

Proceeding Paper

# Investigation of Magnetic Separation and Thermal Treatment Effects, Combined with Additives (Mineral Oxides), on Serpentinized Peridotites from the Gerakini (Chalkidiki, N. Greece) Magnesite Mine <sup>†</sup>

Dimitra Papargyriou <sup>1,2</sup>, Evangelos Tzamos <sup>2,3,4,\*</sup>, Andreas Kasinos <sup>1</sup>, Polykarpos Papageorgiou <sup>1</sup>, Manassis Mitrakas <sup>5</sup> and Anastasios Zouboulis <sup>2</sup> 

<sup>1</sup> Grecian Magnesite S.A., Gerakini, 63100 Athens, Greece; d.papargyriou@grecianmagnesite.com (D.P.);

a.kasinos@grecianmagnesite.com (A.K.); p.papageorgiou@grecianmagnesite.com (P.P.)

<sup>2</sup> Department of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece; zoubouli@chem.auth.gr

<sup>3</sup> North Aegean Slops S.A., 54627 Thessaloniki, Greece

<sup>4</sup> Ecoresources P.C., 54627 Thessaloniki, Greece

<sup>5</sup> Department of Chemical Engineering, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece; mmitraka@auth.gr

\* Correspondence: tzamos@ecoresources.gr

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**Abstract:** Serpentinized peridotite samples—considered nowadays as deposited waste at the magnesite mine of Gerakini (Chalkidiki, N. Greece)—were collected, and their chemical and mineralogical characterization analyzed with Energy-Dispersive X-ray Fluorescence (ED-XRF) and X-ray Diffraction (XRD). Dry magnetic separation was used as a convenient enrichment method; however, no significant effect was shown in the chemical composition of separated (magnetic and non-magnetic) fractions, except for small increases in the olivine, antigorite and enstatite contents, which were observed in the non-magnetic fraction. Finally, the calcination of ground peridotites at 1520 °C, with the addition of CaO, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, presented a negative effect on the structure of the products with regard to their main refractory properties. In contrast, the addition of Cr<sub>2</sub>O<sub>3</sub> and MgO mineral oxides showed improved refractory properties when compared with the initial material.

**Keywords:** magnesite; dunite; serpentinite; chemical–mineralogical characterization; magnetic separation; thermal treatment; refractoriness

## 1. Introduction

Olivine is an anhydrous magnesium iron-silicate mineral with chemical formula 2 (Mg<sup>2+</sup>, Fe<sup>2+</sup>)O.SiO<sub>2</sub>, and is an isomorphic mixture mainly between forsterite (Mg<sub>2</sub>SiO<sub>4</sub>/Fo) and fayalite (Fe<sub>2</sub>SiO<sub>4</sub>/Fa) constituents [1]. Olivine is used in several industrial applications; however, it is noted that its main physicochemical and refractoriness properties are dependent on the content of Fo and Fa fractions [2–4].

Due to the serpentinization process of ultramafic rocks and the consequent alteration of primary minerals into secondary minerals of the serpentine group [5,6], the physicochemical properties of peridotites are gradually degraded, and the resulting materials present rather limited economic and commercial exploitation options [6].

In the Gerakini magnesite mines (N. Greece), peridotites are the host ultramafic rock of magnesite ore [7], covering approximately 80–85% of the excavation site. These rocks are separated from the (useful) magnesite mineral (MgCO<sub>3</sub>) by applying several enrichment processes. The average monthly production of this by-product is estimated

at  $80 \times 10^3$  tn, presenting diverse composition and consisting mainly of forsterite, up to completely degraded peridotites. The continuous deposition of these waste materials due to mining operations will soon start creating potential storage and management problems in the operating mining company.

