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Some Aspects of the Reactivity of Olivine and Serpentine towards Different Chlorinating Gas Mixtures

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The reactivity of olivine and serpentine towards Cl_2+air , Cl_2+N_2 and Cl_2+CO was studied in non isothermal conditions up to 1000 °C. The same samples were also chlorinated in a horizontal experimental set during 2 hours between 500 °C and 1000 °C, under oxidizing and reducing atmospheres. The chlorination products were examined by XRD and SEM.

The iron bearing compounds contained in the olivine and serpentine natural samples can be eliminated through the chlorination or the oxychlorination of these solids at temperatures lower than 900 °C. Carbochlorination of olivine and serpentine is incomplete even at 1000 °C for a reaction time of 2 h. Pure magnesium chloride can be recovered by cooling the gas phase at about 500 °C.

Key Words : Olivine, Serpentine, Chlorination, TGA, Reactivity

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I. INTRODUCTION AND LITERATURE REVIEW

Chlorination of magnesium silicates could be considered as alternative for the extraction of pure magnesium compounds. The literature is relatively poor in this field. This paper describes preliminary results about this topic. It is a part of a larger program devoted to the study of chlorine technology.^[1-3]

Ishii et al.^[4] studied the chlorination of FeO, Fe₂O₃, SiO₂, MgO as well as olivine, protoenstatite and talc between 25 °C and 1000 °C using differential thermal and thermogravimetric analysis (DTA and TGA). According to these authors, the reactivity of MgO towards chlorine is negligible at 640 °C in absence of carbon. In its presence, an exothermic peak is observed at 500 °C corresponding to the formation of MgCl₂. This peak shifts to lower temperatures with increasing the amount of carbon. An endothermic peak was observed at about to 700 °C and attributed to the fusion of MgCl₂. The initial reaction rate was rapid. However, as the reaction progresses, its rate decreases and finally stopped completely at about 55 pct of MgO chlorination. The authors suggest that MgCl₂ formed on the surface of the MgO particles acts as a barrier for further progress of the reaction. They also indicated that chlorination of olivine is only possible in presence of carbon and suggested that two types of magnesium coexist in this solid having different reactivities towards chlorine. Protoenstatite and talc give exothermic peaks at 950 °C and 750 °C, respectively. Equations 1 and 2 describe respectively the interaction of olivine and protoenstatite with Cl₂+C corresponding to these exothermic peaks, while the chlorination of talc proceeded together with its decomposition following equation 3.



II. THERMODYNAMIC STUDY

Olivine and serpentine natural samples contain iron impurities. The evolution of the standard free energy changes (ΔG°) of chlorination of MgO, FeO, Mg₂SiO₄, MgSiO₃ and SiO₂ by chlorine (Eqs. 4 to 10) and by Cl₂+CO (Eqs. 11 to 17) are calculated using data of references 5 and 6. Figures 1 and 2 show the evolution of standard free energy changes, as a function of temperature, for the chlorination and carbochlorination of the considered reactions. Only the chlorination of FeO

by chlorine is thermodynamically favorable in whole explored temperature range. On the other hand, ΔG° of MgO chlorination is slightly positive at temperatures higher than about 500 °C, while the chlorination of SiO₂ is thermodynamically unfavorable up to 1000 °C. However, in the presence of a reducing atmosphere, all the carbochlorination reactions are thermodynamically favorable in the investigated temperature range.

