 doi:10.20944/preprints201806.0362.v1

Peer-reviewed version available at *Minerals* **2018**, *8*, 329; doi:10.3390/min8080329

Article

The Impact of Secondary Phyllosilicate Minerals on the Engineering Properties of Various Igneous Aggregates from Greece

Petros Petrounias [1]*, Panagiota P. Giannakopoulou[1], Aikaterini Rogkala[1], Paraskevi Lampropoulou[1], Eleni Koutsopoulou[1], Dimitrios Papoulis[1], Basilios Tsikouras[2] and Konstantin Hatzipanagiotou[1]

[1] Section of Earth Materials, Department of Geology, University of Patras, 265 04, Patras, Greece; peny_giannakopoulou@windowslive.com (P.P.G.); krogkala@upatras.gr (A.R.); p.lampropoulou@upatras.gr(P.L.); ekoutsop@upatras.gr (E.K); papoulis@upatras.gr (D.P.); k.hatzipanagiotou@upatras.gr (K.H.)

[2] Physical and Geological Sciences, Faculty of Science, Universiti Brunei Darussalam, Jalan Tungku Link, Gadong BE1410, Bandar Seri Begawan, Brunei Darussalam; basilios.tsikouras@ubd.edu.bn;

* Correspondence: Geo.plan@outlook.com

Abstract: This paper investigates the effect of alteration on the physicomechanical properties of igneous rocks from various areas from Greece used as aggregates. The studied lithologies include dunites, harzburgites, lherzolites, gabbros, diabases, dacites and andesites. Quantitative petrographic analysis shows that the tested samples display various percentages of secondary phyllosilicate minerals. Mineral quantification of studied rock samples was performed by using a Rietveld method on X-Ray diffraction patterns of the studied aggregates. The aggregates are also tested to assign moisture content [w (%)], total porosity [n_t (%)], uniaxial compressive strength [UCS (MPa)] and Los Angeles abrasion test [LA (%)]. The influence of secondary phyllosilicate minerals on physicomechanical behavior of tested samples determined using regression analysis and their derived equations. Regression analysis shows positive relationship between the percentage of phyllosilicate minerals of rocks and moisture content as well as with the total porosity values. The relationships between phyllosilicate minerals in the ultramafic and mafic samples and their mechanical properties show that the total rates of phyllosilicate mineral products result negatively in their mechanical properties, while the low percentage of phyllosilicate minerals in volcanic rocks are not able to define set of their engineering parameters.

Keywords: phyllosilicate minerals; serpentine; chlorite; clay minerals; aggregates; physicomechanical properties

---

1. Introduction

Building aggregates are essential raw materials for the construction industry. They are crushed rocks with a key role in creating, maintaining and enhancing the built up environment. The physicomechanical properties of aggregate rocks are significant parameters in any application and in their classification for engineering purposes. The increased number of construction failures has highlighted the importance of understanding mineralogy as a mean to diagnose problems in engineering constructions. Physicomechanical properties depend on the mineralogy, texture (size, shape and arrangement of mineral grains, nature of grains contact, and degree of grain interlocking), alteration and deformation degree of the source rock [1-6]. The mineralogical composition of the aggregates and more specifically their alteration degree strongly influences their mechanical behaviour and in-service performance [7-10]. Increased percentages of certain secondary minerals, such as serpentine, chlorite, talc and smectite affect negatively the physical as well as the mechanical properties of ultramafic aggregates due to their smooth layers, cleavage and platy or fibrous crystal habit [11-14].

Primary minerals form during the original solidification (crystallization) of rocks. They include both the essential minerals used to assign a classification name to the rock as well as the accessory minerals presented in lesser abundance. Secondary minerals are formed in a further stage through which processes such as weathering and hydrothermal alteration take place. Fresh igneous rocks without having sustained weathering or hydrothermal alteration have sufficient strength to meet any engineering requirement however; the effect of ocean-floor metamorphism variously changes their physico-mechanical properties [7]. Hydrothermal alteration can be isochemical, like metamorphism and dominated by mineralogical changes, or metasomatic and results in significant addition or removal of elements. Intense alteration can results in significant volume changes, hence that mass balance approaches using immobile elements are required to fully understand the alteration process [15].

In the present study the main alteration products are phyllosilicate minerals. Phyllosilicates are an important group of minerals which includes micas and clay minerals. The basic structure of the phyllosilicate is based on interconnected six member rings of SiO_4^{-4} tetrahedral that extend outward in infinite sheets. Three out of the 4 oxygens from each tetrahedral are shared with other tetrahedral. This leads to a basic structural unit of $Si_2O_5^{-2}$. Various studies about the occurrence and the transformations of such phyllosilicates have been published in the last 55 years. The collected samples are ultramafic, mafic and volcanic rocks which have been exposed to supergene conditions [16-20] and diagenetic or metamorphic conditions. Phyllosilicate minerals are built of varying proportions of tetrahedral (T) and octahedral (O) layers which are the basic building blocks of this group of minerals. These variations in co-ordination result in minerals of relatively similar structures but of different physical and chemical properties. As a result, there have been many different classifications of phyllosilicate group minerals reported in literature [21]. In this study, the phyllosilicate minerals were studied as alteration products from each different petrographic group, namely ultramafic, mafic and volcanic rock group. This classification allows the comparison of serpentine, mica and swelling clay minerals (vermiculites and smectites), which show a gradual increase in complexity with regards to minerals structure.

Serpentine is the main alteration product of ultrabasic rocks, while chlorite may also be present in minor amounts. Serpentine group and specifically chrysotile is a complex phyllosilicate mineral with a non-typical fibrous morphology. It was proven to be particularly weakness with regards to its mechanical behavior [22]. Serpentinization is the most important alteration process occurring in ultramafic rocks, which accompanies the formation of the ocean floor [4]. During this process, olivine and pyroxene transform to serpentine, a laminate soft mineral which belongs to the phyllosilicate subclass of minerals and forms smooth surfaces [23, 24]. First-order changes to the major element composition of peridotites induced by serpentinization are the addition of 10–12 w_t% water and loss of CaO [25-27]. Chlorite is the most common and abundant altered mineral product of heated seawater-basic rocks of substantive changes in the Ca/Mg ratio of the reacting fluid. Chlorites have been extensively studied in metamorphic, igneous rocks [28,29], sedimentary rocks [30,31] and in geothermal systems and hydrothermal ore deposits [32-34]. The presence of chlorite in aggregates is known to have a critical effect on the freeze-thaw durability of concrete. Clay minerals are the commonest secondary minerals in volcanic rocks (e.g. andesites, rhyodacites). Clay group minerals show a high capacity to absorb and subsequently lose water, which is accompanied by swelling and shrinkage, respectively [35]. Therefore, the capacity of clay minerals to absorb large amounts of water, preferentially along their eminent cleavage, increases the demand of water in a concrete mix, which in turn may have a detrimental impact in the workability of concrete and hence to lead to a weaker and more permeable hardened concrete [32]. Generally, clays are also thought to reduce workability, due to their high surface areas and lamellar structure. Clay minerals have low strength and as a result, if they are present as a coating on aggregates, they might disrupt the bond between the aggregate and the cement paste of the produced concrete. For these reasons, it is of great importance to determine the presence of clay minerals in the aggregates [36-40].

X-ray Diffraction (XRD) is considered the best technique to identify and quantify all minerals present in the studied rock samples. The Rietveld refinement method in XRD quantitative phase analysis has presented advantages over conventional methods [36-40]. The knowledge of the proportion of each phase is an important requirement in assessing the potential use of rocks as aggregates.

This study aims to investigate the effect of petrographic characteristics on aggregate performance based on the results of physicomechanical tests and quantitative analysis of mineralogical composition by the Rietveld method in bulk XRD patterns. More specifically, this paper focuses on the relationship between the engineering properties of the studied aggregates and the ocean-floor alteration products for ultramafic and mafic rocks, as well as the weathering processes products in volcanic rocks including mainly the type and percentage of phyllosilicate minerals.

2. Geological setting

In this study, representative ultramafic and mafic rocks deriving from 4 ophiolite complexes of Greece and volcanic rocks from their surrounding areas are collected in order to study the influence of their alteration degree and especially the impact of their phyllosilicate secondary minerals on their physicomechanical properties. The Veria-Naousa ophiolite complex is located in northern Greece and belongs to Almopias subzone of the Axios geotectonic zone. This complex consists, from base to top, from intense serpentinized lherzolite and harzburgite, interfered by few pyroxenitic dykes [41], as well as gabbro, diabase and pillow basalt. A large number of joints indicate that serpentinized peridotites are highly affected by tectonic processes. The Edessa ophiolites represent remnants of oceanic lithosphere which was thrust out of one or more ocean basins during Upper Jurassic to Lower Cretaceous time [42, 43]. They are tectonically very complex and consist of several tectonic units [44, 45]. The ophiolitic complex includes lherzolite, serpentinized harzburgite with high degree of serpentinization, diorite, gabbro, diabase and basalt. It is dismembered and scattered due to the intensive tectonism. Volcanic rocks are east of the ophiolitic complex and they belong to the Almopias subzone. They are created during pliocenic time and isotopes Sr-Nd method shows that the petrogenesis is of these Pliocene volcanic rocks associated with tectonic environment over SSZ subduction zone for partial melting occurred in the mantle wedge [46, 47]. Gerania complex which belongs to the Pelagonian geotectonic zone is an incomplete and dismembered ophiolite sequence consisting mainly of harzburgite, lherzolite and dunite variably altered [48-50]. The serpentinized peridotites are interrupted by gabbro dykes. The Middle-Late Jurassic Guevgueli Complex represents one of the main ophiolitic complexes of the Vardar Zone and has been sub-divided into two distinct sub-units, which are the East and the West Guevgueli, both including intrusive and volcanic sequences crosscut by several dykes. This complex is intruded by the Fanos Granite and with this together, is sandwiched, through a north-south striking thrust zone, between the Serbomacedonian Massif, to the east, and the Paikon Unit, to the west. The gabbroic rocks of both West and East Guevgueli include olivine gabbro, amphibole gabbro and diorite and their fine-grained varieties (diabases) [51, 52]. The Ag. Theodori volcanic rocks, derived from Crommyonia mark of the western end of the south Aegean volcanic arc includes outcrops of Pliocene dacites which appear spatially related to extensional faults at the margin of the Saronicos basin [53].

