

Chemical, mineralogical and structural features of native and expanded perlite from Macedonia

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Abstract

The physico-mechanical, chemical and mineralogical characteristics of volcanic glass (perlite) from the Mariovo region (Macedonia) as well as the mineralogical changes that occur during its thermal treatment were investigated to demonstrate its utilization for industrial use. The native perlite was characterized by chemical analysis, X-ray powder diffraction (XRPD), infrared (IR) spectroscopy, thermal analysis (TGA/DTA), scanning electron microscopy (SEM-EDX), transmission electron microscopy (TEM), and solid-state NMR. The chemical examination suggests that the perlite represents an acidic volcanic rock with a high percentage of SiO₂ (72.45%), high in alkali metal oxides (4.21 wt.% K₂O, 3.56 wt.% Na₂O), with a loss of ignition 3.54 wt.%. Results from the XRPD indicated major amorphous behaviour, with low amounts of feldspars, quartz, and cristobalite. SEM examinations revealed glassy structure with presence of certain pores (dimensions ranging from 50–100 μm). The determined expansion coefficient was 20 times its original volume. XRPD of expanded perlite compared to the native perlite depicted new intensive peaks of cristobalite. SEM and TEM revealed irregular morphology with broken or ragged edges. On the basis of the chemical and mineralogical composition, the studied perlite is classified as an appropriate material suitable as ceramic flux to lower the sintering temperature.

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1. INTRODUCTION

The Republic of Macedonia is rich in inorganic materials with a wide range of potential use and application, including diatomaceous earth (REKA, et al., 2014; REKA et al., 2017), trepel (a biogenetic rock) (PAVLOVSKI et al., 2011; CEKOVA et al., 2013), pumicite (CEKOVA et al., 2013), dolomite (MAKRESKI et al., 2003; JOVANOVSki et al., 2012), quartzite (JOVANOVSki et al., 2012), bentonite (ŠONTEVSKA et al., 2007) and granite (JOVANOVSki et al., 2012).

Perlite, originates from the term *perlstein* (pearl stone) coined by German petrologists in the nineteenth century for a certain rhyolitic, glassy rock with numerous concentric cracks which on fragmentation yielded pieces vaguely resembling pearls (EVANS, 1993). Perlite was originally identified by its vitreous, pearly lustre and characteristic curved (onion-skin texture) perlitic fractures (BREESE, 1984; KOGEL et al., 2006; KOUKOUZAS, 2006).

Perlite is one of the natural volcanic aluminosilicate glasses (rhyolitic rocks) which formed by the rapid cooling of viscous lava or magma. These include obsidian, perlite, pitchstone, and hydrated volcanic ash or “pumicite” (BREESE, 1984; KOGEL et al., 2006; KOUKOUZAS, 2006; KONGKACHUICHAY and LOHSOONTORN, 2006). The main characteristic of perlite is the content of chemically bonded water. Perlites are classified into three types depending on their water contents as obsidian (water content less than 2 wt. %), perlite (2–5 wt.%) and pitchstone (water content > 5 wt.%). Upon heating (760–900 °C), perlite be-

comes pyroplastic and expands and increases 20 fold in volume. Bound water vaporizes and creates numerous bubbles that provide the exceptional characteristics of the perlite: a porous structure (increased porosity) and low weight (decreased density). Such material is known as expanded perlite; moreover, it expresses a low thermal conductivity, considerable heat resistance and acts as a very good sound absorber. The main components of perlite are the oxides such as SiO₂ (70–75 wt.%), Al₂O₃ (12–18 wt.%) as well as the alkaline oxides (K₂O, Na₂O). Perlite also contains small amounts of other oxides such as Fe₂O₃, CaO, MgO and TiO₂ (ROULIA et al., 2006; BURRIESCI et al., 1985; KAUFHOLD et al., 2014; VARGA et al., 2015).

Perlites, either as native materials or expanded, due to their properties (low density, high porosity, chemical inertness and non-toxicity), are versatile materials and used for the preparation of catalysts, ceiling tiles, pipe insulation, gypsum wallboard, cryogenic insulation, fillers, materials for filtering (filters), aggregates for light cement, removal of heavy metals and adsorption of particulates from the atmosphere, thermal insulators, absorption of oil, roof panels, foams, fire retardants, brick products, horticulture, production of container glass, in the ceramic industry (as a component in the ceramic mass), microorganism carriers, materials for improving the mechanical and thermal properties of cement mortar, and glaze products (AHMADIA et al, 2018; SODEYAMA et al., 1999; ZAFIROVSKI et al., 1987; VIJAYARAGHAVAN and RAJA, 2014; RODRIGUEZ et al., 2016). The application of

perlite for these purposes depends on the physico-chemical characteristics, as well as from its mineralogical composition.