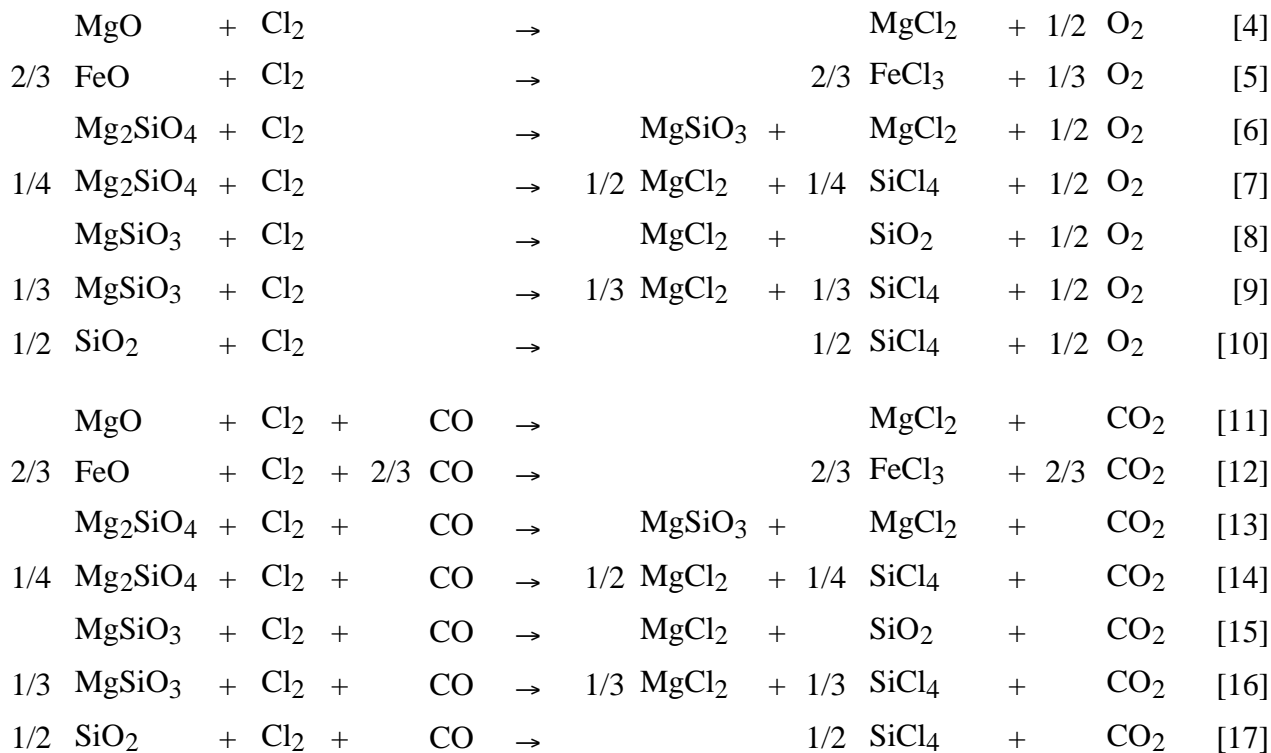


Figure 3 shows the phase stability diagrams for the (Mg, Fe, Si)-O-Cl systems at 800 °C. These diagrams are established using data of reference 6. The estimated experimental partial pressures of Cl₂ and O₂ are indicated in these diagrams for the different chlorination atmospheres. According to these diagrams, oxides of the three elements will react with chlorine in the presence of CO at 800 °C, whereas with the Cl₂+N₂ gas mixture, only iron oxide and MgO could be chlorinated. The thermodynamic probability of chlorination of all the oxides decreases as the oxygen partial pressure increases.

III. MATERIALS AND EXPERIMENTAL PROCEDURE

Natural olivine and serpentine are used for this investigation. X-ray diffraction (XRD) and scanning electron microscope (SEM) analyses of samples are summarized in Figure 4. The main phases identified in these samples are Mg₂SiO₄ and Mg₃Si₂O₅(OH)₄, respectively. However, SEM analysis indicated the presence of iron compounds in these solids. Thermogravimetric (TG)

chlorination tests were realized with 100 mg of sample, using the experimental procedure described previously^[1]. The furnace's heating rate was about 25 °C/ min.

The oxy- and carbochlorination tests with these samples were carried out in a horizontal experimental set described in reference^[1]. This set is essentially composed of a gas metering unit followed by a gas purification one and an automatically controlled electrical furnace. The outlet gas mixture is cooled to condense and to recover volatile chlorides. The exhausted gas mixture is purified before its release to the atmosphere. The reaction products were subjected to SEM and XRD analysis for the identification of formed phases.

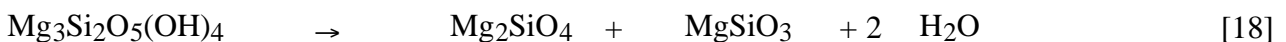
IV. RESULTS AND DISCUSSION

A. Non-isothermal TG measurements

1. Oxychlorination

Figure 5 traces the evolution of the percent (pct) weight loss of olivine and serpentine samples *versus* temperature during their treatments in Cl₂+air gas mixture. The reaction of olivine with this gas mixture starts by a slight weight increase probably due to chlorine adsorption on the sample's surface. The Mg₂SiO₄ sample's weight loss starts at temperature higher than 750 °C. Its reaction rate is low and its weight loss is less than 5 pct even at temperatures approaching 1000 °C. This weight loss is probably due to the chlorination of the iron impurities and the volatilization of the formed ferric chloride.

