Characterization and evaluation of magnesite ore mining procedures by-products from Gerakini mines, Chalkidiki, Greece

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Abstract

Qualitative and quantitative characterization of seven samples (W_1-W_7), which were collected from various grades from "Rachoni" magnesite mine of "Grecian Magnesite SA" company in Gerakini, Chalkidiki, Greece, was performed in this study. The characterization was aiming to their evaluation regarding the possibility of upgrading their properties using various treatment methods (e.g. thermal) under the frame of circular economy. The chemical composition of the samples was determined by Flame Atomic Absorption Spectroscopy (FAAS), after digestion of the samples. Structural characterization of the collected samples was performed by X-Ray Diffraction (XRD), whereas supplementary information on the composition was received by ThermoGravimetric and Differential Thermal Analysis (TG-DTA). The loss of ignition test was also applied in air to estimate the presence of volatile substances (hydroxyls, hydrates, carbonyls) in the minerals. The results of the applied methods reveal the mineral and chemical composition of the samples, as well as their degree of serpentinization. Samples W_1 and W_2 have totally lost their ultramafic characteristics, as a result of the low grade metasomatic processes, that they have been subjected. Sample W_3, beyond the serpentinization process, has been subjected aluminus alteration, resulting the presence of vermiculite and talc. Samples W_4 to W_7, have been subjected serpentinization of different degree each sample, keeping their ultramafic characteristics, mineralogically and petrochemically. These results, indicate that samples W_4, W_5, W_6 and W_7 are the most promising to undergo a suitable (thermal) treatment for the upgrade of their physicochemical characteristics. The presence of magnesite in the samples W_6 and W_7, may more benefit their transformation to forsterite by heat treatment due to the presence of available magnesium.

Introduction

In magnesite-producing mines, the initial extraction of the ore is followed by a series of processes for the separation of magnesite from the host ultramafic rock and the latter is considered as the by-product of the separation processes. Due to the serpentinization of the ultramafic rocks and the consequent alteration of the primary minerals olivine and/or pyroxene mainly to secondary minerals of the serpentine group, the physicochemical properties of these by-products are degraded and their economic and commercial exploitation is currently limited. The purpose of this study, is the qualitative and quantitative characterization of rocks hosting magnesite ore deposits and their evaluation regarding the possibility of upgrading their properties using various treatment methods (e.g. thermal) under the frame of circular economy. For this purpose, samples of various grades were collected from "Rachoni" magnesite mine of "Grecian Magnesite SA" company in Gerakini, Chalkidiki, Greece. Initial investigation and evaluation of the samples was carried out in order to develop appropriate laboratory and industrial technology for the conversion of these wastes into a commercial product (dunite) with added value.

Experimental procedures

To determine the physicochemical properties of these samples, was performed chemical characterization by Flame Atomic Absorption Spectroscopy (FAAS), as well as the determination of the loss on ingnition (LOI). The chemical composition of the samples, was determined by FAAS. For the application of the FAAS method, each sample was crushed (<73μm) and a small quantity (~0.2g) was digested with 1mL $HClO_4$ and 15mL HF in Teflon vials on a sand bath, until incipient dryness. The residue was dissolved using 20mL 6N HCl and diluted to 200mL with ultra-pure water. The loss on ignition test was also applied in air, in 950°C to estimate the presence of volatile substances (hydroxyls, hydrates, carbonyls) in the minerals. Structural characterization of the collected samples was performed by X-Ray Diffraction (XRD), whereas supplementary information on the composition was received by ThermoGravimetric and Differential Thermal Analysis (TG-DTA).

Results and discussion

As for the chemical composition of the samples (Table 1), the following range was determined: SiO_2 37.5-65.2wt%, MgO 5.9-43wt%, Fe_2O_3 1.7-8.1wt%, Al_2O_3 0.45-10.8wt%, CaO 0.3-7.5wt%, Na_2O 0.1-3.3wt%, while were

detected at lower levels the components K_2O, MnO_2, NiO, Cr_2O_3. Based on the content of SiO_2, the samples are distinguished, into two groups: the samples with high silica content (W_1 and W_2) and the samples with low silica content (W_3 to W_7). In samples W_1 and W_2, was also determined the lowest percentage of MgO, while the samples W_3 to W_7 contain the highest. The loss on ignition of the samples ranges from 3.7 to 16% by weight, while this value in serpentine minerals range from 12-13.5% by weight[1] .