Perlite mines are located in several countries around the world, with the leading producers being Turkey, Greece, USA, Japan, Italy and Hungary (SODEYAMA et al., 1999; SODEYAMA and SAKKA, 2005). It is estimated that the Republic of Macedonia contains over 1.18 million tons of perlite (SPASOVSKI and SPASOVSKI, 2012), found in the Tertiary volcanics. The major area is at Nidze Mountain, close to the border with Greece, where perlite is associated with Pliocene latite in the Gradensica deposit (KOGEL et al., 2006). Preparation for excavation was planned in the late 1990s with production expected to reach 80 ktpy (HARBEN and KUZVART, 1997), but no actual extraction occurred.

The aim of this study was to determine, for the first time, the physico-mechanical, chemical and mineralogical characteristics of perlite from the Mariovo region, and to investigate the mineralogical changes that occur during thermal treatment. Therefore, our goal was to resolve the most appropriate valorization of this volcanic rock from this locality as well as to determine its expansion coefficient.

2. MATERIALS AND METHODS

The perlite was collected from the Mariovo region (Fig. 1). The samples were fine-grained of a white to greyish colour, with white phenocrysts, and granulation of 0.2–0.5 mm was used for the measurements. The specific gravity of the natural perlite was determined by pycnometer (as per the standard D 854 – 02 – Standard Test Methods for Specific Gravity of Soil Solids by Water Pycnometer1), while the compressive strength was determined with an automatic press (Automax 5, Controls).

The chemical composition of the volcanic glass was determined using classical silicate analysis. Crude perlite was melted in a mixture of carbonates (Na_2CO_3 and K_2CO_3), whereas the percentages of the various oxides present in the material were determined by complexometric titration (KIRSCHENBAUM, 1983). The alkali metal oxides (Na_2O and K_2O) were determined

by flame photometry using an Evans Electro Selenium Ltd 410 instrument.

The mineralogical characterization was carried out using X-ray powder diffraction (XRPD), thermal analysis (TGA/DTA), scanning electron microscopy (SEM-EDX), transmission electron microscopy (TEM) and infrared spectroscopy (IR). XRPD analysis was performed on a Rigaku Ultima IV X-ray diffractometer equipped with a D/teX high-speed 1-dimensional detector using $\text{CuK}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) in 2θ range from 5 to 60°. The accelerating voltage and the current power were set to 40 kV and 40 mA, respectively.

DTA/TGA analyses of the volcanic glass were performed using a Stanton Redcroft apparatus, under the following experimental conditions: temperature range 20–1000 °C; heating rate 10 °C/min and a thermal treatment duration time of 98 min; sample mass of 19.085 mg, with a ceramic pot as a material carrier. The optical microscopy measurements were conducted on a transmission polarizing microscope SM-POL, Leitz, Wetzlar, Germany.

A scanning electron microscope VEGA3 LMU Tescan Instrument coupled with energy dispersive X-ray spectroscopy (INCA Energy 250 Microanalysis System) was used to quantitatively analyze the products. The voltage of the SE detector was set to 20 kV. A JEOL 2100 transmission electron microscope (TEM) was used to obtain TEM photographs of the volcanic glass. The Perkin-Elmer FTIR system 2000 interferometer was engaged to record the IR spectra in 4000–500 cm^{-1} range using the KBr pellet method. Solid state NMR characterizations of volcanic glass were carried out using a Jeol 400 MHz nuclear resonance spectrophotometer.

In order to determine the expansion coefficient of this volcanic glass, crude perlite was initially dried at 100 °C and subsequently subjected to thermal treatment at 850 °C at which the water trapped in the structure vaporized and escaped resulting in the expansion of the material. The expansion coefficient of perlite is equal to 20 times its initial volume (Fig. 2, right). The bulk density of 62 g/dm^3 (0.062 g/cm^3) was determined for the expanded perlite.