For temperatures less than 500 °C, the serpentine' weight loss is about 1 pct. This weight change is attributed to adsorbed water and partially to constituted one. At temperatures higher than 500 °C, the sample's weight loss is about 16 pct. Treatment of Mg₃Si₂O₅(OH)₄ in nitrogen and using the same experimental conditions leads to a weight loss of about 13 pct that is equal to the calculated weight loss using equation 18. This is probably due to the thermal decomposition of the serpentine and subsequent volatilization of H₂O as described by the following equation.



Consequently, the weight loss of Mg₃Si₂O₅(OH)₄, about 3 pct, may be attributed to the chlorination of the iron bearing compounds and the volatilization of FeCl₃. XRD of the reaction products shows the presence of Mg₂SiO₄ and MgSiO₃. One may underline that MgSiO₃ is thermodynamically stable in Cl₂ as indicated by reactions 8 and 9 (Fig. 1).

2. Chlorination

TG chlorination curves of Mg_2SiO_4 and $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ in the Cl_2+N_2 atmosphere are shown in Figure 6. The curve of olivine indicates that the reactivity of olivine towards the chlorination gas mixture is low. This is in good agreement with the thermodynamic considerations (Figure 1). Only the iron bearing compounds were probably chlorinated up to 1000 °C. The behavior of serpentine in Cl_2+N_2 is almost identical to that in Cl_2+air . However, the obtained weight loss is slightly higher than that corresponding to the thermal decomposition of this solid.

3. Carbochlorination

As expected from the thermodynamic calculations, the carbochlorination of these solids is more favorable than their chlorination with Cl_2+N_2 or Cl_2+air . Figure 7 traces the pct weight loss curves *versus* temperature for the chlorination of magnesium bearing compounds. The olivine begins to react with Cl_2+CO at about 600 °C. The sample weight increases with the temperature rise up to 900 °C. The stabilization of weight loss, beyond this temperature, is due to the overlapping of the sample's rates of carbochlorination and that of MgCl_2 volatilization. The curve of the serpentine carbochlorination first exhibits a weight loss from 500 °C to 700 °C attributed to its thermal decomposition. At temperatures higher than 700 °C, the weight increase is due to the formation of MgCl_2 . Further weight loss above 900 °C is due to the volatilization of magnesium chloride. One may underline that boiling point of MgCl_2 is 1412 °C^[7].

B. Isothermal Treatment in the Horizontal Experimental Set

1. Oxychlorination

Following the preliminary experimentation on the chlorination behavior of these samples in non-isothermal conditions, a series of experiments was performed under isothermal conditions in the temperature range of 500 °C and 1000 °C for a reaction time of two hours using about 3 grams. Figure 8 groups the evolution of pct weight loss of samples as a function of temperature.

The reactivity of olivine towards Cl_2+air is low even for a reaction time of two hours. The observed weight loss of about 8 pct at 1000 °C corresponds probably to the chlorination of iron oxide contained in the sample and probably to partial chlorination of this sample. Analysis of residue shows the presence of Mg_2SiO_4 (Table I) as the only stable phase in all residues obtained by the oxychlorination of olivine. The reaction of serpentine with the oxychlorinating gas mixture

started after its thermal decomposition according to Eq. 18. Again, the chlorination rate of serpentine is low even at 1000 °C. As it is shown in Table I, the XRD analysis confirms the decomposition of serpentine at temperatures higher than 600 °C and the formation of Mg_2SiO_4 and $MgSiO_3$. The absence of magnesium chloride in the reaction product, if formed, can be justified by its volatilization because of the important linear velocity of the gas mixture (about 50 cm/ min.).

Table I - XRD Analysis of the Oxychlorination Residues.

Solid	Temperature of Treatment, °C			
	500	600	800	1000
Olivine	Mg_2SiO_4	Mg_2SiO_4	Mg_2SiO_4	Mg_2SiO_4
Serpentine	$Mg_3Si_2O_5(OH)_4$	$Mg_3Si_2O_5(OH)_4$	$Mg_2SiO_4, MgSiO_3$	$Mg_2SiO_4, MgSiO_3$

