

**МАКЕДОНСКА АКАДЕМИЈА НА НАУКИТЕ И УМЕТНОСТИТЕ**

**ОДДЕЛЕНИЕ ЗА ПРИРОДНО-МАТЕМАТИЧКИ И БИОТЕХНИЧКИ НАУКИ**

**MACEDONIAN ACADEMY OF SCIENCES AND ARTS**

**SECTION OF NATURAL, MATHEMATICAL AND BIOTECHNICAL SCIENCES**

**2013**

**ПРИЛОЗИ**  
**CONTRIBUTIONS**

**34**  
**(1-2)**



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# **ПРИЛОЗИ CONTRIBUTIONS**

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## EDITORIAL

In the period 1969–1979 the journal entitled *Prilozi*, Oddelenie za prirodno-matematički nauki, (*Contributions*, Section of Natural Sciences and Mathematics) was published by the Macedonian Academy of Sciences and Arts.

From 1980 up to 2012 the journal split into *Prilozi*, Oddelenie za matematičko-tehnički nauki, MANU (*Contributions*, Section of Mathematical and Technical Sciences, MASA), and *Prilozi*, Oddelenie za biološki i medicinski nauki, MANU (*Contributions*, Section of Biological and Medical Science, MASA).

Recently, a separate Section of Natural, Mathematical and Biotechnical Sciences has been established at the Macedonian Academy of Sciences and Arts. It has been arranged that *Prilozi/Contributions* is to be the journal of the Section of Natural, Mathematical and Biotechnical Sciences and as of 2013 the journal will be published in a new design in A4 format, twice a year. The Local (National) Editorial Board has been expanded with new members, becoming an International Editorial Board.

The journal publishes original scientific papers, short communications, reviews, professional papers and educational papers from all fields of:

- natural sciences – physics, chemistry, biology, geography, geology;
- mathematical sciences – mathematics, informatics;
- biotechnical sciences – agriculture and food, forestry.

This journal also publishes, continuously or occasionally, the bibliographies of the members of the Macedonian Academy of Sciences and Arts, book reviews, reports on meetings, information on future meetings, important events and dates, and various headings which contribute to the development of the corresponding scientific field.

The original scientific papers report unpublished results of completed original scientific research, whereas the short communications should contain completed but briefly presented results of original scientific research.

The reviews are submitted at the invitation of the Editorial Board. They should be critical surveys of an area in which preferably the author himself is active.

Professional papers report on useful practical results that are not original but help the results of the original scientific research to be adopted into scientific and production use.

Educational papers report on the activities in the laboratory and classroom and the needs of the community of educators in all mentioned fields.

Papers received by the Editorial Board undergo peer review by two anonymous referees (at least one from abroad). The journal is equally opened to foreign and to domestic authors.

*Prilozi/Contributions* is an open access journal and its content is freely available to the public in order to achieve a greater global exchange of knowledge. The electronic version of the journal is accessible on the MANU/MASA website: [www.manu.edu.mk/prilozi](http://www.manu.edu.mk/prilozi).

Gligor Jovanovski  
Editor-in-chief

## TABLE OF CONTENTS

Nenad Novkovski, Albena Paskaleva, Elena Atanassova HYSTERESIS-LIKE FLATBAND VOLTAGE INSTABILITIES IN Al/Ta <sub>2</sub> O <sub>5</sub> -SiO <sub>2</sub> /Si STRUCTURES AND THEIR CONNECTION WITH <i>J-V</i> CHARACTERISTICS .....	7
Irina Petreska, Ljupčo Pejov, Ljupčo Kocarev BIASING FIELD EFFECTS ON ELECTRONIC PROPERTIES IN HALOGENATED PHENYLENE ETHYNYLENE OLIGOMERS .....	19
Marina Stojanovska, Bojan Šoptrajanov, Vladimir M. Petruševski MISCONCEPTIONS IN THE CHEMISTRY TEACHING IN THE REPUBLIC OF MACEDONIA REGARDING THE OXIDATION REACTIONS OF MONOSACCHARIDES .....	27
Aleksandar Pavlov, Zlatko Levkov OBSERVATIONS ON THE GENUS <i>PINNULARIA</i> SECTION <i>DISTANTES</i> (BACILLARIOPHYTA) FROM MACEDONIA; DIVERSITY AND DISTRIBUTION .....	33
Nikola Panov, Milena Taleska, Hristina Dimeska DEMOGRAPHIC ASPECTS OF TERRITORIAL DISTRIBUTION AND URBANIZATION LEVEL IN THE REPUBLIC OF MACEDONIA .....	59
Blažo Boev, Dejan Prelević, Milica Božović, Suzana Erić, Vladica Cvetković OLIVINE WEBSTERITE VEINS CUTTING THE RABROVO SERPENTINITES (SOUTH MACEDONIA): NEW EVIDENCE OF THE ARC SETTING OF THE EAST VARDAR OPHIOLITES? .....	69
Marjan Gusev and Sasko Ristov ANALYSIS OF ASSOCIATIVITY AND CONFLICT MISSES .....	83
Ana Selamovska, Elizabeta Miskoska-Milevska, Olga Najdenovska GENETIC RESOURCES OF TRADITIONAL PEAR VARIETIES IN THE REGION OF SKOPJE .....	93
INSTRUCTIONS FOR AUTHORS .....	101

## СОДРЖИНА

Ненад Новковски, Албена Паскалева, Елена Атанасова НЕСТАБИЛНОСТИ СЛИЧНИ НА ХИСТЕРЕЗИС КАЈ НАПОНОТ НА РАМНИ ЗОНИ ВО СТРУКТУРИ $Al/Ta_2O_5-SiO_2/Si$ И НИВНА ПОВРЗАНОСТ СО <i>J-V</i> КАРАКТЕРИСТИКИТЕ .....	7
Ирина Петреска, Љупчо Пејов, Љупчо Коцарев ЕФЕКТИТЕ ОД НАДВОРЕШНО ЕЛЕКТРИЧНО ПОЛЕ ВРЗ ЕЛЕКТРОНСКИТЕ СВОЈСТВА НА ХАЛОГЕНИРАНИТЕ ФЕНИЛЕН ЕТИНИЛЕН ОЛИГОМЕРИ .....	19
Марина Стојановска, Бојан Шоптрајанов, Владимир М. Петрушевски МИСКОНЦЕПЦИИ ВО НАСТАВАТА ПО ХЕМИЈА ВО РЕПУБЛИКА МАКЕДОНИЈА ВО ВРСКА СО РЕАКЦИОНЕН ОКСИДАЦИЈА КАЈ МОНОСАХАРИДИТЕ .....	27
Александар Павлов, Златко Левков ПРЕГЛЕД НА СЕКЦИЈАТА <i>DISTANTES</i> ОД РОДОТ <i>PINNULARIA</i> ( <i>BACILLARIOPHYTA</i> ) ВО МАКЕДОНИЈА; ДИВЕРЗИТЕТ И ДИСТРИБУЦИЈА .....	33
Никола Панов, Милена Талеска, Христина Димеска ДЕМОГРАФСКИ АСПЕКТИ НА ТЕРИТОРИЈАЛНАТА РАЗМЕСТЕНОСТ И НИВОАТА НА УРБАНИЗАЦИЈА ВО РЕПУБЛИКА МАКЕДОНИЈА .....	59
Блажо Боев, Дејан Прелевиќ, Милица Божовиќ, Сузана Ериќ, Владица Цветковиќ ОЛИВИНСКИ ВЕБСТЕРИТСКИ ЖИЦИ КОИ ГО СЕЧАТ СЕРПЕНТИНСКИОТ МАСИВ НА РАБРОВО (ЈУЖНА МАКЕДОНИЈА), НОВИ СОГЛЕДУВАЊА ЗА ЛАЧНАТА СТРУКТУРА ВО ИСТОЧНИОТ ОФИОЛИТСКИ ПОЈАС НА ВАРДАРСКАТА ЗОНА .....	69
Марјан Гушев, Сашко Ристов АНАЛИЗА НА ПРОМАШУВАЊА ПОРАДИ АСОЦИЈАТИВНОСТ И КОНФЛИКТ .....	83
Ана Селамовска, Елизабета Мискоска-Милевска, Олга Најденовска ГЕНЕТСКИ РЕСУРСИ НА ТРАДИЦИОНАЛНИ СОРТИ КРУШИ ВО СКОПСКИОТ РЕГИОН .....	93
ИНСТРУКЦИИ ЗА АВТОРИТЕ .....	101

