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## First occurrence of dumortierite in Croatia: its chemical composition and appearance as an igneous mineral in leucogranite-hosted pegmatite

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#### **Abstract**

In this article, dumortierite from Croatia is described for the first time. Dumortierite formed in a pegmatite dyke cutting through Cretaceous two-mica leucogranite of the magmatic-metamorphic complex of Mt. Moslavačka Gora. The pegmatite dyke shows a magmatic mineral association of coarse-grained quartz, orthoclase, microcline and albite, less abundant muscovite, biotite, pinkish andalusite and blue-coloured prismatic dumortierite I crystals. Subsequent alteration by titanium-rich hydrothermal fluids led to partial replacement of dumortierite I and andalusite by secondary fibrous to acicular purple dumortierite II enriched in Mg and Ti. During temperature decrease perthite developed in feldspars and at a still later stage, sericite partially replaced not only feldspars but also andalusite and both types of dumortierite along grain boundaries and cracks. Final alteration at very low temperatures caused formation of clay minerals at the expense of feldspars. According to mineral chemical analyses, the feldspars are represented by albite and K-feldspar with a low albite component. Biotite corresponds to annite and its subhedral shape and chemical composition point to magmatic crystallisation from a peraluminous melt derived from a crustal source. Coarse muscovite flakes contain 1.31-1.48 wt.% FeO and 0.56-0.70 wt.% TiO<sub>2</sub>. Their Na/(Na+K) ratios (0.08-0.09) prove a magmatic origin, whereas lower ratios in sericite (0.04-0.06) indicate formation during retrogression. Magmatic muscovite is in textural equilibrium with andalusite, also implying an igneous origin for the latter, which belongs to the S3 textural type of andalusite in felsic igneous rocks. Electron microprobe analyses clearly show a strong positive correlation between Si tetrahedral deficiency (3-Si) and the sum of Al+Ti, (R2= 0.85) in both types of dumortierite, implying Al replacement by Ti. However, Al replacement by Ti is not restricted to Al in the octahedral position, as generally accepted, but most probably also in the tetrahedral position. Distinct pleochroic colours in dumortierite are usually explained by the [Fe/(Fe+Ti)]x100 factor, but according to this study, elevated Mg contents stabilize red to violet coloured dumortierite at higher [Fe/(Fe+Ti)] x100 factors than those previously suggested.

Dumortierite-bearing pegmatite and host two-mica leucogranite show strong chemical similarities in their major, minor and trace element contents. Both rock types have a strong peraluminous character (ASI = 1.6 in pegmatite vs 1.8 in leucogranite), low CaO/Na<sub>2</sub>O ratios (0.11 vs 0.14), high Rb/Ba (74.5 vs 16.4) and Rb/Sr ratios (78.4 vs 43.3) as well as relatively high  $Al_2O_3/TiO_2$  ratios (261 vs 210). For the leucogranitic melt these characteristics indicate derivation from a pelitic source and low melting rates at relatively low temperatures. With respect to the field relationships and the chemical similarities, formation of the pegmatitic melt by fractional crystallisation during solidification of the two-mica leucogranite is inferred. Based on the mineralogical composition, the dumortierite-bearing pegmatite from Mt. Moslavačka Gora may be a member of the abyssal pegmatite class and the AB-BBe subclass. However, its formation by fractional crystallisation from a granitic melt argues against this interpretation, as all other dumortierite-bearing granitic pegmatites occur in high-grade metamorphic host rocks and are thought to be products of anatectic melting of country rocks. Therefore, the investigated pegmatite is quite unique and not fully comparable with any previously described dumortierite-bearing pegmatite worldwide.

**Keywords:** dumortierite, andalusite, granitic pegmatite, Mt. Moslavačka gora, Croatia

## 1. INTRODUCTION

Dumortierite  $[(Al,\Box)Al_6(BO_3)Si_3O_{13}(O,OH)_2]$  is relatively uncommon but is the second most abundant aluminum borosilicate in the Earth's crust after tourmaline. It is the most widespread member of the dumortierite group which also includes very rare magnesiodumortierite  $[(Mg,Ti,\Box)Al_4(Al,Mg)_2(BO_3)Si_3O_{12}(O,OH)_3]$  and

holtite [(Ta,Nb,□,Al)Al<sub>6</sub>(BO<sub>3</sub>)(Si, Sb,As)<sub>3</sub>O<sub>12</sub>(O,OH,□)<sub>3</sub>] (EVANS et al., 2012). Dumortierite occurs as a minor constituent in pegmatite (FUCHS et al., 2005; ČEMPIREK & NOVAK, 2006; PIECZKA et al., 2011; GROAT et al., 2012), granite (PUXEDDU, 2022), aluminous regional metamorphic rocks (VISSER & SENIOR, 1991; WILLNER & SCHREYER, 1991; VRANA et al., 2009;

DOKUKINA et al., 2017; KORSAKOV et al., 2019) and hydrothermally altered rocks (BLACK, 1973; TANER & MARTIN, 1993; CHOO & KIM, 2003; KHALEGHL, 2019).

Dumortierite was first observed at Chaponost, in the Rhône-Alps near Lyons, France, by M.F. Gonnard in November 1879 who named the new mineral after the influential French paleontologist Eugène Dumortier (GONNARD, 1881). The orthorhombic space group of dumortierite (Pmcn) as well as its first general formula were determined by CLARINGBULL & HEY (1958). Its unusually complex crystal structure was resolved by GOLO-VASTIKOV (1965). Later studies revealed the presence of vacancies and water inside the crystal structure (MOORE & ARAKI, 1978; WERDING & SCHREYER, 1983, ALEXANDER et al., 1986). The full occupation of the tetrahedral sites, even if there is a Si-deficiency, was demonstrated by ALEXANDER et al. (1986), who explained this by Al substitution for Si. The same authors postulated that the blue colour of dumortierite can be attributed to Fe<sup>2+</sup>-Fe<sup>3+</sup> charge transfer, and the pale red colour to Fe<sup>2+</sup>-Ti<sup>4+</sup> charge transfer. The most recent refinements of the crystal structure were done by EVANS & GROAT (2012), EVANS et al. (2012) and GROAT et al. (2012) as according to them, dumortierite is strongly pseudohexagonal and contains two types of double chains of Al octahedra running parallel to the c-axis. The Al 2 and Al 3 double chains are characterised by edge-sharing octahedra, whereas the Al 4 double chain consists of face-sharing octahedral dimers. The two types of double chains are linked to one another by corner sharing and form small trigonal channels, which contain BO<sub>3</sub> triangles and large hexagonal channels incorporating the Al 1 chain of face-sharing octahedra. The Al1 chain is connected to the double chain framework via six SiO<sub>4</sub> tetrahedra having two Si 1 and four Si 2 sites. Chemical substitutions occur mostly in the hexagonal channel, for instance Ti<sup>4+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup> at A11 and A1<sup>3+</sup> at Si 1 and Si 2 sites (EVANS et al., 2012). Vacancies occurring at the A11 site are charge compensated by the replacement of O atoms by OH primarily at the O2 and O7 sites (EVANS & GROAT, 2012).

The aim of this study is to present the first known occurrence of dumortierite in Croatia. It was found in a pegmatite dyke cutting a two-mica leucogranite of the Srednja Rijeka quarry (45°42'45.4"N/16°41'31.5"E). The latter is located about 5 km

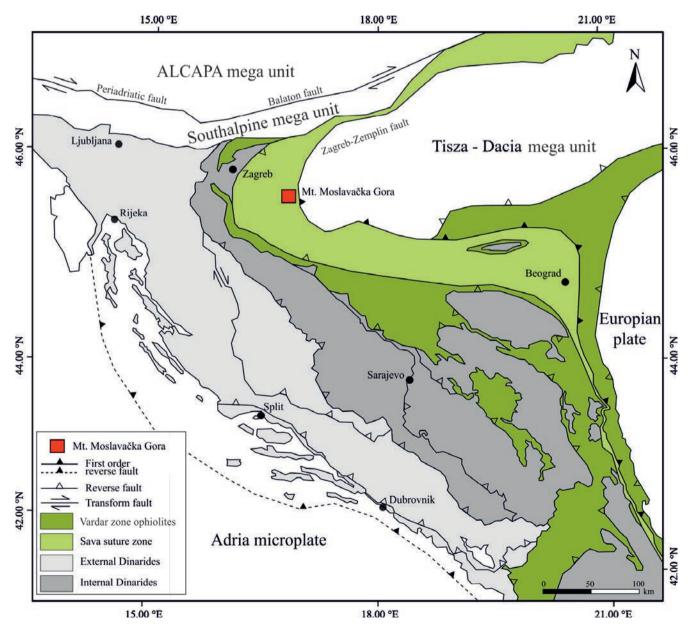


Figure 1. Tectonic map of the northern Dinarides and the surrounding area showing the tectonic subdivision according to SCHMID et al. (2008). The position of Mt. Moslavačka Gora within the Sava suture zone is indicated by the red square.