2. Carbochlorination

Figure 9 shows the evolution of pct weight loss of olivine and serpentine samples during their carbochlorination between 500 °C and 1000 °C. The olivine sample reacts with the gas mixture at 500 °C leading to a weight increase. Between 600 and 700 °C, the weight loss remained constant. This observation agrees with that of Ishii et al.^[4] concerning the presence two types of magnesium, present in the olivine, having different reactivities for the chlorination. Table II confirms the presence of Mg_2SiO_4 and $MgSiO_3$. For temperatures higher than 800 °C, the volatilization of $MgCl_2$ begins leading to a decrease of the sample's weight. As indicated by XRD results of Table II, the phases detected in the chlorination residue are Mg_2SiO_4 and $MgCl_2$ at 500 °C and 600 °C. $MgSiO_3$ was identified at temperatures equal or higher than 800 °C and confirms the reaction described by equation 13. The carbochlorination of olivine is incomplete even at 1000 °C. This is because of the formation of a magnesium chloride and amorphous silica layer that acts as a barrier between the rest of olivine and the carbochlorinating gas mixture. This hypothesis is confirmed by the presence of only $MgCl_2$ as revealed by XRD and that of amorphous silica identified by the SEM analysis.

Serpentine reacted with the Cl_2+CO gas mixture at 500 °C. The observed weight loss up to 800 °C is the algebraic sum of the weight increase due to the chlorination of the iron and magnesium compounds and the weight loss due to the thermal decomposition of the sample (Eq. 18) and the volatilization of $FeCl_3$ and $MgCl_2$. At higher temperatures, the rate of volatilization of $MgCl_2$ seems to be higher than that of its formation. This is confirmed by the presence of silicates in the residue treated at 1000 °C (Table II).

Table II - XRD Analysis of the Carbochlorination Residues.

Solid	Temperature of Treatment °C			
	500	600	800	1000
Olivine	Mg ₂ SiO ₄ , MgCl ₂	Mg ₂ SiO ₄ , MgCl ₂	Mg ₂ SiO ₄ , MgSiO ₃ , MgCl ₂	MgCl ₂
Serpentine	Mg ₃ Si ₂ O ₅ (OH) ₄	MgCl ₂	Mg ₂ SiO ₄ , MgSiO ₃ , MgCl ₂	Mg ₂ SiO ₄ , MgSiO ₃

* MgCl₂ is identified as MgCl₂·6H₂O.

V. CONCLUSIONS

The reactivity of Mg₂SiO₄ and Mg₃Si₂O₅(OH)₄ towards oxychlorinating and chlorinating gas mixtures is low. In both cases, only the iron contained in these minerals is chlorinated and volatilized at temperatures lower than 1000 °C. At temperatures higher than 500 °C, the serpentine is thermally decomposed. These results show that the elimination of the iron compounds from these solids is possible through their chlorination in the temperature range of 800 °C to 1000 °C.

Chlorination and carbochlorination of serpentine and olivine start at about 500 °C and is incomplete at 1000 °C. The serpentine is decomposed to Mg₂SiO₄ and MgSiO₃ at temperatures lower than 800 °C. The iron bearing compounds were fully chlorinated and volatilized at temperatures lower than 900 °C. The magnesium and iron chlorides are recovered by cooling the outlet gases to about 500 °C and 25 °C, respectively. The recovered magnesium chloride is of high purity and identified by XRD as MgCl₂·6H₂O. Such product can be used as a raw material for the fabrication of pure magnesium employed for the production of alloys devoted to the aeronautic sector.

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FIGURE CAPTIONS

- Figure 1 : Standard free energy change of chlorination reactions as a function of temperature^[5, 6].
- Figure 2 : Standard free energy change of carbochlorination reactions as a function of temperature^[5, 6].
- Figure 3 : Phase stability diagram of (a) Mg-O-Cl, (b) Fe-O-Cl and (c) Si-O-Cl systems at 800 °C^[5].
- Figure 4 : Results of SEM and XRD analyses of employed samples.
- Figure 5 : Thermogravimetic analysis of magnesium compounds in Cl₂+air.
- Figure 6 : Thermogravimetic analysis of magnesium compounds in Cl₂+N₂.
- Figure 7 : Thermogravimetic analysis of magnesium compounds in Cl₂+CO.
- Figure 8 : Oxychlorination of magnesium silicates in a horizontal set during 2 hours.
- Figure 9 : Carbochlorination of olivine and serpentine in a horizontal set during 2 hours.

TABLE CAPTIONS

- Table I : XRD Analysis of the Oxychlorination Residues.
- Table II : XRD Analysis of the Carbochlorination Residues.