Table 1. Chemical composition of major and minor oxides in studied samples.

Sample		W_1	W_2	W_3	W_4	W_5	W_6	W_7
MgO	(wt%)	8.1	5.9	32.5	43.0	41.8	39.1	39.7
Fe_2O_3	(wt%)	1.7	6.7	6.8	7.6	8.1	7.2	7.3
Al_2O_3	(wt%)	10.8	1.1	2.9	0.7	0.5	0.5	0.7
CaO	(wt%)	3.8	7.5	1.4	0.6	0.5	0.3	0.4
Na_2O	(wt%)	3.3	0.1	0.5	0.3	0.3	0.4	0.3
SiO_2	(wt%)	64.1	65.2	39.4	43.3	39.2	37.5	38.7
K_2O	(mg/kg)	4730	620	340	720	695	720	745
MnO_2	(mg/kg)	365	1260	1290	1455	1860	1365	1475
NiO	(mg/kg)	509	1814	1586	2900	2955	2802	2621
Cr_2O_3	(mg/kg)	575	570	730	910	320	340	585
LOI	(wt%)	7.3	12.5	16.0	3.7	9.3	14.2	12.4

The XRD patterns, revealed the presence of various serpentine minerals (chrysotile, antigorite, lizardite)[2] in the samples with the highest loss on ignition due to the higher percentage of crystalline water content. In particular, the XRD patterns for the samples W_1 and W_2, in Figures. 1 and 2 respectively, reveal that they consist mainly of quartz and feldspar and carbonate minerals (dolomite and calcite), respectively. This fact, in combination with the increased content of SiO_2 and CaO (Table 1), shows a typical mineral composition that classifies them petrologically as listvanites and confirms the chemical differentiation of the samples in high and low quartz content, as mentioned above. The listvanites are rocks rich in silicon and carbonates. They are products of low degree metasomatic processes of mafic and ultramafic rocks[3].
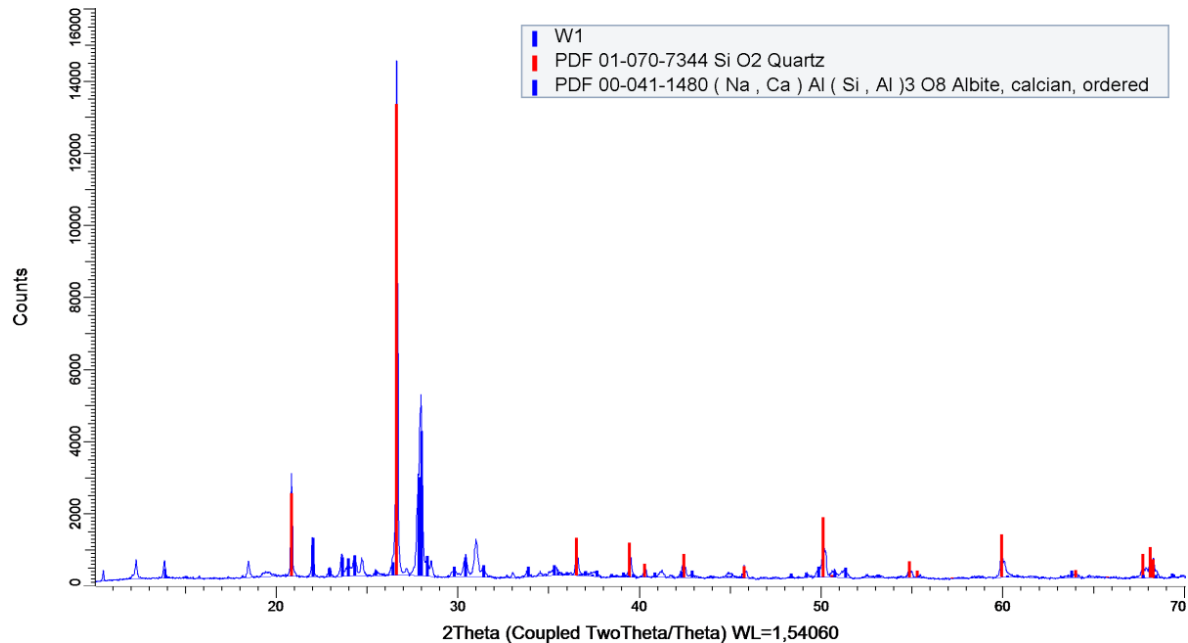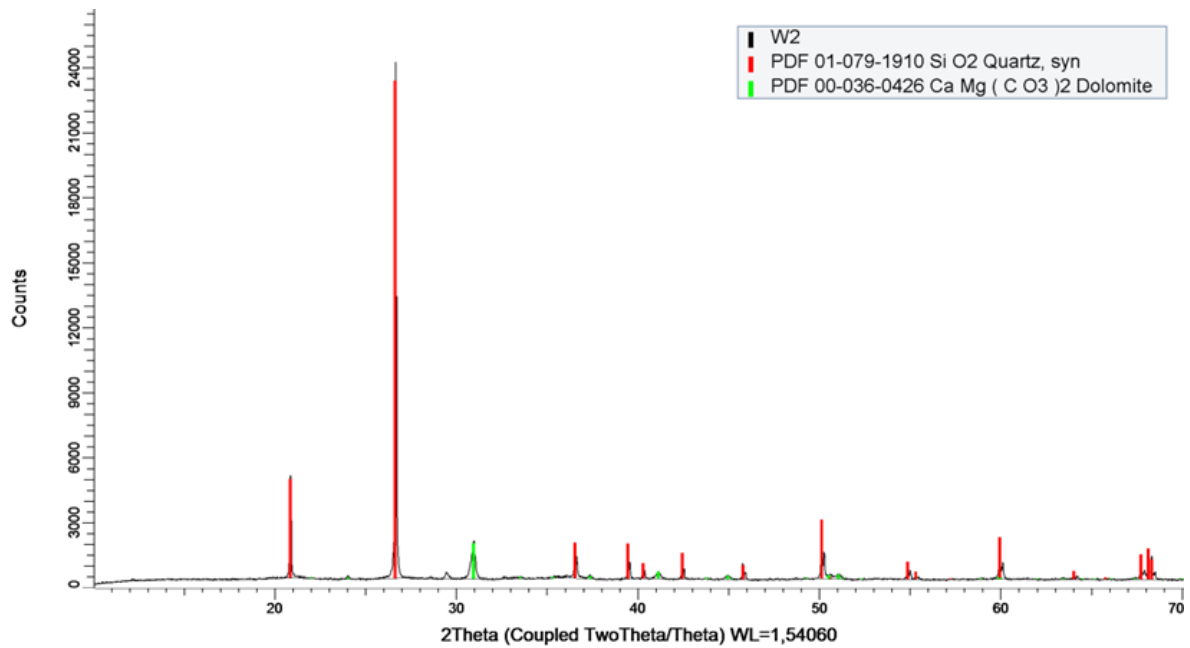