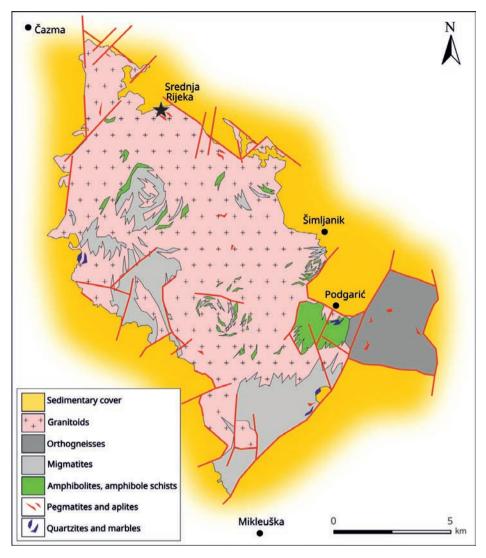


Figure 2. Geological sketch map of the Mt. Moslavačka Gora area modified after CRNKO (1990) and KOROLIJA & CRNKO (1985). The investigated dumortierite-bearing pegmatite is located at Srednja Rijeka quarry (45°42'45.4"N/16°41'31.5"E) and the sample location is marked by a star symbol.

southeast of the city of Čazma in the northern part of Mt. Moslavačka Gora (Fig. 1, 2). Based on petrographic, mineral, chemical and whole rock geochemical data, the mineralogy of dumortierite, the host pegmatite and the surrounding leucogranite are described and their genetic relationships discussed. Finally, data from the studied locality are compared to other dumortierite-bearing pegmatite occurences worldwide.

## 2. GEOLOGICAL SETTING

The described dumortierite occurs in one of the pegmatite dykes cutting a Late Cretaceous two-mica leucogranite of the magmatic-metamorphic complex of Mt. Moslavačka Gora (Fig. 2). The crystalline complex forms an inselberg of about 180 km² in the southwestern part of the Pannonian Basin, which is filled by Neogene and Quaternary sediments (PAMIĆ, 1990). Regarding its position in the regional tectonic framework, the magmatic-metamorphic complex of Mt. Moslavačka Gora was previously deemed to be a part of the Tisia mega unit (PAMIĆ, 1998; PAMIĆ & JURKOVIĆ, 2002), which is characterised by a Variscan metamorphic basement. However, more recent studies recognised a dominant Cretaceous igneous and metamorphic imprint (BALEN & PETRINEC, 2011) and, therefore, it is nowadays attributed to the Sava zone, forming the suture between Europe and the Adria-

derived tectonic units in the Pannonian Basin and the Dinarides (SCHMID et al., 2008) (Fig. 1).

The magmatic-metamorphic complex of Mt. Moslavačka Gora is composed of high- to medium-grade (predominantly migmatite and ortho- and paragneiss) and medium-grade metamorphic rocks (mostly micaschist and amphibolite), with rare intercalations of quarzite and marble (TUĆAN, 1953; BARIĆ, 1972; CRNKO & VRAGOVIĆ, 1990; GARAŠIĆ, 1993; BALEN et al., 2000). This sequence is intruded by various types of granitic rocks, such as two-mica granite, granodiorite, monzogranite and leucogranite (CRNKO & VRAGOVIĆ, 1990; PAMIĆ, 1990) as well as different types of gabbro (KIŠPATIĆ, 1887; TUĆAN, 1953; PAMIĆ, 1987; BALEN et al., 2003). Besides the common granite minerals (quartz, K-feldspar, acid plagiclase, biotite and muscovite), andalusite, sillimanite and tourmaline were recognised in some granitic bodies of Mt. Moslavačka Gora (COHEN, 1887; KIŠPATIĆ, 1887; CRNKO & VRAGOVIĆ, 1990; GARAŠIĆ et al. 2007; BALEN, 2007; BALEN & PETRI-NEC, 2010; BALEN & BROSKA, 2011). Pegmatite and aplite dykes are scarce in the medium-grade metamorphic rocks, but are more frequent and thicker in migmatite and particularly in the granitic rocks (TUĆAN, 1904; CRNKO & VRAGOVIĆ, 1990). The latter also contain different types of enclaves, "for-





Figure 3. Hand specimens of dumortierite-bearing pegmatite from the Srednja Rijeka quarry in Mt. Moslavačka Gora. A) Fine-grained leucogranite (right side) and coarse-grained pegmatite with bluish dumortierite (left side). Both rock types consist of white feldspars, grey quartz, black biotite, silvery-white muscovite and tiny pale pinkish andalusite. B) Pegmatite composed of white feldspars, grey quartz, black biotite flakes and blue dumortierite.

eign" (gneiss, amphibolite xenoliths, etc,) and "cognate" (tourmaline nodules), ranging in size from a few millimetres up to hundreds of metres in size. According to a study by BALEN & PETRINEC (2010), they indicate a complex evolution for at least some of the granitic rocks of Mt. Moslavačka Gora.

Geochronological age data indicate a prolonged period of geological evolution of the magmatic-metamorphic complex of Mt. Moslavačka Gora. Zircon dating revealed an Early Ordovician age (486-491 Ma) for the granitic rocks now metamorphosed to orthogneiss (STARIJAŠ et al., 2010). The granulite facies LP/ HT metamorphic overprint at ~750°C and 3-4 kbar occured in the early Late Cretaceous at about 90 to 100 Ma, as indicated by monazite dating of metapelites (STARIJAŠ et al. 2010). This is in agreement with amphibole Ar-Ar cooling ages of 80-90 Ma determined for amphibolites (BALEN et al. 2001). According to the zircon ages of STARIJAŠ et al. (2010), the two-mica leucogranite crystallised in a late phase of the Cretaceous metamorphic event at 82±1 Ma. Subsequent cooling is documented by Ar-Ar muscovite ages of 73±1 and 74±1 Ma measured in both the pegmatite and two-mica leucogranite (PALINKAŠ et al., 2000; BALEN et al. 2001).

## 3. ANALYTICAL METHODS

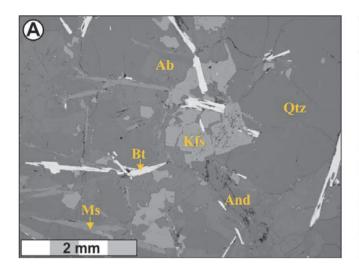
The chemistry of dumortierite and associated minerals in the studied dumortierite-bearing pegmatite was investigated using the Cameca SX51 electron microprobe, equipped with five wavelength-dispersive crystal spectrometers, at the Mineralogical Institute of the University of Heidelberg (Germany). The following operating conditions were applied: accelerating voltage of 15 kV, beam current of 20 nA, about 1  $\mu m$  beam diameter and 10 s counting time for all elements. Calibration standards included natural and synthetic silicates and oxides. The Cameca PAP matrix correction program was applied to the raw data.

Whole rock chemical analyses were performed by Bureau Veritas Commodities Canada Ltd.. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used for the determination of major and minor elements with detection limits ranging from 0.04 to 0.002 wt.%, and inductively coupled plasma mass spectrometry (ICP-MS) for the trace elements showing detection limits in the range from 8 to 0.01 ppm.

#### 4. PETROGRAPHY

The dumortierite-bearing pegmatite dyke is up to 6 cm thick. It consists of coarse-grained quartz, orthoclase, microcline and albite, less abundant muscovite, biotite, pinkish andalusite and blue-coloured dumortierite crystals. In hand specimens (Fig. 3) and back-scattered electron (BSE) images (Fig. 4), the rock shows no indications of postmagmatic deformation. Quartz grains are irregularly shaped, often with amoeboid grain boundaries. In cross polarised light they show weak undulose extinction. They commonly enclose smaller flakes of biotite and/or muscovite. Microcline grains vary in size from 1.0 up to 3.5 mm whereas orthoclase grains are usually coarser (up to 6.0 mm). Both K-feldspars are subhedral to anhedral in shape, perthitic (Fig. 4B) and partially altered to sericite and clay minerals. Fine-grained intergrowths of quartz and microcline are also observed. Biotite flakes and quartz grains are locally enclosed in orthoclase. Albite occurs as subhedral to anhedral grains with common polysynthetic twinning lamellae and varies in size from 4.0 to 15.0 mm (Fig. 4A). It contains various mineral inclusions: microcline, biotite. quartz and dumortierite and also shows alteration to sericite and clay minerals. Muscovite forms subhedral to anhedral flakes up to 0.7 mm in size (Fig. 4A). In some cases, it is intergrown with biotite at the rims. Tiny muscovite (sericite) flakes or aggregates occur at the rims and within cracks of andalusite and dumortierite (Fig. 4B). Biotite flakes vary in size from 0.5 up to 1.9 mm and are commonly subhedral in shape (Fig. 4A). They are pleochroic ranging from light brown to deep brown (Fig. 5). Andalusite occurs as prismatic euhedral to subhedral crystals ranging from 0.1 to 0.5 mm in thickness and from 0.2 to 0.9 mm in length. It shows strong pleochroism from colourless and pale pinkish to pink colour (Fig. 5). The colour is not homogeneous but partly shows a normal concentric zoning with straight to curved gradational boundaries, but sector zoning is also observed. At the rims, andalusite shows replacement by polycrystalline sericite aggregates and dumortierite (Dum II) (Fig. 5).

The microscopic studies identified **two types of dumortierite** crystals: Dum I and Dum II. The Dum I crystals are subhedral, prismatic and up to 26 mm in size. They are strongly pleochroic ranging from colourless to azure blue (Fig. 6). Dum II represents bundles of parallel fibrous or acicular crystals, which



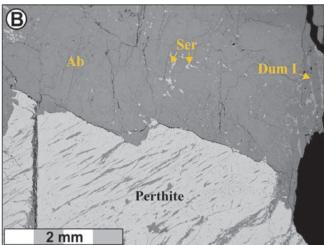
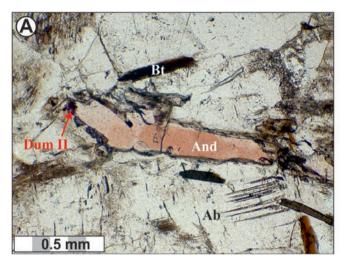


Figure 4. Back-scattered electron (BSE) images of dumortierite-bearing pegmatite. A) The mineral assemblage includes coarse-grained quartz (Qtz), K-feldspar (Kfs), albite (Ab), muscovite (Ms), biotite (Bt) and andalusite (And). B) Perthitic K-feldspar (Kfs), albite (Ab) slightly altered to sericite (Ser) and dumortierite (Dum I), which is replaced by sericite (Ser) along the cracks.



