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PETROLOGICAL AND GEOCHEMICAL COMPARISON OF RODINGITES FROM KIMI-EVIA ISLAND WITH OUTCROPS FROM ADJACENT REGIONS

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Abstract

The present study is focused on the geochemical and petrological comparison between rodingites from the Kimi region in Central Evia (Greece) with those from East and West Othris, as well as with rodingites from Skyros island. Based upon their whole rock geochemical and petrographical data it is suggested that rocks from Skyros island and Kimi-Evia display similar features. Kimi-Evia and Skyros rodingites are characterized by their highly comparable REE patterns with significant LREE enrichments. This is most likely attributed to the effects of carbonic rich fluids, enhancing the transfer of REE via CO_3^{-2} *ligands. The West Othris rodingites display similar MREE and HREE patterns with the least fractionated rodingites from Kimi-Evia and Skyros, whereas the LREE are significantly depleted. The East Othris rodingites differ from all other rodingite occurrences, since they exhibit much lower ΣREE contents. Rodingitization in all studied areas was associated with serpentinization processes and was evolved in several metasomatic stages, in which vesuvianite was formed during the last episodes at relatively low temperatures.*

Keywords: *metasomatism, rodingites, vesuvianite, petrography, serpentinization, geochemistry*

Περίληψη

Η παρούσα έρευνα εστιάζει στη γεωχημική και πετρολογική σύγκριση μεταξύ των ροδιγκιτών της περιοχής της Κύμης στην Κεντρική Εύβοια (Ελλάδα) και εκείνων των παρακείμενων περιοχών της Ανατολικής, Δυτικής Όθρυς και της νήσου Σκύρου. Από την εν λόγω σύγκριση προκύπτει το συμπέρασμα ότι οι ροδιγκίτες των περιοχών της Κύμης και της Σκύρου εμφανίζουν κοινά πετροχημικά και πετρολογικά χαρακτηριστικά όπως τα παρόμοια πεδία τιμών σπανίων γαιών και ιδίως ο εμπλουτισμός σε ελαφριές σπάνιες γαίες (REE). Το γεγονός αυτό πιθανότατα οφείλεται στην επίδραση διαλυμάτων πλούσιων σε ανθρακικά ιόντα τα οποία ενισχύουν τη μεταφορά των σπανίων γαιών μέσω συμπλόκων CO3-2. Οι ροδιγκίτες της Δυτικής Όθρυς παρουσιάζουν παρόμοια πεδία ελαφρών (LREE) και μέσων σπανίων γαιών (MREE) σε σχέση με τα λιγότερο διαφοροποιημένα πετρώματα της Κύμης και της Σκύρου, ενώ οι ελαφριές σπάνιες γαίες παρουσιάζουν σημαντική απόπλυση. Οι ροδιγκίτες της Ανατολικής Όθρυς διαφέρουν από αυτούς των υπόλοιπων περιοχών καθώς εμφανίζουν σημαντικά χαμηλότερες τιμές συνόλου σπανίων γαιών (ΣREE). Η ροδιγκιτίωση σχετίζεται άμεσα με τα φαινόμενα σερπεντινίωσης και εξελίχθηκε σε πολλά μετασωματικά στάδια. Ο σχηματισμός του βεζουβιανίτη έλαβε χώρα στο τελευταίο μετασωματικό επεισόδιο σε συνθήκες χαμηλών θερμοκρασιών.

Λέξεις κλειδιά: *μετασωμάτωση, ροδιγκίτες, βεζουβιανίτης, πετρογραφία, σερπεντινίωση, γεωχημεία*

1. Introduction

Rodingites are Ca-rich and silica undersaturated metasomatized rocks that appear within serpentinized peridotites (e.g. Coleman, 1967; Hatzipanagiotou and Tsikouras, 2001; Li et al., 2004, 2007; Tang et al., 2018). Their formation is attributed to serpentinization and in some cases to autometasomatic processes (e.g. Hall and Ahmed, 1984; Hatzipanagiotou et al., 2003; Frost and Beard, 2007; Zharikov et al., 2007; Klein, 2009). In each of the studied areas rodingites appear as dykes within serpentinized ultramafic rocks or as replacing products of massive gabbroic rocks. The effect of the metasomatic processes and the hydrous fluids is also confirmed by the significant listwanite occurrences in most of the studied areas. The study of rodingitization contributes to the scientific knowledge of metasomatic processes and the associated hydrous metasomatic fluids that were evolved in many successful stages during T decrease as a result of exhumation.