3. Materials and Methods

Ultramafic, mafic and volcanic samples from the studied areas were collected according to EN 932-1 [54] standard. Petrographic features of studied samples were examined using a combination of petrographic methods. The mineralogical and textural characteristics of the samples were examined on thin sections using a polarizing microscope (Leica Microsystems Leitz Wetzlar, Germany) according to EN-932-3 [55] standard for petrographic description of aggregates. The mineralogical composition of the studied samples was determined with X-Ray Diffraction. The XRD method took place by using a Bruker D8 advance diffractometer, with Ni-filtered CuKα radiation. Random powder mounts were prepared by gently pressing the powder into the cavity holder. The scanning

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 22 June 2018 doi:10.20944/preprints201806.0362.v1

Peer-reviewed version available at *Minerals* **2018**, *8*, 329; doi:10.3390/min8080329

area for bulk mineralogy of specimens covered the 2θ interval 2–70°, with a scanning angle step size of 0.015° and a time step of 0.1 s. The <2 μm clay fraction was separated by settling and dried on glass slides at room temperature. For each < 2 μm specimen, the clay minerals were scanned from 2 to 30° 2θ and identified from three XRD patterns (after air-drying at 25°C, after ethylene glycol treatment and heating at 490°C for 2 h). The mineral phases were determined using the DIFFRACplus EVA 12® software (Bruker-AXS, USA) based on the ICDD Powder Diffraction File of PDF-2 2006 while the semi-quantitative analyses was performed by TOPAS 3.0 ® software, based on the Rietveld method refinement routine. The routine is based on the calculation of a single mineral-phase pattern according to the crystalline structure of the respective mineral, and the refinement of the pattern using a non-linear least squares routine. The quantification errors were calculated for each phase according to Bish and Post [37].

Samples in the form of grains were gold coated and analyzed by using Secondary Electron Images (SEI) to determine the surface texture of their microroughness according to BS 812 Part 1 [56] which outlines six qualitative categories, e.g. glassy, smooth, granular, rough, crystalline, honeycomb and porous.

The engineering/physicomechanical properties of ultramafic, mafic and volcanic rocks were determined by the following laboratory tests: moisture content, total porosity, uniaxial compressive strength, Los Angeles abrasion value. Moisture content (w) is an important physical parameter for the quality of aggregates. In this study moisture content (w) was examined in accordance to the AASHTO T-255 [57] standard. Total porosity (nt) is a basic factor for rock strength, as a small change in pore volume can leads to an appreciable mechanical effect. This test was calculated by using specimens of rocks according to the I.S.R.M 1981[58] standard. The Los Angeles abrasion (LA) test, measures the resistance of an aggregate in abrasion, attrition and grinding. This test was carried out in accordance to the ASTM C-131 [59] standard using the "B" gradation. The uniaxial compressive strength (UCS) is one of the most significant engineering properties of rocks. The UCS test was carried out on 6 cylindrical rock specimens with height/diameter ratio between 2 and 3, and their diameters ranging from 51 to 54 mm (ASTM D-2938 [60]) for the elaboration of uniaxial compressive strength test, and the average values were used for each set of specimens.

4. Results

4.1. Petrographic features

Thin sections from each sample were examined using a petrographic microscope. The studied ultramafic samples comprise serpentinized dunite (GE.37), harzburgite (ED.59, ED.115) and lherzolite (BE.103, GE.42) with variable degrees of serpentinization. Dunite presents cataclastic and locally granular textures. Primary assemblage includes mostly olivine (forsteritic) and scarce relic crystals of orthopyroxene (Figure 1a). Infrequent opaque minerals (mainly chromite) are present, too. The primary assemblage of the harzburgite constitutes less than 20% of the mode and comprises relics of orthopyroxene, rare clinopyroxene, olivine and Cr-spinel. The lherzolite shows cataclastic, porphyroclastic and locally protogranular textures, the primary assemblage includes olivine (forsteritic), orthopyroxene and clinopyroxene. Opaque minerals (mainly Al-spinel) are present in small amounts. Serpentine is the main alteration product of all samples (Figure 1b), showing mesh, ribbon, bastite and intersertal textures. Chlorite, talc and magnetite are also products of hydrothermal alteration.

The studied mafic samples comprise diabase (BE.43, ED.110, KIL.2 and KIL.3), low grade metamorphism gabbro (ED.26) and low grade metamorphism diabase (ED.24). The low grade metamorphism gabbro consists mainly of clinopyroxene (Figure 1c) and presents high percentage of chlorite. The chlorite displays large crystals which are unevenly distributed in the structure of the studied sample. Primary textures have been obliterated by deformation. The diabase samples exhibit porphyritic, ophitic and subophitic textures. The mineral assemblage is similar to that of gabbros including clinopyroxene and subhedral plagioclase. In some cases the plagioclase is partially to completely transformed to sericite. Ilmenite, magnetite, titanite and zircon are present in small amounts, less than 5% of the mode. Chlorite, actinolite, epidote and prehnite are considered as secondary phases (Figure 1c). Among the secondary minerals, chlorite presents uniform distribution in diabases (BE.43, ED.110, KIL.2), filling up the gaps existing due to the subophitic texture which is dominant in this lithology (Figure 1c).

The studied volcanic samples comprise dacite (GE.22, GE.23) and andesite (BE.81, BE.82 and BE.101) with variable degrees of alteration. Dacite shows porphyritic texture. It is dominated by quartz, plagioclase, hornblende, biotite and sanidine. The quartz is usually rounded and displays sharp boundaries to the matrix. Andesite has distinct porhyritic texture and is characterized mainly by the presence of mostly tabular sanidine phenocrysts. It is rich in clinopyroxene and biotite phenocrysts set in a holocrystalline groundmass of fluidal texture (Figure 1f). Plagioclase phenocrysts occur in all samples and are strongly zoned showing normal and oscillatory reverse zoning. Biotite is ubiquitous, showing intensive pleochroism in the shade of straw yellow to dark brown-reddish. Common accessory minerals include apatite, titanite, zircon and magnetite.

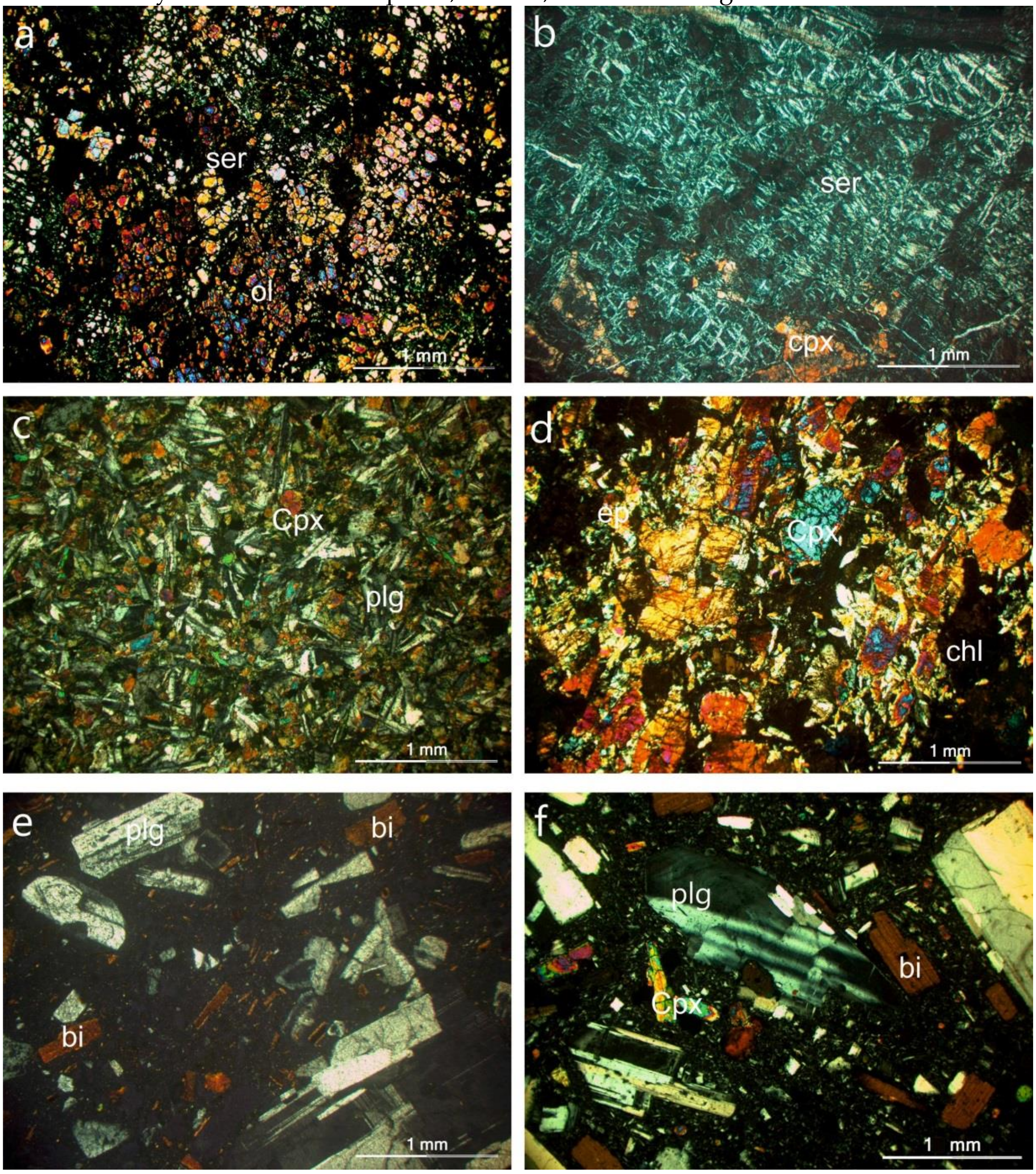

Figure 1. Photomicrographs of: (**a**) Granular and cataclastic texture in a dunite clinopyroxene (sample GE.17, XPL); (**b**) Mesh texture in a serpentinized lherzolite (sample BE.103, XPL); (**c**) diabase showing subophitic texture with clinopyroxene and plagioclase crystals (sample KIL.2); (**d**) Low grade metamorphism gabbro where clinopyroxene has been altered to epidote and chlorite (sample ED.26, XPL); (**e**) Dacite showing porphyritic texture with phenocrysts of plagioclase and biotite (sample GE.22, XPL); (**f**) Andesite showing porphyritic texture with phenocrysts of plagioclase, biotite and

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 22 June 2018 doi:10.20944/preprints201806.0362.v1

Peer-reviewed version available at Minerals 2018, 8, 329; doi:10.3390/min8080329

clinopyroxene (sample BE.81, XPL); ep: epidote, cpx: clinopyroxene, chl: chlorite, ser: serpentine, plg: plagioclase, bi: biotite, ol: olivine.