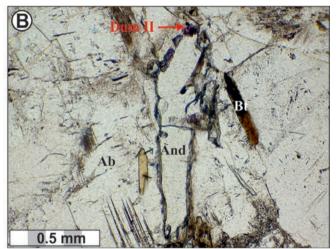
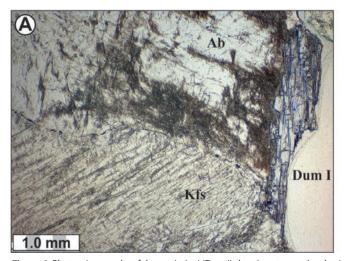


Figure 5. Photomicrographs of andalusite (And), showing strong pleochroism from pale pinkish to pink colour and zoning expressed by the intensity of the colour. It is slightly replaced by sericite and Ti-rich red-violet dumortierite (Dum II) at the rims. Biotite (Bt) flakes are pleochroic from light brown to deep brown.



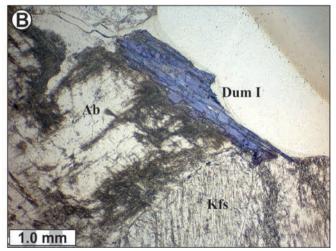


Figure 6. Photomicrographs of dumortierite I (Dum I) showing strong pleochroism from pale blue to colourless. The subhedral prismatic crystal is associated with K-feldspar and albite intensely altered to dark brown clay minerals.

are up to 1.4 mm long. Their strong pleochroism ranges from colourless to red-violet (Fig. 7). A zoned subhedral prismatic dumortierite crystal is also observed. It exhibits a blue to colourless

pleochroic core overgrown by a colourless to red-violet pleochroic rim (Fig. 8). Small muscovite flakes (sericite) replace both types of dumortierite along rims and cracks (Fig. 4B).

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1.0 mm

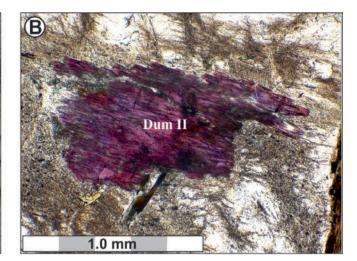
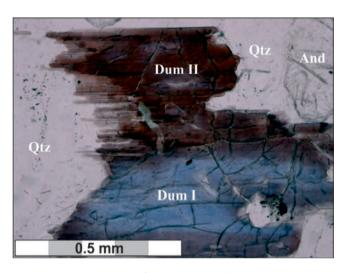


Figure 7. Photomicrographs of dumortierite II (Dum II) showing strong pleochroism from very pale violet to colourless. Dumortierite forms bundles of parallel fibrous or acicular crystals in a mineral assemblage with pleochroic light to deep brown biotite (Bt) and feldspar (Fsp), which is strongly altered to dark brown clay minerals



**Figure 8.** A photomicrograph of a zoned prismatic dumortierite crystal exhibiting a blue to colourless pleochroic core overgrown by a colourless to red violet pleochroic rim.

#### 5. MINERAL CHEMISTRY

Chemical compositions of **feldpars** are given in Table 1. Their chemical formulae were calculated on the basis of 8 oxygens and the total Fe was determined as FeO. The analysed plagioclase Ab<sub>91-98</sub>An<sub>1.4-8</sub>Or<sub>0.6-1</sub> corresponds to albite, whereas K-feldspar contains only minor Na (0.069 to 0.105 pfu). The Fe content is very low, varying from 0.000 to 0.001 pfu in albite and from 0.000 to 0.003 pfu in K-feldspar.

The chemistry of **mica minerals** is shown in Table 2. Their chemical formulae were calculated on the basis of 11 (O,OH) and total Fe as Fe<sub>2</sub>O<sub>3</sub> for muscovite but as FeO for biotite. Coarse **muscovite** flakes (analyses MG-27 and MG-28) and fine-grained muscovite (sericite) replacing andalusite and dumortierite (analyses MG-02, MG-04, MG-11, MG-14) show compositional differences. The coarse muscovite flakes are richer in Ti (0.028-0.034 pfu), Fe (0.073-0.082 pfu), Mg (0.033-0.040 pfu) and Na (0.078-0.082 pfu) but poorer in Al<sub>tot</sub> (2.786-2.827 pfu) than the sericite (Ti = 0.003-0.013 pfu, Fe = 0.000-0.031 pfu, Mg = 0.003-0.011 pfu, Al<sub>tot</sub> = 2.873-2.924 pfu). The analysed **biotite** flakes are characterised by high Al<sub>tot</sub> (1.852-1.894 pfu) and high Fe (1.737-1.776 pfu), have a moderate variation in Al<sup>IV</sup> (1.336-1.373

pfu) and a narrow range of high Fe<sup>2+</sup>/(Fe<sup>2+</sup>+Mn+Mg) ratios (0.829 to 0.836). This corresponds to a common annite composition according to the classification diagram of DEER et. al. (1982). The concentration of Ti varies from 0.165 to 0.173 pfu. The content of K is in the range of 0.895 and 0.930 pfu and Na ranges from 0.010 to 0.013 pfu, yielding low Na/(Na+K) ratios (0.010 to 0.014).

The chemical composition of **andalusite** is displayed in Table 3. The chemical formulae of andalusite were calculated on the basis of 3 cations and 5 oxygens and total Fe as Fe<sub>2</sub>O<sub>3</sub>. Except for Si and Al, only Fe shows a noticeable concentration varying from 0.016 to 0.017 pfu. The distribution of Fe is not homogeneous but produces a chemical zoning. The zoning is expressed by the intensity of the pinkish colour, whereby the colour intensity is positively correlated with the Fe content.

The chemical composition of **dumortierite** is presented in Table 4. Its chemical formulae were calculated on the basis of 17 (O,OH), assuming that the contents of  $B_2O_3$  and  $H_2O$  correspond to 6.20 wt. % and 1.30 wt. %, respectively, in accordance with the measured values of these components in FUCHS et al. (2005). The Dum I crystals occurring as large prismatic grains have lower Mg contents (0.033-0.055 pfu) and Ti (0.001-0.011 pfu) than the smaller Dum II crystals occurring as fibrous or acicular crystals (Mg: 0.047-0.087 pfu; Ti: 0.043-0.064 pfu). The differences in Fe abundance (0.038-0.072 pfu vs 0.037-0.057 pfu) and Al/Si ratios (2.35-2.47 vs 2.27-2.49) are not significant. A Si deficiency (<3.0 pfu) is observed in 95% of the EPMA spot analyses.

## 6. BULK CHEMISTRY OF DUMORTIERITE-BEARING PEGMATITE AND TWO-MICA LEUCOGRANITE

The chemical composition of dumortierite-bearing pegmatite (sample MG-D-PG-13) and host two-mica leucogranite (sample MG-D-G13) is given in Table 5. The two rocks show great similarities with respect to both major and trace elements, and the obtained values are in accordance with published analyses for leucogranite from Srednja rijeka from BALEN & PETRINEC (2011).

With respect to the major elements, the investigated rocks are characterised by high contents of SiO<sub>2</sub> (72.67 in pegmatite versus 75.30 wt. % in leucogranite), Al<sub>2</sub>O<sub>3</sub> (15.63 vs 14.67 wt. %) and Na<sub>2</sub>O (3.35 vs 3.58 wt. %), and low contents of TiO<sub>2</sub> (0.06 vs 0.07 wt. %), Fe<sub>2</sub>O<sub>3</sub> (0.55 vs. 0.79 wt. %), MgO (0.06 vs 0.08 wt.

**Table 1.** Electron microprobe compositions of feldspars.

Mineral	Albite					K-feldspars		
Analysis	MG-06	MG-08	MG-10	MG-22	MG-23	MG-09	MG-25	MG-26
SiO <sub>2</sub>	68.25	67.64	67.72	66.02	65.89	64.39	64.74	64.57
TiO <sub>2</sub>	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
$Al_2O_3$	19.99	20.07	20.54	21.51	21.51	18.95	18.84	18.69
$Cr_2O_3$	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
FeO	0.01	0.00	0.00	0.03	0.03	0.03	0.01	0.09
MnO	0.00	0.00	0.00	0.05	0.04	0.00	0.00	0.00
CaO	0.29	0.32	0.56	1.78	1.79	0.00	0.00	0.00
Na <sub>2</sub> O	11.74	11.53	11.32	10.87	10.74	0.77	1.17	1.03
K <sub>2</sub> O	0.13	0.17	0.18	0.14	0.20	15.53	14.61	15.08
Σ	100.41	99.73	100.32	100.41	100.21	99.67	99.37	99.46
Si	2.974	2.967	2.953	2.891	2.891	2.978	2.989	2.988
Ti	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Al	1.026	1.038	1.056	1.110	1.112	1.033	1.025	1.019
Cr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe <sup>2+</sup>	0.000	0.000	0.000	0.001	0.001	0.001	0.000	0.003
Mn	0.000	0.000	0.000	0.002	0.001	0.000	0.000	0.000
Ca	0.014	0.015	0.026	0.084	0.084	0.000	0.000	0.000
Na	0.991	0.981	0.957	0.923	0.914	0.069	0.105	0.092
K	0.007	0.010	0.010	0.008	0.011	0.916	0.861	0.890
Σ	5.012	5.009	5.002	5.019	5.015	4.998	4.981	4.994

Chemical formula was calculated on the basis of 8 oxygen and total Fe was determined as FeO.