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Figures

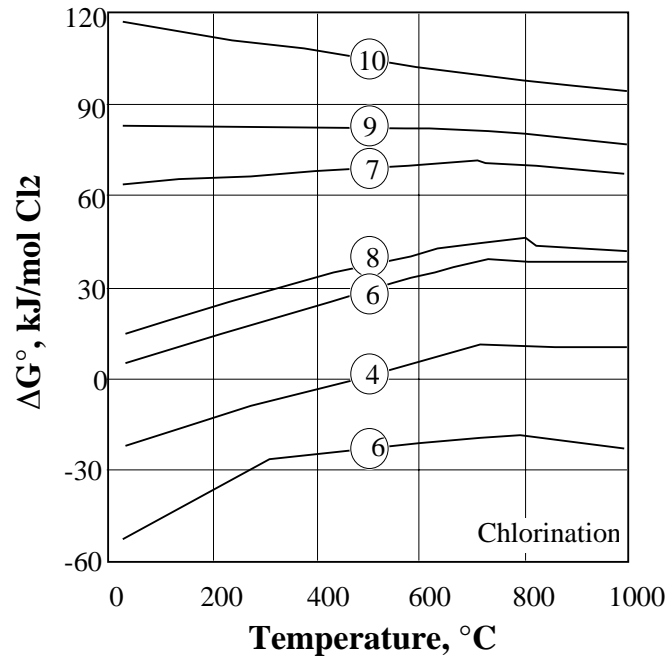


Figure 1 - Standard free energy change of chlorination reactions as a function of temperature^[5,6].

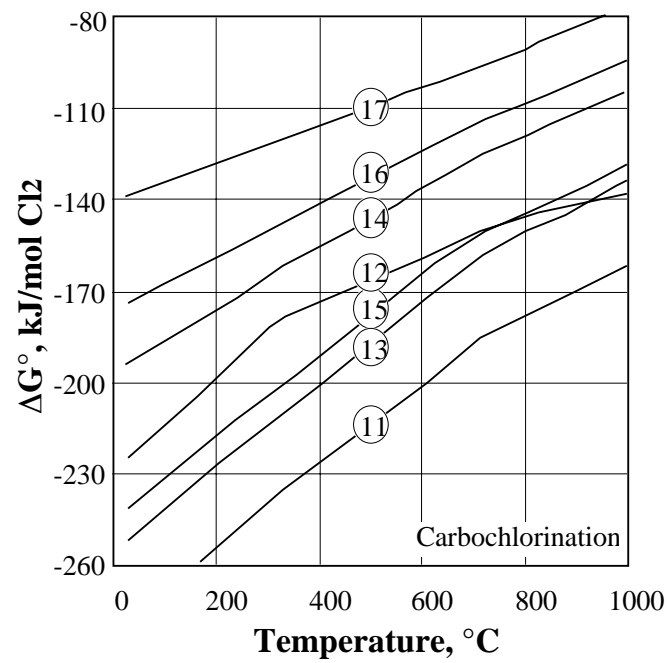
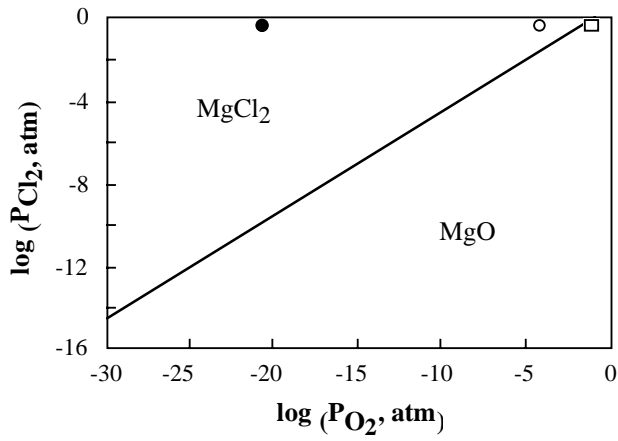
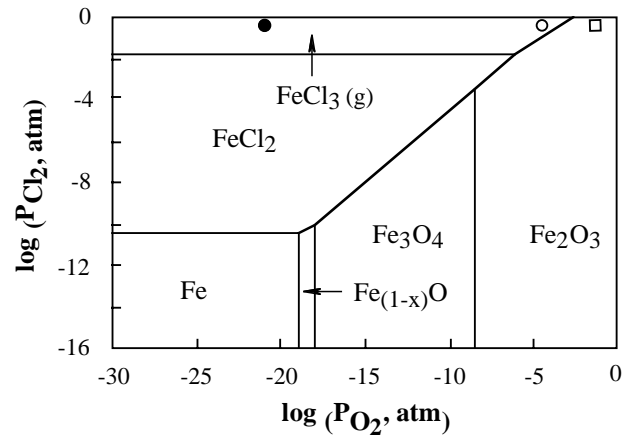