The aim of this study is to evaluate the main chemical and mineralogical characteristics of these waste rocks (peridotites). The study also aims to investigate the possibility of enriching these waste- (as they are currently considered) or by-products with the application of a convenient magnetic separation process [8,9], alongside the investigation of the effect of thermal treatment and with the addition of different metal oxides (CaO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, MgO, Cr<sub>2</sub>O<sub>3</sub>), [1–4,10]. The aim is to initially develop a laboratory-based—but later a potentially industry-applicable—technology, regarding the conversion of a waste material into a useful product with commercial added value, i.e., applying the principles of a circular economy to mining operations.

## 2. Materials and Methods

Thirteen representative samples of serpentinized peridotites were collected—nine from different selected sites of the main excavation mining area (Rachoni), and two from the already-existing waste stockpiles. These samples were initially crushed with a jaw crusher down to 14 mm, which is the grain size suitable for the subsequent application of magnetic separation. Then, further grinding of these samples was performed (down to less than 63  $\mu\text{m}$ ), to be used for their detailed chemical and mineralogical analysis.

Chemical analysis was performed using Energy-Dispersive X-ray Fluorescence spectroscopy (ED-XRF) with the fusion beads method, adding LiB<sub>4</sub>O<sub>7</sub> as dilution material in the Spectro Xlab 2000 analyzer (Spectro, Kleve, Germany). X-ray Diffractometry (XRD) was used for the mineralogical analysis of samples by applying the SIEMENS–D5000 analyzer (40 KV, 30 mA) with Cu-K $\alpha$  radiation (Siemens, Madison WI, USA). Magnetic separation was performed using the industrial dry magnetic rotary separator (neodymium–iron magnet, field intensity of 15,000–16,000 G), attempting to remove the Fe<sup>2+</sup>-silicates fraction to enrich the residuals and to improve the chemical composition of the product.

Finally, for the thermal treatment experiments, two selected samples were used from different locations of the Gerakini mine's excavation site, with sizes of less than 63  $\mu\text{m}$ . Several mineral oxides (CaO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, MgO and Cr<sub>2</sub>O<sub>3</sub>) were added to these samples, then the mixtures were pressed to form cylindrical specimens. These specimens were calcined (thermally treated) in a programmed electrical furnace under air atmosphere, using heating and cooling rates of 4  $^{\circ}\text{C min}^{-1}$  and a dwell time of 2 h at 1520  $^{\circ}\text{C}$ . After that, the volume shrinkage, which occurred due to the firing treatment, was evaluated using a caliper and the  $(V_0 - V_1)/V_0$  ratio, whereas the indicators 0 and 1 refer to the dimensions of the same sample before and after the firing process.

## 3. Results and Discussion

### 3.1. Chemical and Mineralogical Characterization

The chemical and the mineralogical composition of the serpentinized peridotites samples obtained from the mine area are summarized in Tables 1 and 2, respectively. The samples W1–W3 present substantially different chemical compositions to the others, as also confirmed by the XRD diagrams; this is because they are more (geologically) degraded samples, due to a higher degree of serpentinization with the primary mineral phases of quartz and talc; therefore, these samples are considered of minor interest for further investigation/re-use purposes.

The average composition of sample W4-E6743 is: MgO  $42 \pm 3\%$ , SiO<sub>2</sub>  $41 \pm 3.5\%$ , FeO  $7.1 \pm 0.4\%$ , and LoI  $6.5 \pm 3\%$ . However, the mineralogical phase analysis reveals that olivine is the main mineral constituent, and antigorite and enstatite are secondary. The higher LoI of samples W6 and W7 is related to the presence/incorporation of MgCO<sub>3</sub>.

**Table 1.** Chemical analysis by Energy-Dispersive X-ray Fluorescence spectroscopy (XRF) and the respective loss of ignition (LoI).