Figure 1. XRD pattern of sample W_1.

Figure 2. XRD pattern of sample W_2.

The sample W_3, consists of vermiculite-quartz-serpentine-talc-amphiboles-carbonates (Figure 3). The presence of the phyllosilicate mineral vermiculite, indicates that sample W_3 has subjected, except of serpentinization, and aluminus alteration[4].
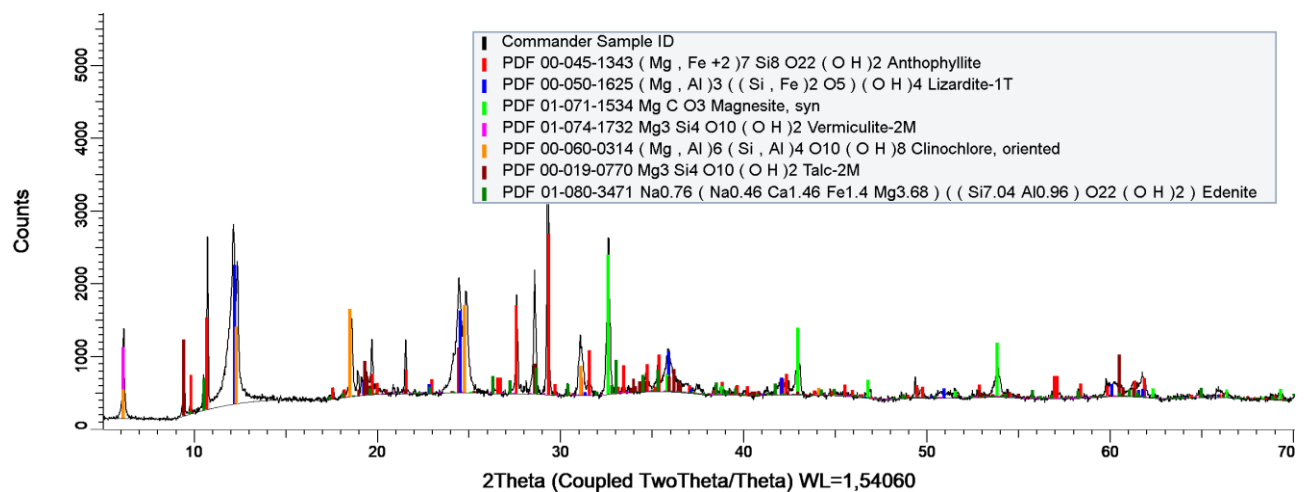