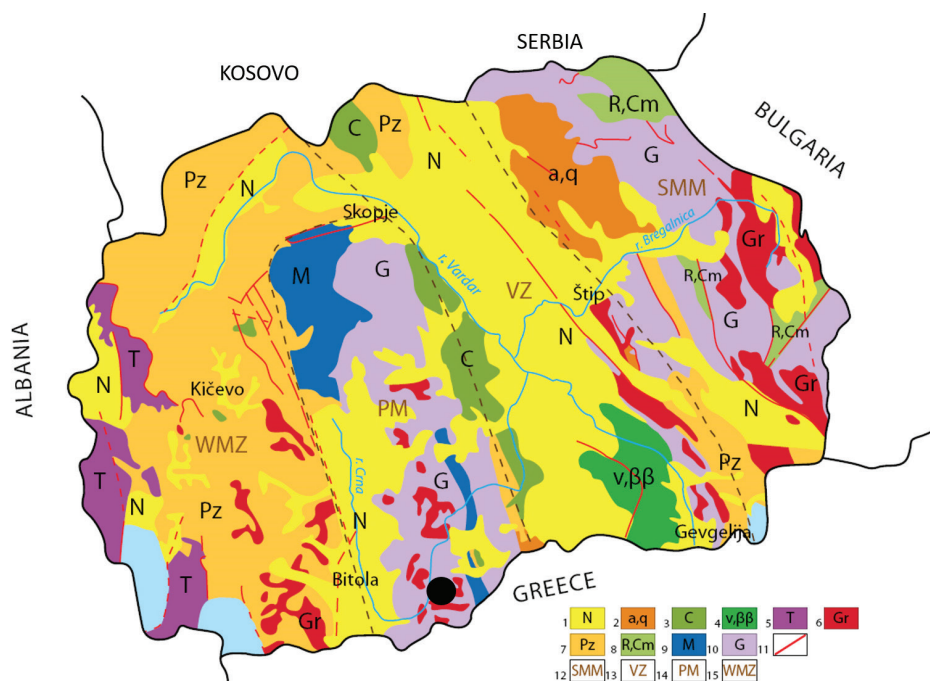


Figure 1. A geological map of Macedonia pinpointing the locality (black circle) from where the perlite was excavated.

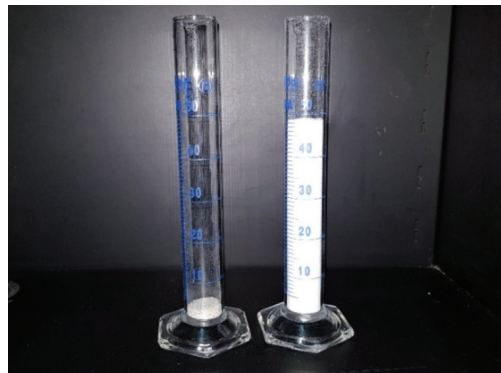


Figure 2. Natural (crude) perlite from Mariovo region (up). Comparison of the volume of the same mass (3.1 g) of perlite and expanded perlite (down). The volume of 2.5 ml of native perlite versus the volume of 50 ml of the expanded perlite.

3. RESULTS AND DISCUSSION

3.1. Physico-mechanical properties of perlite

The perlite was excavated from the Mariovo region (Fig. 1). The following physico-mechanical properties were determined for the native perlite (Fig. 2, left): white to light grey colour, odourless, with clearly visible black particles of glass. The specific gravity of the natural perlite was determined by pycnometer (Standard D 854 – 02 - Standard Test Methods for Specific Gravity of Soil Solids by Water Pycnometer) as 2.23–2.40 g/cm³, while the compressive strength was in the range from 4.20 to 5.30 MPa.

The process of expanding the natural perlite was monitored by expansion in industrial vertical expansion furnaces. In order to obtain the maximum expansion at this grain size (0.2–0.5 mm), perlite was preheated at 350–400 °C for a period of 4–5 seconds and afterwards heated at 850 °C in the high temperature furnace for 2–3 seconds.

3.2. Chemical analysis of perlite

The chemical composition of the volcanic rock (Table 1) was determined with the classical chemical silicate analysis. The loss of ignition (LOI) was determined while heating perlite at 1000 °C for a period of 1 hour; LOI was 3.54% and lies within the typical range for perlites (3–5%).