Sample	MgO	SiO <sub>2</sub>	CaO	FeO wt. %	Al <sub>2</sub> O <sub>3</sub>	MnO	NiO	LoI
W1	11.2	63.5	4.10	1.5	10.4	0.04	0.05	7.3
W2	8.20	62.6	7.5	6.2	1.40	0.11	0.18	12.5
W3	34.3	39.7	1.5	5.3	2.4	0.10	0.18	15.7
W4	43.3	42.9	0.56	7.1	0.65	0.14	0.30	3.8
W5	41.5	38.8	0.49	7.5	0.50	0.19	0.32	9.5
W6	40.1	37.6	0.29	6.8	0.45	0.13	0.32	14.1
W7	39.5	38.6	0.47	6.7	0.60	0.14	0.29	12.4
W8	40.2	43.6	0.92	7.4	0.82	0.15	0.30	5.7
W9	39.2	44.2	0.74	7.2	0.80	0.14	0.28	6.5
W10	39.7	43.2	0.81	7.1	1.05	0.15	0.29	7.1
W11	41.3	39.9	0.27	6.9	0.65	0.13	0.32	9.3
E6382	39.8	43.1	0.60	7.1	0.70	0.14	0.30	7.3
E6743	44.8	38.0	0.55	6.7	0.65	0.15	0.28	6.8

**Table 2.** Mineralogical analysis using X-ray Diffractometry (XRD).

Sample	Main Phase	Secondary Phases
W1	Quartz	Enstatite, antigorite, vermiculite
W2	Quartz	dolomite
W3	Talc	Quartz, antigorite, magnesite, enstatite
W4	Olivine	Antigorite, enstatite, quartz
W5	Olivine	Antigorite, vermiculite, traces of enstatite
W6	Antigorite	Olivine, magnesite, traces of talc and quartz
W7	Antigorite	Olivine, enstatite, magnesite, talc, traces of quartz
W8	Olivine	Antigorite, enstatite
W9	Olivine	Antigorite, enstatite, talc
W10	Olivine	Antigorite, enstatite, talc
W11	Olivine	Antigorite, enstatite, talc
E6382	Olivine	Antigorite, enstatite
E6743	Olivine	Antigorite

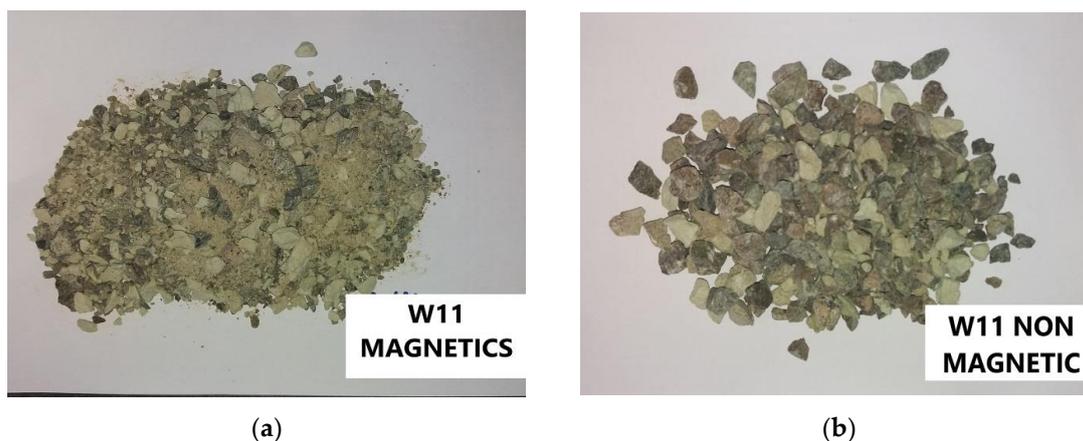
### 3.2. Dry Magnetic Separation

Regarding the application of magnetic separation as a typical mineral enrichment method, four representative samples from the mine area were selected (W4, W6, W9 and W11) with grain sizes of 0–14 mm, and passed through the industrial rotary magnet. The distribution of the material between the two fractions showed that the non-magnetic fraction was higher (65–75%) in comparison to the magnetic one.

The particle size analysis of the separated fractions showed a higher concentration of material in the 0–5 mm size in the magnetic fraction and for all the examined samples, in contrast to the non-magnetic fraction, for which the material was present in higher concentrations in the 5–10 mm size. This indicates that better separation can be achieved for the smaller-sized granulometry. A macroscopic view of the examined fractions is shown in Figure 1, with the fractions of the W11 sample as an example.

