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Influence of Grinding Contamination on High-Temperature Phases of Pyrophyllite

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Abstract

Phases formed at high temperatures from ground pyrophyllite in porcelain and agate mortars have been studied by X-ray diffraction. Cordierite ($2MgO.2Al_2O_3.5SiO_2$) as one crystalline phase appears in ground samples in a hard porcelain mortar after being treated above 1300°C, due to the reaction of enstatite ($MgO.SiO_2$), derived from the balls used, with mullite (mainly $3Al_2O_3.2SiO_2$) and cristobalite (SiO_2) originating from the decomposed pyrophyllite sample during heating. After milling experiments using agate mortar and balls, the formation of cristobalite at lower temperatures, in ground as opposed to unground materials in hard porcelain, is attributed to contamination resulting from the mill and balls used.

Die Phasen, die bei hohen Temperaturen aus Pyrophyllit gebildet wurden, das zuvor in Porzellan- oder Achatmühlen gemahlen wurde, sind mittels Röntgendiffraktometrie untersucht worden. Cordierit ($2MgO.2Al_2O_3.5SiO_2$) tritt oberhalb 1300°C als eine der kristallinen Phasen in Proben auf, die in Hartporzellanmühlen gemahlen wurden. Er ist das Reaktionsprodukt von Enstatit ($MgO.SiO_2$) aus dem Mahlkugelabrieb mit Mullit (überwiegend $3Al_2O_3.2SiO_2$) und Cristobalit (SiO_2), welche aus dem sich bei der Temperaturbehandlung zersetzenden Pyrophyllit stammen. Nach Versuchen mit Mahlgefäßen und Kugeln aus Achat tritt die Cristobalitbildung bei niedrigeren Temperaturen als bei Materialien auf, die in Hartporzellanmühlen gemahlen wurden, was auf eine Achatkontamination durch Mahlgefäß und Kugeln zurückgeführt wird.

On a étudié, par le relevé des spectres de diffraction RX, les phases formées à haute température selon que l'on broie la pyrophyllite dans des mortiers de porcelaine ou d'agate. La cordiérite ($2MgO.2Al_2O_3.5SiO_2$), en tant que phase cristalline, apparaît après traitement au-dessus de 1300°C d'échantillons broyés dans un mortier en porcelaine dure. On explique cette formation par la réaction de l'enstatite ($MgO.SiO_2$) provenant des billes utilisées avec la mullite (essentiellement $3Al_2O_3.2SiO_2$) et la cristobalite (SiO_2) issues de la décomposition de l'échantillon de pyrophyllite durant le traitement thermique. Lorsque l'on broie dans un mortier et avec des billes en agates, la formation de cristobalite à plus basse température est attribuée à la contamination résultant des médias utilisés.

1 Introduction

Several authors[1–4] have paid attention to the study of the thermal reaction of pyrophyllite. Most of the work has been centred on the effects shown by heating up to 1000°C. However, investigation of the reactions which occur between 1000 and 1500°C has not been as extensive. The exothermic effects at 1215°C and 1325°C in the DTA curves are attributed to the formation of mullite and cristobalite, respectively.[4]

It is well known that grinding of clay minerals produces various effects on their structure and properties.[5] The significant processes involved in the preparation of ceramic raw materials have been studied, especially those for kaolinite,[6] montmorillonite or bentonite[7] and illite.[8] In a previous paper[9] the authors have studied the influence of mechanical and thermal treatment on pyrophyllite showing the formation of mullite at lower temperatures (1000°C) than in non-mechanically treated samples. However, the influence of mechanical treatment in mullite and cristobalite formation that occurs between 1000 and 1500°C is not yet well understood.

Little consideration has been given so far to the contamination produced by the materials of the pot

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and balls used during grinding. These materials may also have influence on the new phases formed at low and high temperatures.[10,11] Gammage & Glasson[12] have demonstrated the wear of porcelain-made mill components during the ball milling of calcium carbonate. Barba *et al.*[13] have studied the effect of contaminants during ball milling of Al_2O_3 powders. Pérez-Rodríguez *et al.*[14] have demonstrated the appearance of cordierite phase and the formation of cristobalite and mullite at lower temperature in ground, as opposed to unground, in both ordered and disordered kaolinites due to the effects of contamination coming from the hard porcelain mill.

The purpose of the present work is: (i) to study the influence of mechanical treatment of pyrophyllite in the formation of new phases that occurs between 1000 and 1500°C, and (ii) to show the influence that mill components have during the grinding of pyrophyllite, particularly on the new crystalline phases formed after thermal treatment.

2 Experimental Procedure

Pyrophyllite from Hillsboro supplied by Ward's N.S. Est. Inc., Rochester, NY was used. The natural sample was crushed, lightly ground, sieved to pass 50 μm and used in that form. The mineralogical composition determined by X-ray diffraction (Fig. 1(a)) showed pyrophyllite ($\approx$85 wt%) and minor quantities of andalusite ($\approx$10 wt%) and kaolinite ($\approx$5 wt%). The chemical contents (wt%), found by atomic absorption to be Fe_2O_3 (0·2), CaO (0·10), MgO (0·09), TiO_2 (0·60), Na_2O (0·08) and K_2O (0·02), are not relevant, as is expected for a material with a high proportion of pyrophyllite (SiO_2, 63·92 wt%; Al_2O_3, 30·28 wt%).