## OLIVINE WEBSTERITE VEINS CUTTING THE RABROVO SERPENTINITES (SOUTH MACEDONIA): NEW EVIDENCE OF THE ARC SETTING OF THE EAST VARDAR OPHIOLITES?

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The study reports petrography and mineral chemistry data about an ultramafic vein that cuts the Rabrovo serpentinite (near Valandovo, Southern Macedonia). The serpentinite occurs as a block within a shearing zone of the East Vardar Zone tectonic mélange. The vein corresponds to medium-grained olivine websterite that sometimes displays cumulate-like textures. It is composed of low-Al orthopyroxene ( $Mg\#[\text{mol MgO} \cdot 100 / (\text{MgO} + \text{FeO}^{\text{I}})] \sim 85$ ,  $\text{Al}_2\text{O}_3 < 2$  wt.%), clinopyroxene ( $Mg\# = 82\text{--}86$ ), olivine ( $Mg\# \sim 84$ ) and spinel ( $\text{Cr}\#[\text{mol Cr}_2\text{O}_3 / (\text{Cr}_2\text{O}_3 + \text{Al}_2\text{O}_3)] \sim 0.4$ ), which, according to geothermometric calculations, equilibrated at 750–850 °C. Its pyroxene-rich modal composition suggests that this rock cannot represent a normal lithospheric mantle. Instead, it is supposed that it was formed via magmatic precipitations in the mantle lithosphere. In addition, the Rabrovo olivine websterite shows similar mineral chemical compositions to many other orthopyroxene-rich lithologies worldwide, which origin is commonly associated with subduction settings. Therefore, its presence is considered as additional evidence that the East Vardar ophiolites represent typical supra-subduction ophiolites.

**Key words:** ultramafic rock; orthopyroxene; subduction; Balkan Peninsula

### INTRODUCTION

The Balkan Peninsula is known from the existence of several ophiolite belts which are part of a much broader ophiolite domain that can be traced from the Western Mediterranean to the Himalaya. From the west to the east they are: Dinaridic ophiolite belt, Western Vardar ophiolites and Eastern Vardar ophiolites (e.g. [1, 2] and references therein). The geotectonic setting of all these ophiolite belts was mainly determined on the basis of the igneous members of ophiolites, mostly pillow lavas and diabase dykes, and only partly by studying depletion degrees of the underlying mantle peridotites [3–5]. Only very rare studies from this region were aimed at investigating orthopyroxene-rich lithologies [6]. On the other hand, it is very well known that ophiolites containing this lithology are commonly interpreted as originating from subduction-related settings (e.g. [7]).

The East Vardar Zone has the most pronounced supra-subduction signature of all the Balkan ophiolite belts. This setting was first, at least indirectly, suggested by [3] Maksimović and Majer (1981) and [8] on the basis of the higher depletion extent found in the East Vardar peridotites with respect to the Dinaride and West Vardar peridotites. The most striking evidence came from a recent study of ophiolite-related volcanic rocks of the Demir Kapija ophiolites in south Macedonia [9]. Moreover, based on the composition of mantle xenoliths entrained in Palaeogene mafic alkaline rocks of East Serbia, some authors [10, 11] argued that the mantle underneath the present day East Serbia also possesses supra-subduction signatures. These authors further postulated that this subcontinental mantle slice may, in fact, represent suboceanic mantle portions that were accreted during the closure of the East Vardar Zone (see also [12]). One of the strong-

est independent evidence for this hypothesis was derived from the presence and characteristics of a sub-group of olivine websterite xenoliths. [13] studied these orthopyroxene-rich xenoliths in detail and concluded that they represented lithospheric precipitates of boninite-like magmas similar to those commonly found in sub-arc settings.

In this study we report and discuss petrography and mineral chemistry of a pyroxene-rich vein cutting the serpentinite of Rabrovo (south Macedonia). The serpentinites geotectonically belong to the narrow East Vardar Zone ophiolite belt, and this is the first occurrence of orthopyroxene-rich lithology in this ophiolite zone. In a separate paper we shall present the full whole rock and mineral major and trace element geochemistry of this lithology, whereas in this study we focus on the major element compositions of main minerals. By comparing the compositions of the minerals from the Rabrovo websterite vein with those occurring in the olivine websterite xenoliths reported by [13], we shed more light on the significance of orthopyroxene-rich lithologies for determining the geotectonic setting of their host ophiolites.

### GEOTECTONIC SETTING

The present day geology of Macedonia is generally interpreted as having resulted by collision between the continental margins of Adria and Eurasia [14–16]. The central parts are dominated by the Pelagonides and the Vardar Zone *s.l.* The Pelagonides are composed of Precambrian rocks extending northward from the Skutari–Peč line to the Drina–Ivanjica metamorphic unit [2, 17–21]. The Vardar Zone *s.l.* is represented by the Western and the East Vardar ophiolitic units (*sensu* [2]). The East Vardar ophiolites occur in the southeast part of Macedonia, where they are represented by the largest ophiolitic complex of Demir Kapija. The whole ophiolitic section is unconformably covered by the Upper Tithonian reef limestones, which are, in the northwest and the south-east covered by upper Eocene-Pliocene and Pliocene-Quaternary sediments, respectively. In the west, the East Vardar ophiolites have tectonic relationship with the Pelagonian unit, whereas the north-eastern tectonic contact with the Serbo-Macedonian Massif is characterized by a mylonite zone, and sporadically by tectonic *mélange*. Within this heterogeneous *mélange*-like zone occur numerous ophiolite-related rock associations, which are spatially detached from the main body of the Demir Kapija complex. They are represented by variably sized blocks of diabases, gabbros and serpentinites, often containing pyroxene-rich veins.

### EXPERIMENTAL SECTION

Ten samples of the studied ultramafic vein were cut to produce chips for further scanning electron and microprobe investigations. The samples are first investigated petrographically using transmitted-light microscope in order to select the freshest rocks. The five freshest samples are studied on major element chemistry of the main minerals. Mineral chemistry was determined by electron microprobe (JEOL JXA 8900RL) at the Department of Geosciences, University of Mainz (Germany), using wavelength-dispersive analysis and a range of natural and synthetic standards. The data were corrected using the CITZAF procedure [22]. Detection limits were between 0.01 and 0.07 wt%. Operating conditions were generally 15 kV (20 kV) accelerating voltage, 12 nA beam current, 1–5  $\mu\text{m}$  beam diameter and 15–30 s counting time on peak.