The present study aims to conduct a petrographical, geochemical and mineralogical comparison between the rodingite samples of Kimi area and those from East Othris, West Othris and Skyros island. In addition, it aims to outline similarities and differences amongst rodingites from the aforementioned areas in order to contribute to the ongoing research conducted that focuses on the interpretation of the metasomatic evolution and geotectonic environment of their formation.

2. Geological Setting

Rodingites from Kimi-Evia island are found within serpentinized ultramafic rocks of the Pelagonian flysch, which exhibits an Upper Cretaceous-Paleocene age (I.G.M.E. Geological Map of Greece, Kymi Sheet, 1981; Katsikatsos, 1970). It consists of typical sedimentary rocks such as sandstones, shales, cherts, along with limestone intercalations, peridotitic bodies (I.G.M.E. Geological Map of Greece, Kymi Sheet, 1981; Robertson, 1990) and ophicalcites (Paraskevopoulos and Kanakis, 1972; Robertson, 1990). The flysch presents a chaotic structure similar with that of an ophiolitic mélange. Ultramafic rocks are serpentinized and sheared and crossed by talc schists, magnesite and pyroxenite veins. Rodingites appear as dykes of E-W or NNE-SSW direction with a thickness ranging from 15 cm to 2 m within serpentinized ultramafic host rocks. They exhibit zoning characterized by specific mineral assemblages from their margin to their core. Chlorite rich zones are found between the rodingites and the surrounding serpentinites that surround them. The marginal areas are chlorite and/or diopside rich, whereas the core areas are rich in garnet and/or vesuvianite. A third transitional zone between the core and the rodingite margins often occurs consisting of the aforementioned minerals in various proportions.

The Othris area is located in central Greece and includes rocks from the Pelagonian and Sub-Pelagonian geotectonic zones (Smith et al., 1975; Ferrière, 1982; Katsikatsos, 1992; Papanikolaou, 1997, 2009; Smith and Rassios, 2003; Ferrière et al., 2012; Koutsovitis et al., 2013). In East Othris the Jurassic ophiolitic rocks near Vrinena (Rassios, 1990) and Eretria (Ferrière, 1982; Economou and Naldrett, 1984; Migiros et al., 1997) encompass rodingites (Koutsovitis et al., 2013). In Vrinena rodingites appear as massive bodies or in the form of dykes associated with gabbroic and doleritic rocks respectively (Koutsovitis et al., 2013). In Eretria rodingites are present as dykes of 1.5 m thickness within serpentinized harzburgites or as irregular bodies associated with gabbroic rocks (Koutsovitis et al., 2013). Chlorite rich margins appear near the contact between the rodingite dykes and serpentinites. In the Aerino and Velestino regions rodingites belong to a post-flyschic tectonic nappe, associated with gabbroic and gabbroic/doleritic rocks respectively (Koutsovitis et al., 2013). Rodingites are also present in SE Othris within ophiolitic mélange occurrences overthrusted above the volcano-sedimentary rocks of the Sub-Pelagonian zone (Koutsovitis et al., 2013).

West Othris area is located in Central Greece including a transition from continental to pelagic Mesozoic sedimentary rocks called Mirna Group (Hynes, 1974; Menzies and Allen, 1974; Smith et al., 1975; Smith, 1993; Tsikouras et al., 2009), occurrences of dismembered ophiolitic rocks (Tsikouras et al., 2009), as well as the Sipetorrema lava unit (Smith et al., 1975) and the Kournovon dolerite unit (Tsikouras et al., 2009). Rodingites occur as dykes of 5-20 cm width within the serpentinized harzburgite and can be divided into two groups based on the presence of significant amounts of well-formed calcite crystals (Tsikouras et al., 2009). The peridotitic rocks are in contact with an ophiolitic mélange consisting of dolerite, basalt, red chert and serpentinized peridotite, which overlies a Late Cretaceous-Tertiary flysch (Tsikouras et al., 2009).