The results obtained from the chemical composition of perlite indicate that the analyzed perlite represents an acidic volcanic rock with a high percentage of SiO₂ (72.48%) and substantial amounts of Al₂O₃ (13.15%). The alkali metal oxides (K₂O and Na₂O) are present at 4.21% and 3.56% respectively, (representing high percentages) indicates that the analyzed raw material is suitable for container glass.

Table 1. Chemical composition of perlite.

Oxides	Mass %
SiO ₂	72.48
Al ₂ O ₃	13.15
Fe ₂ O ₃	1.23
TiO ₂	0.15
CaO	1.13
MgO	0.35
K ₂ O	4.21
Na ₂ O	3.56
LOI	3.54
Total	99.80

3.3. X-ray powder diffraction analysis of the native and expanded perlite

Results of the XRPD analysis of the perlite (Fig. 3, top) depicts the amorphous behaviour of the sample manifested by the appearance of one complex “hump” widely positioned between 15 and 30° (2θ) with the most maxima peaking in the 22–26.7° range as a result of the high percentage of the aluminosilicate glass phase associated by small amounts of crystalline phases. The small quantities of the crystalline phases are mainly represented by feldspars, quartz and cristobalite. Feldspars are represented as plagioclases (13.50°, 25.76°, 29.98°, 33.64°, 35.40°, 42.66°, 49.74°), K, Na-feldspars (23.70°, 27.40°, 27.66°), and microcline (27.66, 29.49, 50.58). The less pronounced presence of SiO₂ polymorphs

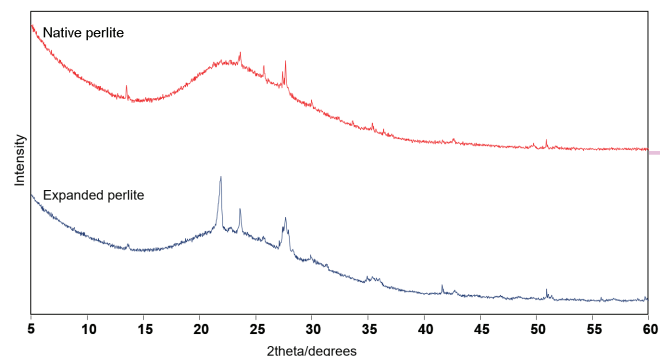


Figure 3. XRPD analysis of native perlite (top) and expanded perlite (bottom).

are represented by α -quartz (26.67°) and cristobalite (21.94°). The presence of crystalline modifications in the volcanic rock is correlated to the origin of perlite, with more crystallites being formed in the slow cooling of the lava.

Results of the XRPD analysis of the expanded perlite (Fig. 3, bottom) again demonstrated the amorphous behaviour of the sample manifested by the appearance of one complex “hump” extended between 15 and 30° (2θ) with the most maxima peaking in the 22–26.7° range as a result from the high percentage of aluminosilicate glass. Compared to the native perlite, the expanded perlite shows an evident increase in the amount of cristobalite (21.94°, 28.44, 31.40, 36.00) present.

3.4. Infrared spectral analysis of the native and the expanded perlite

The IR spectrum of native perlite (Fig. 4, top) exhibits an absorption band at 786 cm⁻¹ attributed to the bending vibrations of the Si-O-Si framework, whereas the band at 1078 cm⁻¹ is a result of

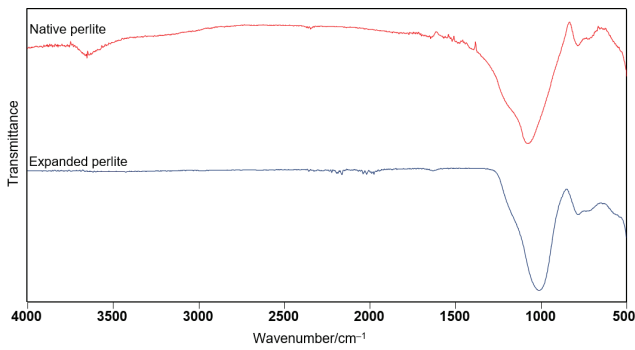


Figure 4. IR spectrum of native perlite (top) and expanded perlite (bottom).

the stretching vibrations of the Si-O-Al units (SODEYAMA et al., 1999; MAKRESKI et al., 2009). The band at 1644 cm^{-1} is due to bending vibrations from the absorbed water (ROULIA et al., 2006; VARUZHANYAN et al., 2006; MAKRESKI et al., 2009), whereas the band at 3650 cm^{-1} is due to the stretching vibration of the absorbed water molecules (SODEYAMA et al., 1999; LI and TOMOZAWA, 1994).