### RESULTS

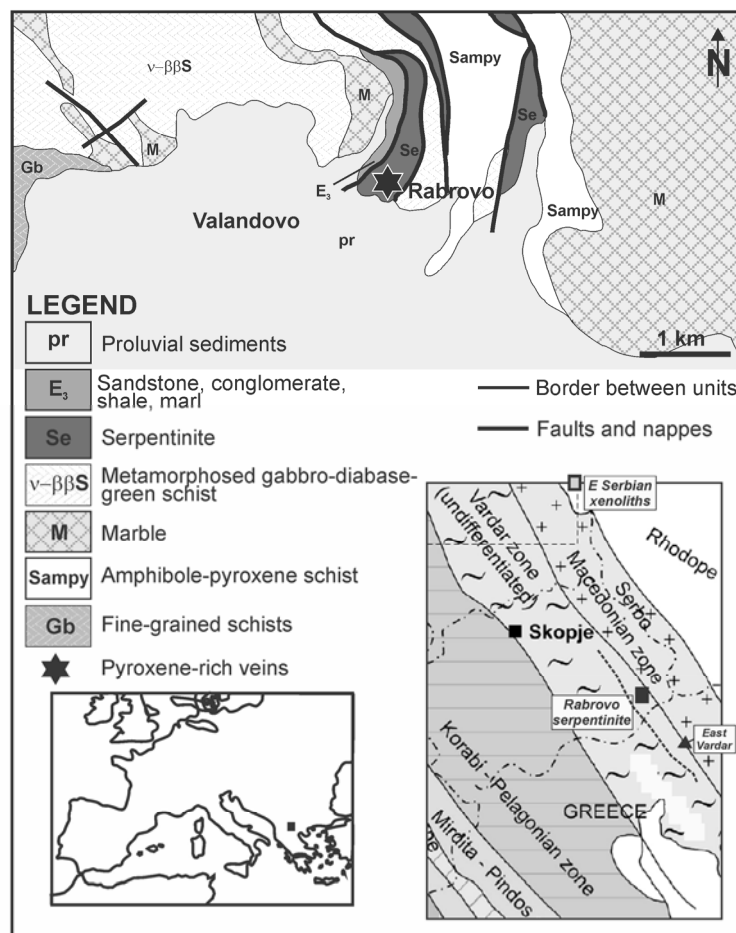
#### Field occurrence and petrography of the orthopyroxene-rich veins

The studied pyroxene-rich veins are found cutting a serpentinite block from the tectonic *mélange* of the East Vardar Zone. The serpentinite crops out near Rabrovo, along the road Valandovo–Strumica. It appears as a ~1 km long and a few hundreds of meters wide lens-like body that exhibits sharp tectonic contacts with the adjacent medium – to lowgrade metamorphic rocks of the Serbo-Macedonian Massif (Figure 1; [23]).

The pyroxene-rich vein represents, in fact, an approximately 1–1.5 m thick veining zone (Figure 2a). The veining zone consists of numerous pyroxene-rich individual veins ranging in thickness from only a few millimeters to >15 cm. Both host serpentinite and pyroxene-rich veins are strongly sheared and at places mylonitized and no evidence of true magmatic contacts can be observed. Therefore, the veins sometimes have typical lens-like forms or dismembered bands that resemble typical boudins.

These suggest that the presently observed contacts resulted from shearing during mylonitization and that boudin-like structures are probably formed by stretching along the shear foliation and shortening perpendicular to this. The serpentinite is composed of rare relicts of olivine and pyroxene set in a fine-grained matrix of serpentine minerals. In this stage of investigation it is not clear whether they represent remnants of mantle peridotites or those originating from the bottom of oceanic crust.





**Figure 1.** Geological sketch of the Rabrovo area. Compiled from the Basic Geological Map of SFR Yugoslavia 1:100000, Sheet: Gevgelija [23]; The inset is after [21]

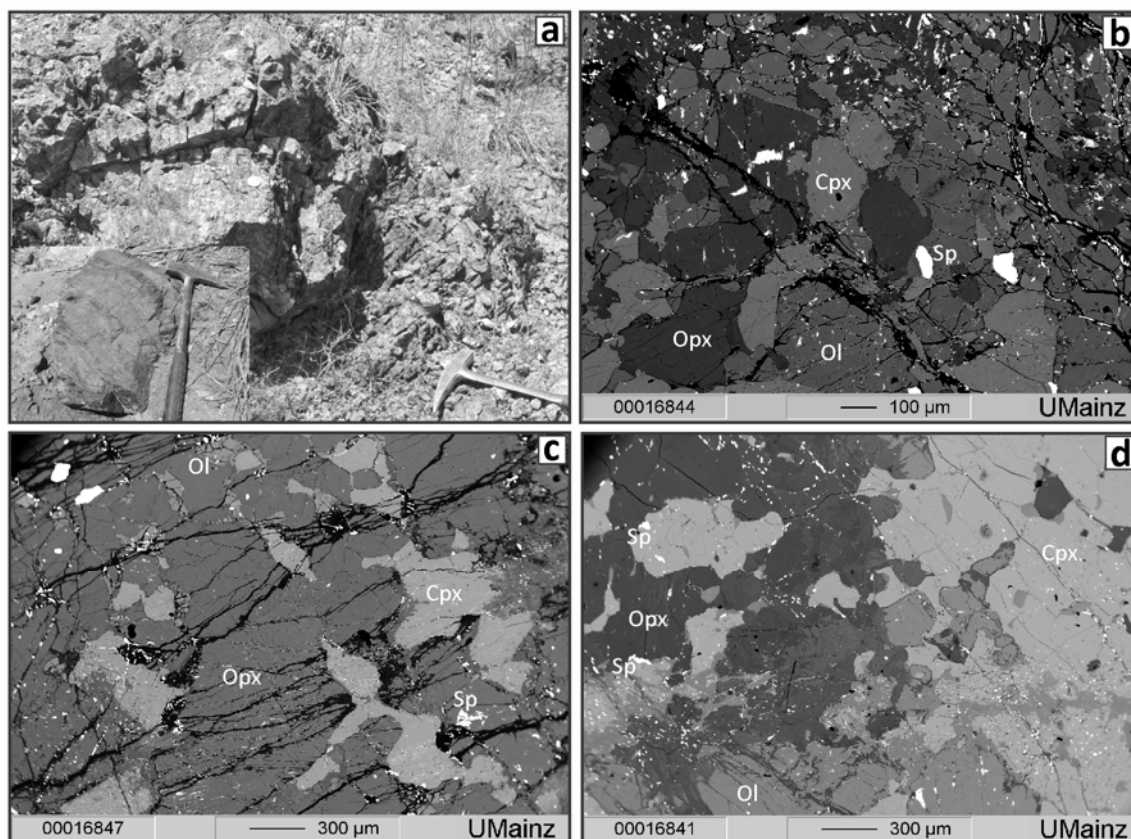
The pyroxenite veins have medium- to fine-grained granular texture. At mm scale the phases are merely undeformed and display sharp and mostly curvilinear contact suggesting good equilibration. It is composed of variable proportions of olivine, orthopyroxene, clinopyroxene and spinel. Apart of these predominant phases a few grains of altered amphibole are also found in some veins. The modal composition is very variable, showing considerable differences at cm and even mm scale. The differences are mostly related to different proportions of olivine and two pyroxenes. Irrespectively to the wide range in modal composition, this rock differs from normal mantle peridotites by having less than 50 % olivine, and can be classified as olivine websterite. Orthopyroxene often predominates over clinopyroxene and forms the main crystal network (Figure 2b). It is subhedral and tabular in shape and usually displays tiny exsolution lamellae (Figures 2b, d). Clinopyroxene often appears filling interstitial spaces in-between orthopyroxene crystals and giving cumulitic characteristics (Figure 2c). It sometimes forms larger pools that enclose smaller orthopyroxene grains (Figure 2d). These textural relationships can

suggest that orthopyroxene crystallized shortly before and/or partly simultaneously to clinopyroxene. Olivine is, most probably, an earlier phase that crystallized before the pyroxenes. Sometimes it appears as subhedral to almost idiomorphic crystal indicating free crystallization in open space (Figure 2b). It is rather fresh with serpentinization developed only along cracks. Spinel is represented by tiny, subhedral and mostly equidimensional to slightly elongated grains. They are isolated and enclosed by more coarse-grained silicates (Figure 2c, d).