%) and CaO (0.36 vs 0.51 wt. %). Only the  $K_2O$  content is significantly higher in dumortierite-bearing pegmatite (6.13 wt.%) than in the host two-mica leucogranite (3.86 wt.%). The aluminium-saturation index (ASI), which is defined by the molar ratio of  $Al_2O_3/(CaO+Na_2O+K_2O)$ , is comparable (1.6 vs. 1.8), indicating a strong peraluminous character of the rocks.

In comparison to the host two-mica leucogranite, the dumortierite-bearing pegmatite is slightly enriched in Co (4.5 vs 0.2 ppm), Rb (298 vs 229 ppm) and Pb (22.0 vs 5.3 ppm), but depleted in Ba (4 vs 14 ppm). Low concentrations of Sr (3.8 and 5.3 ppm) and Zr (31.9 and 29.8 ppm) are typical for both rock types. The trace element compositions normalised to the upper continental crust (TAYLOR & McLENNAN, 1985) demonstrate great similarities (Fig. 9A). Both rocks exhibit a slight, up to threefold en-

richment in Cs, Rb, K and Ta, whereas all other trace elements are depleted. The depletion is strong for Ba and Sr but only moderate for Zr and Ti.

The rare earth element (REE) concentrations of dumortierite-bearing pegmatite and the host two-mica leucogranite are presented in Table 6. The Eu value for dumortierite-bearing pegmatite is missing because it is below the detection limit. The total sum of REE (ΣREE) is low (18.15 and 17.85 ppm) and the individual REE abundances are 5 to 15 times higher than those in chondrite (SUN & McDONOUGH, 1989). In the chondrite-normalised REE diagram, the investigated rocks display identical REE patterns. They are relatively flat with a weak M-type tetrad effect (Fig. 9B) and a pronounced negative Eu anomaly (Eu/Eu\* = 0.06 for pegmatite and 0.08 for leucogranite, where

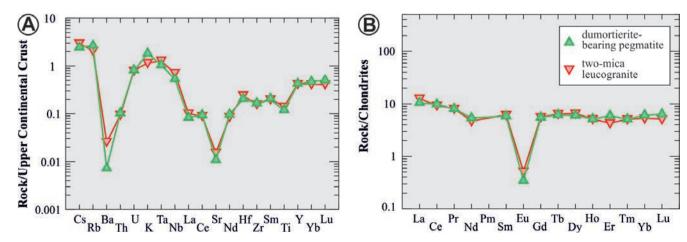


Figure 9. Chemical composition of dumortierite-bearing pegmatite and two-mica leucogranite from Mt. Moslavačka Gora. A) Trace element composition normalised to the upper continental crust with the values from TAYLOR & MCLENNAN (1985). B) Chondrite-normalised REE pattern using the values from SUN & MCDON-OUGH (1989).

Geologia Croatica

0.829

0.834

0.833

0.836

0.836

Fe/(Fe+Mn+Mg)

Moctor         Moctor<	Mineral	muscovite						Mineral	biotite				
4.6581         4.6581         4.648         0.4710         4.589         4.645         50.2         33.24         33.30         33.30           4.6581         4.658         4.648         47.10         45.89         46.57         50.20         33.24         33.30         33.30           2.714         3.706         3.668         3.70         4.627         50.20         12.70         20.7	Analysis	MG-02	MG-04	MG-11	MG-14	MG-27	MG-28	Analysis	MG-24	MG-29	MG-30	MG-32	MG-31
10,000   1,0		fine-grained	fine-grained	fine-grained	fine-grained	coarse-grained	coarse-grained						
10.06   0.07   0.07   0.02   0.05	SiO <sub>2</sub>	45.81	45.93	46.48	47.10	45.89	46.57	SiO <sub>2</sub>	33.24	33.30	33.39	32.15	33.67
37.14         37.00         36.63         37.22         36.18         35.90         41.94         19.97         19.85         15.86           0.03         0.03         0.03         0.04         0.05         0.04         0.05         0.00	TiO <sub>2</sub>	90:0	0.07	0.07	0.27	0.56	0.70	TiO <sub>2</sub>	2.77	2.76	2.80	2.69	2.90
10.05	Al <sub>2</sub> O <sub>3</sub>	37.14	37.00	36.63	37.22	36.18	35.90	$AI_2O_3$	19.97	19.85	19.86	19.66	19.87
10.05   0.00   0.04   0.56   1.31   1.48   FeO   26.74   26.72     10.01   0.00   0.00   0.00   0.10   0.01   0.00   0.	Cr <sub>2</sub> O <sub>3</sub>	0.03	00:00	00:00	0.01	0.00	0.00	Cr <sub>2</sub> O <sub>3</sub>	0.00	90:0	0.00	0.02	0.01
0.01         0.00         0.00         0.10         0.00         0.10         0.00 <t< td=""><td>FeO</td><td>0.05</td><td>00:00</td><td>0.04</td><td>0.56</td><td>1.31</td><td>1.48</td><td>FeO</td><td>26.74</td><td>26.72</td><td>26.45</td><td>25.67</td><td>26.25</td></t<>	FeO	0.05	00:00	0.04	0.56	1.31	1.48	FeO	26.74	26.72	26.45	25.67	26.25
0.03         0.04         0.05         0.11         0.34         0.41         MgO         2.48         251           0.04         0.00         0.00         0.01         0.00	MnO	0.01	00:00	00:00	0.00	0.10	0.00	MnO	0.84	0.77	0.89	0.87	0.93
10,0   0,00   0,00   0,01   0,01   0,00   0,01   0,00	MgO	0.03	0.04	0.05	0.11	0.34	0.41	MgO	2.48	2.51	2.46	2.37	2.51
0.44         0.40         0.24         0.61         0.61         0.61         0.62         0.63         0.69 <t< td=""><td>CaO</td><td>00:00</td><td>00:00</td><td>00:00</td><td>0.01</td><td>0.00</td><td>0.01</td><td>CaO</td><td>0.00</td><td>0.01</td><td>0.00</td><td>0.00</td><td>0.00</td></t<>	CaO	00:00	00:00	00:00	0.01	0.00	0.01	CaO	0.00	0.01	0.00	0.00	0.00
10,54   10,66   10,39   10,06   10,29   9,82   5,00   8,97   8,89   9,410   9,411   9,389   9,561   9,527   9,552   5   5   9,508   9,495   9,495   9,411   9,389   9,561   9,527   9,552   5   5   9,508   9,495   9,495   9,495   9,411   9,389   3,041   3,065   3,069   3,069   3,069   0,003	Na <sub>2</sub> O	0.44	0.40	0.24	0.27	0.61	0.65	Na <sub>2</sub> O	0.08	90.0	0.08	0.08	0.08
3.060         3.069         3.081         95.27         95.27         95.29         5.440         94.95           3.060         3.069         3.103         3.081         3.082         3.081         3.082         3.0	K <sub>2</sub> O	10.54	10.66	10.39	10.06	10.29	9.82	K <sub>2</sub> O	8.97	8.89	60'6	8.92	8.87
3.666         3.069         3.103         3.061         3.041         3.067         5140         2.640         2.647           0.003         0.003         0.004         0.013         0.028         0.034         1.766         0.165           1.2924         2.914         2.881         2.873         2.827         2.786         Al         1.669         0.165           0.001         0.000	Ы	94.10	94.11	93.89	95.61	95.27	95.52	Σ	92.08	94.95	95.03	92.41	95.08
3.060         3.065         3.085         3.041         3.067         5.440         2.640         2.647           0.003         0.003         0.004         0.013         0.028         0.034         17.00         0.165         0.175         0.1													
4 0003         0.004         0.013         0.028         0.034         The control of t	iS	3.060	3.069	3.103	3.085	3.041	3.067	Si	2.640	2.647	2.651	2.627	2.664
2924         2914         2881         2873         2.827         2.786         41         1.869         1.859         1.859           9001         0.000         0.000         0.000         0.000         0.000         0.000         0.000         0.000         0.000         0.000         0.005	<sub>=</sub>	0.003	0.003	0.004	0.013	0.028	0.034	ı	0.166	0.165	0.167	0.165	0.173
0.001         0.000         0.000         0.000         0.000         0.000         0.000         0.000         0.000         0.000         0.000         0.000         0.005 <th< td=""><td>74</td><td>2.924</td><td>2.914</td><td>2.881</td><td>2.873</td><td>2.827</td><td>2.786</td><td>ΑΙ</td><td>1.869</td><td>1.859</td><td>1.859</td><td>1.894</td><td>1.852</td></th<>	74	2.924	2.914	2.881	2.873	2.827	2.786	ΑΙ	1.869	1.859	1.859	1.894	1.852
0.003         0.000         0.002         0.031         0.003         6.04         1.776         1.771         1.777         1.771         1.771         1.771         1.772	Ċ	0.001	00000	0.000	0.000	0.000	0.000	Ċ	0.000	0.004	0.000	0.001	0.000
0,000         0,000 <th< td=""><td>-e<sup>3+</sup></td><td>0.003</td><td>0.000</td><td>0.002</td><td>0.031</td><td>0.073</td><td>0.082</td><td>Fe<sup>2+</sup></td><td>1.776</td><td>1.776</td><td>1.757</td><td>1.754</td><td>1.737</td></th<>	-e <sup>3+</sup>	0.003	0.000	0.002	0.031	0.073	0.082	Fe <sup>2+</sup>	1.776	1.776	1.757	1.754	1.737
0.0003         0.0004         0.011         0.033         0.040         Mg         0.293         0.298           0.000         0.000         0.000         0.000         0.000         0.001         0.001         0.001           0.057         0.052         0.030         0.034         0.078         0.082         Na         0.012         0.010           0.089         0.909         0.885         0.841         0.870         0.825         K         0.909         0.902           0.050         6.951         6.910         6.888         6.955         6.918         X.720         7.712           0.050         0.054         0.033         0.039         0.082         0.091         Na/(Na+K)         0.013         0.135           0.054         0.055         0.033         0.039         0.082         0.091         Na/(Na+K)         0.013         0.135           0.055         0.056         0.092         0.092         0.092         0.093         0.032         0.092         0.091         0.013         0.013         0.092         0.092         0.093         0.092         0.093         0.092         0.093         0.092         0.093         0.092         0.093         0.09	Mn	0.000	0.000	0.000	0.000	0.005	0.000	Mn	0.056	0.052	0.060	0.060	0.062
0.000         0.000         0.000         0.000         0.000         0.000         0.001 <th< td=""><td>Mg</td><td>0.003</td><td>0.004</td><td>0.004</td><td>0.011</td><td>0.033</td><td>0.040</td><td>Mg</td><td>0.293</td><td>0.298</td><td>0.291</td><td>0.288</td><td>0.296</td></th<>	Mg	0.003	0.004	0.004	0.011	0.033	0.040	Mg	0.293	0.298	0.291	0.288	0.296
0.057         0.056         0.034         0.078         0.082         Na         0.012         0.010           0.898         0.999         0.885         0.841         0.870         0.825         K         0.999         0.902           0.059         0.054         6.910         6.888         6.955         6.918         X         7.720         7.712           0.060         0.054         0.033         0.039         0.082         0.091         Na/Na+K)         0.013         0.010           Al <sup>II</sup> Al <sup>II</sup> 1.360         1.353           Al <sup>II</sup> 0.509         0.509         0.506	Ça	0.000	00000	0.000	0.000	0.000	0.001	Ca	0.000	0.001	0.000	0.000	0.000
0.898         0.909         0.881         0.870         0.825         K         0.909         0.902           0.6950         6.951         6.910         6.888         6.955         6.918         \$2.125         7.720         7.712           0.054         0.033         0.039         0.082         0.091         Na/(Na+K)         0.013         0.010           0.054         0.035         0.039         0.082         0.091         Na/(Na+K)         0.1360         1.353           0.054         0.504         0.509         0.506         0.506           0.054         0.505         0.505         0.505	Na	0.057	0.052	0:030	0.034	0.078	0.082	Na	0.012	0.010	0.012	0.013	0.012
6,950         6,910         6,888         6,955         6,918         \$\text{2}\$         7,720         7,712           0,060         0,054         0,033         0,039         0,082         0,091         Na/Na+K)         0,013         0,010           All N         1,360         1,350         1,353           All N         1,360         0,506           All N         0,509         0,506           All N         0,509         0,506	~	0.898	606'0	0.885	0.841	0.870	0.825	¥	0.909	0.902	0.921	0.930	0.895
0.060         0.054         0.033         0.039         0.082         0.091         Na/(Na+K)         0.013         0.010           All V         1.360         1.353         1.353         1.353         1.353         1.353           All V         All V         1.360         0.506         0.506         0.506	Z	6.950	6.951	6.910	6.888	6.955	6.918	Σ	7.720	7.712	7.718	7.732	7.691
1.360 1.353 0.509 0.506 An+Mg 2.125 2.125	Na/(Na+K)	090'0	0.054	0.033	0.039	0.082	0.091	Na/(Na+K)	0.013	0.010	0.013	0.013	0.014
0.509 0.506 2.125 2.125								Alıv	1.360	1.353	1.349	1.373	1.336
2.125 2.125								ΑΙ <sup>νι</sup>	0.509	0.506	0.510	0.521	0.516
								Fe+Mn+Mg	2.125	2.125	2.108	2.102	2.095