The chemical analysis and the LoI determination of the fractions did not show any significant differences between the magnetic and the non-magnetic fractions, nor with the composition of raw samples, i.e., before the application of the separation process (Table 3). However, the FeO content of the magnetic fraction was between 1 and 1.5 wt. %, which is greater compared to that of the non-magnetic fraction.

However, the mineralogical analysis—as obtained from the XRD measurements—revealed a small increase in olivine, serpentine and enstatite minerals in the non-magnetic fraction for all the examined samples, except for sample W9, where a decrease in serpentine content can be noted (Figure 2c).



**Figure 1.** The sample W11 fractions after the application of magnetic separation: (a) magnetic fraction; (b) non-magnetic fraction.

**Table 3.** Chemical analysis using XRF and LoI of magnetic and non-magnetic fractions.

Sample	MgO	SiO <sub>2</sub> wt. %	CaO	FeO	LoI
<b>W4</b>	<b>43.3</b>	<b>42.9</b>	<b>0.56</b>	<b>7.1</b>	<b>3.8</b>
Magnetic	42.4	39.9	0.65	8.2	4.9
Non-magnetic	44.7	43.5	0.51	6.4	3.2
<b>W6</b>	<b>40.1</b>	<b>37.6</b>	<b>0.29</b>	<b>6.8</b>	<b>14.1</b>
Magnetic	41.2	36.1	0.45	7.5	13.3
Non-magnetic	39.7	37.9	0.25	6.2	14.5
<b>W9</b>	<b>39.2</b>	<b>44.2</b>	<b>0.74</b>	<b>7.2</b>	<b>6.5</b>
Magnetic	38.7	43.1	0.95	7.9	8.1
Non-magnetic	40.9	44.8	0.61	6.6	5.7
<b>W11</b>	<b>41.3</b>	<b>39.9</b>	<b>0.27</b>	<b>6.9</b>	<b>9.3</b>
Magnetic	40.8	39.6	0.41	7.7	8.8
Non-magnetic	41.6	40.2	0.24	6.6	9.6

### 3.3. Thermal Treatment

To evaluate the calcination (thermal treatment) effect, two samples (E6382 and E6743) were selected; they presented different chemical compositions, especially regarding the olivine percentage. The olivine content of the E6382 and E6743 samples were calculated as  $65 \pm 4$  wt. % and  $93 \pm 3\%$ , respectively, using quantitative analysis of XRD patterns with JADE XRD data analysis software. In Figure 3a,b, the pressed pellets of peridotite sample E 6382 before and after calcination are shown, respectively. As can be noted, the calcination had a negative effect on the pellet structure, with the appearance of melted material and relative volume shrinkage.

Further investigation of this effect showed that the addition of CaO, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> mineral oxides caused the extensive melting and volume shrinkage of the respective specimens; these were found to be proportional to the percentage of added oxides, with the major impact shown by the addition of SiO<sub>2</sub> (Figures 4–6). Contrarily, by adding the oxides of MgO and Cr<sub>2</sub>O<sub>3</sub> to the examined specimens, an improvement in refractoriness can be observed (Figures 7 and 8, respectively).

With the aim of cross-checking the negative effect of adding Ca, Al and Si oxides, the same experiment was performed for sample E6743, which consisted mainly of olivine, and showed the lowest melting point upon application of calcination in comparison with the E6382 sample, as shown in Figure 9. The addition of Ca or Al oxides showed no significant effect on the refractoriness properties; however, by adding SiO<sub>2</sub>, the negative effect was

more obvious, with increasing volume shrinkage and melting of the pellet when comparing these samples with the initial sample (without additives) (Figures 10–12).