### Mineral chemistry

The studied minerals from the Rabrovo olivine websterite veins have relatively uniform major element compositions. The results of microprobe investigations are given in Tables 1–4. The classification diagram of pyroxenes of Morimoto et al. [24] is given in Figure 3.

**Orthopyroxene** corresponds to enstatite with an average composition of  $En_{85}Fs_{14}W_1$ .



**Figure 2.** Field photos and BSE images of the studied olivine websterite. a – Field outcrop of the Rabrovo olivine websterite; the inset displays cm-thick interfingering of serpentinite and olivine websterite rocks; b – granular texture with subhedral to almost euhedral orthopyroxene and olivine and subordinate anhedral clinopyroxene; c – a cumulate-like texture with interstitial clinopyroxene surrounded by orthopyroxene; d – a larger clinopyroxene pool in the olivine websterite (right-hand side of the photo)

It is characterized by uniform Mg# [mol MgO\*100/(MgO + FeO<sup>t</sup>)] values mostly ranging between 84 and 86. Al<sub>2</sub>O<sub>3</sub> and CaO contents are relatively low and range from 1 to 1.5 wt.%, and from 0.3 to 0.6 wt.%, respectively. Chromium and nickel contents vary between 0.15 wt.% and 0.4 wt.% and ~0.5 wt.% Cr<sub>2</sub>O<sub>3</sub> and NiO, respectively. Al<sub>2</sub>O<sub>3</sub>, CaO and Cr<sub>2</sub>O<sub>3</sub> contents in this orthopyroxene are comparable from those found in orthopyroxene from the East Vardar peridotites, and are remarkably lower than those displayed by orthopyroxene from peridotite of Dinaride and West Vardar ophiolites [25, 26]. In comparison to orthopyroxene from East Serbian mantle xenoliths, there is a clear compositional similarity with orthopyroxene from spinel-poor olivine websterite xenoliths (Figure 4). The origin of these olivine websterite xenoliths is interpreted in terms of lithospheric crystallization of high-Si-Mg boninite-like magmas [11].

**Clinopyroxene** shows narrow compositional transitions from diopside to augite with an average formula of En<sub>~46</sub>Fs<sub>~8</sub>W<sub>~46</sub>. It is also characterized by relatively uniform Mg#s mostly between 85 and 86. Elements that commonly reflects the fertility of the

magmatic source are present in very low concentrations, for instance: Al<sub>2</sub>O<sub>3</sub> = 1–1.6 wt.%, TiO<sub>2</sub> = 0.04–0.06 wt.% and Na<sub>2</sub>O < 0.1 wt.%. Chromium contents are moderate and range between 0.3–0.4 wt.% Cr<sub>2</sub>O<sub>3</sub>. In Figure 5 is given Mg# vs Al<sub>2</sub>O<sub>3</sub> (wt.%) plot for clinopyroxene. It is evident that the clinopyroxene that occurs in the studied olivine websterite veins is compositionally very similar to the clinopyroxene from olivine websterite mantle xenoliths derived from the East Serbian subcontinental mantle [11, 13].

**Olivine** is relatively uniform and corresponds to Fo<sub>83–85</sub>. It is characterized by low calcium contents (CaO = 0.02–0.08 wt.%) and rather uniform nickel concentrations ranging 0.24–0.28 wt.% NiO.

**Spinel** is chromium rich with Cr#[molCr<sub>2</sub>O<sub>3</sub>/(Cr<sub>2</sub>O<sub>3</sub> + Al<sub>2</sub>O<sub>3</sub>)] ranging between 0.38 and 0.45 and Fe#[mol FeO<sup>t</sup>/(MgO + FeO<sup>t</sup>)] values about 0.5. Average olivine-spinel compositions plot off the "mantle array" ([27]; not shown), because their olivine shows lower Fo contents for the given high Cr# in spinel. The same is observed for the East Serbian olivine websterite xenoliths [10, 11], although spinels from the xenoliths have higher Cr#s (> 0.65).

**Table 2.** Microprobe analyses of clinopyroxene from olivine websterite of Rabrovo (in %)

No.	308	309	310	311	312	313	314	315	316	317
<b>SiO<sub>2</sub></b>	51.50	51.74	50.38	51.51	51.26	51.63	51.26	51.82	51.18	51.37
<b>TiO<sub>2</sub></b>	0.05	0.05	0.06	0.06	0.06	0.07	0.06	0.04	0.06	0.07
<b>Al<sub>2</sub>O<sub>3</sub></b>	1.18	1.20	1.11	1.35	1.24	1.24	1.35	1.39	1.35	1.27
<b>FeO</b>	5.18	5.56	6.76	5.36	5.28	5.10	5.06	5.14	4.94	5.08
<b>MnO</b>	0.11	0.11	0.16	0.13	0.12	0.11	0.11	0.10	0.13	0.12
<b>MgO</b>	16.76	17.15	17.68	16.91	17.07	16.83	16.91	16.71	16.80	16.81
<b>CaO</b>	23.11	22.47	20.54	23.06	23.11	23.04	23.17	22.99	22.91	22.95
<b>Na<sub>2</sub>O</b>	0.05	0.06	0.09	0.06	0.10	0.06	0.04	0.08	0.07	0.06
<b>Cr<sub>2</sub>O<sub>3</sub></b>	0.41	0.42	0.36	0.49	0.41	0.43	0.42	0.43	0.45	0.45
<b>NiO</b>	0.02	0.04	0.03	0.03	0.01	0.03	0.01	0.01	0.03	0.04
<b>Total</b>	98.37	98.80	97.18	98.96	98.67	98.52	98.40	98.71	97.91	98.22
<b>Site allocations (6 O)</b>										
<b>Si</b>	1.916	1.915	1.894	1.905	1.898	1.917	1.904	1.921	1.910	1.913
<b>Al</b>	0.052	0.052	0.049	0.059	0.054	0.054	0.059	0.061	0.059	0.056
<b>Fe<sup>3</sup></b>	0.033	0.033	0.056	0.037	0.048	0.029	0.037	0.019	0.030	0.032
<b>T</b>	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
<b>Al</b>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
<b>Fe<sup>3</sup></b>	0.073	0.074	0.098	0.082	0.093	0.071	0.083	0.069	0.078	0.075
<b>Ti</b>	0.001	0.001	0.002	0.002	0.002	0.002	0.002	0.001	0.002	0.002
<b>Cr</b>	0.012	0.012	0.011	0.014	0.012	0.012	0.012	0.013	0.013	0.013
<b>Ni</b>	0.001	0.001	0.001	0.001	0.000	0.001	0.000	0.000	0.001	0.001
<b>Mg</b>	0.913	0.911	0.889	0.901	0.893	0.914	0.903	0.916	0.906	0.909
<b>Fe<sup>2</sup></b>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
<b>Mn</b>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
<b>M1</b>	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
<b>Mg</b>	0.016	0.035	0.102	0.031	0.050	0.018	0.034	0.007	0.029	0.024
<b>Fe<sup>2</sup></b>	0.056	0.066	0.058	0.047	0.022	0.058	0.037	0.071	0.046	0.052
<b>Mn</b>	0.003	0.004	0.005	0.004	0.004	0.003	0.004	0.003	0.004	0.004
<b>Ca</b>	0.921	0.891	0.828	0.914	0.917	0.917	0.922	0.913	0.916	0.916
<b>Na</b>	0.003	0.004	0.007	0.004	0.007	0.004	0.003	0.005	0.005	0.004
<b>K</b>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
<b>M2</b>	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
<b>En</b>	46.122	47.010	48.671	46.245	46.498	46.351	46.372	46.194	46.527	46.407
<b>Fs</b>	8.170	8.724	10.690	8.431	8.259	8.044	7.962	8.128	7.873	8.059
<b>Wo</b>	45.707	44.266	40.639	45.324	45.243	45.605	45.666	45.677	45.600	45.535
<b>Mg#</b>	84.951	84.347	81.992	84.580	84.918	85.212	85.347	85.037	85.527	85.204
<b>Fe<sub>2</sub>O<sub>3</sub></b>	3.767	3.823	5.451	4.264	5.062	3.582	4.286	3.158	3.858	3.796
<b>FeO</b>	1.790	2.120	1.855	1.523	0.725	1.877	1.203	2.299	1.468	1.664
<b>100Ca/(Ca+Mg)</b>	49.774	48.497	45.503	49.497	49.316	49.594	49.616	49.719	49.497	49.526
<b>Cr/(Cr+Al)</b>	18.989	18.993	17.911	19.607	18.178	18.756	17.435	17.349	18.120	19.103
<b>(Si+Mg)/(Al+Na)</b>	51.533	50.534	51.564	45.089	46.416	48.989	45.871	43.058	44.082	47.370
<b>Al p.f.u.</b>	0.052	0.052	0.049	0.059	0.054	0.054	0.059	0.061	0.059	0.056