4.2. X-Ray Diffraction and Quantitative analysis of aggregates

Representative XRD patterns of samples from all the studied lithologies are shown in Figure 2. The XRD patterns of random powder mounts from the studied ultramafic rocks revealed that serpentine is the main alteration product in all samples (Table 1). In serpentinized dunite (GE.37), olivine, orthopyroxene, spinel and traces of magnetite and talc are also present in full accordance with the petrographic studies. In serpentinized harzburgite samples (ED.59, ED.115), serpentine is abundant; magnetite and spinel appear as minor mineral phases. Chlorite is also present in sample ED.59 and clinopyroxene in ED.115. In serpentinized lherzolite samples (BE.103, GE.42) serpentine is the main phase, clinopyroxene, garnet and spinel are present. Traces of chlorite are also present in sample GE.42.

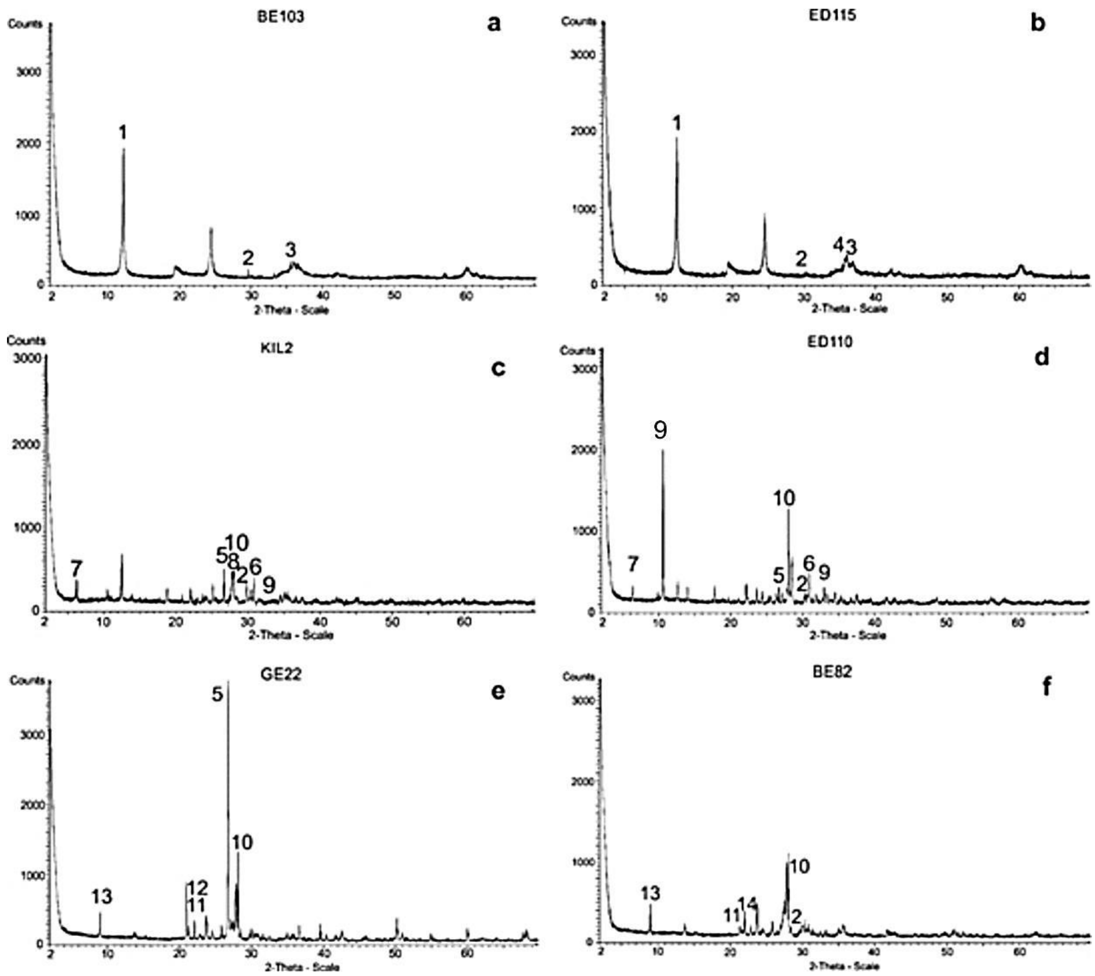

Figure 2. X-ray diffraction patterns of representative aggregate rocks: (**a**) Serpentinized lherzolite (sample BE.103); (**b**) Serpentinized harzburgite (sample ED.115); (**c**) Diabase (sample KIL.2); (**d**) Diabase (sample ED.110); (**e**) Dacite (sample GE.22); (**f**) Andesite (sample BE.82); 1:serpentine, 2: clinopyroxene, 3: spinel, 4: magnetite, 5: quartz, 6: epidote, 7: chlorite, 8: titanite, 9: actinolite, 10: plagioclase, 11:K-feldspars, 12: chromite, 13: mica, 14: hematite.

Representative X-Ray diffraction patterns of the clay fraction from all types of lithologies are presented in Figure 3. The clay fraction of serpentinized peridotites is dominated by serpentine and locally talc. Chlorite was also present in serpentinized harzburgites. The clay fraction of low grade metamorphism mafic rocks consists mainly of chlorite. Smectite and Illite were identified in andesites

Peer-reviewed version available at *Minerals* **2018**, *8*, 329; doi:10.3390/min8080329

and dacites. Serpentine and talc are identified by the characteristic reflections at 7.3A° and 9.3A° respectively, which are not affected upon ethylene glycol treatment. Chlorite shows the characteristic reflections at 14.2A°, 7.1A° and 3.55A°, which remain unaffected after ethylene glycol treatment. Illite is identified by the reflections at 10A°, 4.97A°, 4.48A° and 3.3A°. Smectite is identified by the characteristic reflection at 15.4A° and at 17A° after ethylene glycol treatment which shifts at 10A° after heating.

In the ultramafic rock samples the dominant secondary mineral is serpentine (Table 1) and only in two of the studied samples secondary chlorite has been detected (Samples ED.59 and GE42). Smectite could not be identified neither on bulk nor by clay fraction sample analysis due to its minor percentage (below detection limits). Also in mafic rock samples the dominant secondary mineral is chlorite. The amount of smectite (if present) in the samples of these lithologies is below the detection limit in all samples.

In the volcanic rock samples the percentage of smectite increases compared to the other lithologies. As can be seen from Table 1 and clay fraction patterns the sample BE.82 presents containing of 2.8% montmorillonite, in contrast to sample BE.101 which presents contains only 0.4% montmorillonite (Table 1, Figure 3).

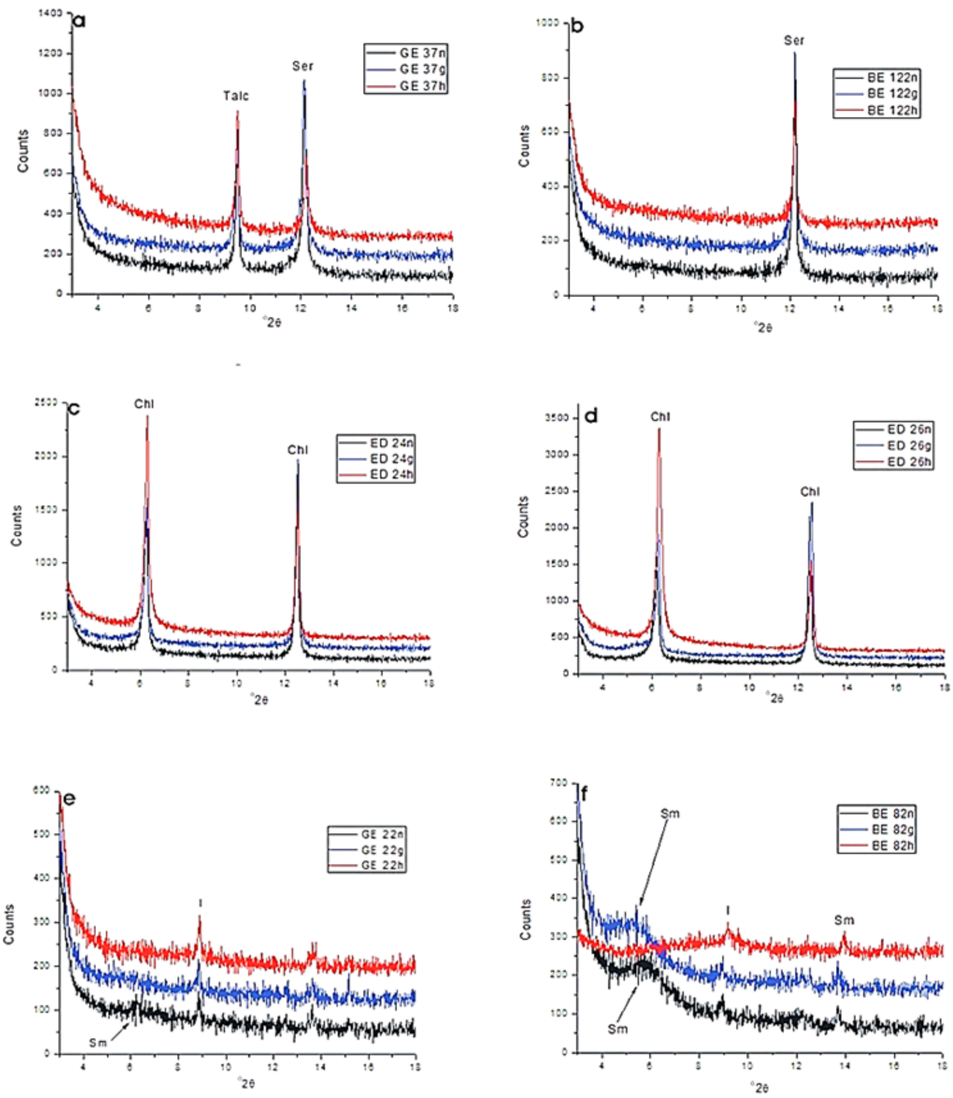

Figure 3. X-ray diffraction patterns of the clay fraction of representative studied samples: (**a**) Dunite (sample GE.37); (**b**) Serpentinized harzburgite (sample BE.122); (**c**) Diabase (sample ED.24); (**d**) Gabbro (sample ED.26); (**e**) Dacite (sample GE.22); (**f**) Andesite (sample BE.82); sample numbers are given in the inserts (n: air-dried, g: glycolated, h: heated, Sm: smectite, I: illite, Ser: serpentine, Talc: talc, Chl: chlorite).