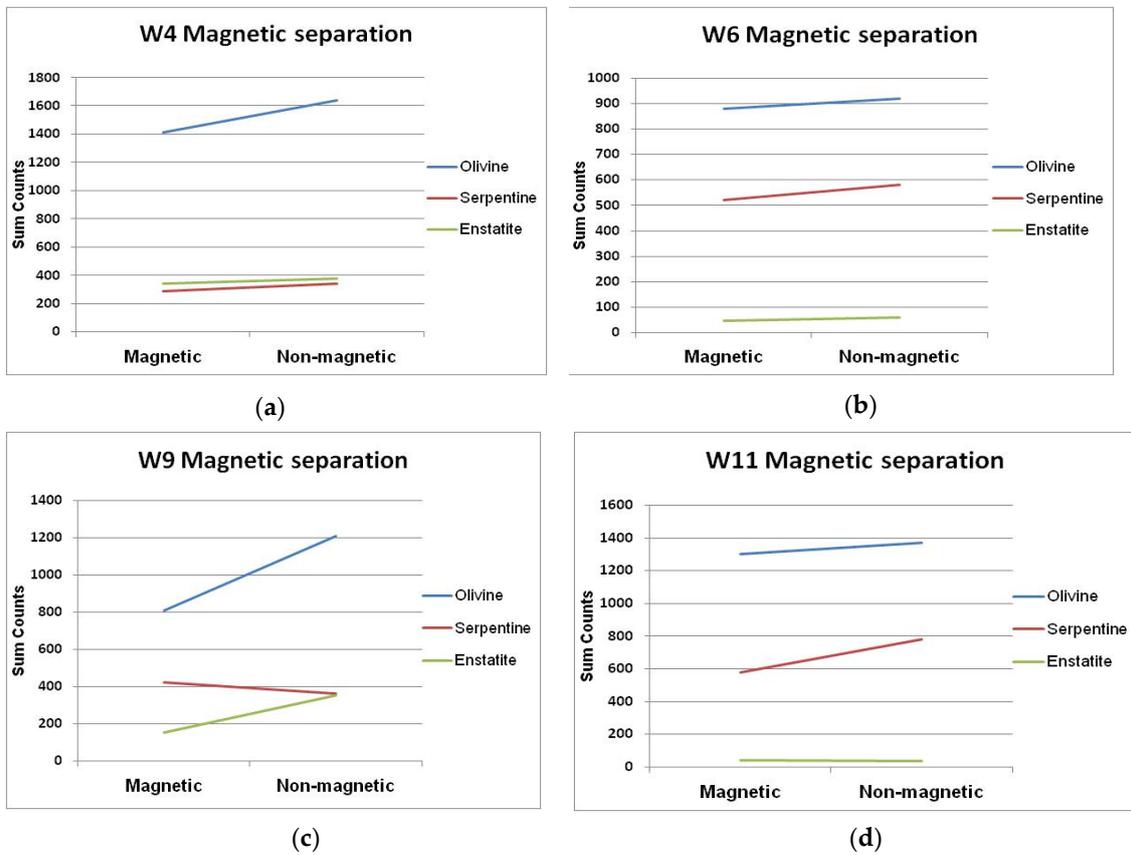


Figure 2. Diagrams of main diffraction peak count variations in the XRD patterns for the samples: (a) W4; (b) W6; (c) W9; and (d) W11.

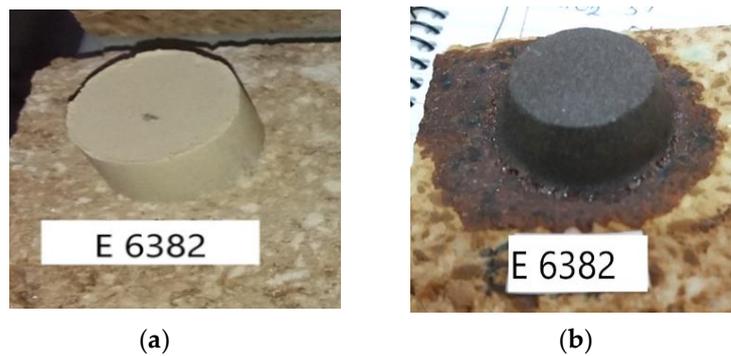


Figure 3. Peridotite sample E6382: (a) Before calcination; (b) after calcination.