Skyros is located in the central Aegean Sea and belongs to North Sporades island complex. It is composed of the Pelagonian tectonic zone, the Eohellenic tectonic nappe and the Skyros Unit. The Eohellenic nappe is overthrusted above the Pelagonian basement rocks and consists mainly of an ophiolitic mélange

(Katsikatsos, 1992; Pe-Piper and Piper, 2002). The Skyros ophiolite among others is composed of highly deformed serpentinite occurrences intruded by rodingite dykes (Karkalis et al., 2016), while other rocks include basaltic lavas, gabbroic rocks, doleritic dykes and ophicalcites.

3. Materials and Methods

In our research several samples from the rodingite core zones were collected for petrographical and geochemical investigations. The petrographic study was performed at the Department of Mineralogy and Petrology at the National and Kapodistrian University of Athens and was accomplished by the study of thin sections under the polar microscope. Several rodingite samples from the region of Kimi were analyzed for whole rock chemistry at ACME Laboratories in Canada using ICP-MS method.

4. Results

4.1. Petrography

Kimi rodingites are divided into two groups namely Group-I and Group-II that correspond to non-carbonated and carbonated dykes respectively. The core zones of both groups are rich in vesuvianite and garnet. Accessory minerals in both cases include diopside, chlorite, prehnite, opaque Fe-Ti-oxides, while Group-II rodingites additionally includes calcite within cavities of the rodingite matrix (Fig. 1b). Their textures range from cryptocrystalline to fine grained, characterized by idiomorphic garnet and vesuvianite grains. Chlorite and diopside, which are the main accessory phases appear intergranular between garnet grains. These rocks are crosscut by secondary metasomatic veins which mostly include fine grained garnet, clinopyroxene, chlorite and vesuvianite.

The Skyros rodingites (Karkalis et al., 2016) consist of hydrogarnet, vesuvianite, chlorite, diopside and prehnite. Their texture ranges from cryptocrystalline to fine grained, characterized from a garnet-chlorite rich groundmass, with prehnite porphyroblasts (Fig. 1a) and a few calcite occurrences. In addition, secondary metasomatic veins consisting of hydrogarnet, diopside usually crosscut the rodingite groundmass.

The East Othris rodingites are divided into two types (Koutsovitis et al., 2013). Type-1 rodingites mainly include prehnite, clinopyroxene (relict or secondary), amphibole, chlorite ± hydrogarnet ± pumpellyite ± white mica ± calcite. Hornblende is associated with clinopyroxene, while chlorite appears mainly intergranular between prehnite and amphibole or in the form of veinlets. Type-2 rodingites exhibit many similarities with both groups of Kimi rodingites. They mainly include hydrogarnet (± garnet), clinopyroxene and chlorite (± vesuvianite), while prehnite, pumpellyite, amphibole, calcite, Fe–Ti oxides, spinel and titanite can rarely occur. In many cases garnet appears as porphyroblast, (like in Kimi rodingites), whereas clinopyroxene can either appear as small neoblasts or relict grains replaced by garnet and chlorite. Vesuvianite occurs in the form of dispersed aggregates or within veinlets, whereas chlorite is usually present between garnet and clinopyroxene, which is also observed in Kimi rodingites.