Peer-reviewed version available at Minerals 2018, 8, 329; doi:10.3390/min8080329

The quantification results of the mineralogical composition from the studied aggregate rocks, by the Rietveld method in bulk and clay fraction XRD patterns, are presented in Table 1. The obtained compositions are consistent with the petrographic observations under the polarizing microscope.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 22 June 2018 doi:10.20944/preprints201806.0362.v1

Peer-reviewed version available at *Minerals* **2018**, *8*, 329; doi:10.3390/min8080329

Table 1. Mineralogical composition of the studied rock samples (-: not detected). The quantification errors calculated for each phase according to Bish and Post [37] are estimated to be ~1%.

Samples	ED.59	ED.115	BE.103	GE.42	GE.37	BE.43	ED.26	ED.24	ED.110	KIL.2	KIL.3	BE.82	GE.22	GE.23	BE.81	BE.101
Ol	-	-	-	-	43.7	-	-	-	-	-	-	-	-	-	-	-
Opx	-	-	-	-	3.9	-	-	-	-	-	-	-	-	-	-	-
Cpx	-	1.1	5.1	5.5	-	6.6	26.5	27.0	3.1	25.9	19.4	7.6	-	-	8.7	5.9
Sp	5.3	7.1	6.5	5.0	6.3	-	-	-	-	-	-	-	-	-	-	-
Qtz	-	-	-	-	-	6.0	-	-	2.1	5.1	4.2	-	30.5	15.8	-	-
Plg	-	-	-	-	-	46.5	2.0	-	46.0	39.9	51.1	52.8	31.0	45.7	55.1	56.2
Kfs	-	-	-	-	-	-	-	-	-	-	1.3	25.2	30.5	19.4	25.1	30.1
Bi	-	-	-	-	-	-	-	-	-	-	-	5.6	2.1	9.4	6.1	2.4
Ttn	-	-	-	-	-	2.5	4.1	2.5	-	1.7	0.9	-	-	-	-	-
Ilm	-	-	-	-	-	-	2.0	-	-	-	-	-	-	-	-	-
Mgt	5.7	3.2	-	-	4.6	4.0	-	-	-	-	-	-	-	-	-	-
Hem	-	-	-	-	-	-	-	-	-	-	-	2.0	-	-	1.0	1.1
Ap	-	-	-	-	-	2.4	-	-	-	-	-	-	-	-	-	-
Crs	-	-	-	-	-	-	-	-	-	-	-	-	2.0	4.8	-	-
Ser	84.0	88.6	87.0	83.0	35.0	-	-	-	-	-	-	-	-	-	-	-
Chl	5.0	-	-	4.0	-	10.0	25.0	23.0	7.2	9.6	7.2	-	-	-	-	-
Act	-	-	-	-	-	15.0	-	-	33.2	6.8	9.4	-	-	-	-	-
Ep		-	-	-	-	6.5	21.8	27.5	8.4	11.0	6.5	-	-	-	-	-
Talc	-	-	-	-	6.5	-	-	-	-	-	-	-	-	-	-	-
Prh	-	-	-	-	-	-	8.3	20.0	-	-	-	-	-	-	-	-
Pmp	-	-	-	-	-	-	10.3	-	-	-	-	-	-	-	-	-
Ath	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Grt	-	-	1.4	2.5	-	-	-	-	-	-	-	-	-	-	-	-
Il	-	-	-	-	-	-	-	-	-	-	-	3.8	2.5	4.2	3.1	3.9
Sm	-	-	-	-	-	-	-	-	-	-	-	2.8	1.4	0.7	0.9	0.4

4.3. Scanning Electron Microscopy (SEM)

4.3.1. Surface texture of the studied aggregates

Surface texture is an expression of the microroughness of aggregate particles, and mainly depends on the petrographic features of rocks. The surface textures of the aggregate particles were studied using secondary electron images (SEI). Differences in microroughness are apparent between different lithotypes (ultramafic, mafic and volcanic rock samples). The surface of the particles appears rough microroughness with decreasing alteration degree (Figure 4).

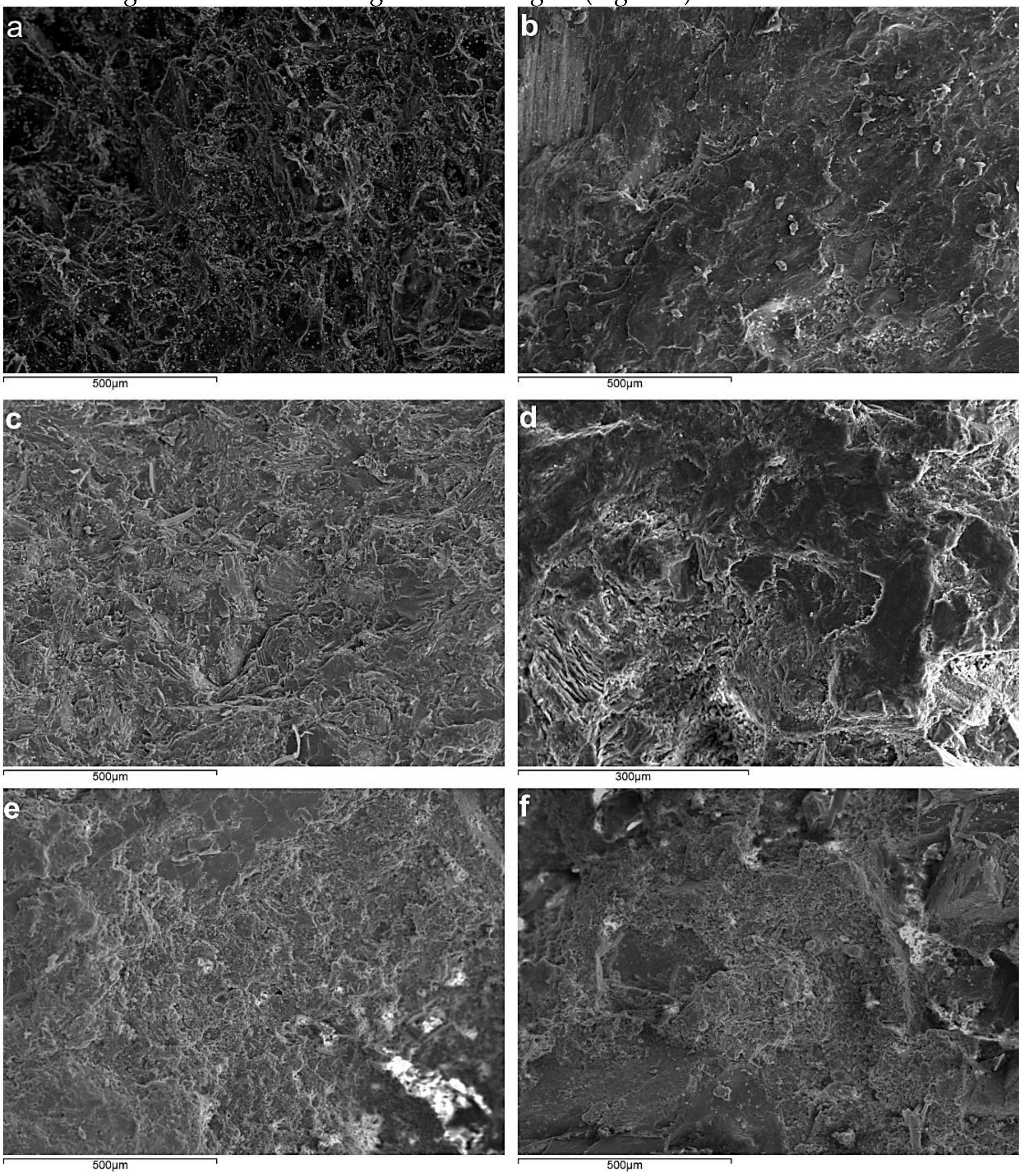

Figure 4. Back scattered images showing the surface texture of representative studied rocks. Differences in the mineralogical and textural features are also observed: (**a**) Harzburgite (sample GE.28); (**b**) Lherzolite (sample BE.103); (**c**) Diabase (sample KIL.2); (**d**) Low grade metamorphism gabbro (sample ED.26); (**e**) Andesite (sample BE.101); (**f**) Andesite (sample BE.82).

Peer-reviewed version available at *Minerals* **2018**, *8*, 329; doi:10.3390/min8080329

4.3.2. SEM study of clay minerals

Selected samples were observed by SEM for the study of smectite. The selected samples were those that smectite was identified using XRD analysis. The study revealed (Figures 5a-d) that typical smectite morphology can be observed only in the volcanic samples (BE.101, GE.23). The smectite flakes that were identified are formed as the result of the partial alteration of plagioclase surfaces in volcanic rocks (Figures 5c and d). The limited alteration that was observed is in agreement with the low amount of smectite. It should be noted that a number of EDS analyses were performed on the surfaces of the samples but the results cannot conclusive due to the small size of the smectite flakes and the low amount of smectite (the analyses were not only from smectite but also from the surrounding minerals). Despite that the characteristic smectite (Figs 5a-d) images in the surface aggregate particles may determine any engineering construction.