Chemical formulas were calculated on the basis of 11 (O, OH) and total Fe was determined as  $Fe_2O_3$  for muscovite, and as FeO for biotite.

**Table 3.** Electron microprobe compositions of andalusite.

Analysis	MG-19	MG-20
SiO <sub>2</sub>	36.23	35.97
TiO <sub>2</sub>	0.06	0.04
$Al_2O_3$	62.82	62.88
$Cr_2O_3$	0.00	0.03
FeO	0.72	0.76
MnO	0.00	0.03
Σ	99.83	99.72
Si	0.981	0.976
Ti	0.001	0.001
Al	2.006	2.011
Cr	0.000	0.001
Fe <sup>3+</sup>	0.016	0.017
Mn	0.000	0.001
Σ	3.006	3.010

Chemical formulas were calculated on the basis of 13 cations and 5 oxygen, and total Fe as Fe $_2$ O $_3$ .

 $Eu/Eu^* = Eu_N/(\sqrt{(Sm_N^*Gd_N)})$ . The  $(La/Yb)_N$  ratios, usually used for the evaluation of REE fractionation, are low and very similar in both rocks (1.74 and 2.39).

### 7. DISCUSSION

## 7.1. Mineral chemistry and ion substitutions in dumortierite

Two types of dumortierite can be distinguished in the studied pegmatites on the basis of their textural and optical properties. The large prismatic Dum 1 grains with the colourless to azure blue pleochroism and Dum II appearing as smaller bundles of parallel fibrous or acicular crystals with a colourless to red-violet pleochroism are also characterised by their different chemical compositions. Dum I crystals have lower contents of Mg and Ti (0.033-0.055 pfu and 0.001-0.011 pfu) than Dum II (0.047-0.087 pfu and 0.043-0.064 pfu.), whereas the difference in Fe<sup>2+</sup> is not significant (Table 4). However, it is interesting to note, that Fe<sup>2+</sup> shows a moderately negative correlation with the sum of Ti and Mg in Dum I, but a clear positive correlation in Dum II (Fig. 10A).

Table 4. Electron microprobe compositions of selected durmotierite analyses.

Analysis	MG-06-1 Dum I	MG-06-3	MG-06-5 Dum I	MG-06-7	MG-06-12 Dum II	MG-06-13
	prismatic	Dum I prismatic	prismatic	Dum I prismatic	fibrous	Dum II fibrous
	crystal	crystal	crystal	crystal	aggregate	aggregate
SiO <sub>2</sub>	30.26	29.57	30.29	30.43	29.79	31.16
TiO <sub>2</sub>	0.04	0.13	0.04	0.15	0.72	0.59
B <sub>2</sub> O <sub>3</sub> *	6.20	6.20	6.20	6.20	6.20	6.20
Al <sub>2</sub> O <sub>3</sub>	62.15	61.87	61.65	61.42	60.75	60.09
Cr <sub>2</sub> O <sub>3</sub>	0.02	0.00	0.01	0.03	0.06	0.02
FeO	0.68	0.76	0.89	0.64	0.58	0.70
MnO	0.05	0.04	0.02	0.03	0.02	0.01
MgO	0.25	0.25	0.24	0.26	0.48	0.60
CaO	0.01	0.03	0.01	0.00	0.00	0.00
Na <sub>2</sub> O	0.01	0.02	0.02	0.02	0.01	0.00
K <sub>2</sub> O	0.00	0.01	0.00	0.01	0.00	0.02
H <sub>2</sub> O*	1.30	1.30	1.30	1.30	1.30	1.30
Σ	100.96	100.16	100.66	100.49	99.90	100.68
Si	2.926	2.887	2.940	2.956	2.916	3.022
Ti	0.003	0.009	0.003	0.011	0.053	0.043
В	1.035	1.045	1.039	1.040	1.047	1.038
Al	7.083	7.119	7.054	7.032	7.008	6.869
Cr	0.002	0.000	0.001	0.002	0.005	0.002
Fe <sup>2+</sup>	0.055	0.062	0.072	0.052	0.047	0.057
Mn	0.004	0.003	0.002	0.003	0.002	0.001
Mg	0.036	0.036	0.034	0.037	0.070	0.086
Ca	0.001	0.003	0.001	0.000	0.000	0.000
Na	0.002	0.004	0.003	0.003	0.001	0.000
К	0.000	0.001	0.000	0.001	0.000	0.003
Н	0.839	0.847	0.842	0.842	0.849	0.841
Σ	10.949	10.970	10.952	10.939	10.950	10.922
Al/Si	2.42	2.47	2.40	2.38	2.40	2.27
[Fe/(Fe+Ti)]x100	95	87	96	82	47	57

Chemical formulas were calculated on the basis of 17 oxygens, total Fe as FeO.

<sup>\*</sup>It is assumed that  $B_2O_3 = 6.20$  wt. % and  $H_2O = 1.30$  wt. %, on the basis of paper FUCHS et al. (2005).