**Table 1.** Microprobe analyses of orthopyroxene from olivine websterite of Rabrovo (in %)

No.	10	12	13	14	15	16	19	20	21	22	23	24	25	26	27	59	61	63	65	94
<b>SiO<sub>2</sub></b>	55.66	56.80	56.90	56.54	56.48	56.36	55.84	56.02	56.32	56.00	55.81	55.85	55.22	55.36	55.72	53.32	53.48	53.42	53.49	55.27
<b>TiO<sub>2</sub></b>	0.02	0.02	0.03	0.04	0.03	0.02	0.03	0.03	0.03	0.03	0.02	0.03	0.04	0.03	0.04	0.03	0.01	0.03	0.03	0.02
<b>Al<sub>2</sub>O<sub>3</sub></b>	1.39	1.35	1.37	1.35	1.37	1.35	1.43	1.41	1.38	1.36	1.35	1.35	1.33	1.34	1.31	1.29	1.31	1.35	1.39	1.38
<b>FeO</b>	9.19	8.97	9.13	9.11	9.10	9.28	9.08	9.08	9.09	9.24	9.21	9.10	9.09	9.08	9.12	9.29	9.22	9.35	9.19	9.54
<b>MnO</b>	0.27	0.26	0.25	0.25	0.25	0.25	0.25	0.25	0.27	0.23	0.25	0.26	0.25	0.24	0.24	0.25	0.24	0.26	0.26	0.27
<b>MgO</b>	32.46	32.22	32.11	31.79	31.90	31.91	31.99	31.87	31.99	31.87	31.95	32.00	31.71	32.06	31.92	32.03	32.01	32.10	31.84	31.94
<b>CaO</b>	0.58	0.54	0.55	0.56	0.58	0.55	0.64	0.65	0.59	0.66	0.65	0.65	0.63	0.63	0.61	0.59	0.58	0.54	0.54	0.48
<b>Cr<sub>2</sub>O<sub>3</sub></b>	0.37	0.35	0.34	0.35	0.36	0.34	0.32	0.32	0.31	0.32	0.29	0.31	0.30	0.30	0.30	0.25	0.26	0.26	0.26	0.26
<b>NiO</b>	0.04	0.06	0.05	0.05	0.04	0.06	0.05	0.05	0.05	0.06	0.07	0.05	0.07	0.05	0.05	0.05	0.05	0.04	0.03	0.05
<b>Total</b>	99.97	100.57	100.72	100.02	100.11	100.11	99.63	99.68	100.04	99.76	99.60	99.60	98.64	99.09	99.31	97.10	97.15	97.35	97.03	99.20
<b>Site allocations (6 O)</b>																				
<b>Si</b>	1.944	1.972	1.973	1.975	1.972	1.969	1.959	1.965	1.968	1.964	1.959	1.960	1.957	1.951	1.961	1.914	1.918	1.912	1.922	1.948
<b>Al</b>	0.056	0.028	0.027	0.025	0.028	0.031	0.041	0.035	0.032	0.036	0.041	0.040	0.043	0.049	0.039	0.054	0.055	0.057	0.059	0.052
<b>Fe<sup>3</sup></b>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.032	0.026	0.031	0.019	0.000
<b>T</b>	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
<b>Al</b>	0.001	0.027	0.029	0.030	0.028	0.025	0.018	0.024	0.025	0.020	0.015	0.016	0.013	0.007	0.016	0.000	0.000	0.000	0.000	0.005
<b>Fe<sup>3</sup></b>	0.045	0.000	0.000	0.000	0.000	0.000	0.013	0.000	0.000	0.006	0.017	0.014	0.020	0.033	0.013	0.078	0.074	0.079	0.069	0.038
<b>Ti</b>	0.001	0.001	0.001	0.001	0.001	0.000	0.001	0.001	0.001	0.001	0.000	0.001	0.001	0.001	0.001	0.001	0.000	0.001	0.001	0.001
<b>Cr</b>	0.010	0.010	0.009	0.010	0.010	0.010	0.009	0.009	0.009	0.009	0.008	0.009	0.008	0.008	0.008	0.007	0.007	0.007	0.007	0.007
<b>Ni</b>	0.001	0.002	0.001	0.001	0.001	0.002	0.001	0.001	0.002	0.002	0.002	0.001	0.002	0.001	0.001	0.001	0.001	0.001	0.001	0.001
<b>Mg</b>	0.943	0.961	0.959	0.958	0.960	0.964	0.958	0.965	0.964	0.963	0.958	0.959	0.956	0.950	0.961	0.913	0.917	0.912	0.922	0.947
<b>Fe<sup>2</sup></b>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
<b>Mn</b>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
<b>M1</b>	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
<b>Mg</b>	0.747	0.707	0.701	0.698	0.700	0.698	0.715	0.702	0.703	0.703	0.714	0.715	0.719	0.734	0.714	0.801	0.795	0.801	0.784	0.731
<b>Fe<sup>2</sup></b>	0.224	0.260	0.265	0.266	0.266	0.271	0.254	0.266	0.266	0.265	0.254	0.253	0.249	0.235	0.256	0.169	0.176	0.170	0.188	0.243
<b>Mn</b>	0.008	0.008	0.007	0.007	0.007	0.007	0.008	0.007	0.008	0.007	0.008	0.008	0.008	0.007	0.007	0.008	0.007	0.008	0.008	0.008
<b>Ca</b>	0.022	0.020	0.020	0.021	0.022	0.021	0.024	0.024	0.022	0.025	0.024	0.024	0.024	0.024	0.023	0.023	0.022	0.021	0.021	0.018
<b>Na</b>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
<b>K</b>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
<b>M2</b>	1.000	0.995	0.993	0.992	0.994	0.998	1.000	1.000	0.998	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
<b>En</b>	85.01	85.27	85.02	84.91	84.92	84.74	84.89	84.82	84.93	84.63	84.69	84.84	84.78	84.94	84.87	84.71	84.83	84.74	84.84	84.53
<b>Fs</b>	13.90	13.71	13.94	14.02	13.96	14.20	13.90	13.94	13.94	14.11	14.08	13.93	14.02	13.86	13.96	14.16	14.06	14.23	14.13	14.57
<b>Wo</b>	1.09	1.02	1.04	1.07	1.12	1.05	1.22	1.24	1.13	1.26	1.24	1.23	1.21	1.20	1.16	1.13	1.10	1.03	1.03	0.91
<b>Mg#</b>	85.95	86.15	85.91	85.83	85.88	85.64	85.93	85.89	85.90	85.71	85.75	85.90	85.81	85.97	85.87	85.68	85.78	85.62	85.72	85.30