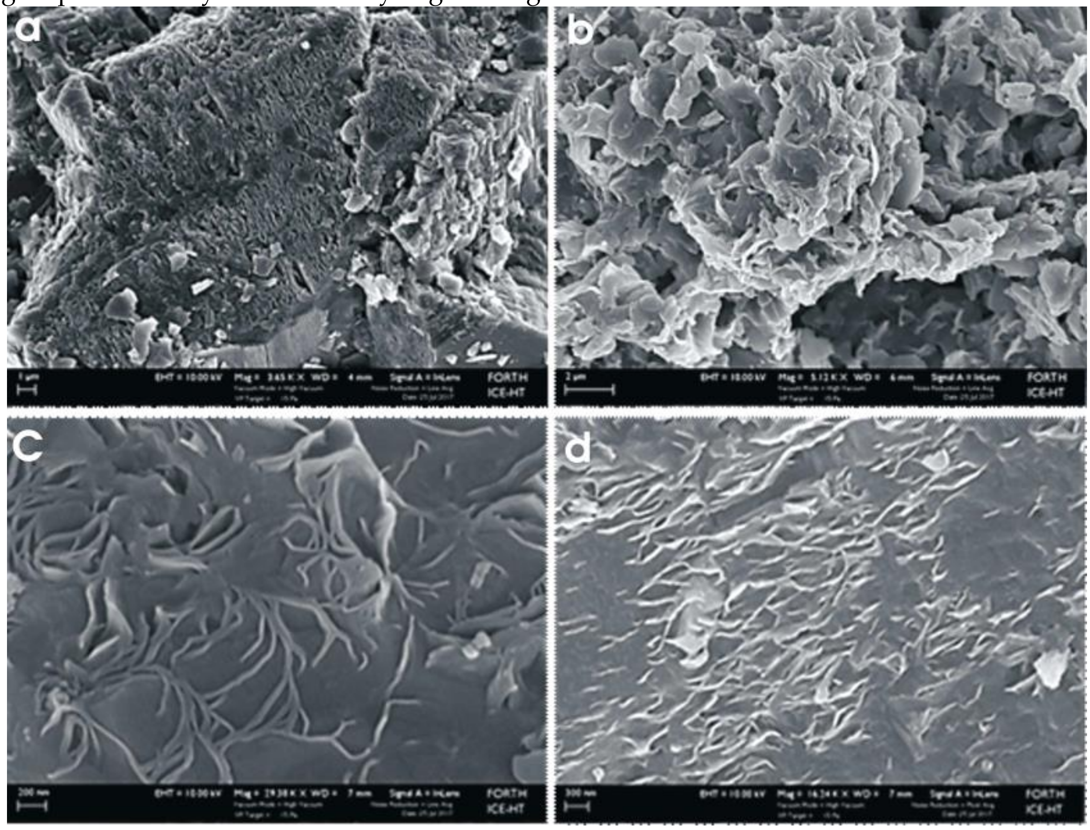

Figure 5. (**a**), (**c**) Smectite flakes on plagioclase surfaces of andesite (sample BE.101); (**b**), (**d**) Characteristic smectite flakes on plagioclase crystals of dacite (sample GE.23).

4.4. Physicomechanical properties of aggregates

The moisture content, the total porosity, the Los Angeles abrasion value and the uniaxial compressive strength of the studied aggregate rocks were determined. As shown in the table below (Table 2), the moisture content ranges between 0.20 and 2.13%, with dacite (GE.23) having the highest value. The total porosity ranges between 0.48 and 11.93%, with dacite (GE.22) having the highest value. Concerning the Los Angeles abrasion test, the resistance in abrasion of the studied rocks ranges between 7.31 and 58.04%, with the diabase (ED.110) presented as the most resistant in abrasion compared to the altered dacite which is the less resistant aggregate. The uniaxial compressive strength of the tested rocks ranges between 20 MPa and 148 MPa, where the most serpentinized harzburgite (ED.59) presents the lower strength and a lightly altered diabase is the most durable aggregate rock (ED.110).

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 22 June 2018 doi:10.20944/preprints201806.0362.v1

Peer-reviewed version available at Minerals 2018, 8, 329; doi:10.3390/min8080329

Table 2. Physical and mechanical properties of tested samples.

Samples	Lithology	w (%)	n_t (%)	LA (%)	UCS (MPa)
BE.103	Lherzolite	1.94	4.99	28.97	32.00
GE.37	Dunite	0.43	0.76	17.36	100.00
ED.59	Harzburgite	1.52	6.29	40.36	20.00
ED.115	Harzburgite	2.10	4.53	20.77	28.00
GE.42	Lherzolite	1.60	4.00	25.62	38.00
BE.43	Diabase	0.25	0.53	8.72	150.00
ED.26	Gabbro	0.60	1.74	20.68	65.00
ED.24	Diabase	0.52	0.84	14.15	91.33
ED.110	Diabase	0.20	0.86	7.31	148.00
KIL.2	Diabase	0.20	0.66	9.31	122.34
KIL.3	Diabase	0.14	0.48	10.77	126.72
BE.81	Andesite	0.90	10.15	23.98	45.00
BE.82	Andesite	1.14	10.76	35.00	35.62
BE.101	Andesite	1.70	11.62	55.00	37.47
GE.22	Dacite	1.47	11.93	58.04	25.00
GE.23	Dacite	2.13	8.40	50.62	33.11

5. Discussion

The ocean-floor metamorphism has variably affected the collected ultramafic and mafic samples. During this process primary minerals from ultramafic and mafic rocks are often transformed to secondary ones as a result of the ocean-floor metamorphism process. This process is usually accompanied by a variable degree of metamorphism depending on the parent rock and the general context (i.e. pressure, temperature, hydrological features) of its formation. As a result, primary mineral assemblages are usually replaced by secondary hydrated minerals such as serpentine, amphibole and chlorite as reported for the ultramafic and mafic rocks of the present study. In volcanic settings, the mineral composition and porous structure of the primary rocks can be intensively altered by various processes (i.e. hydrothermal), resulting in changes of their physical and mechanical properties. Moreover, weathering in volcanic samples is the commonest alteration cause. During the weathering of the investigated volcanic samples Ca, Mg, K, Na, Rb and Sr generally show a rapid, early loss which can be correlated with the alteration of volcanic glass to smectite and illite. Based on the results of this study, the understanding of the phyllosilicate secondary mineral behavior is of great importance in order to diagnose plausible problems in engineering constructions.

Many researchers have studied the relationships between the physical and mechanical tests in order to investigate the impact of the alteration degree of various rock samples or other petrographic characteristics (i.e. the structural complexity of serpentine) and how they affect the engineering properties of rocks [9,10,12,22]. Regression analysis is the commonest statistical method for the investigation the interdependence of the physical and mechanical parameters. Mechanical parameters such as UCS reduce as the porosity increases, while mechanical properties decrease as the alteration degree of rocks used as aggregates increases. Sabatakakis et al. [61] and Diamantis et al. [11] suggested correlations between UCS and porosity for several lithotypes studied. In this study, strong correlations were observed between the physical and mechanical properties. As it can be seen from Figure 6 the critical mechanical parameters such as L.A (%) and UCS (MPa) are influenced by the total porosity n_t (%) and the moisture content w (%). The logarithmic equation (R^2 =0.82) seems to fit better between UCS and porosity (Figure 6a) while the relationship between Los Angeles abrasion value and porosity (Figure 6c) is better described by the liner equation (R^2 =0.76). Moreover, there are good correlations between the mechanical parameters and the moisture content as shown in Figures 6b, d. The best logarithmic equation (R^2 =0.90) is found between moisture content and uniaxial compressive strength. These great relationships (Figure 6) verify the hypothesis of many researchers for the interdependence between the physical and mechanical parameters. This is probably due to the fact that the minerals which have the ability to restrain water in their structure are likely to fail more easily under mechanical stress than minerals that are unable to restrain water. In the studied samples a great range in the mechanical properties of the rocks was observed (Table 2). This could be due to internal discontinuities, as a result of the different degrees of alteration due to the formation of secondary phyllosilicate minerals which are able to restrain water in their structure. Thus, knowledge of the presence and type of the secondary phyllosilicate minerals seems to be a determinant factor for the investigation of the physical and mechanical properties.

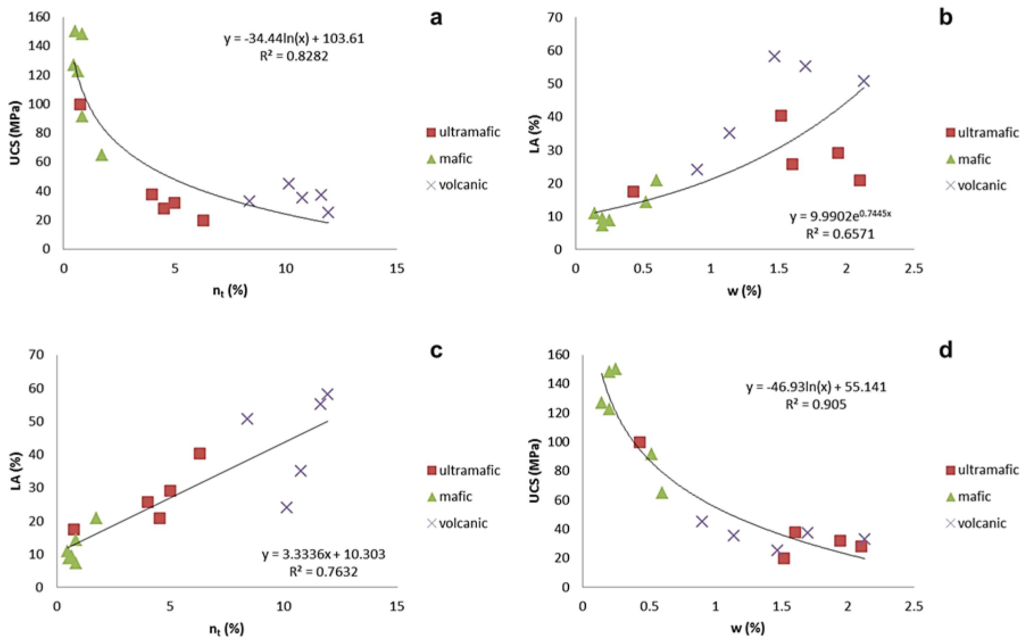

Figure 6. (**a**) The uniaxial compressive strength test [UCS (MPa)] versus the total porosity [n_t (%)] of the studied rocks; (**b**) The Los Angeles abrasion test [LA (%)] versus the moisture content [w (%)] of the studied rocks; (**c**) The Los Angeles abrasion test [LA (%)] versus the total porosity [nt (%)] of the studied rocks; (**d**) the uniaxial compressive strength test [UCS (MPa)] versus the moisture content [w (%)] of the studied rocks.