Figure 3. XRD pattern of sample W_3

The samples W_4 to W_7 consists mainly of olivine (forsterite) - serpentine – pyroxenes. Olivine and serpentine are the main phases in these 4 samples. The above mineral composition of these samples is a typical of ultramafic rocks hosting magnesite deposits and have subjected different degree of serpentinization. In Figures 4 and 5 are presenting the XRD patterns for the samples W_4 and W_5, respectively.
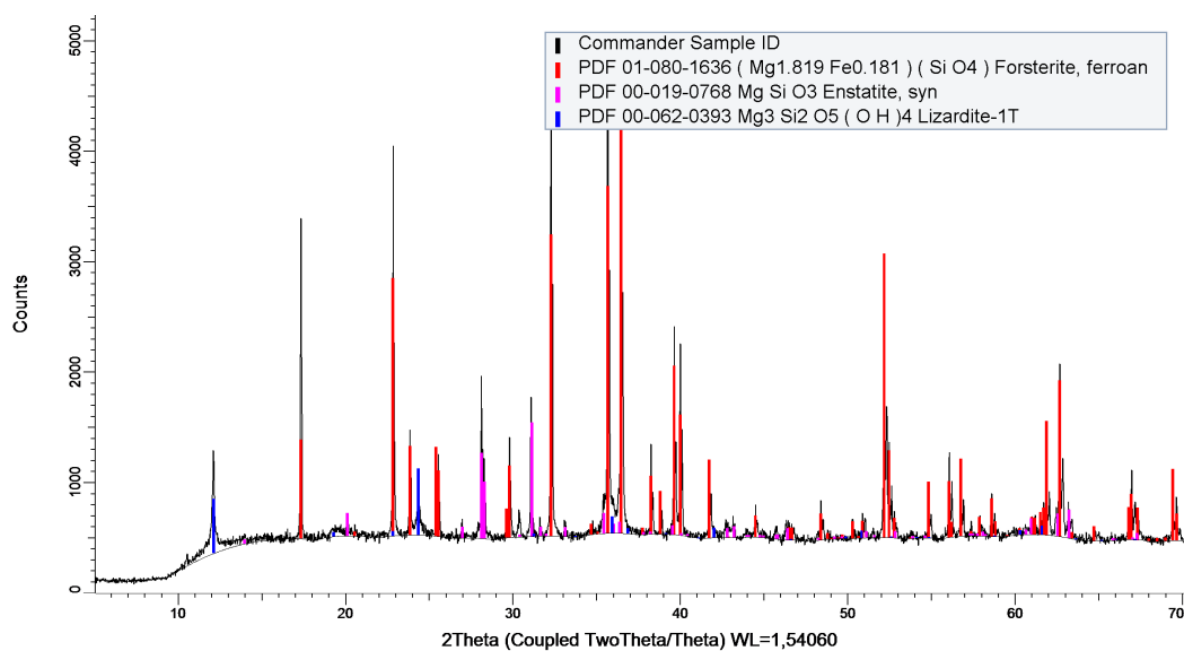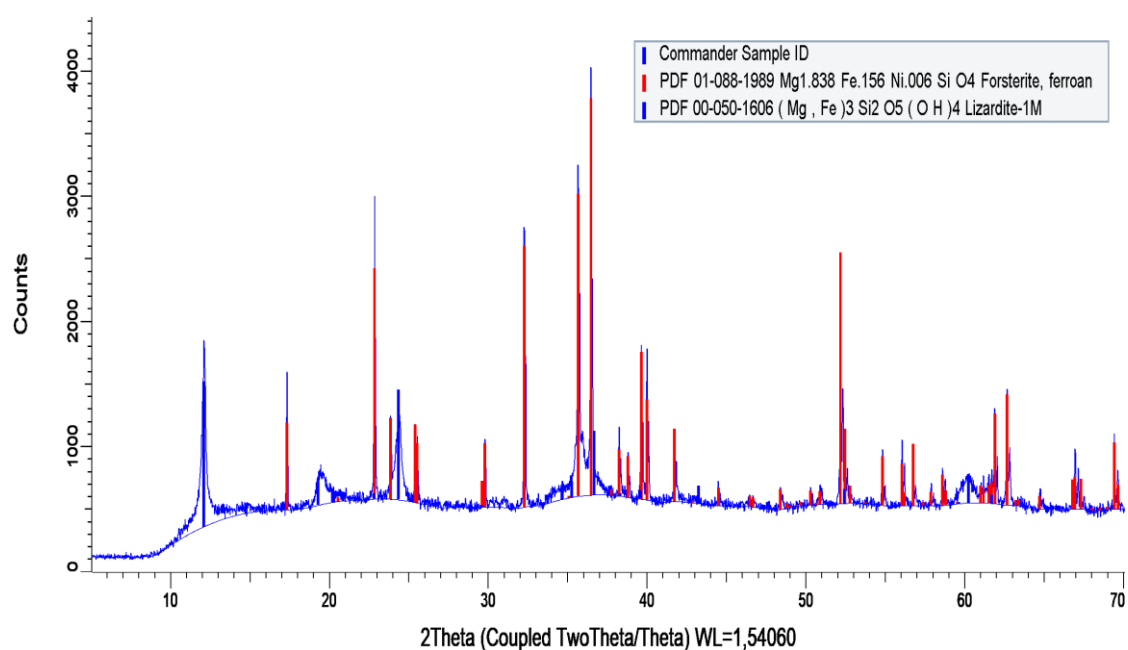
Figure 4. XRD pattern of sample W_4.