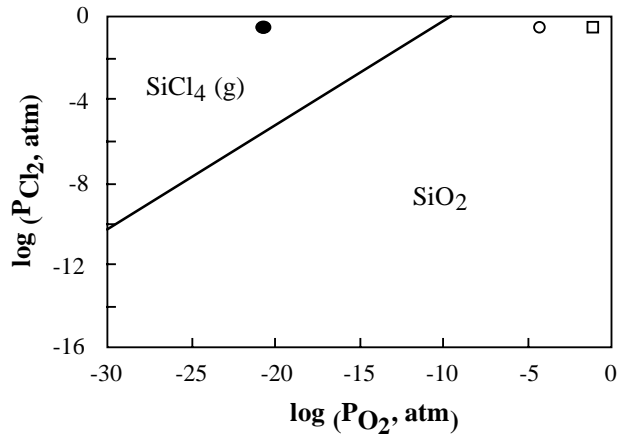
Figure 2 - Standard free energy change of carbochlorination reactions as a function of temperature^[5,6].



(a)



(b)



(c)

- : Estimated range of experimental conditions for oxychlorination,
- : Estimated range of experimental conditions for chlorination,
- : Estimated range of experimental conditions for carbochlorination.

Figure 3 - Phase stability diagram of (a) Mg-O-Cl, (b) Fe-O-Cl and (c) Si-O-Cl systems at 800 °C[5].

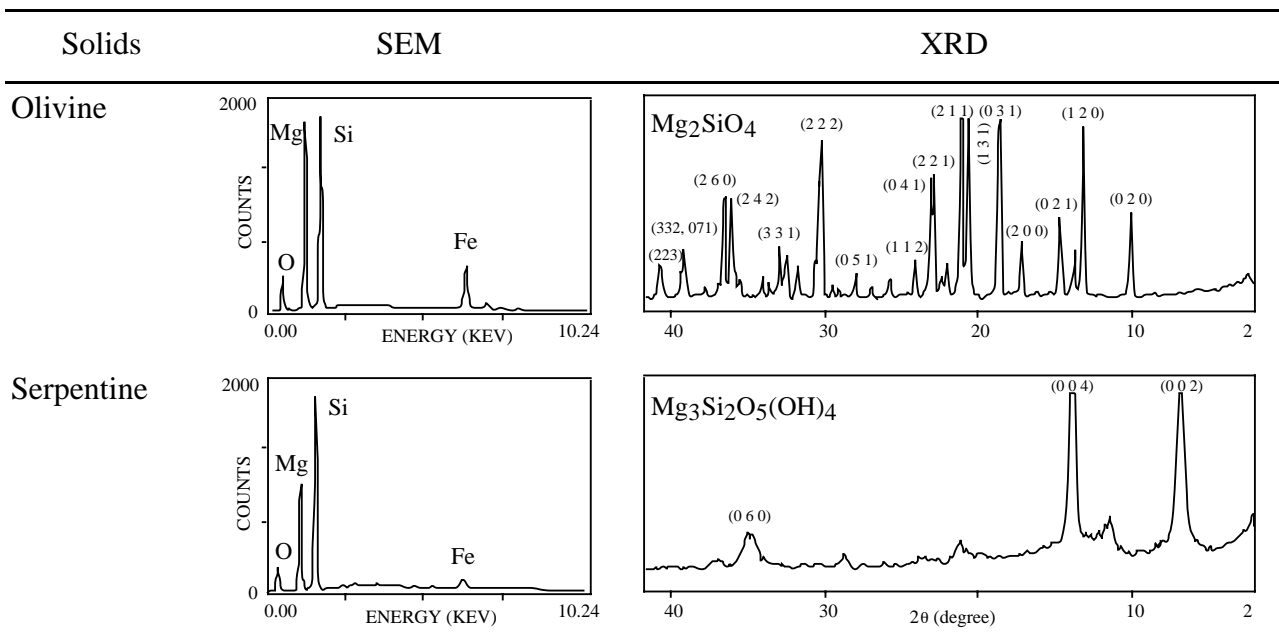


Figure 4 - Results of SEM and XRD analyses of employed samples.