As results of the thermal treatment and water loss during the expansion of perlite, the bands at 1644 cm^{-1} and 3650 cm^{-1} that were previously discussed at the native perlite (Fig. 4, bottom), bands due to bending vibrations from the absorbed water and the stretching vibration of the absorbed water molecules (ROULIA et al., 2006; VARUZHANYAN et al., 2006; MAKRESKI et al., 2009), as expected, are missing in the IR spectrum of the expanded perlite (Fig. 4, bottom). The band at 785 cm^{-1} and 1047 cm^{-1} are ascribed to the Si-O stretching vibrations of Si-O-Si and Si-O-Al, respectively (SODEYAMA et al., 1999).

3.5. Optical microscopy

The results of the light microscopy demonstrated the sample composition of an isotropic glassy mass (Fig. 5) with the presence of glassy-isotropic fine-grained particles/microlites ($0.03\text{--}0.1\text{ mm}$). In the fine-grained mass of the raw material, besides the microlites, phenocrysts of quartz with dimensions varying from 2 to 3 mm are observed, corroded in the mass itself (Fig. 5).

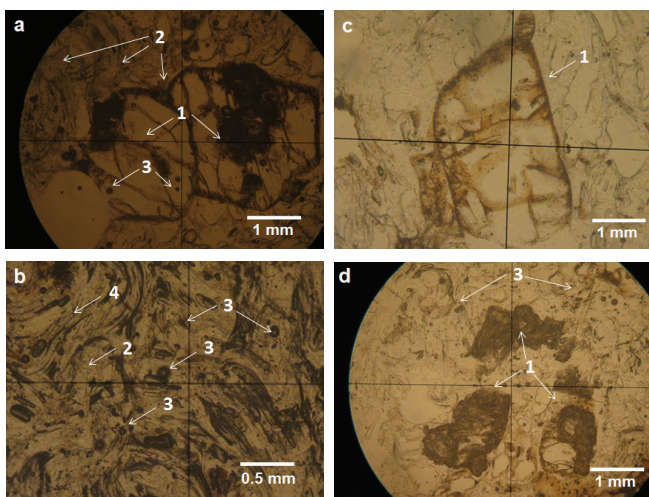


Figure 5. Optical photomicrographs of perlite: a) 2-3 mm quartz phenocryst (1) and microlite (3) embedded in the glassy mass (2) with indications of corrosion of the crystal; b) isotropic microlites (3) with prevalence of turbulent, fluidal movement (4) of the glassy phase (2); c) corroded phenocryst (1) from the glassy mass; d) microlite (3) and corroded phenocrysts (1) of pigmented isotropic minerals (most likely carriers of Fe, Ti and Mn) from the glassy mass.

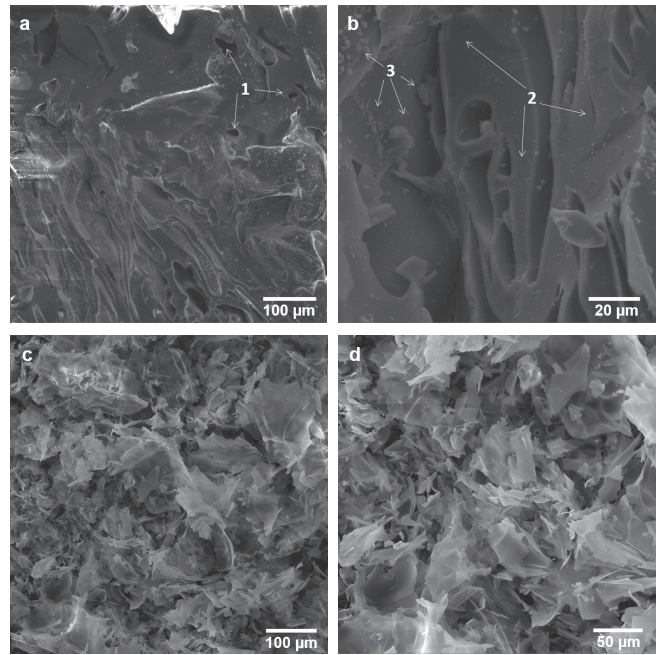


Figure 6. SEM photomicrographs of crude perlite (a,b) and the expanded perlite (c,d). Perlite shows open pores (1), glassy mass (2), and tiny crystals (3).