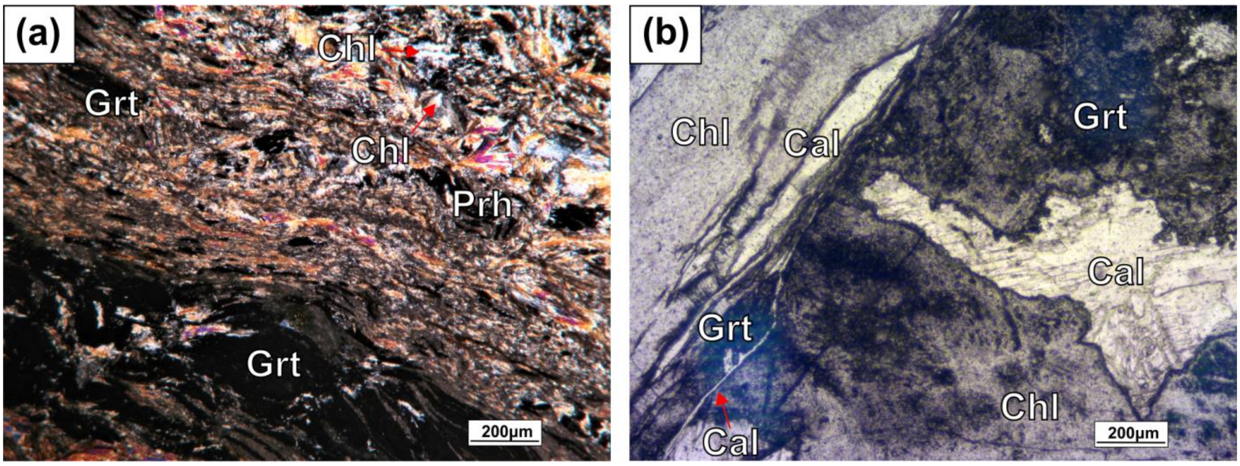

Fig. 1: Photomicrographs of: (a) Skyros rodingite, consisting of chlorite (Chl) garnet (Grt) and prehnite (Prh). (b) Group-II Kimi rodingite consisting mainly of a groundmass rich in chlorite (Chl) and garnet (Grt), with calcite (Cal) cavities and veins.

The West Othris rodingites are divided into two groups based on the presence of significant amounts of well-formed calcite crystals (Tsikouras et al., 2009). The calcite bearing subgroup mainly presents blasto-subophitic texture and doleritic origin. It is composed of clinopyroxene, chlorite, garnet, calcite, titanite ± ilmenite, whereas vesuvianite is difficult to be distinguished due to its anisotropic character and small size.

Table 1: Representative whole rock major and rare earth element (ppm) compositions of the studied rodingites from the region of Kimi. Major elements and Rare Earth Elements (REE) were measured by ICP-MS, b.d.l.: below detection limit.

Major Elements			**Rare Earth Elements**		
Sample	**EROD26M**	**EROD18**	**Sample**	**EROD26M**	**EROD18**
Rock Type	Rodingite	Rodingite	Rock Type	Rodingite	Rodingite
Group	Group-I	Group-II	Group	Group-I	Group-II
SiO_2	37.36	34.05	La	55.50	56.30
Al_2O_3	16.63	16.52	Ce	137.40	103.30
Fe_2O_3	2.55	0.22	Pr	14.43	10.31
MgO	4.75	1.67	Nd	45.80	35.50
CaO	34.47	38.14	Sm	11.93	6.50
Na2O	b.d.l.	0.05	Eu	0.43	1.28
K_2O	b.d.l.	b.d.l.	Gd	14.41	5.42
TiO_2	0.03	0.02	Tb	3.08	0.75
P_2O_5	0.01	0.02	Dy	23.03	4.25
MnO	0.23	b.d.l.	Ho	4.67	0.73
LOI	3.7	9.2	Er	14.47	2.13
Sum	99.79	99.91	Tm	2.24	0.30
TOT/C	0.06	2.29	Yb	15.08	1.81
TOT/S	b.d.l.	b.d.l.	Lu	2.03	0.30

The calcite-free subgroup mainly includes clinopyroxene + garnet + chlorite + titanite ± apatite. Clinopyroxene and garnet occur as local granoblastic segregations within the rodingite, while subhedral to euhedral neoblastic diopside overgrows garnet. In cases of chlorite dominance, the texture is lepidoblastic.

4.2. Whole rock Chemistry

Kimi rodingites exhibit higher CaO contents compared to those of Skyros and Othris regions, which generally present the highest and lowest SiO_2 contents respectively (Fig. 2a). The alkali contents are strongly depleted in Kimi-Evia, Skyros and West Othris rodingites, whereas the East Othris rodingites are less depleted (Fig. 2b). Rodingite samples have been plotted in the ACF ternary diagram (Fig. 3).