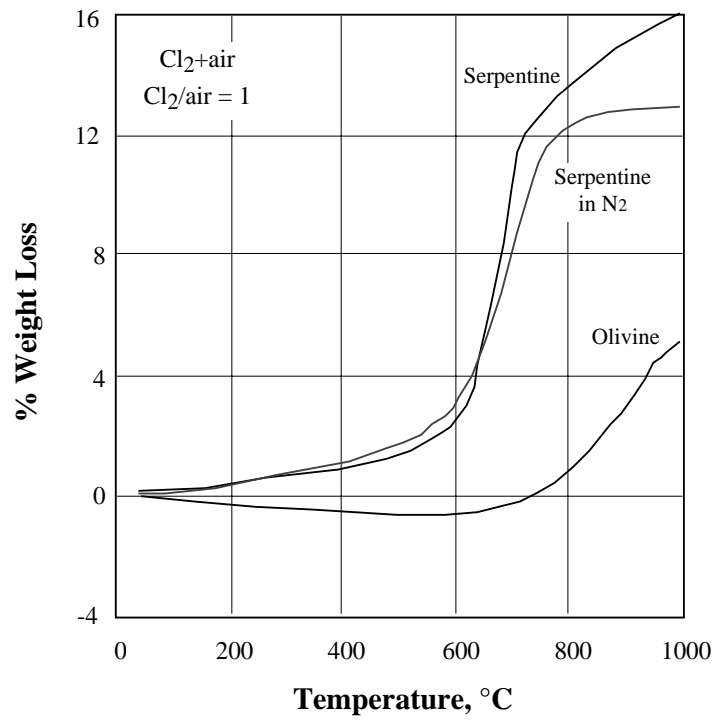


Figure 5 - Thermogravimetric analysis of magnesium compounds in Cl₂+air.

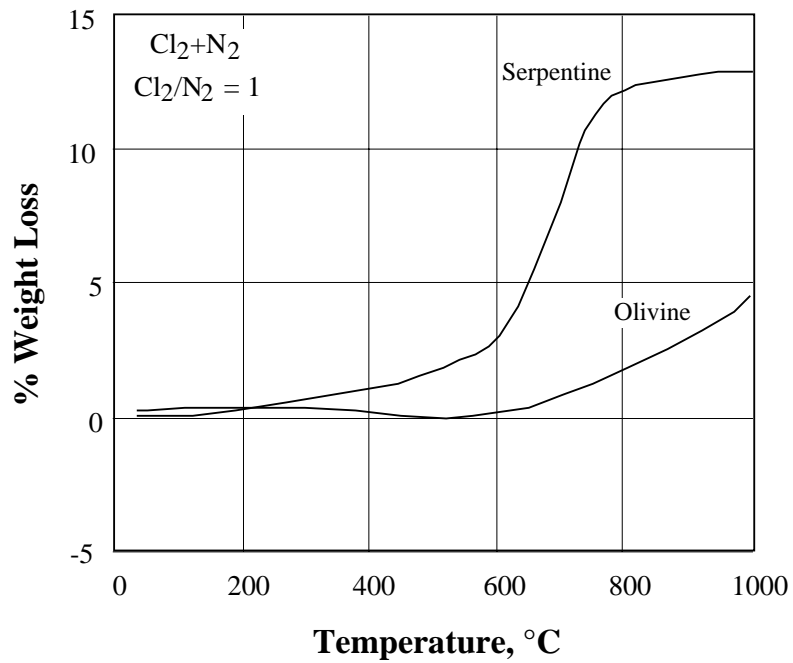


Figure 6 - Thermogravimetric analysis of magnesium compounds in Cl₂+N₂.

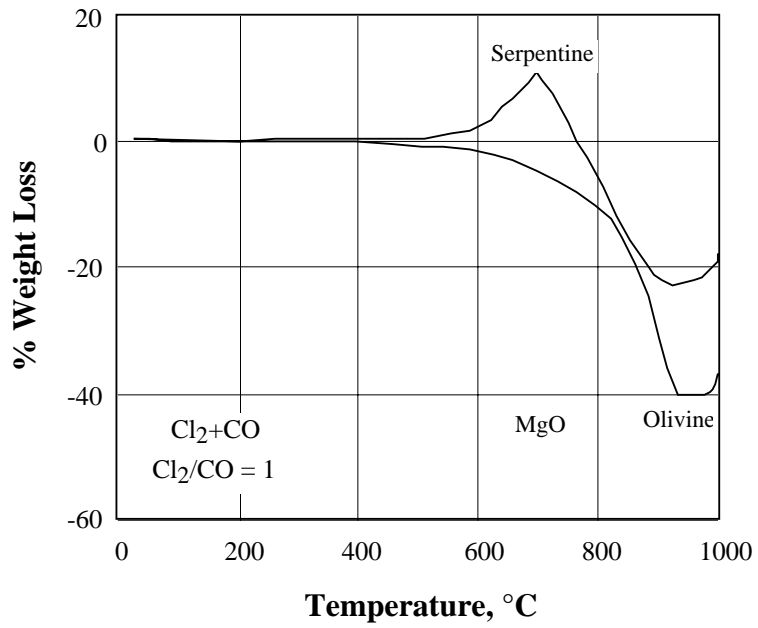


Figure 7 - Thermogravimetric analysis of magnesium compounds in $\text{Cl}_2 + \text{CO}$.