**Table 5.** The major and trace element analyses of dumortierite bearing pegmatite and two-mica leucogranite.

Dumortierite bearing Two-mica pegmatite leucogranite MG-D-G13 Sample MG-D-PG13 wt.% SiO<sub>2</sub> 72.67 75.3 TiO<sub>2</sub> 0.06 0.07  $Al_2O_3$ 15.63 14.67  $Cr_2O_3$ <0,002 <0,002 Fe<sub>2</sub>O<sub>3</sub> 0.55 0.79 MnO 0.02 0.03 MaO 0.06 0.08 CaO 0.36 0.51 3.58 Na<sub>2</sub>O 3.35 K<sub>2</sub>O 6.13 3.86  $P_2O_5$ 0.28 0.25 LOI 0.9 0.8 TOT/C <0,02 <0,02 TOT/S < 0.02 < 0.02 99.99 99.98 1.80 ASI 1.60 210.00 Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> 261.00 CaO/Na<sub>2</sub>O 0.11 0.14 maa Ba 4 14 2 Be <1 4.5  $C_0$ 0.2 10.9 Cs 9.0 Ga 18.6 19.2 Hf 1.2 1.4 Nb 13.3 17.7 297.9 229.4 Rb Sn 10 13 5.3 Sr 3.8 2.8 Ta 2.3 Th 1.0 1.1 2.3 U 2.2 <8 <8 ٧ 2.7 W 3.8 Zr 31.9 29.8 9.1 9.4 Υ Мо <0,1 <0,1 0.4 Cu 1.1 Pb 22.0 5.3 28 Zn 36 Ni 1.9 0.5 1.7 As 1.4 Cd 0.1 <0,1 Sb 0.1 <0,1 Bi 5.4 2.3 Ag 0.1 <0,1 17.7 Au 28.6 0.01 <0,01 Hq ΤI 0.2 0.3 Se <0,5 <0,5 7 Sc 6 Rb/Ba 74.5 16.4 Rb/Sr 78.4 43.3

**Table 6.** REE composition of dumortierite bearing pegmatite and two-mica leucogranite.

ppm	Dumortierite bearing pegmatite	Two-mica leucogranite
Sample	MG-D-PG13	MG-D-G13
La	2.50	3.00
Ce	6.00	5.70
Pr	0.77	0.77
Nd	2.50	2.20
Sm	0.89	0.94
Eu	<0,02	0.03
Gd	1.13	1.15
Tb	0.23	0.24
Dy	1.52	1.66
Но	0.29	0.29
Er	0.98	0.71
Tm	0.13	0.13
Yb	1.03	0.90
Lu	0.16	0.13
ΣREE	18.15	17.85
Eu/Eu*	0.06	0.09
(La/Yb) <sub>N</sub>	1.74	2.39

This indicates complex substitution reactions which will depend on many factors, including bulk chemistry of the host rock, fluid composition and p-T conditions. The differences in chemical composition certainly affect the pleochroic colours of dumortierite.

ALEXANDER et al. (1986) tried to explain distinct pleochroic colours in dumortierites by an [Fe/(Fe+Ti)]x100 factor. They postulated a pale red colour at [Fe/(Fe+Ti)]x100 < 25, a purple colour at [Fe/(Fe+Ti)]x100 = 25 and a blue colour at [Fe/(Fe+Ti)]x100 > 25. However, according to the data presented in this study, the blue pleochroic colour appears at [Fe/(Fe+Ti)]x100 = 82 - 99, while in contrast to the study of ALEXANDER et al. (1986), the red to violet pleochroic colour is observed at [Fe/(Fe+Ti)]x100 = 38 - 57 (Table 4, Fig. 10B). The deviating results could be due to a slightly different chemical composition of the examined dumortierite crystals.

The samples used by ALEXANDER et al. (1986) are characterised by lower Mg contents (mostly less than 0.020 pfu) and lower [Fe/(Fe+Ti)]x100 ratios (mostly less than 32) than the dumortierite crystals investigated in this study. Interestingly, the red to violet pleochroic dumortierite from this study shows a strong positive correlation between [Fe/(Fe+Ti)]x100 and Mg content (Fig. 10B). This may indicate a stabilisation of the red to violet colour by Mg even at [Fe/(Fe+Ti)]x100 factors exceeding 25.

The Si tetrahedral deficiency in dumortierite is conventionally balanced by Al, based on the evidence of tetrahedral Al in natural (ALEXANDER et al., 1986) and synthetic dumortierite (WERDING & SCHREYER, 1983). In this study, not only is the Si tetrahedral deficiency confirmed, but there is also a positive correlation between 3-Si and Al ( $R^2 = 0.51$ ). The correlation is moderate if Dum I and Dum II are taken together, but is better when the two types are considered separately (Fig. 10C). However, when Ti is included in the substitution, there is a strong cor-

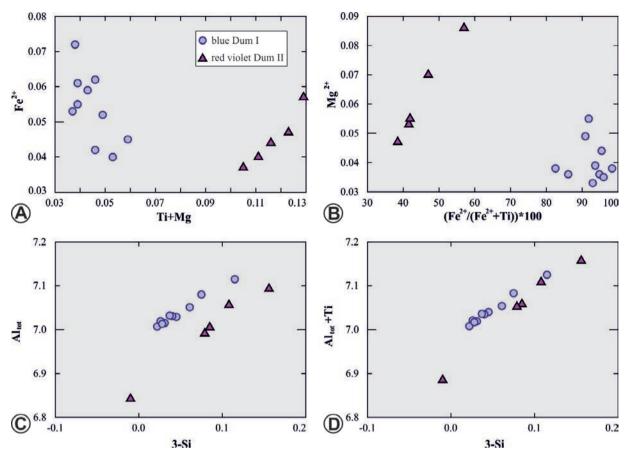


Figure 10. Chemical composition of dumortierite from Mt. Moslavačka Gora. A)  $Fe^{2+}$  vs (Ti+Mg) diagram showing a clear positive correlation between  $Fe^{2+}$  and the sum of Ti and Mg in the crystal lattice of red to violet Dum II but a moderately negative correlation for blue Dum I crystals. B) In the  $Mg^{2+}$  vs (Fe/(Fe+Ti))x100 ratio diagram, a strong positive correlation is visible for Dum II, whereas Dum I shows a moderately negative correlation. C) In the  $AI_{tot}$  vs 3-Si diagram, all dumortierite analyses taken together show a badly defined moderately positive correlation  $(R^2 = 0.51)$  but when considering Dum I and Dum II separately, a well defined correlation is visible. D) In the  $AI_{tot}$  +Ti vs 3-Si diagram, a strong positive correlation  $(R^2 = 0.85)$  is visible, suggesting that Ti in dumortierite replaces not only AI in octahedra, but also together with AI may substitute for Si in the tetrahedral position.

relation between 3-Si and Al+Ti ( $R^2 = 0.85$ ). This suggests that Ti replaces not only Al in the octahedral position, as generally accepted (EVANS et al., 2012), but also together with Al it substitutes for Si in the tetrahedral position (Fig. 10D). The results of this study clearly indicate that higher Al and Ti contents in the crystal structure compensate for a higher Si tetrahedral deficiency.

WERDING & SCHREYER (1990) found that dumortierites synthesised at low pressures (3-5 kbar) exhibit higher Al/Si ratios of 2.77-2.94 than those synthesised at high pressures (15 to 20 kbar), which yield Al/Si ratios of 2.33-2.55. In this study, the measured Al/Si ratios for Dum I and Dum II range from 2.35-2.47 and 2.27-2.49, respectively (Table 4). This might be interpreted as crystallisation of the investigated dumortierite at elevated pressure. However, due to the presence of magmatic andalusite in the mineral assemblage of the pegmatite, pressures of >5 kbar can be excluded. This supports the assumption by WERDING & SCHREYER (1990), who proposed that the Al/Si ratio of natural dumortierite depends not only on the pressure but also on additional components (Fe, Mg, Ti) present in its crystal structure.

## 7.2. Mineral chemistry of mica minerals and their origin

In the investigated dumortierite-bearing pegmatite two types of muscovite can be distinguished. Coarse muscovite flakes are in textural equilibrium with the other minerals of the pegmatite mineral assemblage and are obviously of magmatic origin. In contrast, tiny flakes of retrograde muscovite (sericite) partly replace K-feldspar, andalusite and dumortierite along the crystal rims and cracks. They also show chemical differences, as the coarse flakes are richer in Ti, Fe, Mg and Na but poorer in Al than sericite (Table 2). Furthermore, the coarse muscovite flakes are characterised by Na/(Na+K) ratios of 0.08 to 0.09, whereas in the sericite the Na/(Na+K) ratios range from 0.04 to 0.06. These values prove a magmatic origin for the coarse muscovite flakes, because according to MONIER et al. (1984), the Na/(Na+K) ratios in muscovite of magmatic origin are greater than 0.06.

The chemical composition of magmatic biotite depends on the chemistry of the parent magma and therefore might be used to estimate the pressure-temperature conditions during crystallisation, the chemical affinity and the origin of the plutonic host rock (TANG et al., 2019). Nevertheless, due to the sensitivity of the biotite chemistry to the coexisting mineral assemblage, subsequent hydrothermal activity and metamorphic overprinting, its primary composition may be disturbed. Therefore, caution is recommended when using discrimination and petrogenetic diagrams involving biotite chemistry (SAMADI et al., 2021). All analysed biotite flakes of the dumortierite-bearing pegmatite are classified as annite. Its magmatic origin is supported both by petrographic criteria, such as a subhedral morphology (Fig. 4A, 5A and 5B), and also by its chemical composition. In the ternary TiO<sub>2</sub>\*10-(FeO+MnO)-MgO diagram of NACHIT et al. (2005), all biotite

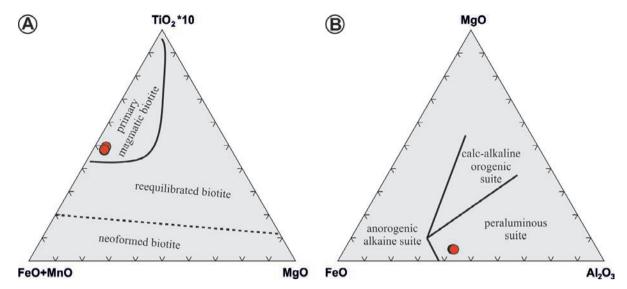
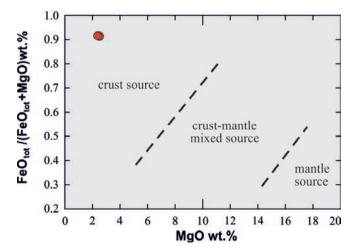


Figure 11. Chemical composition of biotite from the dumortierte-bearing pegmatite of Mt. Moslavačka Gora. A) In the ternary (TiO<sub>2</sub>\*10)-(FeO+MnO)-MgO diagram of NACHIT et al. (2005), all biotite analyses plot in the field of magmatic biotite. B) According to the ternary MgO-FeO<sub>tot</sub>-Al<sub>2</sub>O<sub>3</sub> diagram of ABDEL-RAHMAN (1994), the biotite analyses indicate the peraluminous nature of the host rock.

analyses plot in the field of primary magmatic biotite (Fig. 11A). The aluminum-saturation of the host magma can be estimated by plotting the biotite analyses in the ternary MgO-FeO<sub>tot</sub>-Al<sub>2</sub>O<sub>3</sub> diagram of ABDEL-RAHMAN (1994). In this diagram, the biotite analyses indicate the peraluminous nature of the dumortierite-bearing pegmatite (Fig. 11B). The source of the biotite parental melt was determined with the FeO<sub>tot</sub> /(FeO<sub>tot</sub> + MgO)-MgO diagram by ZHOU (1986), which indicates a crustal source for the biotite (Fig. 12).