5.1. The impact of secondary phyllosilicate minerals on engineering properties of ultramafic rocks

The studied ultramafic rocks derived from 3 ophiolite complexes of Greece have been variably affected by serpentinization as it can be seen in Table 1 and have been described in 4.1 (Figures 1a, b). The primary minerals of the studied ultramafic rocks have been converted to secondary mineral phases as a result of ocean-floor metamorphism process. In order to present the effect of the secondary phyllosilicate minerals in the engineering properties of aggregates the U_{ph} index was proposed for the ultramafic rocks and was used in the correlation analysis with engineering parameters. This petrographic index U_{ph} (%) is the sum of the secondary phyllosilicate minerals present in ultramafic rocks and can be described by the following equation:

$$U_{ph} = \text{Serp}\ (\%) + \text{Chl}\ (\%) + \text{Talc}\ (\%), \quad (1)$$

The sum of the phyllosilicate minerals (U_{ph} index), reflects the degree of alteration of the studied ultramafic rocks and may influence their physicomechanical properties. The regression analysis was applied among the petrographic data and the physicomechanical properties of the ultramafic samples in order to clarify the relationships between the secondary phyllosilicate minerals and the engineering properties. The petrographic index U_{ph} displays significant correlations with all the studied physicomechanical properties. As it can be seen in Figure 7 strong representative correlations exist between U_{ph} and UCS and as well as porosity. The U_{ph} index is positively correlated with the physical parameters such as porosity (Figure 7a) presenting logarithmic trend (R^2 =0.97), the value of porosity tends to increase when the sum of phyllosilicate minerals content increases.

The increasing ability of ultramafic rocks which contain high contents of phyllosilicate minerals such as serpentine, chlorite, talc, to incorporate water can be explained by the fact that these platy or tabular secondary minerals have the capability to adsorb water. These minerals usually form foliated masses which contribute to the development of more porous areas. The other minerals of ultramafic rocks (primary and secondary) don't have similar effect on their physical properties maybe due to their crystal structure. The degree of alteration and the formation of secondary hydrated minerals combined with their structure may lead to various property changes. On the other hand, ultramafic rocks with low degree of alteration tend to have low porosity and permeability, massive crystalline structures and generally have better physicomechanical performance.

On the other hand, an inverse relationship (R^2= 0.97) was found between U_{ph} and uniaxial compressive strength (Figure 7b) suggesting that these phyllosilicate minerals are the determinant factors among the other minerals (primary and non phyllosilicate secondary minerals) influencing the mechanical performance of aggregates. Figures 7a and 7b support the interpretation mentioned above in figure 6, because these phyllosilicate minerals, due to their platy and layered character, form foliated masses which lead to the development of larger pores and open surfaces which are responsible for mechanically weaker rocks as these areas disturb the cohesiveness of rock's structure. In the studied ultramafic rocks, the secondary phyllosilicate minerals due to their low hardness in conjunction with their phyllosilicate structure create different microroughness. As can be seen in figure 4, with decreasing alteration (i.e. decreasing contents of secondary phyllosilicate minerals) (Table 1) the surface of the particles appears rough microroughness (Figure 4). This is explained by the platy and soft nature of phyllosilicate minerals and mainly by serpentine structure. The low microtopography results in considerable reduce of mechanical properties which hence influence the engineering constructions, because the smooth surfaces of the particles of ultramafic rocks, due to low microroughness, do not favor strong adherence with the cement paste in the concrete [22].

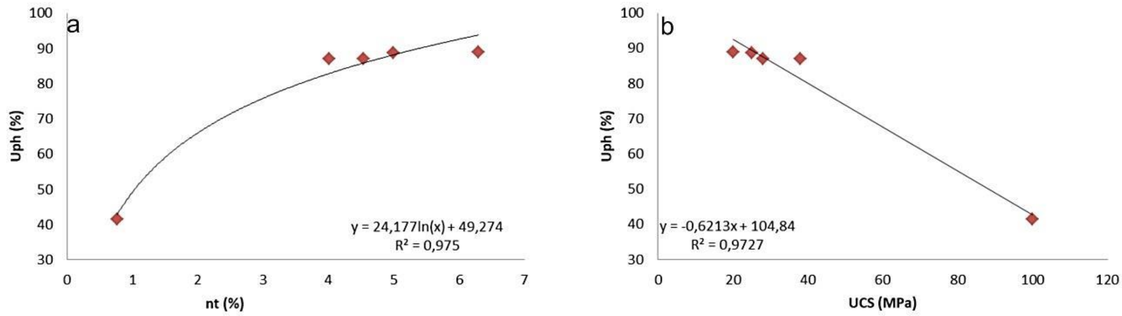

Figure 7. (**a**) The index [Uph (%)] versus the total porosity [nt (%)] of the studied ultramafic rocks; (**b**) the index [Uph (%)] versus the uniaxial compressive strength test [UCS (MPa)] of the studied ultramafic rocks.

The statistical significance of these correlations was also evaluated using the t-test and the p-value, as they don't present normal distribution. The significant values of the t-test compared to the critical t-table values, as well as the p-values of these pairs, for confidence levels even higher than the 95%, strongly suggest the validity of these relationships (Table 3) enhancing the hypothesis of the influence of the secondary phyllosilicate minerals on the engineering properties of the studied ultramafic rock samples.

Table 3. Paired t-test results for the statistical correlations of the indices U_{ph} and UCS, nt. The listed critical t-table values are for the relevant freedom degrees (dF) and for confidence levels of 99% (a=0.01), 98% (a=0.02), 95% (a=0.05) and 90% (a=0.10).

Pair	T-test	dF	p-value	T-table values			
				a=0.01	a=0.02	a=0.05	a=0.10
U_{ph}(%)-UCS(MPa)	-1.342	5	0.2371	3.364	2.756	2.015	1.475
U_{ph}(%)-n_t(%)	-6.270	3	0.0081	4.540	3.481	2.353	1.637

5.2. The impact of secondary phyllosilicate minerals on engineering properties of mafic rocks

The studied mafic rocks from 3 different ophiolite complexes of Greece display chlorite as the main phyllosilicate alteration product as shown in Table 1 and in Figure 1. Chlorite primary occurs as an hydrothermal alteration product of ferromagnesian minerals in igneous rocks and especially in mafic altered rocks. This case study focuses on the content of phyllosilicate minerals, as they seem to significantly influence the engineering performance of mafic rocks. Several scientists classified mafic igneous rocks according to the micropetrographic indexes. Weinert [62] classified mafic rocks according to the total percentage of secondary minerals. In order to present the effect of the secondary phyllosilicate minerals on the engineering properties of aggregates, the M_{ph} index was also employed for the mafic rocks. In this case study, the sum of the phyllosilicate minerals in mafic rocks (M_{ph}) constitutes only of the chlorite content and can be described by the following equation:

$$M_{ph} = \text{Chl } (\%), \quad (2)$$

Regression analysis was applied between the (M_{ph}) index and the physicomechanical properties of the mafic rock samples. The moisture content of the studied mafic samples show strong positive relationships (R^2= 0.98) with the M_{ph} (Figure 8a). Although the contribution of other hydrated secondary minerals (Table 1) in the total moisture content cannot be excluded, the strong positive correlation between Mph and w (%) suggests that chlorite is the main mineral phase that determines the moisture content in the studied mafic rocks. Moreover, a strong negative correlation (R^2 =0.88) exists between M_{ph} and UCS (Figure 8b). The above mentioned correlations indicate that the mechanical strength decreases as the percentage of chlorite increases. The mechanical behavior of the studied mafic rocks can better be explained by the contribution of the petrographic methods employed in the present study. The content of secondary phyllosilicate minerals, described by the Mph index, in combination with the microtopography of some mafic samples compared to other mafic samples seems to control their mechanical behavior as aggregates. The combination of petrographic methods is able to interpret the best microtopography of some mafic samples in relation to other mafic samples as well as the final best mechanical behavior of them as aggregates. Samples with a low percentage of chlorite (Table 1, sample ED.110) which is evenly distributed as shown from the microscopic studies (Figure 1c), exhibit higher microroughness (Figure 4c) and better mechanical behavior (Table 2). On the other hand, samples with high percentage of chlorite which is unevenly distributed in the structure of the rock (Figure 1d), is observed to create lower microroughness (Figure 4d) and inferior mechanical behavior (Table 2), as the extensive areas of chlorite probably create failure points to the material under mechanical stress such as uniaxial compressive strength and Los Angeles abrasion (Table 2). This can better be explained by the crystal structure of chlorite which is a hydrated phyllosilicate mineral. The ability of chlorite to adsorb and retain water in the layers of its structure (Figure 8a) decreases the uniaxial compressive strength (Figure 8b), as the numerous layers can act as surfaces of weakness for the rocks.

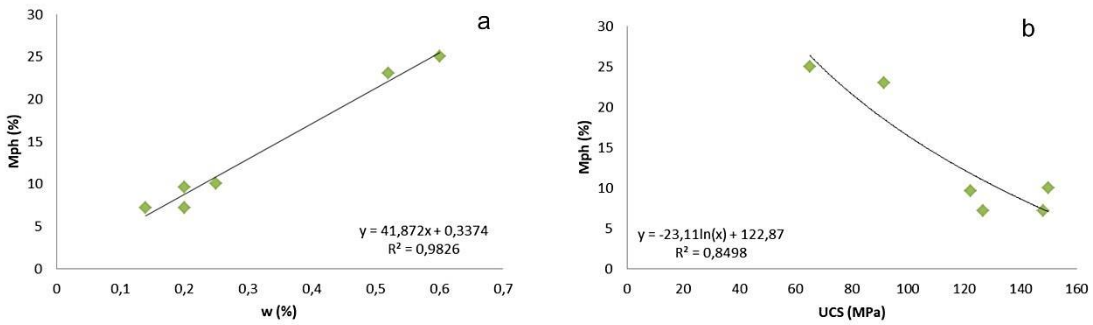

Figure 8. (**a**) The index [M_{ph} (%)] versus the moisture content [w (%)] of the studied mafic rocks; (**b**) the index [M_{ph} (%)] versus the uniaxial compressive strength test [UCS (MPa)] of the studied mafic rocks.

The statistical significance of the R^2 values is appraised again using the t-test and the p-value, as they don't present normal distribution. In this study, the mafic studied samples with different degrees of alteration were selected in order to obtain a representative sample population. The significant values of the t-test compared to the critical t-table values, as well as the p-values of these pairs. For confidence levels even higher than the 95%, strongly suggest the validity of these relationships (Table 4) enhancing the hypothesis of the influence of the phyllosilicate secondary minerals on the engineering properties of the studied mafic rock samples.