**Table 3.** Microprobe analyses of olivine from olivine websterite of Rabrovo (in %)

No.	49	51	53	55	57	67	68	80	82	84	89	90	91
<b>SiO<sub>2</sub></b>	39.12	39.31	39.16	38.77	38.68	39.30	38.94	39.06	38.96	39.26	39.79	39.32	39.53
<b>FeO</b>	14.65	14.56	14.21	14.50	14.44	14.27	14.21	15.43	15.60	15.18	14.70	14.64	14.62
<b>MnO</b>	0.25	0.25	0.22	0.21	0.22	0.23	0.25	0.27	0.26	0.26	0.25	0.24	0.23
<b>MgO</b>	45.90	45.79	45.99	45.78	45.25	45.83	45.68	44.84	44.86	44.90	45.99	45.79	45.68
<b>CaO</b>	0.02	0.02	0.01	0.04	0.08	0.06	0.09	0.07	0.05	0.06	0.02	0.02	0.03
<b>Cr<sub>2</sub>O<sub>3</sub></b>	0.03	0.02	0.03	0.04	0.02	0.05	0.04	0.03	0.04	0.03	0.02	0.01	0.03
<b>NiO</b>	0.24	0.23	0.25	0.24	0.24	0.24	0.22	0.21	0.22	0.22	0.25	0.25	0.25
<b>Total</b>	100.20	100.17	99.87	99.57	98.94	99.98	99.43	99.91	99.99	99.91	101.01	100.28	100.37
<b>Site allocations (4 O)</b>													
<b>Si</b>	0.982	0.986	0.984	0.979	0.983	0.986	0.983	0.987	0.984	0.990	0.989	0.986	0.989
<b>Z</b>	0.982	0.986	0.984	0.979	0.983	0.986	0.983	0.987	0.984	0.990	0.989	0.986	0.989
<b>Ti</b>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
<b>Al</b>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
<b>Fe<sup>2+</sup></b>	0.307	0.305	0.299	0.306	0.307	0.300	0.300	0.326	0.330	0.320	0.306	0.307	0.306
<b>Mn</b>	0.005	0.005	0.005	0.004	0.005	0.005	0.005	0.006	0.005	0.006	0.005	0.005	0.005
<b>Mg</b>	1.717	1.712	1.723	1.724	1.714	1.715	1.720	1.688	1.689	1.688	1.705	1.711	1.704
<b>Ca</b>	0.001	0.001	0.000	0.001	0.002	0.002	0.002	0.002	0.001	0.002	0.000	0.001	0.001
<b>Na</b>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
<b>K</b>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
<b>Cr</b>	0.000	0.000	0.001	0.001	0.000	0.001	0.001	0.001	0.001	0.001	0.000	0.000	0.001
<b>Ni</b>	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.004	0.004	0.004	0.005	0.005	0.005
<b>X</b>	2.036	2.028	2.032	2.041	2.034	2.027	2.033	2.027	2.031	2.020	2.021	2.029	2.021
<b>Mg#</b>	84.81	84.86	85.23	84.91	84.82	85.13	85.14	83.82	83.68	84.06	84.80	84.79	84.78
<b>Fo</b>	84.60	84.64	85.03	84.73	84.62	84.92	84.92	83.58	83.45	83.82	84.58	84.58	84.57
<b>Fa</b>	15.15	15.10	14.74	15.05	15.15	14.83	14.82	16.13	16.28	15.90	15.17	15.17	15.18

**Table 4.** Microprobe analyses of spinels from olivine websterite of Rabrovo (in %)

No.	45	46	47	48	73	75	77	78	122	123	124	125	126
<b>SiO<sub>2</sub></b>	0.02	0.06	0.03	0.08	0.09	0.06	0.05	5.91	0.93	0.06	0.02	0.02	0.04
<b>TiO<sub>2</sub></b>	0.11	0.11	0.11	0.10	0.07	0.08	0.07	0.07	0.16	0.16	0.15	0.17	0.16
<b>V<sub>2</sub>O<sub>3</sub></b>	0.40	0.39	0.38	0.40	0.37	0.35	0.40	0.27	0.37	0.33	0.37	0.37	0.38
<b>Al<sub>2</sub>O<sub>3</sub></b>	29.57	29.25	29.63	30.83	33.21	33.46	33.62	25.41	32.25	34.36	34.26	34.54	33.60
<b>Cr<sub>2</sub>O<sub>3</sub></b>	36.59	36.89	36.85	34.85	32.31	32.47	32.14	25.59	32.09	31.77	31.95	31.76	32.11
<b>FeO<sub>t</sub></b>	22.83	23.81	22.91	22.91	23.83	23.30	23.13	27.24	23.00	22.30	22.59	22.60	22.86
<b>MnO</b>	0.26	0.32	0.27	0.27	0.27	0.26	0.25	0.48	0.23	0.21	0.22	0.22	0.23
<b>MgO</b>	10.14	9.66	10.09	10.29	10.06	10.40	10.54	9.79	11.01	11.19	11.07	11.08	10.89
<b>CaO</b>	0.08	0.04	0.04	0.03	0.10	0.12	0.19	2.08	0.02	0.01	0.01	0.00	0.01
<b>NiO</b>	0.08	0.07	0.06	0.06	0.07	0.06	0.08	0.05	0.10	0.12	0.12	0.13	0.11
<b>Total</b>	100.08	100.60	100.38	99.83	100.38	100.56	100.48	96.89	100.15	100.51	100.76	100.90	100.39
<b>Cr</b>	0.889	0.897	0.892	0.844	0.774	0.773	0.765	0.740	0.779	0.750	0.754	0.747	0.764
<b>Ti</b>	0.003	0.002	0.003	0.002	0.002	0.002	0.002	0.002	0.004	0.004	0.003	0.004	0.004
<b>V</b>	0.008	0.008	0.008	0.008	0.007	0.007	0.008	0.007	0.007	0.007	0.007	0.007	0.007
<b>Al</b>	1.071	1.061	1.070	1.114	1.186	1.189	1.194	1.096	1.167	1.210	1.205	1.212	1.192
<b>Fe<sup>3+</sup></b>	0.018	0.020	0.016	0.020	0.021	0.019	0.021	0.146	0.031	0.019	0.019	0.018	0.021
<b>Fe<sup>2+</sup></b>	0.533	0.554	0.538	0.529	0.541	0.529	0.521	0.395	0.496	0.501	0.508	0.509	0.512
<b>Mn</b>	0.007	0.008	0.007	0.007	0.007	0.007	0.006	0.015	0.006	0.005	0.006	0.006	0.006
<b>Mg</b>	0.464	0.443	0.461	0.470	0.454	0.467	0.473	0.534	0.504	0.498	0.492	0.491	0.488
<b>Co</b>	0.002	0.001	0.001	0.001	0.002	0.003	0.005	0.061	0.001	0.000	0.000	0.000	0.000
<b>Ni</b>	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.003	0.003	0.003	0.003	0.003
<b>Mg#</b>	0.47	0.44	0.46	0.47	0.46	0.47	0.48	0.57	0.50	0.50	0.49	0.49	0.49
<b>Cr#</b>	0.45	0.46	0.45	0.43	0.39	0.39	0.39	0.40	0.40	0.38	0.38	0.38	0.39