The content of Ti in biotite is extensively used as a geothermometer. However, the incorporation of Ti in biotite is additionally influenced by the biotite crystal chemistry (especially the MgO/(MgO+FeO) ratio), the mineral assemblage of the host rock and the pressure (HENRY et al., 2005). Biotites from dumortierite-bearing pegmatite are not suitable for geothermometry for several reasons: i) the measured  $X_{\rm Mg}={\rm Mg/(Mg+Fe)}$  values are 0.141 to 0.146 and, therefore, outside of the calibration range of the Ti-in-biotite geothermometer after HENRY et al. (2005), which is calibrated for  $X_{\rm Mg}=0.275$ -1.000; and ii) the absence of minerals indicating Ti-saturation, such as ilmenite or rutile. Both reasons may lead to underestimated temperatures. A strong pos-



**Figure 12.** In the  $FeO_{tot}$  /( $FeO_{tot}$  + MgO) vs MgO diagram after ZHOU (1986), all biotite analyses from dumortierite-bearing pegmatite plot in the field of a crustal source.

itive correlation between the total Al (<sup>T</sup>Al) content in biotite and the solidification pressure of the host granitic rock was found by UCHIDA et al. (2007). They expressed this correlation as an empirical equation:

$$P (kb) = 3.03 \text{ x}^{T} \text{Al-}6.53 (\pm 0.33)$$

where <sup>T</sup>Al is the total Al content in biotite, calculated on the basis of 22 oxygens. Using this geobarometer, an approximate solidification pressure of 4.70 to 4.95 kbar (470 to 495 MPa) is estimated for the studied dumortierite-bearing pegmatite. This is consistent with solidification at a depth of 15.7 to 16.5 km. However, this pressure range is not in accordance with the presence of andalusite in the mineral assemblage of the dumortierite-bearing pegmatite. Even though there is an ongoing discussion about the precise location of the Al<sub>2</sub>SiO<sub>5</sub> triple point in the P-T space, most petrologists agree that it is somewhere between 3.8 kbar at 500°C and 4.5 kbar at 550°C (PATTISON, 2001). Most probably, the primary biotite composition was changed during late magmatic/ hydrothermal activity and no precise pressure conditions can be determined from the biotite.

## 7.3. Chemistry of andalusite and its origin

In andalusite the chemical substitution of Si and Al is restricted to only a few trace elements such as Fe, Mn, Ti and Cr. In a comprehensive paper on magmatic andalusite, CLARKE et al. (2005) found that FeO contents in the range of 0.08 to 1.71 wt% are typical of andalusite of magmatic origin. In the andalusite of the dumortierite-bearing pegmatite, only Fe was found in noticeable concentrations of 0.72 to 0.76 wt. %, which are in agreement with a magmatic origin. Also the chemical equilibrium of andalusite with coexisting minerals is an important criterion to prove a magmatic origin. CLARKE et al. (2005) analysed 108 samples of and alusite-bearing felsic igneous rocks and concluded that biotite coexisting with andalusite has  $Al^{IV} \sim 2.68 \pm 0.07$  pfu and muscovite is characterised by 0.57 to 4.01 wt. % FeO and 0.02 to 2.85 wt. % TiO2. As the investigated biotite from the dumortieritebearing pegmatite contains only 1.336 to 1.373 Al<sup>IV</sup> pfu, it seems not to be in equilibrium with andalusite. In contrast, the FeO

(1.31-1.48 wt. %) and  $\text{TiO}_2$  (0.56-0.70 wt. %) contents of muscovite fulfil the criteria.

Besides chemical criteria, textural criteria can also be useful to identify an igneous origin for andalusite (CLARKE et al., 2005). On the one hand, the single euhedral to subhedral andalusite grains in the dumortierite-bearing pegmatite are comparable in size with the other minerals (biotite, muscovite) present and fit to the S3 textural type of andalusite in felsic igneous rocks (textural classification after CLARKE et al., 2005). However, no mineral inclusions typical for metamorphic andalusite, such as, for instance, carbonaceous material defining a chiastolite cross, are present. Taking into account both chemical and textural criteria, an igneous origin is likely for the andalusite of dumortierite-bearing pegmatite.

Although the replacement of andalusite by muscovite may take place under magmatic conditions (CLARKE et al., 2005), the textural relationships with fine-grained muscovite and additional Dum II suggest a replacement at subsolidus hydrothermal conditions in the studied dumortierite-bearing pegmatite.

The stability field of magmatic andalusite in a granitic host rock is defined by the water-saturated granite solidus, the andalusite-sillimanite polymorphic transformation reaction and the stability field of muscovite (CLARKE et al., 2005). Among the many factors that favour crystallisation of andalusite from magma (overview in CLARKE et al., 2005), the following are significant in the studied dumortierite-bearing pegmatite: i) an excess of Al<sub>2</sub>O<sub>3</sub> (ASI = 1.60), ii) increased boron content (presence of dumortierite) may contribute to lowering of the granite solidus, and iii) the presence of small amounts of transition element solid solution in andalusite (presence of Fe<sup>3+</sup>-rich pinkish cores) may contribute to broadening the andalusite stability field. Furthermore, water-saturated melting reactions at low temperature and pressure are known to favour crystallisation of andalusite (CLARKE et al., 2005).

## 7.4. Relationships of dumortierite-bearing pegmatite and two-mica leucogranite and genesis of the granitic melt

The strong similarities in major, minor and trace element contents of dumortierite-bearing pegmatite and the host two-mica leucogranite (Fig. 9A and 9B) clearly indicate their common origin. The chemical similarities in addition to the spatial relationship are a strong argument that the pegmatite melt developed by fractional crystallisation during solidification of the two-mica leucogranite. For this reason, it is important to discuss the formation of the two-mica leucogranite to understand the chemical composition of the dumortierite-bearing pegmatite.

The two-mica leucogranite is strongly peraluminous (ASI = 1.8), enriched in Cs, Rb, U, K, Ta and Nb and characterised by a low CaO/Na<sub>2</sub>O (0.14) and high Rb/Ba (16.4) as well as Rb/Sr (43.3) ratios. The low CaO/Na<sub>2</sub>O and high Rb/Ba and Rb/Sr ratios reflect a low amount of plagioclase in the source because plagioclase readily incorporates Ca, Ba and Sr, but not Rb (HARRIS & INGER, 1992). In contrast, micas are rich in K and Rb but poor in Ca, Ba and Sr. According to SYLVESTER (1998), pelite-derived melts usually have CaO/Na<sub>2</sub>O ratios less than 0.3. This indicates melting of a plagioclase-poor and mica-rich source, represented by mica-rich schists and paragneiss derived from a pelitic protolith.

According to SYLVESTER (1998), the Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> ratio of strongly peraluminous granite melts commonly reflects the melting temperature, even though pressure and water addition have

to be taken into account. In fact, an increase of the melting temperature leads to increasing breakdown of Ti-bearing phases (ilmenite, biotite) and, consequently, to a decrease of the  $\rm Al_2O_3/TiO_2$  ratio. The  $\rm Al_2O_3/TiO_2$  ratio of the investigated two-mica leucogranite is 210 and corresponds to relatively low temperatures and a low degree of melting. This is in accordance with temperatures calculated by BALEN & BROSKA (2011) for the crystallisation of a two-mica granite with tourmaline nodules from Mt. Moslavačka Gora. They determined zircon and monazite saturation temperatures of ~730°C and ~720°C, respectively.

On the basis of chemical and isotopic data, GARAŠIĆ et al. (2007) concluded that the two-mica leucogranite from Mt. Moslavačka Gora formed by the melting of continental crust in a collisional environment. As potential field evidence for crustal melting in a collisional environment, BALEN & BROSKA (2011) described the occurrence of metapelitic xenoliths within the two-mica granite. The authors emphasised that the strong muscovite depletion in the metapelitic xenoliths argues for their restitic nature.

According to SYLVESTER (1998), strongly peraluminous granitic intrusions occur as a consequence of post-collisional processes in various orogens. The European Alps and Himalayas are regarded as high pressure collisions characterised by overthickened crust. In this environment, melting is caused by the radioactive decay of K, U and Th, and strongly peraluminous granitic melts with high  $Al_2O_3/TiO_2$  ratios develop at relatively low temperatures (<875°C). In contrast, the European Variscides and the Lachlan Fold Belt (Australia) are defined as high temperature collisions with less crustal thickening ( $\leq$  50 km), where anatexis is related to the upwelling of hot asthenosphere, resulting in hot ( $\geq$  875°C) melts having low  $Al_2O_3/TiO_2$  ratios.

Even though the  $Al_2O_3/TiO_2$  ratio in the two-mica leucogranite from Mt. Moslavačka Gora is high and corresponds to low melting temperatures, high pressure metamorphism and an overthickened crust is lacking in the area. Therefore, similarities with the genesis of the peraluminous leucogranites of the European Alps are highly questionable. As the majority of the strongly peraluminous granites of the European Variscides are the result of high temperature melting and are characterised by low  $Al_2O_3/TiO_2$  ratios, they also exhibit minor similarities with the two-mica leucogranite from Mt. Moslavačka Gora. Taking all arguments into account, it seems that the two-mica leucogranite of Mt. Moslavačka Gora is quite unique and not comparable with the majority of the peraluminous granites from the European Alps, Himalayas and European Variscides.