Table 4. Paired t-test results for the statistical correlations of the indexes M_{ph} and UCS, w. The listed critical t-table values are for the relevant freedom degrees (dF) and for confidence levels of 99% (a=0.01), 98% (a=0.02), 95% (a=0.05) and 90% (a=0.10).

Pair	T-test	dF	p-value	T-table values			
				a=0.01	*a=0.02*	*a=0.05*	*a=0.10*
M_{ph}-UCS (MPa)	10.534	5	0.0001	3.364	2.756	2.015	1.475
M_{ph}-w (%)	-3.740	4	0.0197	3.746	2.998	2.131	1.533

5.3. The impact of secondary phyllosilicate minerals on engineering properties of volcanic rocks

The studied volcanic rocks from Greece (Veria and Ag. Theodori) display smectite and illite as the main phyllosilicate alteration products. Weathering reactions mainly involve the transformation of feldspars from andesites and dacites to the smectite and illite. This case study focuses on the content of secondary phyllosilicate minerals of volcanic rocks. In order to present the effect of the secondary phyllosilicate minerals in the engineering properties of aggregates, the V_{ph} index was employed for the volcanic rocks. The V_{ph} index is an expression of the sum of the secondary phyllosilicate minerals present and can be described by the following equation:

$$V_{ph} = Sm\ (\%) + ill\ (\%), \tag{3}$$

The V_{ph} index and the physicomechanical properties of the volcanic rock samples were also studied. The statistical processing between the V_{ph} index and the engineering tests did not show up any clear correlation among the test variables (Figures 9 a, b, Table 2). This may be due to the very low percentage of clay minerals (smectite and illite) within the studied volcanic rocks (Table 1), presenting a range of values between 3.9% - 6.6%. The traces of clay minerals identified on the surface of volcanic rocks by SEM images (Figure 5), do not seem to affect the microroughness of the volcanic aggregates particles (Figure 4). These percentages of clay minerals described by the V_{ph} index do not seem to determine the engineering parameters of the rocks (Figure 9), probably due to their different hydration and swelling properties. Smectite belongs to the swelling types of clays while illite is a non-

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 22 June 2018 doi:10.20944/preprints201806.0362.v1

Peer-reviewed version available at *Minerals* **2018**, *8*, 329; doi:10.3390/min8080329

swelling clay mineral which however, is structurally very closely related to smectite. From an engineering point of view, the most complicated rocks in the construction industry are volcanic rocks containing swelling clay minerals [22]. This may due to the fact that even the low percentage of smectite and illite is capable to adsorb water in their phyllosilicate structure during the preparation of engineering constructions. These swelling clay minerals may swell up to 700%-800% [63] hence causing severe destruction to their host rocks.

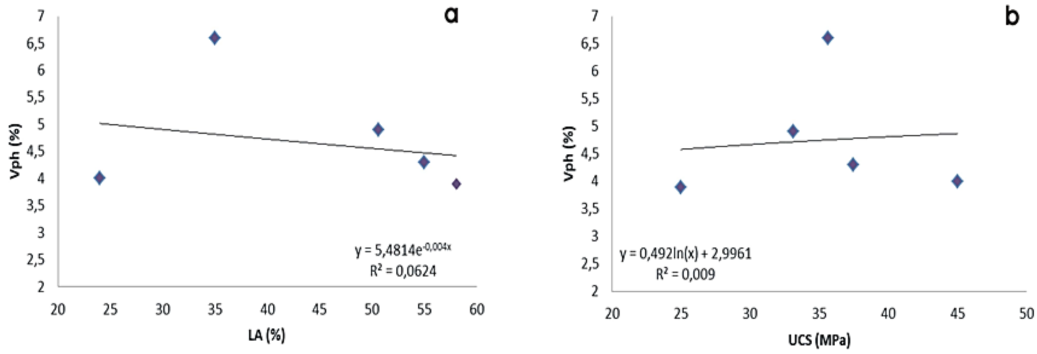

Figure 9. (**a**) The index [V_{ph} (%)] versus the Los Angeles abrasion test [LA (%)] of the studied volcanic rocks; (**b**) the index [V_{ph} (%)] versus the uniaxial compressive strength test [UCS (MPa)] of the studied volcanic rocks.

5. Conclusions

This paper investigates the impact of the presence and type of secondary phyllosilicate minerals of ultramafic, mafic and volcanic rocks with a variable degree of alteration on the engineering properties of these studied rocks when used as aggregates. The studied samples presented various percentages and types of secondary phyllosilicate minerals depending on their different parent rocks. For this purpose a combination of petrographic methods was employed and the physicomechanical properties of these various igneous rocks were studied. The conclusions of this study are summarized below:

-In ultramafic rocks, the sum of the secondary phyllosilicate minerals (serpentine, chlorite and talc) expressed by the U_{ph} index may constitute a secure index to determine their physicomechanical properties and hence to be used for the estimation of possible failures on engineering constructions.

-In mafic rocks, the content of chlorite expressed by the M_{ph} index can be a secure index for the identification of the quality of mafic aggregates in various construction applications.

-In the volcanic rock samples studied, the sum of phyllosilicate minerals (smectite and illite) expressed by the V_{ph} index can not constitute a secure index which can be generally used in volcanic rocks. This happens due to the low percentage of smectite and illite which don't present correlations with the physicomechanical properties. However the percentage of smectite and illite, even in minor amounts, due to their swelling behavior can be responsible for the severe failures in a wide range of applications.

The presence and type of secondary phyllosilicate minerals seems to have a significant negative impact on the quality of the studied rocks as aggregates. The combination of petrographic methods and the engineering properties constitutes a useful tool for the evaluation of rocks as aggregates.

Author Contributions: Petros Petrounias participated in the fieldwork, the elaboration of laboratory tests, the interpretation of the results, coordinated the research and wrote the manuscript; Panagiota P. Giannakopoulou participated in the fieldwork, the elaboration of laboratory tests, the interpretation of the results and contributed to the manuscript writing; Aikaterini Rogkala participated in the fieldwork, performed the SEM work, the interpretation of the results and contributed to the manuscript writing; Paraskevi Lampropoulou carried out the XRD analyses and participated in the interpretation of the results; Eleni Koutsopoulou participated in the elaboration of laboratory tests, the mineralogical analyses and mineral quantification of the samples the interpretation of the results and contributed to the manuscript writing; Dimitrios Papoulis participated in the elaboration of the mineralogical analyses of clay minerals and the interpretation of the results; Basilios Tsikouras participated in the fieldwork, the interpretation of the results and the coordination of the research; and Konstantin Hatzipanagiotou participated in the interpretation of the results and the coordination of the research.

Acknowledgments: The authors wish to thank Dr. Drakopoulos of the Foundation for Research and Technology-Hellas (FORTH) Institute of Chemical Engineering and High Temperature Chemical Processes (ICE/HT) Rio-Patras, Greece and A.K Seferlis of the Laboratory of Electron Microscopy and Microanalysis, University of Patras for his assistance with the microanalyses and SEM micrographs.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Shakoor, A.; Bonelli, R.E. Relationship between petrographic characteristics, engineering index properties and mechanical properties of selected sandstones. Bull. Ass. Eng. Geol. **1991**. XXVII, 55-71.
2. Haney, M.G.; Dhakoor, A. The relationship between tensile and compressive strengths for selected sandstones as influenced by index properties and petrographic characteristics. Proc. 7th Int. IAEG Cong. Lisbon. Portugal. **1996**, IV, 3013-3021.
3. Turgul, A.; Zarif, I.H. Correlation of mineralogical and textural characteristics with engineering properties of selected granitic rocks from Turkey. *Eng. Geol*. **1999**, 51, 303-317.
4. Smith, M.R.; Collis, L. Aggregates: Sand, Gravel and Crushed Rock Aggregates for Construction Purposes; Spec. Publ. 17; The Geological Society: London, UK, **2001**.
5. Miskovsky, K.; Tabora, D.M.; Kou, S.Q.; Lindqvist, P.A. Influence of the mineralogical composition and textural properties on the quality of coarse aggregates. *J. Mater. Eng. Perform.* **2004**, 13 (2), 144-150.
6. Al-Oraimi, S.K.; Taha, R.; Hassan, H.F. The effect of the mineralogy of coarse aggregate on the mechanical properties of high- strength concrete. Constr. *Build. Mater*. **2006**, 20, 499-503.
7. Rigopoulos, I.; Tsikouras, B.; Pomonis, P.; Hatzipanagiotou, K. The influence of alteration on the engineering properties of dolerites: the example from the Pindos and Vourinos ophiolites (northern Greece). *Int. J. Rock Mech. Min. Sci*. **2010**, 47 (1), 69-80.
8. Yilmaz, N.G.; Goktan, R.M.; Kibici, Y. Relations between some quantitative petrographic characteristics and mechanical strength properties of granitic building stones. *Int. J. Rock Mech. Min. Sci*. **2011**, 48, 506-513.
9. Petrounias, P.; Rogkala, A.; Kalpogiannaki, M.; Tsikouras, B.; Hatzipanagiotou, K. Comparative study of physico-mechanical properties of ultrabasic rocks (Veria-Naousa ophiolite) and andesites from central Macedonia (Greece). *Bull. Geol. Soc. Gr*. **2016**, 50, 1989-1998.
10. Giannakopoulou, P.P.; Tsikouras, B.; Hatzipanagiotou, K. The interdependence of mechanical properties of ultramafic rocks from Gerania ophiolitic complex. *Bull. Geol. Soc. Gr.* **2016,** 50, 1829-1837.
11. Diamantis, K.; Gartzos, E.; Migiros, G. Study on uniaxial compressive strength, point load strength index, dynamic and physical properties of serpentinites from Central Greece: Test results and empirical relations. *Eng. Geol*. **2009**, 108, 199-207.
12. Rigopoulos, I.; Tsikouras, B.; Pomonis, P.; Hatzipanagiotou, K. The impact of petrographic characteristics on the engineering properties of ultrabasic rocks from northern and central Greece. *Q. J. Eng. Geol. Hydrogeol.* **2012**, 45, 423-433.
13. Pola, A.; Crosta, G.; Fusi, N.; Barberini, V.; Norini, G. Influence of alteration on physical properties of volcanic rocks. *Tectonophysics*. **2012**, 566-567, 67-86.
14. Ündül, Ö. Assessment of mineralogical and petrographic factors affecting petro-physical properties, strength and cracking processes of volcanic rocks. *Eng Geol.* **2016**, 210, 10-22.
15. Gresens, R.L. Composition-volume relationships of metasomatic. Chem. Geology. **1967**, 2, 47-65.