3.6. Scanning electron microscopy (SEM-EDX) and transmission electron microscopy (TEM) of the native and expanded perlite

The results from the SEM of crude perlite (Figs. 6a,b) confirm the findings from the optical microscopy. The evidence of open pores and the fluid character of the glassy phase are depicted in Fig. 6a, whereas Fig. 6b illustrates compact glassy mass of the perlite with presence of the tiny crystals.

Scanning electron microscopy (SEM) was also employed to study the induced material alteration by the expansion process (Fig. 6c, d). During the heat treatment, the grains start to soften superficially and the outer shell becomes smooth, while the water trapped in the thin layers escaped resulting in expansion of the grain. The grains explode vigorously with considerable morphological alteration (ROULIA et al., 2006).

The expanded perlite particles exhibited irregular morphology with broken or ragged edges. The perlite particles exhibit some internal cellular structure. The microstructure of the expanded perlite is characterized by vast open pores (small channels which form a dense network) and some isolated holes and cells.

According to the area spectrum of EDX analysis, the presence of O, Na, Al, Si and K elements in the structure of the native perlite was quantitatively determined (Fig. 7). Namely, the chemical composition and weight percentage of the elements in perlite (O: 51.40%, Na: 2.00%, Al: 6.72%, Si: 35.03%, and K: 4.84%) correspond to the prevailing glassy phase in perlite (Fig. 7a, c). On the other hand, the chemical composition obtained from carefully selected spheres with dimensions smaller than $1\text{--}5\text{ }\mu\text{m}$ (O: 63.19%, Al: 7.04%, and Si: 29.76%) served as evidence for the presence of crystalline aluminosilicates in perlite (Fig. 7b, d).

The results from the transmission electron microscopy of the crude perlite show that the main mass of perlite is volcanic glass (Fig. 8). TEM also shows that the glassy mass of native perlite nests presence of very fine crystalline phases, with dimensions ranging from $10\text{--}50\text{ nm}$ (Fig. 8). These results correspond to

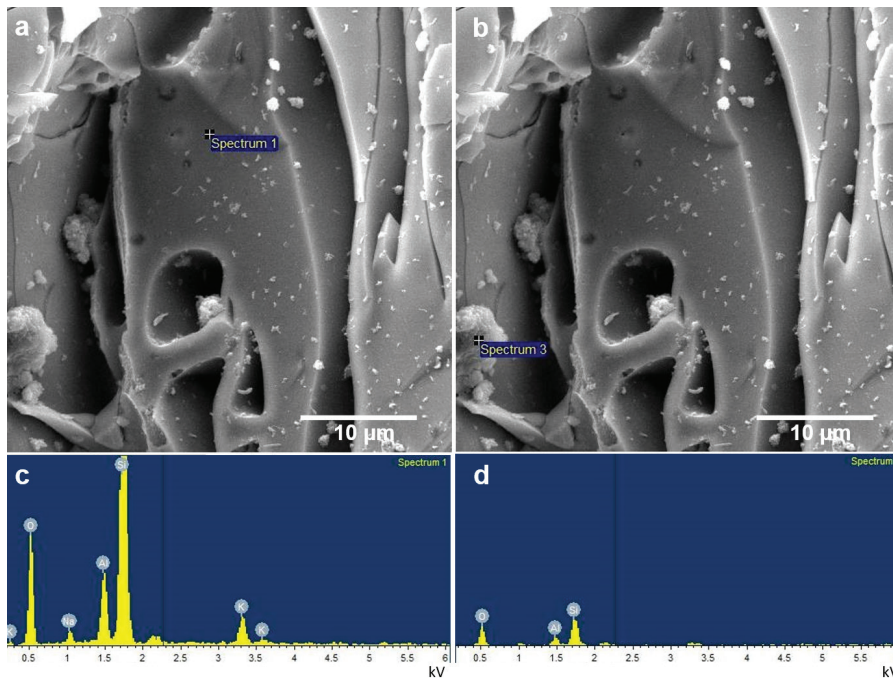


Figure 7. SEM photomicrographs of native perlite: the glassy/amorphous (a) and crystalline phase (b) and the corresponding element content as determined by EDS (c, d).

