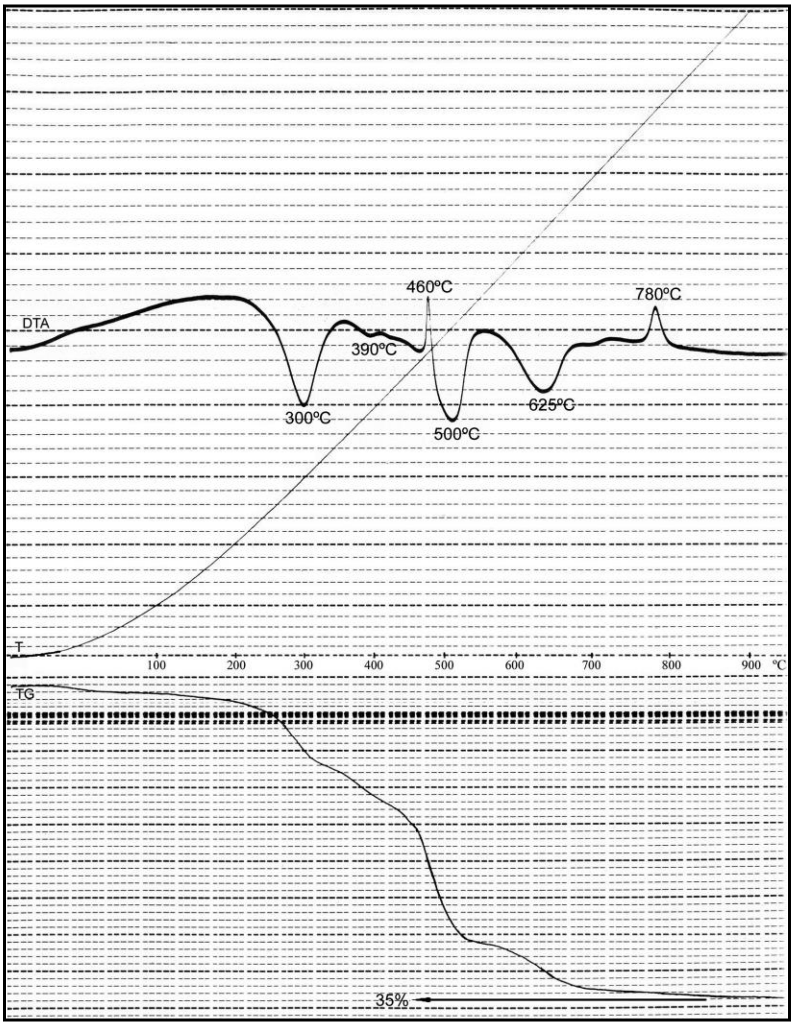

Fig. 10. Thermal derivatogram of the sample from joints filling developed in ultrabasic massive from Tişoviţa

Results and interpretation

The optical features, crystal habit and the mode of aggregation of the fibrous mineral which prevails in the joints are concordant with the results obtained from the interpretation of the X-ray diffractogram and the interpretation of the thermal curves in DTA analysis. It can be concluded that this fibrous mineral is nesquehonite.

The chlorite-magnesite domains in the host rock are interpreted as the result of the interaction between the dunite and some CO_2-bearing hydrothermal fluids. In a later lower temperature-stage, these fluids are also responsible for the deposition of the nesquehonite in the joints. The olivine alteration to serpentine group minerals in the dunitic domains has taken place in two stages. The first stage has involved the formation of the low-Fe serpentine and the second the formation of the greenalite at lower temperatures (<300°C).

In the studied samples it has been proved: i) the presence of some minerals from the serpentine group having various iron contents which range up to the greenalite type; ii) the presence of some minerals of talc group also with variable iron contents ranging up to the minnesotaite. The minerals mentioned above are formed on the fayalite component from the olivine. The SiO_2 and CO_2-rich hydrothermal solution took both magnesium ions and iron ions and made possible reaction of the following types:

4 olivine+$2CO_2$+$4H_2O$ → serpentine + 2 magnesite (1)
3 olivine+$4H_2O$+SiO_2 → greenalite (2)
greenalite+$3CO_2$ → minnesotaite+3 magnesite+$3H_2O$ (3)
magnesite + $3H_2O$ → nesquehonite (4)

Conclusions

The mineralogical-petrographical study (optical microscopy, XRD, thermal analyses) of the samples from transitional zone of Iuţi-Tişoviţa-Plavişeviţa ophiolitic complex reveals the presence of the association of secondary minerals predominantly magnesian minerals (serpentine + minnesotaite + greenalite + nesquehonite). From this association the serpentine minerals are formed by metasomatic processes on the initial dunitic rock. The nesquehonite is formed in the latest genetic stage through direct deposition from the solution.

The fracturing in an extensional regime has resulted in the formation of a complex system of joints filled through hydrothermal deposition with carbonate + serpentine + talc or carbonate + serpentine + chlorite + talc.

From this association of magnesian minerals developed in fissures that affected ophiolitic massive from Tişoviţa can be noticed the presence in high quantity of nesquehonite, rare mineral, that so far is not cited in serpentinites from Romania.

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Recommended for publication by Department of "Geology and Prospecting of Mineral Deposits", Faculty of Geology and Prospecting