The Kimi-Evia and Skyros rodingites are evidently Ca-rich, which is further confirmed by their abundance in grossular, vesuvianite and usually calcite, while East and West Othris rodingites plot closer to the chlorite compositional field. Magmatic protoliths are absent from Kimi-Evia, and therefore geochemical comparisons were accomplished with the use of magmatic rocks from the areas of East Othris, West Othris and Skyros island. In all cases Kimi rodingites exhibit a clear enrichment in CaO and depletion in Na_2O and K_2O contents, a pattern which is also observed when comparing the Othris and Skyros rodingites with their magmatic protoliths.

The REE-Chondrite normalized patterns of the Kimi-Evia rodingites are characterized by their REE enrichment and high fractionation between LREE and HREE.

Specifically, the LREE (26.04-237.55 X CN) are higher than the MREE (2.49-108.94 X CN) and more comparable with the HREE (11.24-115.00 X CN). The negative Eu anomalies are in many cases significant ranging from 0.09 to 0.64. The rodingite from Skyros (Karkalis et al., 2016) displays similar patterns with the least enriched in REE rodingites from Kimi-Evia. West Othris rodingites (Tsikouras et al., 2009) exhibit similar MREE and HREE patterns with the least fractionated rodingites from Kimi-Evia and Skyros, whereas the LREE are significantly depleted.