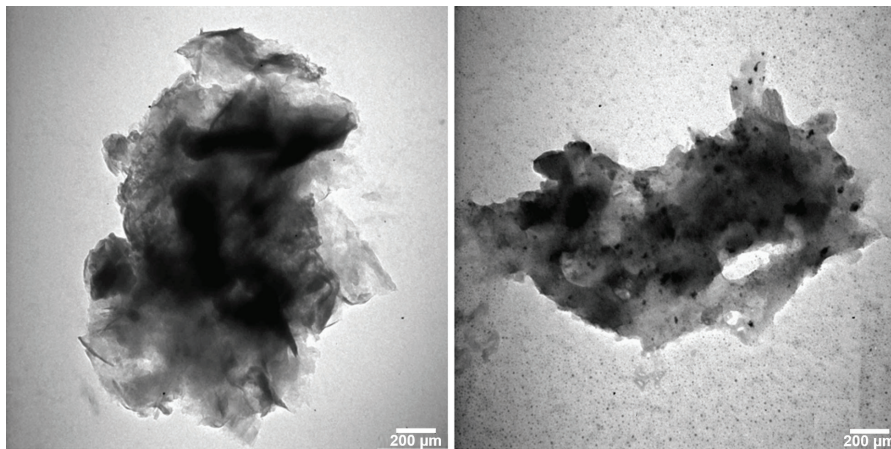


Figure 8. TEM photomicrographs of the glassy mass in perlite (left) and the crystalline phases in the volcanic glass (right).

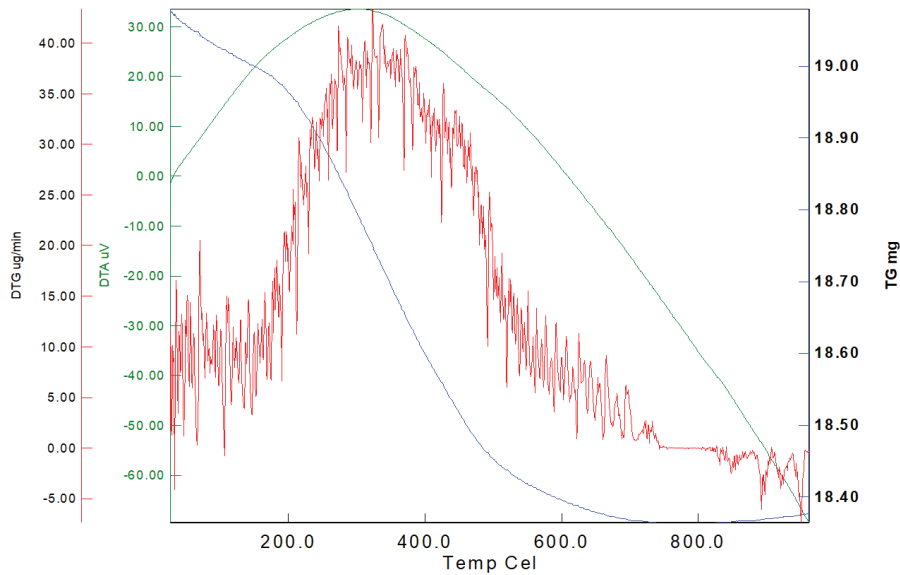


Figure 9. The DTA/TGA curves of native perlite.

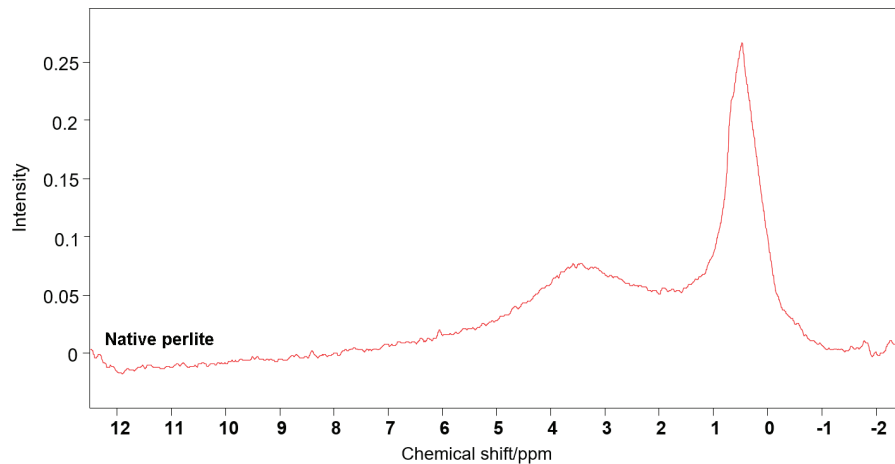


Figure 10. Solid state ^1H NMR spectrum of the native perlite (volcanic glass).