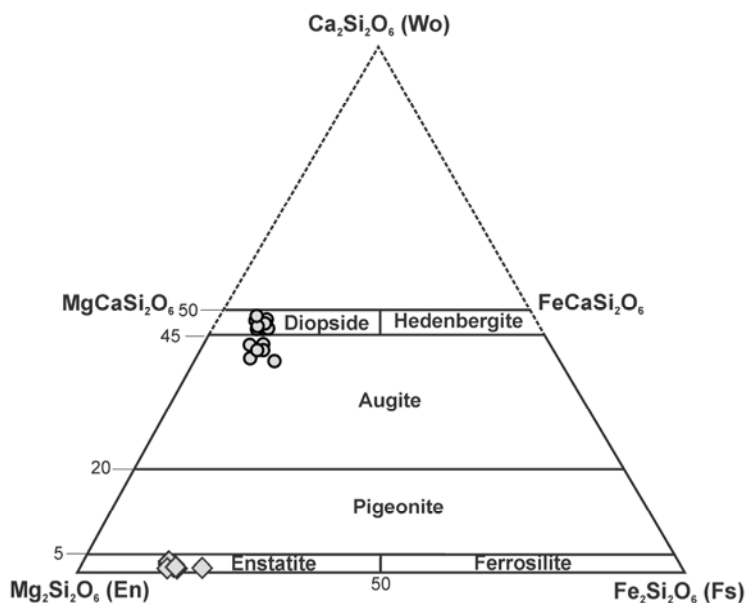


Figure 3. Diagram of classification of pyroxenes [24]

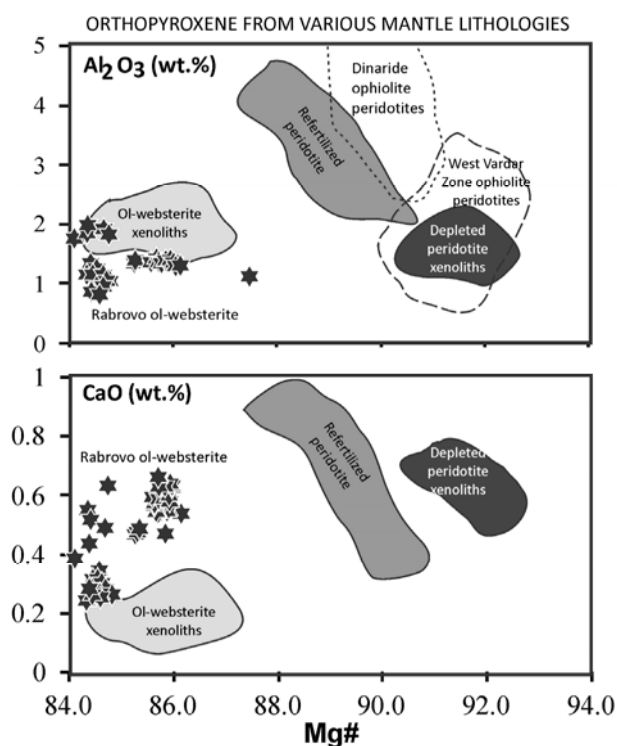


Figure 4. Mg# [mol MgO\*100/(MgO + FeO<sup>1</sup>)] vs Al<sub>2</sub>O<sub>3</sub> (a) and CaO (b) plots for orthopyroxene; data for the composition of orthopyroxene from other lithologies are from: [11, 13] for orthopyroxene from various East Serbian mantle xenoliths and [25] for orthopyroxene from Dinaride and West Vardar peridotites

#### Geothermometric calculations

Temperatures were calculated using the olivine-spinel [28–30], clinopyroxene-only [31] and

orthopyroxene-only [32] geothermometers for pressures ranging between 2 and 5 kbars. The results of geothermometric calculations are shown in Table 5. The average calculated temperature according to different geothermometers varies between 750 and 850°C.

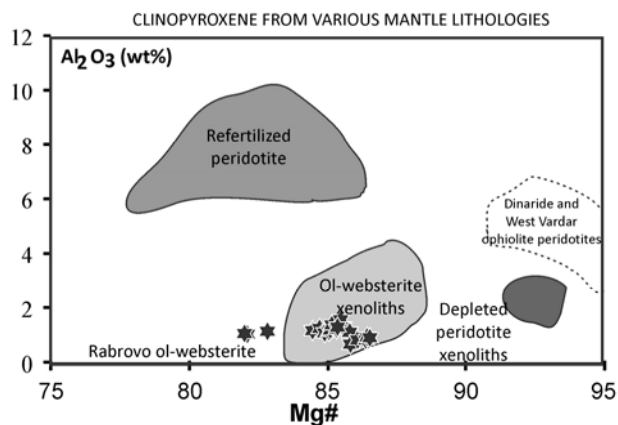


Figure 5. Mg# [mol MgO\*100/(MgO + FeO<sup>1</sup>)] vs Al<sub>2</sub>O<sub>3</sub> plot for clinopyroxene; data for the composition of clinopyroxene from other lithologies are from: [11, 13] for clinopyroxene from various East Serbian mantle xenoliths and [25] for clinopyroxene from Dinaride and West Vardar peridotites

## DISCUSSION

#### The origin of the olivine websterite veins

The olivine websterite veins found cutting the Rabrovo serpentinite are characterized by remarkably

fertile compositions. Such compositions fall outside the main compositional trends of common mantle peridotites. These veins are ortho- and clinopyroxene-rich and all their Fe-Mg silicates have relatively low Mg# (< 87) to be in equilibrium with typical mantle silicates. These characteristics indicate that this lithology cannot be regarded as 'normal' upper mantle. It is generally accepted that such pyroxene-rich rocks are related to magmatic modifications of the upper mantle i.e. that they

result from percolations and precipitations of mafic/ultramafic magma and formation of pyroxene-rich domains in the mantle lithosphere [33, 34]. Besides the formation of magmatic mafic and ultramafic veins, this process is also responsible for metasomatic refertilization of previously depleted lithospheric mantle. In such a way, previously variably depleted lherzolite/harzburgite mantle peridotite is transformed into clinopyroxene-rich lherzolite and, in some cases, even wherlites domains [35].