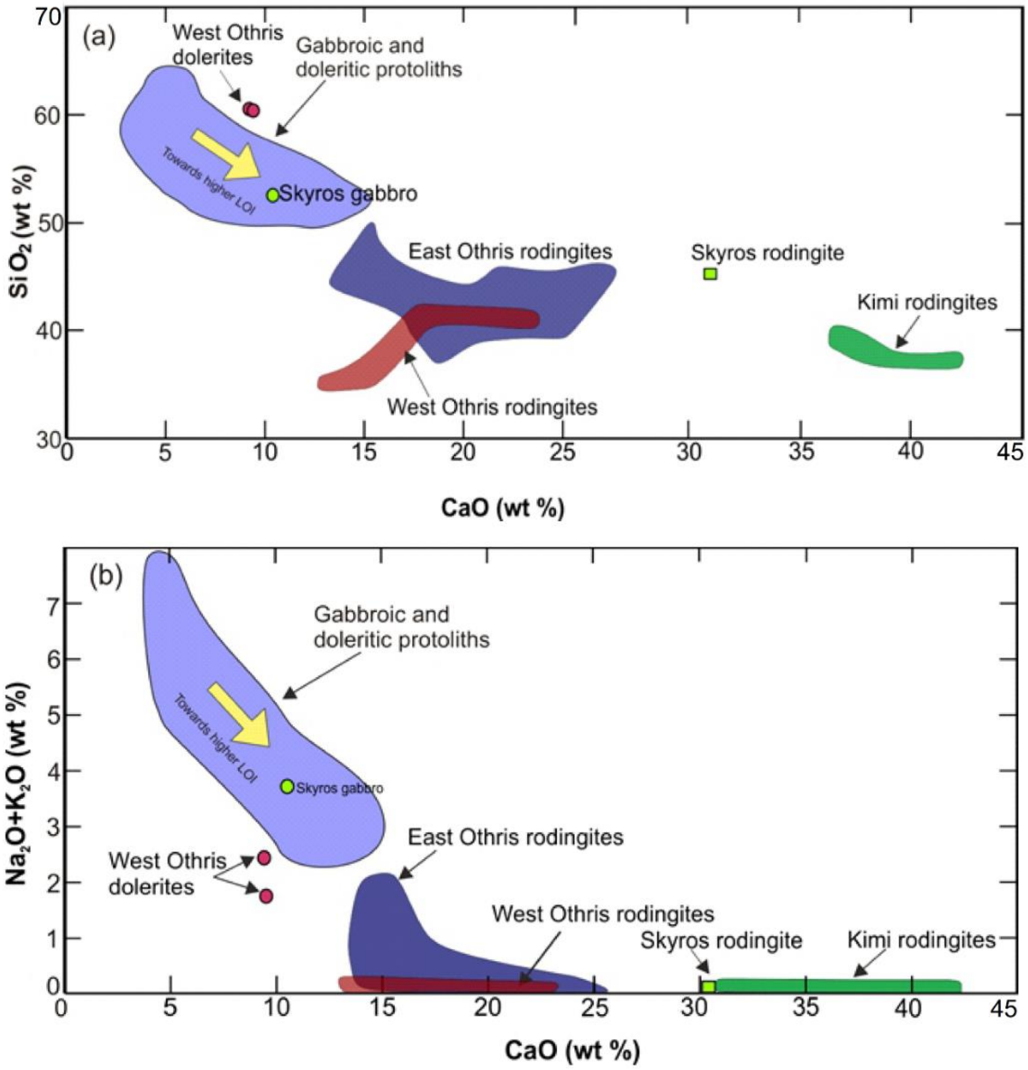

Fig. 2: Binary diagrams of (a) SiO_2 (wt.%) vs. CaO (wt.%) (b) Na_2O + K_2O (wt.%) vs. CaO (wt.%). Data plotted are from Koutsovitis et al. (2013) for East Othris; Tsikouras et al. (2009) for West Othris; Karkalis et al. (2016) for Skyros island rocks and Karkalis (2018) for Kimi-Evia rodingites.

They differ in presenting either positive or slightly negative Eu anomalies. The East Othris rodingites (Koutsovitis et al., 2013) display different REE-Chondrite normalized patterns compared to rodingites from the other three studied regions, since their ΣREE contents are much lower. These rocks have been derived from the rodingitization of boninitic rocks (Koutsovitis et al., 2013) and are also characterized by the absence of any significant Eu anomaly.