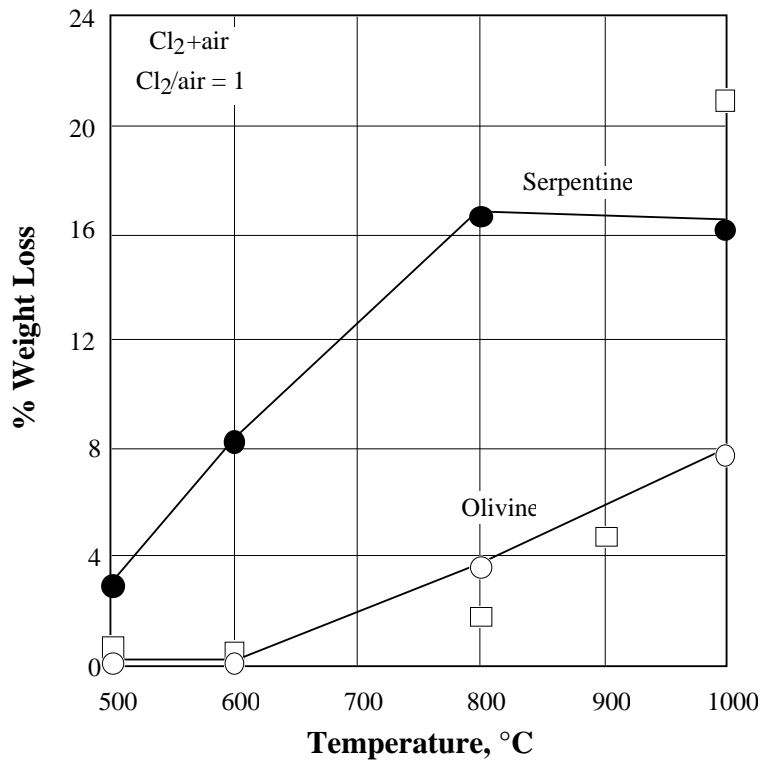


Figure 8 - Oxychlorination of magnesium silicates in a horizontal set during 2 hours.

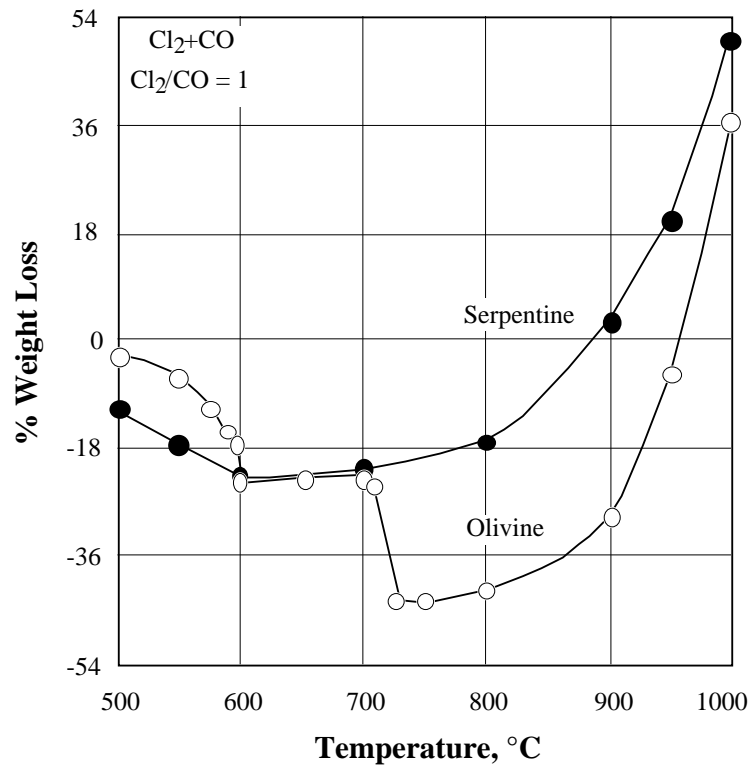


Figure 9 - Carbochlorination of olivine and serpentine in a horizontal set during 2 hours.