XRPD observations where the amorphous phase prevailed and a relatively low crystalline phase (tiny crystals) was observed. These results are also complementary with the composition of volcanic glass observed by EDX measurement.

3.7. Thermal examinations

The thermogravimetric analysis (TGA) and the differential thermal analysis (DTA) of the analyzed raw volcanic rock indicates weight loss in three temperature intervals (Fig. 9). The first temperature interval is between 20 and 215 °C resulting with a subtle weight loss of 0.68% attributed to the loss of adsorbed water on the perlite surface. The major mass loss of 2.69% occurs in the temperature interval from 215–477 °C and is a consequence of the hydroxyl groups release. Bearing in mind the absence of organic matter due to the lack of determined carbon (according to the chemical analysis), we suggest that the remaining chemically bonded water (0.43%) (ROULIA et al., 2006; CELIK et al., 2013), is released in the temperature interval from 477–826 °C.

3.8. Solid state (CP-MAS) ^1H NMR spectroscopy

The ^1H CP-MAS NMR spectra of the crude perlite (Fig. 10) consists of two peaks. The first maximum around 0.3 ppm is very intensive and relatively narrow, whereas the second weak and broad peak evolves around 3.5 ppm. This second peak exhibits a broad appearance due to the overlapping of the signals from the homonuclear dipolar interactions and chemical shift distribution caused by sample disorder, reflecting the predominant amorphous nature of the analyzed specimen.

The obtained spectrum compares well with previous published solid state ^1H NMR spectra of perlite from other regions (ZUJOVIC et al., 2018). However, the lower or more narrow but intensive signal at 0.3 ppm serves as an indicator for the crystallinity phase of the sample that was also depicted from the collected XRPD spectrum (see Fig. 3, top).

4. CONCLUSIONS

The first full characterization of the unexpanded and expanded perlite from Mariovo allows the following conclusions to be drawn:

i) Chemical analysis of the volcanic rock suggests that the raw material represents acidic volcanic rock, with a high percentage of SiO_2 (72.48%), whereas the presence of Al_2O_3 is 13.52%. The percentage of alkali metal oxides, K_2O and Na_2O is 4.21% and 3.56% respectively.

ii) Results from the XRD examination suggest a high percentage of amorphous phase, with the minimal presence of crystalline forms. The crystalline phase is mainly composed of feldspars, and SiO_2 polymorphs (quartz and cristobalite).

iii) The results from the optical microscopy confirm the results from the XRD analysis; the volcanic rock is composed of an isotropic amorphous glassy mass with the presence of fine-grained particles-microlite.

iv) The SEM results are commensurate with the findings delivered by optical microscopy. SEM photomicrographs undoubtedly report on the fluid character of the glassy mass and the compact glass mass of the perlite with the presence of tiny crystals and pores. On the other hand, the SEM results from the *expanded* perlite revealed the presence of open pores (small channels which form a dense network) and some isolated holes and cells in its microstructure. The simultaneous presence of these open pores and isolated holes delivers extremely high transpiring power (absorb water and then release the water in the form of vapour) and high strength, respectively. The difference is pronounced by the fact that the transpiring characteristic plays a pivotal role in the thermal insulation property of the material, whereas high strength is needed for structural lightweight concrete.

v) Total mass loss of 3.80 wt.% observed during the TG treatment was correlated with trapped water escaping from the volcanic rock.

vi) The IR spectrum provides valuable information regarding the presence of adsorbed water in perlite (1644 cm^{-1} and 3650 cm^{-1} bands) that was essentially excreted during the expansion process (the corresponding bands disappeared).

Due to the low proportion of a crystalline phase fortified by the abovementioned results, it can be concluded that analyzed volcanic rock (perlite), represents valuable starting material for production of high quality expanded perlite. As a result of the high percentage of alkali metal oxides, the high percentage of SiO_2 , the volcanic glass (perlite) can be utilized as a raw material for the production of container glass. The high percentage of the glassy phase, high percentage of SiO_2 and alkali metal oxides makes perlite from Mariovo an attractive material for the production of acid resistant glazing materials.

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