Figure 5. XRD pattern of sample W_5.

The XRD patterns from samples W_6 (Figure 6) and W_7, indicate that they have similar mineral composition. They consists of olivine, serpentine and appears also magnesite.
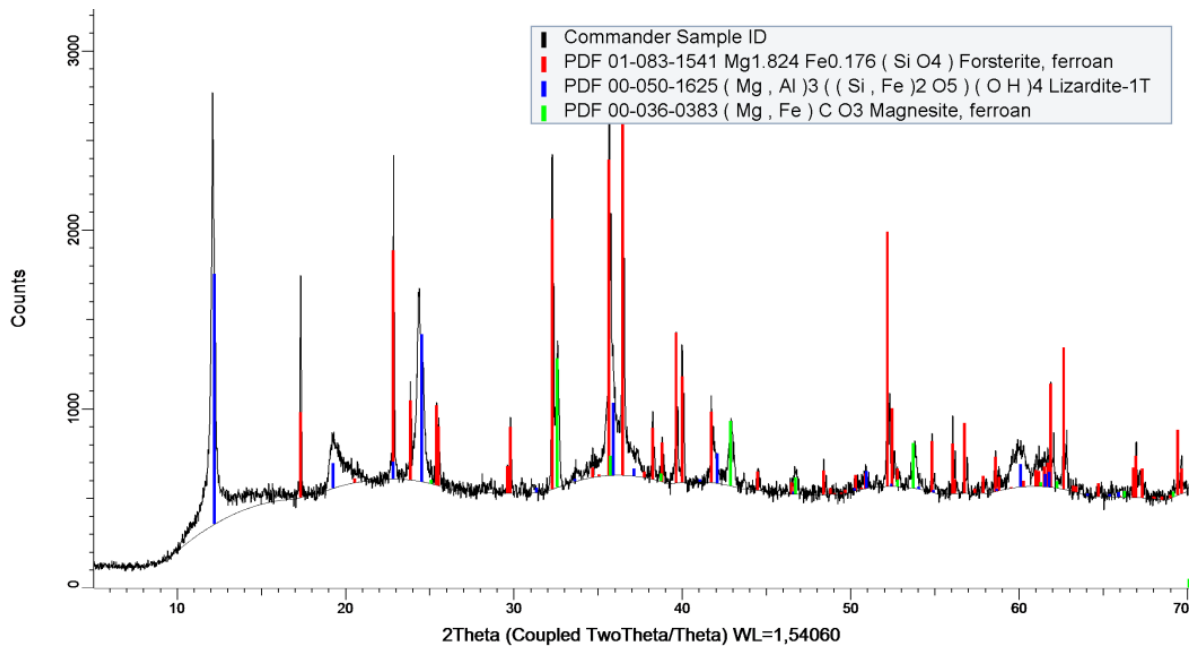
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Figure 6. XRD pattern of sample W_6.