Figure 4. Peridotite sample E6382 with the CaO addition after calcination.

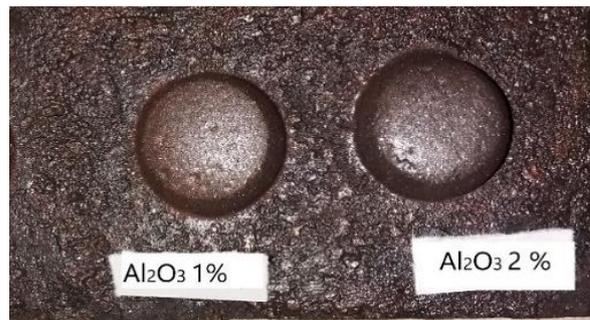


Figure 5. Peridotite sample E6382 with the Al<sub>2</sub>O<sub>3</sub> addition after calcination.



Figure 6. Peridotite sample E6382 with the SiO<sub>2</sub> addition after calcination.

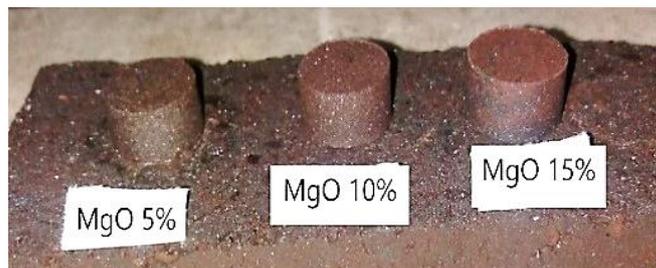


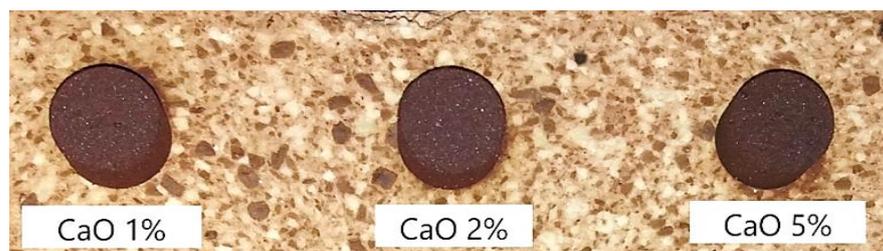
Figure 7. Peridotite sample E6382 with the MgO addition after calcination.



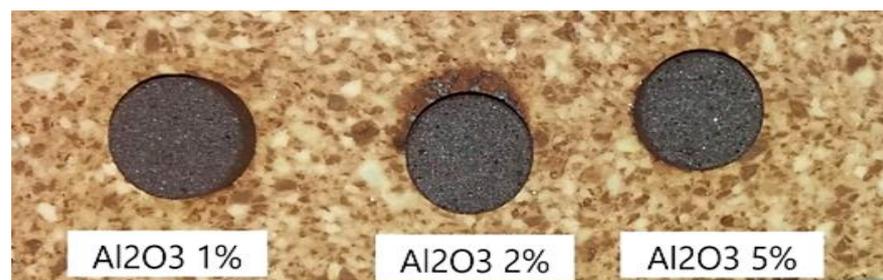
Figure 8. Peridotite E6382 with the Cr<sub>2</sub>O<sub>3</sub> addition after calcination.



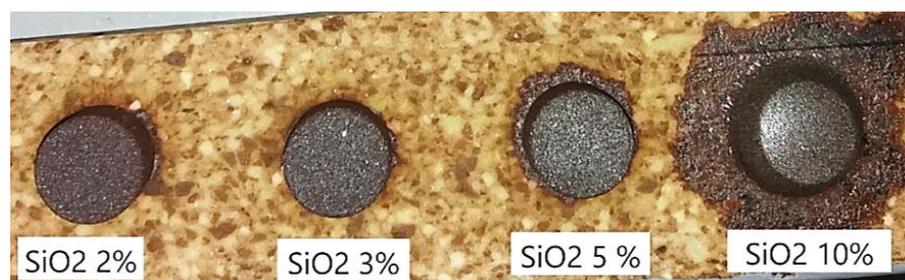
Figure 9. Peridotite sample E6743 without additives after calcination.