**Table 5.** Calculated temperatures according to different geothermometers

<b>Olivine-spinel geothermometer</b>	
[27] Fabriés, 1979	690–770 °C (average = 732, SEE = 25°C) n = 12
[28] Roeder et al., 1979	660–770 °C (average = 709, SEE = 36°C) n = 12
[29] Ballhaus et al., 1991	630–700 °C (average = 766, SEE = 25°C) n = 12
<b>Clinopyroxene only geothermometer</b>	
[30] Nimis and Taylor, 2000	770–950 °C (average = 845, SEE = 51°C) n = 20
<b>Orthopyroxene only geothermometer</b>	
[31] Witt-Eickschen and Seck, 1991	690–890 °C (average = 772, SEE = 60°C) n = 20

However, the above mentioned modifications of the normal upper mantle material commonly produces clinopyroxene-rich lithologies and, additionally, such lithologies contain typically Fe-Ti-Al-Ca rich silicates. By contrast, the Rabrovo olivine websterite possesses a list of other characteristics that are unusual for lithologies having formed by modifications caused by mafic melts. First, the Rabrovo olivine websterite is rich in orthopyroxene (> 50 %vol.) that usually predominates over clinopyroxene. It is generally known that this mineral normally decrease in abundance during mafic metasomatism because this phase is not stable in Si-undersaturated magmas or those close to silica saturation [36].

The presence of orthopyroxene-rich mantle rocks have been reported by many authors [7, 37–39]. The origin and evolution of these lithologies have been variously interpreted. Namely, by: (i) deserpentinization of the normal peridotitic upper mantle (e.g. [40]), (ii) metasomatism induced by percolating Si-rich melts/fluids [7, 37], or (iii) direct crystallization from a silica saturated melt (e.g. [41]). The first two interpretations are not likely scenarios for the origin of melts from which the Rabrovo olivine websterite crystallized. On the contrary, these rocks show many characteristics that can be associated with crystallization of Si-rich lithospheric magmas. This is indicated from textural relationships that are found in the studied olivine websterite, at first

place, from the presence of cumulate-like texture (see Figure 2c). Moreover, these rocks lack fibrous orthopyroxene or olivine relicts in orthopyroxene, which are commonly found after deserpentinization and/or fluid-induced metasomatic processes. Mineral chemistry data also support this conclusion. Namely, Mg# and NiO contents of the orthopyroxene from the Rabrovo olivine websterite is rather low (< 87 and <0.06 wt.%, respectively), to support an origin via deserpentinization and fluid-induced metasomatism. Therefore, it is more logical that the studied olivine websterite veins originated by crystallization of a primarily silica- and Mg-rich, presumably, boninite-like magma. Early crystallization of orthopyroxene, which is suggested by textural relationships, indicates silica-saturated or oversaturated melts, most probably with more than 53 wt.% SiO<sub>2</sub> (e.g. [42]). Higher modal abundance of clinopyroxene in combination with relatively low Mg# in olivine and pyroxenes and somewhat higher CaO contents in orthopyroxene, can suggest that these olivine websterites crystallized from evolved magmas.

### Geodynamic implications

Notwithstanding which interpretation for the origin of the Rabrovo olivine websterite we adopt, it is very likely that the formation of these rocks was associated with a supra-subduction setting.



Similar orthopyroxene-rich mantle domains are found at many places worldwide: Papua New Guinea [7], USA [38, 43, 44], Kamchatka [40], Canada [45], Andes [46], Philippines [47], Zabargard peridotite, Red Sea [48], and Cabo Ortegal peridotite, Spain [49]. Most these localities have a close spatial and temporal relation to subduction.

It is worth noting that the studied olivine websterite veins are found cutting a serpentinite block from the East Vardar Zone mélange. It is known that the East Vardar ophiolite is dominated by harzburgites and is considered to be the most depleted one in the Balkan Peninsula. As previously mentioned, [10, 11, 13] argued that orthopyroxene-rich mantle xenoliths in Serbia also originated as lithospheric precipitates of arc-related magmas. They suggested that these high-Mg and high-Si magmas resulted from melting of a highly refractory harzburgitic source, most probably due to a H<sub>2</sub>O flux. Such melting processes are very common in fore-arc regions. Analogously, the formation of the studied olivine websterite vein could have resulted from melting of highly refractory mantle peridotites in the presence of H<sub>2</sub>O flux and depression of melting temperatures. The orthopyroxene-rich mantle xenoliths differ from the studied olivine websterite by having abundant carbonate and displaying much higher Cr# values in their spinels. However, this cannot disturb the postulated petrogenetic analogy of these two lithologies. As shown by Cvetković and coauthors [10, 11, 13] the carbonate present in the East Serbian orthopyroxene-rich mantle xenoliths is unrelated to their original composition but was likely introduced via later metasomatic processes. On the other hand, higher Cr#s in spinels from the xenoliths can be explained because the source from which this lithology originated was associated with higher degree of depletion.

The fact that there is a contrast in Fe–Mg distribution between the silicates of the olivine websterite and normal depleted peridotite suggests that these websterite domains did not reside long in the mantle before they were tectonically emplaced and reworked in the mélange. This is corroborated by a very large range temperature range that is obtained by thermometric calculations, which can suggest fast and incomplete equilibration. This, in turn, indicates that subduction processes that were responsible for subduction, the most likely candidate is the Mesozoic subduction related to closure of the Tethyan Ocean [21].

## CONCLUSIONS

The presence of olivine websterite veins cutting the Rabrovo serpentinite block in the mélange is considered as evidence that the East Vardar Zone ophiolite belt formed in a supra-subduction setting. Textural relationships suggest that the olivine websterite vein represents relicts of magmatic precipitates at crustal or subcrustal (?) depths. The average temperature of equilibration is estimated to 750–850 °C. Low Mg# values in silicates of the studied olivine websterite suggests that these magmas did not reside long in the lithosphere. Major element chemical compositions of the main minerals composing the olivine websterite indicate that the studied veins formed by crystallization of silica saturated, MgO-rich primary magmas that commonly originate by melting of highly depleted peridotite in sub-arc settings. This study strongly suggests that the investigation of pyroxene-rich lithospheric rocks can be very useful palaeotectonic indicators, especially recording possible effects of subduction processes.

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**ОЛИВИНСКИ ВЕБСТЕРИТСКИ ЖИЦИ КОИ ГО СЕЧАТ СЕРПЕНТИНСКИОТ МАСИВ  
НА РАБРОВО (ЈУЖНА МАКЕДОНИЈА): НОВИ СОГЛЕДУВАЊА ЗА ЛАЧНАТА  
СТРУКТУРА ВО ИСТОЧНИОТ ОФИОЛИТСКИ ПОЈАС  
НА ВАРДАРСКАТА ЗОНА**

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Во трудот е прикажана петрографијата и хемијата на минералите од ултрабазичните жилни карпи кои ги сечат серпентинитите на Раброво (во близината на Валандово, југоисточна Македонија). Серпентинитите се појавуваат во вид на блокови во раседните зони од тектонскиот меланж во источната вардарска субзона. Жилните карпи одговараат на средно зрнести оливински вебстерити и понекогаш покажуваат кумулатни текстури. Изградени се од ортопироксен, клинопироксен оливин и спинел. Составот на пироксенот укажува на тоа дека тие не се репрезент на нормална литосверска обвивка. Врз основа на главните карактеристики на офиолитите од источната вардарска субзона може да се констатира дека тие претставуваат типични супра субдукциски офиолити.

**Клучни зборови:** ултрабазични карпи; ортопироксени; субдукција; Балкански Полуостров