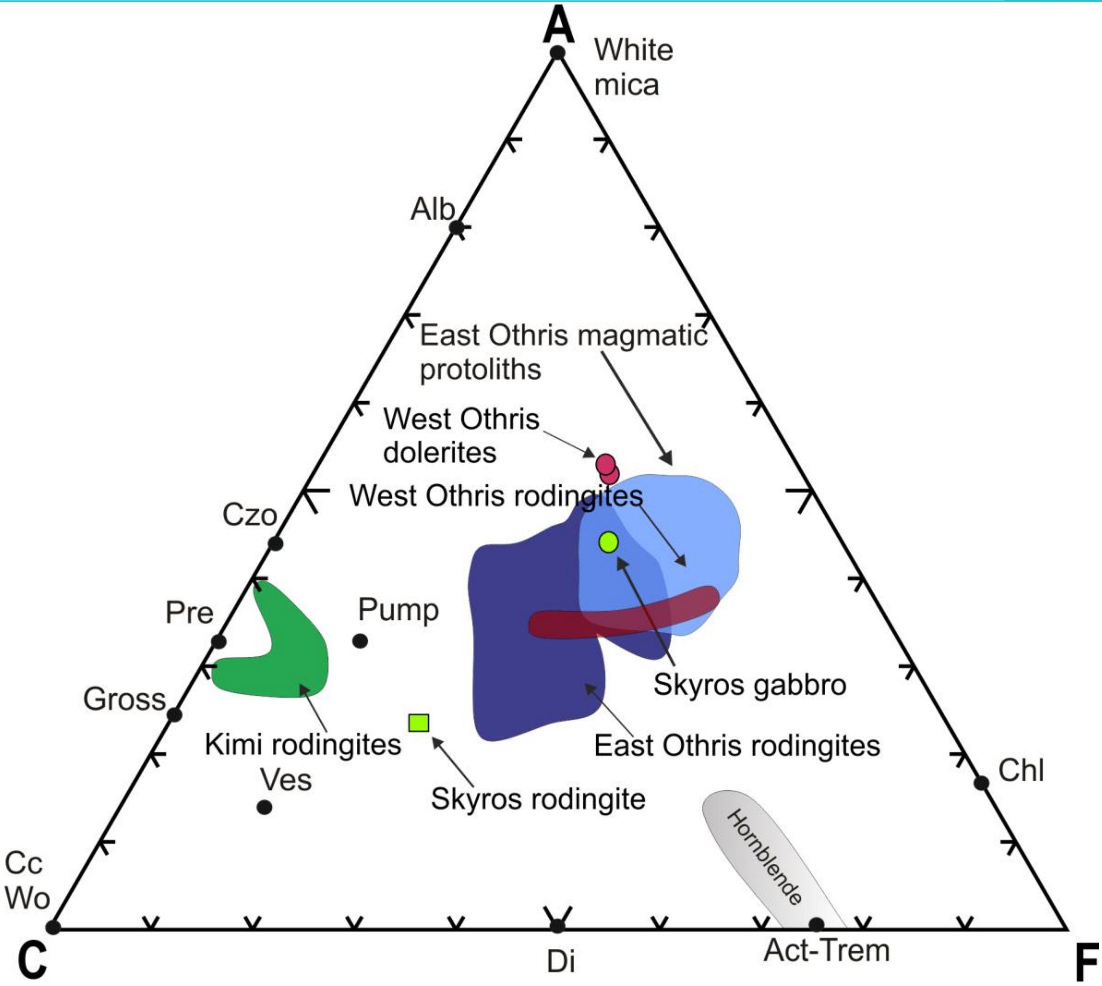

Fig. 3: ACF diagram for rodingites and their protoliths showing their compositional variations. Data plotted are from Koutsovitis et al. (2013) for East Othris; Tsikouras et al. (2009) for West Othris; Karkalis et al. (2016) for Skyros island rocks and Karkalis (2018) for Kimi-Evia rodingites.

5. Discussion

In accordance to the literature of rodingites internationally, Kimi rodingites exhibit a clear enrichment in CaO and depletion in SiO_2 and alkalis, which is also observed in rodingites from East and West Othris and Skyros island. Kimi rodingites present higher CaO contents compared to those of East-West Othris and Skyros, due to their higher amounts of hydrogarnet and vesuvianite, which is regarded as a late stage mineral phase during rodingitization (Li et al., 2007; Normand and Williams-Jones, 2007; Koutsovitis et al., 2013). Since rodingitization is highly associated with serpentinization processes, Ca^{+2} was released from the ultramafic serpentinized rocks during the clinopyroxene breakdown in the form of $CaOH^{+}$ (e.g. Coleman, 1977; Schandl et al., 1989; O' Hanley et al., 1992; O' Hanley, 1996; Schandl and Mittwede, 2001; Frost and Beard, 2007; Bach and Klein, 2009; Koutsovitis et al., 2013). However, an alternative scenario is proposed by Frost et al. (2008), who associates the CaO enrichment in rodingites with the silica release during anorthite breakdown, while Ca remains in quite high amounts. Silica release is indicative of clinopyroxene breakdown and feldspar dissolution of the gabbroic protoliths which form grossular and prehnite (Coleman, 1977; Schandl et al., 1989; O'Hanley et al., 1992; Schandl and Mittwede, 2001; Frost and Beard, 2007; Bach and Klein ,2009; Li et al., 2004, 2008; Koutsovitis et al., 2013).