**Figure 10.** Peridotite sample E6743 with the CaO addition after calcination.



**Figure 11.** Peridotite sample E6743 with the Al<sub>2</sub>O<sub>3</sub> addition after calcination.



**Figure 12.** Peridotite sample E6743 with the SiO<sub>2</sub> addition after calcination.

#### 4. Conclusions

Several samples considered as waste/by-products were collected from the magnesite mine area, and a detailed chemical and mineralogical analysis was conducted using Energy-Dispersive X-ray Fluorescence (ED-XRF) and X-Ray Diffractometry (XRD) methods, respectively. The average chemical analysis of the examined specimen W4-E6743 was found to be: MgO  $42 \pm 3\%$ , SiO<sub>2</sub>  $41 \pm 3.5\%$ , FeO  $7.1 \pm 0.4\%$ , and LoI  $6.5 \pm 3\%$ , whereas the mineralogical phase analysis revealed that olivine was the main mineral constituent, and that antigorite and enstatite were secondary.

The process of dry magnetic separation as an enrichment method presented no particular effect with regard to the chemical composition between the separated fractions, although it revealed small increases in olivine, antigorite and enstatite in the non-magnetic fraction.

Finally, the calcination of peridotite specimens at 1520 °C, with the addition of mineral oxides (CaO, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>), presented a negative effect on the structure of the products regarding the main refractory properties, in contrast with the addition of Cr<sub>2</sub>O<sub>3</sub> and MgO oxides, which showed an improvement in them when compared with the initial material.

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## References

1. Furlani, E.; Aneggi, E.; Maschio, S. Sintering behavior of waste olivine and olivine/alumina blends. *Materials* **2014**, *7*, 4773–4788. [[CrossRef](#)] [[PubMed](#)]
2. Sarkar, R. Olivine-the potential industrial mineral: An overview. *Trans. Indian Ceram. Soc.* **2002**, *61*, 80–82. [[CrossRef](#)]
3. Küçüköğlü, Ö.; Yücel, O. Production of Olivine-Based Refractories from Domestic Sources. In Proceedings of the 18th International Metallurgy & Materials Congress, Istanbul, Turkey, 29 September–1 October 2016; pp. 220–222.
4. Birch, R.E.; Harvey, F.A. *Forsterite and Other Magnesium Silicates as Refractories*; Annual Meeting American Ceramic Society, Refractories Division: Buffalo, NY, USA, 1935; pp. 176–192.
5. Moody, J.B. Serpentinization: A review. *Lithos* **1976**, *9*, 125–138. [[CrossRef](#)]
6. Diamantis, K. Engineering Geological Properties of the Ultrabasic Rocks in Othrys and Kallidromo Mountains (Central Greece). Ph.D. Thesis, Agricultural University of Athens, Athens, Greece, 2010.
7. Shand, A.M. *The Chemistry and Technology of Magnesia*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2006; pp. 5–30.
8. Belley, F.; Ferré, E.C.; Martín-Hernández, F.; Jackson, M.J.; Dyar, M.D.; Catlos, E.J. The magnetic properties of natural and synthetic (Fe, Mg<sub>1-x</sub>)<sub>2</sub>SiO<sub>4</sub> olivines. *Earth Planet. Sci. Lett.* **2009**, *284*, 516–526. [[CrossRef](#)]
9. Nemat, S.; Ramezani, A.; Emami, S.M. Possible use of serpentine from Abdasht chromite mines into the refractory and ceramic industries. *Ceram. Int.* **2016**, *42*, 18479–18483. [[CrossRef](#)]
10. Nguyen, M.; Sokolář, R. Influence of different raw material mixtures with olivines on synthesis and properties of forsterite ceramics. *AIP Conf. Proc.* **2019**, *2170*, 020012.