The TG-DTA diagrams, indicates that the percentage on loss on ignition of the samples is in good agreement with weight loss from the diagrams. From the TG-DTA diagrams of the samples W_1 and W_2 (Figure 7 and 8 respectively) and W_3 is resulting that it is not observed the formation of forsterite, The endothermic peak near ~790°C, in the TG-DTA diagram for the sample, W_2, represents and decomposition of dolomite[5].
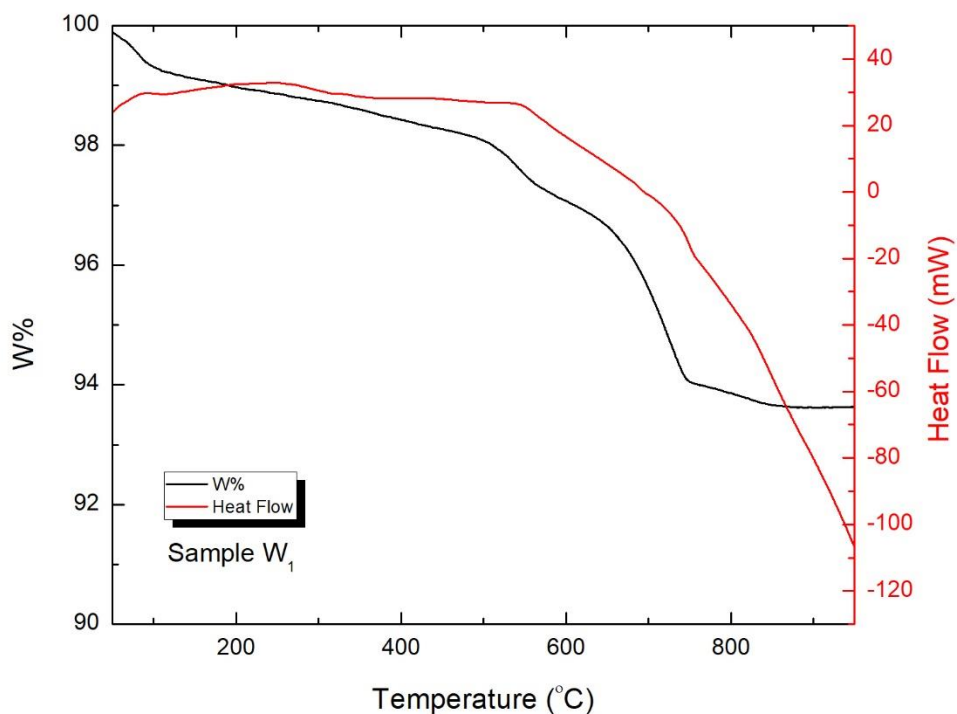