### 7.5. Genesis of the dumortierite-bearing pegmatite

Comparing the chemical characteristics of dumortierite-bearing pegmatite and two-mica leucogranite, the ASI, the contents of Cs, Rb, U, K, Ta and Nb as well as the Rb/Ba and Rb/Sr ratios of the pegmatite are higher, whereas the CaO/Na<sub>2</sub>O ratio is lower than that of the leucogranite. All these features are compatible with fractional crystallisation of a granitic melt and the formation of a residual melt which subsequently crystallised as pegmatite.

The primary mineral assemblage of the pegmatite consists of blue dumortierite I (Dum I), andalusite, biotite, muscovite, plagioclase, K-feldspar and quartz. With respect to the presence of magmatic andalusite, crystallisation occured at shallow crustal levels, maybe at 5-6 km depth as for the nearby two-mica granite (BALEN & BROSKA (2011).

Later circulation of Ti-rich hydrothermal fluids led to the partial replacement of primary Dum I by secondary purple Dum II enriched in Mg and Ti. Additional Dum II formed at the expense of magmatic andalusite. During the temperature decrease, perthite formed in feldspar and at still lower temperatures, sericite partially replaced, not only feldspars, but also andalusite and both types of dumortierite along grain boundaries and cracks. The last alteration includes the formation of clay minerals at the expense of feldspars. The dumortierite-bearing pegmatite lacks deformation and, therefore, is associated with a late to post-tectonic phase of the continental collision along the Sava suture zone.

The formation of dumortierite instead of tourmaline in the pegmatite may be explained by the high  $Al_2O_3$  (15.63 wt. %) content and quite low content of iron and magnesium oxides in the melt (Fe<sub>2</sub>O<sub>3</sub> = 0.55 wt.%; MgO = 0.06 wt.% in dumortierite-bearing pegmatite). In fact, tourmaline occurs frequently in the two-mica granite and the host two-mica leucogranite of Mt. Moslavačka Gora. In the two-mica leucogranites, it is characterised by a chemical zoning and a schorl-foitite composition (GARAŠIĆ et al., 2007). BALEN & PETRINEC (2011) recognised differences between tourmaline occurring in nodules within the two-mica granite and disseminated tourmaline in cross-cutting leucogranite dykes.

## 7.6. Classification of dumortierite-bearing pegmatite

According to the presented data, the dumortierite-bearing pegmatite from Mt. Moslavačka Gora developed by fractional crystallisation of a granitic melt and based on the modal mineral composition, it is a granitic pegmatite. Except for minor amounts of dumortierite and andalusite, no special minerals are observed and there is only slight enrichment of some rare elements (e.g. Cs, Rb, U, Ta and Nb).

With respect to the most commonly used classification of granitic pegmatite by ČERNY & ERCIT (2005), the studied dumortierite-bearing pegmatite can be attributed to the abyssal class and AB-Bbe subclass, when considering the mineralogical composition only. Some elements typical for the LCT family are enriched, but even though the Li content is not determined, no strong enrichment is indicated by the absence of typical Li-rich minerals. However, the abyssal pegmatite class is known to occur in high-grade metamorphic host rocks of upper amphibolite to granulite facies, and frequently originated by anatectic melting (ČEMPIREK & NOVAK, 2006). Additionally, the AB-BBe subclass is often considered as an indicator for high pressure metamorphic conditions in the country rocks (ČEMPIREK & NO-VAK, 2006). In contrast, the investigated dumortierite-bearing pegmatite of Mt. Moslavačka Gora developed by magmatic differentiation from a two-mica leucogranite and the presence of magmatic and alusite as well as the data concerning the regional geological evolution argue against a relationship with high pressure metamorphic conditions. For these reasons, it does not represent a typical abyssal pegmatite.

Alternatively, the classification of granitic pegmatites by WISE et al. (2022) can be applied. According to this classification, the studied dumortierite-bearing pegmatite belongs to Group 3 pegmatites, because of its strongly peraluminous nature, the mineral composition consisting of quartz, K-feldspar, plagioclase, muscovite, biotite, primary and lusite and a B-mineralization expressed by dumortierite. However, WISE et. al (2022) claim that Group 3 pegmatites occur in high-grade metamorphic areas and are direct products of the anatexis (DPA) of amphibo-

lite- to granulite-facies metamorphic metapelite, amphibolite, paragneiss and migmatite. In contrast, the dumortierite-bearing pegmatite crystallised from a residual granitic melt (RGM in terms of WISE et al., 2022).

In summary, it is difficult to classify the dumortierite-bearing pegmatite from Mt. Moslavačka gora using the existing classification schemes.

## 7.7. Comparison of dumortierite-bearing pegmatite with other dumortierite occurrences worldwide

According to the literature mentioned in the introduction, dumortierite is relatively rare, but most frequently found as a minor component in alumina-rich regional metamorphic rocks. Additionally, it appears in acidic magmatic rocks, such as granite and granitic pegmatite, and within hydrothermally altered rocks.

The rare dumortierite-bearing pegmatite dykes almost all occur in high-grade metamorphic areas, and they are thought to represent products of the anatexis of metapelitic country rocks. For instance, dumortierite-bearing pegmatite dykes are known from several localities in the Gföhl Unit of the easternmost Moldanubian Mega unit located in the Bohemian Massif in Austria (FUCHS et al., 2005) and the Czech Republic (CEMPIREK & NOVAK, 2006). They are all characterised by a small thickness, Al-rich mineral assemblages and elevated contents of light elements (B, Be). Their host rocks show a polyphase Variscan metamorphic evolution with a granulite facies HP/HT metamorphic overprint (CEMPIREK & NOVAK, 2006). With respect to their mineral composition and the tectonic environment, they are classified as abyssal pegmatites of the AB-BBe subclass, according to the classification of ČERNÝ & ERCIT (2005). Similar abyssal pegmatite dykes of the AB-BBe subclass were reported from other high-grade metamorphic terranes, for example from Antarctica (SCHÜSSLER & HENJES-KUNST, 1994; GREW, 1998), Norway (HUIJSMANS et al., 1982), Sri Lanka (GREW et al., 1995) or India (MAHAPATRA & CHAKRABARTY, 2011). Due to the frequent occurrence of dumortierite-bearing abyssal pegmatite dykes in high pressure metamorphic terranes, ČERNÝ & ERCIT (2005) suggested that dumortierite-bearing abyssal pegmatites may be a good indicator of HP metamorphism.

Dumortierite-bearing pegmatite dykes related to a parental granite, as the one described from Mt. Moslavačka Gora, are obviously extremely rare. In the literature, only one example is described that is associated with the Szabo Bluff granite located in the Queen Maud Mountains in Antarctica. However, dumortierite occurs there solely as an alteration product of andalusite (BURT & STUMF, 1983) and, therefore, this occurrence is not fully comparable.

## 8. CONCLUSIONS

The investigated pegmatite dyke from Mt. Moslavačka Gora is characterised by a magmatic mineral assemblage of quartz, orthoclase, microcline and albite, and less abundant muscovite, biotite, pinkish andalusite and blue-coloured dumortierite.

Dumortierite is present as large prismatic grains with a colourless to azure blue pleochroism (Dum I) and as smaller bundles of parallel fibrous or acicular crystals with a colourless to redviolet pleochroism (Dum II). Both types show differences in their chemical composition. Dum I crystals have lower contents of Mg (0.033-0.055 pfu) and Ti (0.001-0.011 pfu) than Dum II crystals (0.047-0.087 pfu and 0.043-0.064 pfu, respectively). A strong correlation between 3-Si and Al+Ti ( $R^2=0.85$ ) in both Dum I and Dum II suggests that Ti replaces Al in the octahedral position but

also together with Al, may substitute for Si in the tetrahedral position. The presented data confirm that the Al/Si ratio in natural dumortierite depends not only on pressure conditions but also on additional components, such as Fe, Mg or Ti, in its crystal structure. Most probably, an elevated Mg content favours a red to violet colour at comparable [Fe/(Fe+Ti)]x100 factors.

Coarse-grained magmatic muscovite shows Na/(Na+K) ratios varying between 0.08 and 0.09. Biotite chemistry corresponds to annite and indicates not only a magmatic origin but also the peraluminous nature and crustal source of the parental melt of the dumortierite-bearing pegmatite. Calculations of the pressure during solidification using the Al (<sup>T</sup>Al) content in biotite as a geobarometer yielded pressures of 470 to 495 MPa. These values are not in accordance with the presence of andalusite in the magmatic mineral assemblage. Most probably the biotite chemistry is slightly influenced by late hydrothermal fluids.

Andalusite forms euhedral to subhedral grains which are comparable in size to the magmatic muscovite and biotite. Because of these textural criteria and additional chemical criteria defined by CLARKE et al. (2005), it is part of the magmatic mineral assemblage.

Dumortierite-bearing pegmatite and the host two-mica leucogranite show strong similarities in major, minor and trace element contents. These chemical similarities, in addition to the spatial relationships, argue for the development of the pegmatite melt by fractional crystallisation during solidification of the twomica leucogranite.

The investigated pegmatite is quite unique and not fully comparable with any described dumortierite-bearing pegmatite worldwide. Most dumortierite-bearing granitic pegmatites occur in high-grade metamorphic host rocks and are thought to be products of anatectic melting of the country rocks. Even if the mineralogical composition of the dumortierite-bearing pegmatite from Mt. Moslavačka Gora allows a classification in the abyssal pegmatite class and the AB-BBe subclass, its formation by fractional crystallisation from a granitic melt is not in accordance with such an interpretation.

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