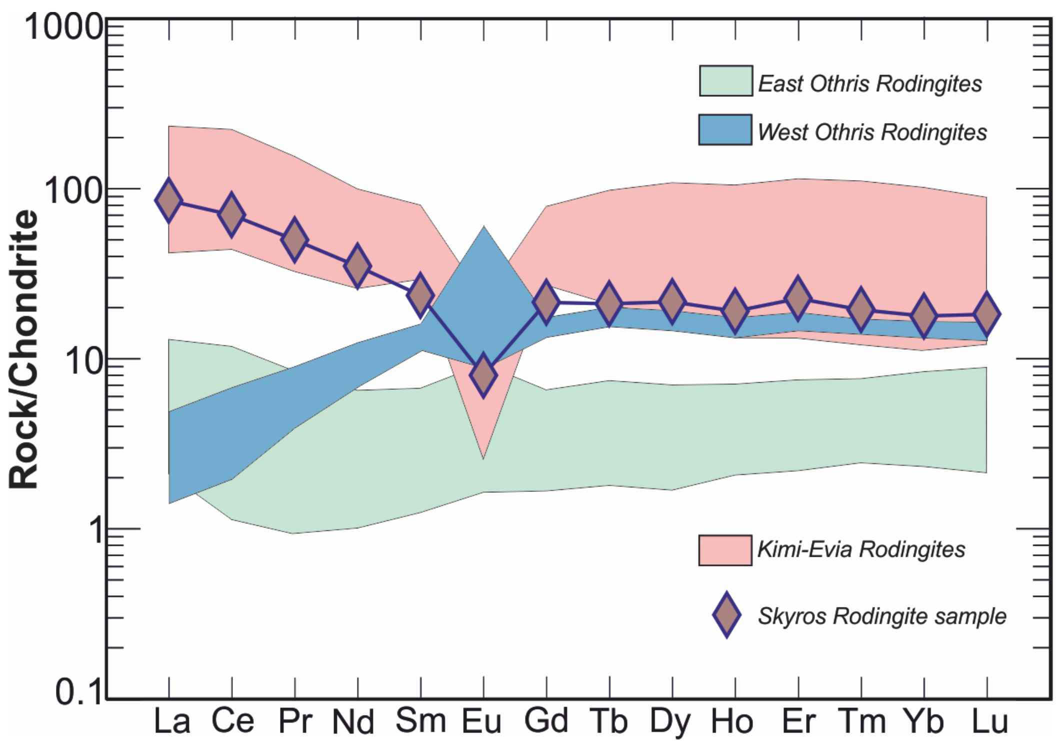

Fig. 4: Chondrite-normalized REE patterns [normalizing factors from McDonough and Sun (1995)] of the rodingite samples from the regions of Kimi (Evia island, Central Greece), Skyros island (Karkalis et al., 2016), West Othris (Tsikouras et al., 2009) and East Othris (Koutsovitis et al., 2013).

The source of REE is most probably that of the mafic protoliths, which is likely enhanced with the breakdown of plagioclase, but also pyroxene dissolution from the adjacent peridotites (Tsikouras et al., 2009). Regarding the REE enrichments noticed in the Kimi rodingites, compared to those of East-West Othris and Skyros island, it could be assumed that the main factor for the enhancement of the REE mobility is the effect of LREE-bearing carbonate complexes (e.g. Wendlandt and Harrison, 1979; Gimeno-Serrano et al., 2000; Tsikouras et al., 2009). These complexes are very soluble when calcite is formed, due to decrease of CO_3^{-2} activity (Caruso and Simmons, 1985; Tsikouras et al., 2009), resulting in LREE precipitation. Subsequently the presence of higher calcite amounts in Kimi rodingites compared to those of East-West Othris and Skyros island is most probably the main reason for the abundant LREE contents. Moreover, the presence of two distinct rodingite groups in the region of Kimi-Evia that correspond to carbonate-bearing and carbonate-free types, is indicative of the occurrence of two main metasomatic events, characterized by different XCO_2 conditions.

6. Conclusions

The present study provides a preliminary petrographical and geochemical comparison between rodingites among the areas of Kimi-Evia, Skyros island and Othris region. Rodingites of each area exhibit similar petrographical structures and mineralogical compositions, characterized by the presence of garnet, vesuvianite and calcite in various amounts. Based upon their whole rock chemical data, all rodingite samples exhibit sub-parallel HREE patterns, whereas their LREE patterns range among the different areas.

Rodingites of Kimi-Evia exhibit similar features with those of Skyros island, characterized by their highly comparable REE patterns with significant LREE enrichments. LREE mobilization was probably associated with leaching processes, where carbonic rich fluids promoted LREE transfer via CO_3^{-2} ligands.

On the other hand, the Othris rodingites are characterized by their depleted LREE contents, whereas East Othris rodingites exhibit much lower ΣREE contents compared to the other areas. Metasomatism in each case of the studied rodingites is strongly associated with serpentinization and was evolved in several metasomatic events, while vesuvianite was formed during the last metasomatic episode at relatively low temperatures. The presence of calcite in several rodingite samples from Kimi-Evia, accompanied with their high LREE contents is indicative of the XCO_2 importance in the metasomatic processes.

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