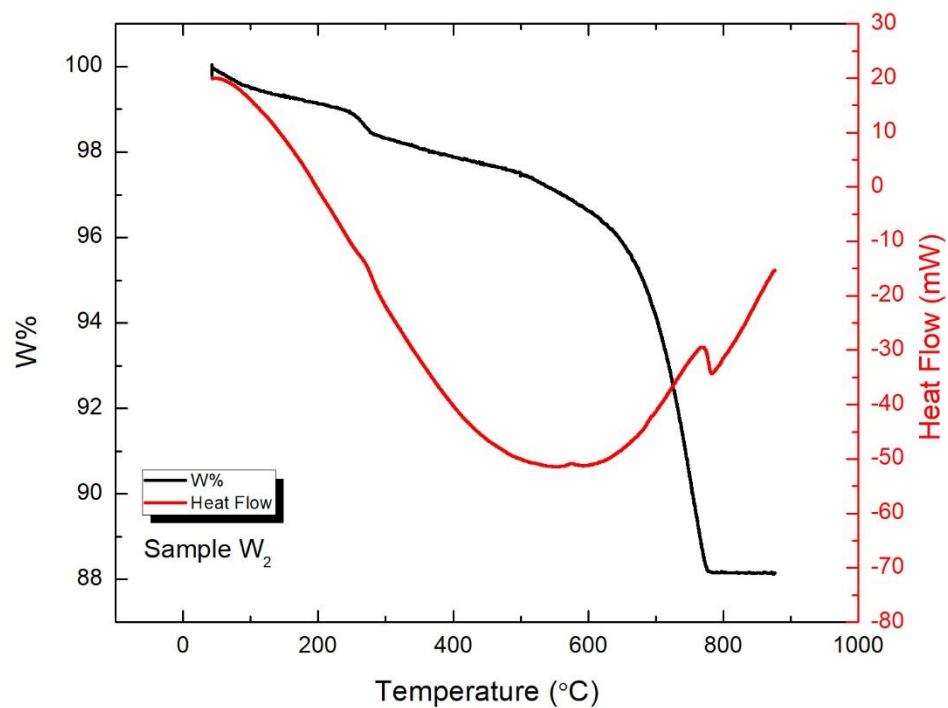
Figure 7. TG-DTA curves of sample W_1.

Figure 8. TG-DTA curves of sample W_2.

In the TG-DTA diagram for the sample W_4, after the release of the structural water (endodermic reaction) is observed a very small exothermic peak due to the formation of forsterite in ~830°C (Figure 9).
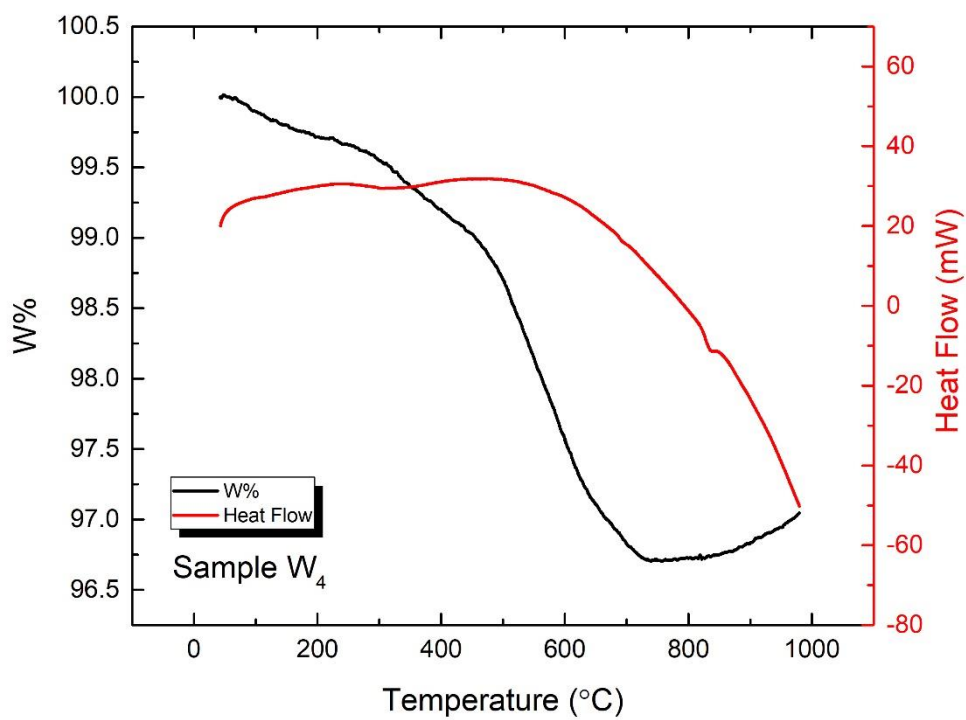

Figure 9. TG-DTA result of sample W_4.