16. Veniale, F.; van der Marel, H.D. An interstrat- ified saponite-swelling chlorite mineral as a weathering product oflizardite rock from St. Margherita Staffora (Pavia Province), Italy. *Beitr. Miner. Petrogr.* **1963**, 9, 198-245.
17. Wildman, W.E.; Jackson, M.L.; Whittig, L.D. Iron-rich montmorillonite formation in soils derived from serpentinites. *Soil Sci. Soc. Amer. Proc.* **1968,** 32, 787-794.
18. Ducloux, J.; Mennier, A.; Velde, B. Smectite, chlorite and a regular interstratified chlorite-vermiculite in soils developed on a small serpentinite body Massif Central, France. *Clay Mins.* **1976.** 11, 121-135.
19. Garcia, A.; Delgado, M. Mineralogia de las fracciones arenosas de suelos desarrolados sobre serpentinas en la Sierra de Carratraca (Malaga). *Anal. Edafol. Agrobiol.* **1978,** 37, 599-620.
20. Istok, J.D.; Harward, M.E. Influence of soil moisture on smectite formation in soils derived from serpentite. *Soil. Sci. Soc. Am. J.* **1982**. 46, 1106-1108.
21. Hurlbut, C.S.; Sharp, W.E. Dana's Minerals and How to study Them (After Edward Salisbury Dana), fourth ed. John Wiley & Sons, Inc., New York, **1998**, 248–257.
22. Petrounias, P.; Giannakopoulou, P.P.; Rogkala, A.; Stamatis, P.M.; Tsikouras, B.; Papoulis, D.; Lampropoulou, P.; Hatzipanagiotou, K. The Influence of Alteration of Aggregates on the Quality of the Concrete: A Case Study from Serpentinites and Andesites from Central Macedonia (North Greece). *Geosciences.* **2018**, 8,
23. Escartin, J.; Hirth, G.; Evans, B. Strength of slightly serpentinized peridotites: implications for the tectonics of oceanic lithosphere. Geology. **2001**, 29, 1023-1026.
24. Frost, B.R.; Beard, J.S. On silica activity and serpentinization. *J. Petrol.* **2007**, 48, 1351-1368.
25. Shervais, J.W.; Kolesar, P.; Andreasen, K. Afield and chemical study of serpentinization – Stonyford, California: chemical flux and mass balance. *Int. Geol. Rev.* **2005**, 47, 1-23.
26. Deschamps, F.; Godard, M.; Guillot, S.; Hattori, K. Geochemistry of subduction zone serpentinites: a review. *Lithos* **2013**, 178, 96-127.
27. Malvoisin, B. Mass transfer in the oceanic lithosphere: Serpentinization is not isochemical. *Earth Planet. Sci. Lett*. **2015,** 430, 75-85.
28. Morad, S. Mica Alteration Reactions in Jurassic Reservoir sandstones from the Haltenbanken Area, offshore Norway. *Clays Clay Miner.* **1990**, 38, 584-590.
29. Bettison, L.A.; Schiffman, P. Compositional and Structural variations of phyllosillicates from the Point Soil ophiolite, California. *Am. Mineral.* **1988**, 79, 671-695.
30. Stoch, I.; Sikora, W. Transformation of micas in the process of kaolinitization of granites and gneisses. *Clays Clay Miner.* **1976**, 24, 156-162.
31. Srodon, J.; Ebert, D.D. Illite. Rev. Mineral. **1984**, 13, 495-544.
32. Innoue, A.; Utada, M. Further investigations of a conversion series of dioctahedral mica/smectite in the Shinzan hydrothermal alteration area, north- east Japan. *Clays Clay Miner.* **1983,** 31, 401-412.
33. Kranidiotis, P.; MacLean, W.H. Systematics of chlorite alteration at the Phelps Dodge massive sulfide deposit, Matagami, Quebec. *Econ. Geol.* **1987**, 82, 1898-911.
34. Shikazono, N.; Kawahata, H. Compositional differences in chlorite from hydrothermally altered rocks and hydrothermal ore deposits. *Can. Mineral*. **1987**, 25, 465-474.
35. Tiwari, B.; Ajmera, B. Consolidation and swelling behavior of major clay minerals and mixtures. *Appl. Clay Sci.* **2011**, 54 (3-4), 264-273.
36. Bish, D.L.; Howard, S.A. Quantitative phase analysis using the Rietveld Method. *J. Appl. Cryst.* **1988**, 21, 86–91.
37. Bish, D.L.; Post, J.E. Quantitative mineralogical analysis using the Rietveld full pattern fitting method. *Am. Mineral*. **1993**, 78, 932–940.
38. McCusker, L.B.; Von Dreele, R.B.; Cox, D.E.; Louer, D.; Scardi, P. Rietveld refinement guidelines. J. *Appl. Crystallogr.* **1999**, 32, 36–50.
39. Hillier, S. Accurate quantitative analysis of clay and other minerals in sandstones by XRD: Comparison of a Rietveld and a reference intensity ratio (RIR) method and the importance of sample preparation. *Clay Miner*. **2000**, 35, 291–302.
40. Gualtieri, A.F. Accuracy of XRPD QPA using the combined Rietveld-RIR *Method. J. Appl. Crystallogr*. **2000**, 33, 267–278.

41. Rogkala, A.; Petrounias, P.; Tsikouras, B.; Hatzipanagiotou, K. New occurrence of pyroxenites in the Veria-Naousa ophiolite (north Greece): Implications on their origin and petrogenetic evolution. *Geosciences*. **2017**, 7, 92; doi:10.3390/geosciences7040092.
42. Decourt, J.; Aubouin, J.; Savoyat, E.; et al. Le sillon mesohellenique et la zone pelagonienne. *Bull. Soc. Geoli. Fr.* **1977**, 1, 32-70.
43. Michailidis, K.M. Zoned chromites with high MN-contents in the Fe-Ni-Cr-laterite ore deposits from the Edessa area in Northern Greece. *Miner. Deposita*. **1990**, 25, 190-197.
44. Pe-Piper, G.; Piper, D.J.W. The igneous rocks of Greece. The Anatomy of an Orogen. Beitrge zur Regionalen Geologie der Erde (Series). Stuttgart. Gebrder Borntaeger.2002; doi: 10.1017/S0016756803218021.
45. Saccani, E.; Photiades, A.; Santato, A.; Zeda, O. New evidence for supra-subduction zone ophiolites in the Vardar zone of northern Greece: Implications for the tectonomagmatic evolution of the Vardar oceanic basin. *Ofioliti*. **2008**, 33, 65–85.
46. Boccaletti, M.; Manetti, P.; Peccerillo, A. The Balkanides as an Instance of Back-Arc Thrust Belt: Possible relation with the Hellinides. *Geol. Soc. Amer.Bull.* **1974**, 85, 1077-1084.
47. Eleftheriadis, G.; Castorina, F.; Soldatos, T.; Masi, U. Geochemical and Sr-Nd isotopic evidence for the genesis of the Late Cainozoic Almopia volcanic rocks (Central Macedonia, Greece). *Min & Petrol.* **2003**, 78, 21-36.
48. Clément, B. Evolution géodynamique d'un secteur des Hellénides internes: l'Attique-Béotie (Gréce continentale), Thesis Univ, Lille, **1983**.
49. Vacondios, I. Etude metallogenique des chromites liees aux ophiolites de type Mediterranee occdentale ou orientale: le chromites de Tinos et des Gerannees. Ph.D. thesis, Patras, **1997**, 98.
50. Danelian, T.; Robertson, A.H.F. Palaeogeographic implications of the age of radiolarian-rich sediments in Beotia (Greece). *Bull. Geol. Soc. Gr.* **1998**, 32, 21–29.
51. Zachariadis. P.; Kostopoulos. D.; Reischmann. T.; Himmerkus. F.; Matukov D.; Sergeev. S. U-Pb ion-microprobe zircon dating of subduction-related magmatism from northern Greece: The ages of the Guevgueli, Thessaloniki and Chalkidiki igneous complexes. *Geophys. Res. Abstr.* **2006,** 8: SRef-ID: 1607-7962/gra/EGU06-A-055560.
52. Saccani. E.; Bortolotti. V.; Marroni. M.; Pandolfi. L.; Photiades. A.; Principi. G. The Jurassic association of backarc basin ophiolites and calc-alkaline volcanics in the Guevgueli complex (Northern Greece): Implication for the evolution of the Vardar zone. *Ofioliti*. **2008**,33:209-227.
53. Freyberg, B. V. Geologie des Isthmus von Korinth. Erlanger Geologische Abhandlungen, 95. Erlangen: Junge and Sohn, Universitats-Buchdruckerei. **1973.**
54. EN 932-1. Part 1: Composition, specifications and conformity criteria for common cements, European standard, **2011**.
55. EN 932. Part 3: Procedure and terminology for simplified petrographic description, European standard, **1996.**
56. BS 812. Methods for sampling and testing of mineral aggregates, sands and fillers, Part 1: methods for determination of particle size and shape, London, **1975.**
57. AASHTO T255. Standard method of test for total evaporable moisture content of aggregate by drying, **2000**.
58. I.S.R.M. Suggested Methods. “Rock Characterization Testing and Monitoring”, Editor E. Brown, Pergamon Press, **1981**.
59. ASTM C-131. Resistance to abrasion of small-size coarse aggregate by use of the Los Angeles machine. American Society for Testing and Materials, Philadelphia, **1989**.
60. ASTM D-2938. Standard test method of unconfined compressive strength of intact rock core specimens. Annual Book of Standards, 4.08. American Society for Testing and Materials, Philadelphia,**1986.**
61. Sabatakakis, N.; Koukis, G.; Tsiambaos, G.; Papanakli, S. Index properties and strength variation controlled by microstructure for sedimentary rocks. *Eng. Geol.* **2008**, 97, 80-90.
62. Weinert, H.H. Basic igneous rocks in road foundations. CSIR Research Report No. 218, Soil Mechanics Division, National Institute for Roads Research, Pretoria, **1964**, 47.
63. Taylor, R.K.; Smith, T.J. The engineering geology of clay minerals; swelling, shrinking and mudrock breakdown. *Clay Miner.* **1986**, 21, 235–260.