On the contrary, in the samples W_5, W_6 and W_7 is observed significant formation of forsterite, with the highest rate of formation being observed in the samples W_6 and W_7 in ~850°C[6]. In the TG-DTA curve of the sample W_6 (Figure 8), is observed the loss of crystal waters from 550 to 700°C, in the form of an endothermic reaction, while near to ~850°C is observed the exothermic peak which attributed to formation of forsterite[6]. The fact that the sample W_6 contains lizardite and magnesite, concludes that lizardite in combination with excess magnesite, favor the formation of a higher amount of forsterite in relation with the magnesite-free samples (Reaction 1). The total loss on ignition for the sample W_6 is ~12,5%wt.%.
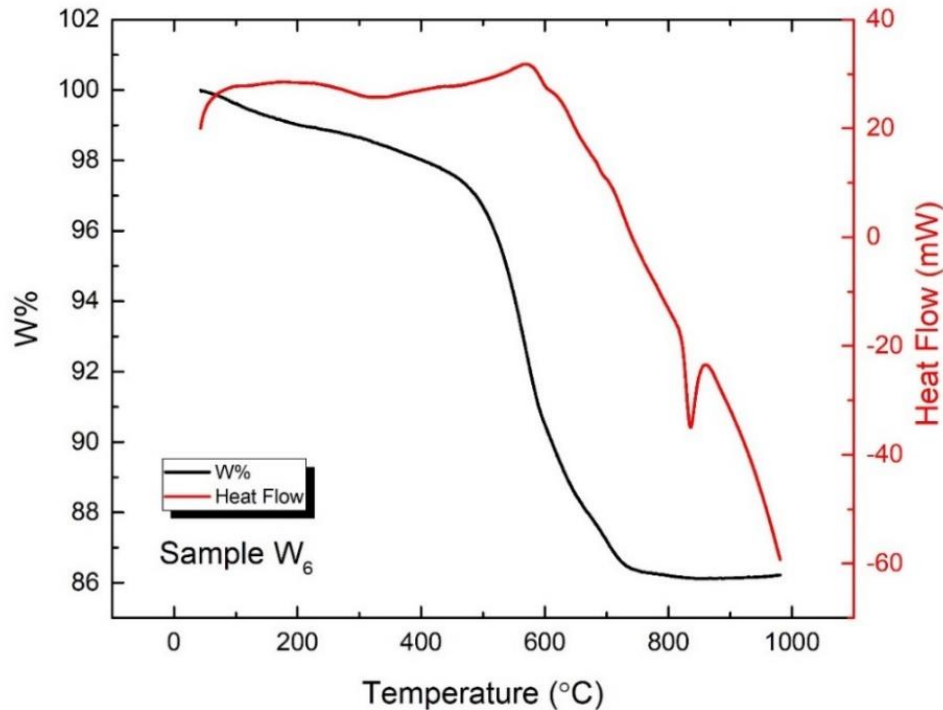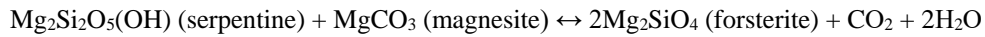
$$Mg_2Si_2O_5(OH) \text{ (serpentine)} + MgCO_3 \text{ (magnesite)} \leftrightarrow 2Mg_2SiO_4 \text{ (forsterite)} + CO_2 + 2H_2O$$

Figure 8. TG-DTA curves of sample W_6.

Conclusions

The results of the applied methods revealed the mineral and chemical composition of the samples, as well as their degree of serpentinization and indicate that samples W_4, W_5, W_6 and W_7 are the most promising to undergo a suitable (thermal) treatment for the upgrade of their physicochemical characteristics. This conclusion is based on their mineralogical composition: they consist mainly of serpentine and forsterite (the magnesium-rich end-member of olivine). Thermal treatment is expected to lead to the decomposing of serpentine and to the forming of "second generation" forsterite, thus upgrading the properties of this material. It should be noted that samples W_6 and W_7 also contain magnesite; the presence of magnesite in these particular samples could assist further during their thermal treatment because of the excess in available magnesium. According to the serpentinization chemical reaction:

$$2Mg_2SiO_4 \text{ (forsterite)} + CO_2 + 2H_2O \rightarrow Mg_2Si_2O_5(OH) \text{ (serpentine)} + MgCO_3 \text{ (magnesite)},$$
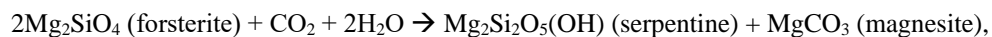
magnesite is going to be needed to reverse this chemical reaction, resulting the formation greater quantity of forsterite, which is the main target of the ongoing research.

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