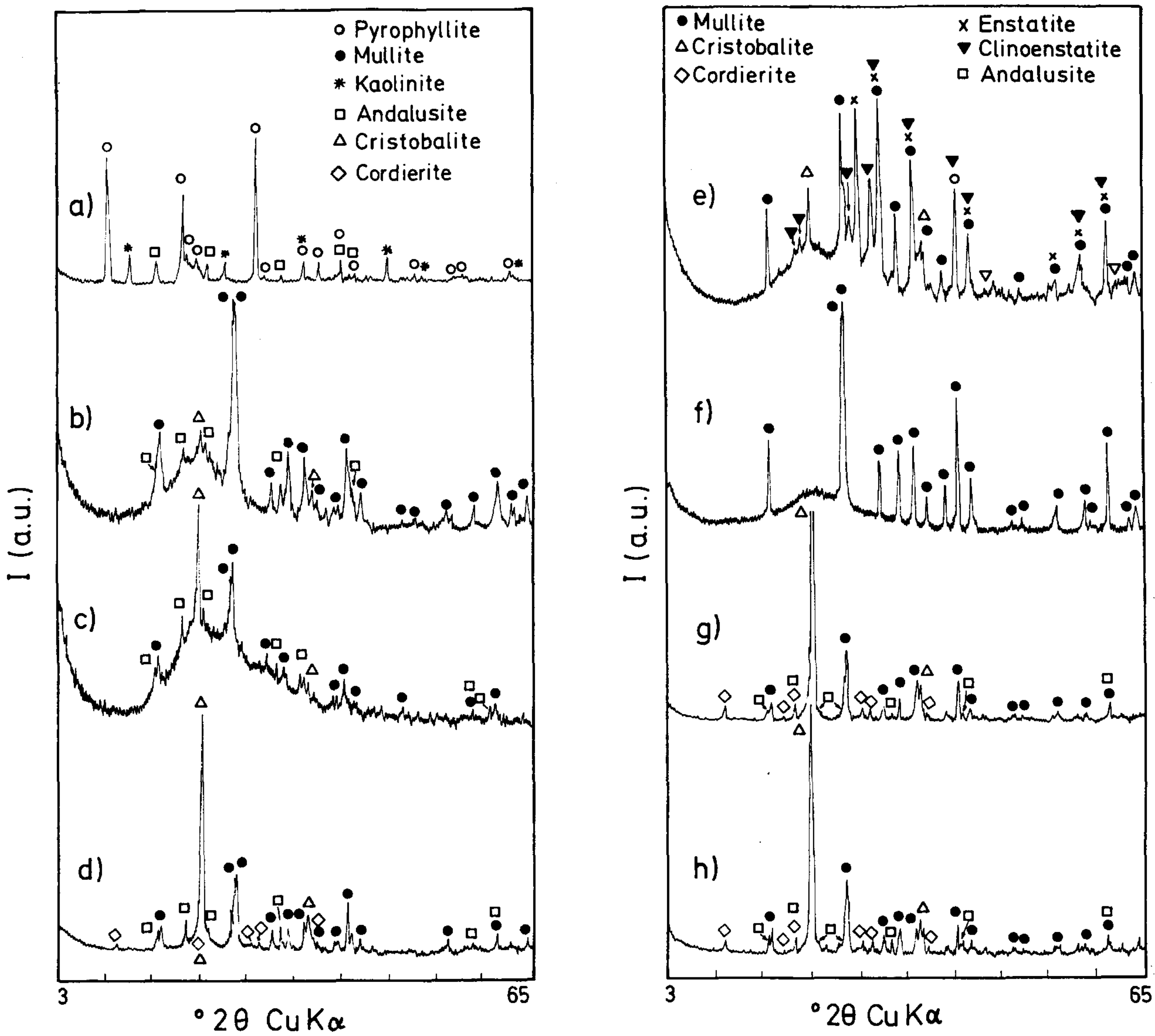

Fig. 1. X-Ray diffraction diagrams of (a) original pyrophyllite; (b) after heating at 1300°C; (c) sample ground for 32 min in hard porcelain mill after heating at 1300°C; (d) sample ground for 60 min in hard porcelain mill after heating at 1300°C; (e) ground powder obtained from the hard porcelain mill or residue (see the text); (f) fragments obtained from the porcelain pot used in the grinding experiments; (g) pyrophyllite ground for 8 h in the agate mortar mixed with 10 wt% of residue (see XRD pattern in part (f)), after heating at 1300°C; (h) original (unground) pyrophyllite mixed with 10 wt% of residue after heating at 1300°C.

The loss on ignition at 1000°C of 4·74 wt% is in good agreement with that calculated for the pyrophyllite content.

Dry grinding of pyrophyllite was conducted in a ball mill (model S-1 Retsch, F. Kurt Retsch, Haan, Germany) at a rate of 250 rpm, from a minimum of 5 min to a maximum of 325 min. Weighed samples of 2·200 g were used for each experiment. The grinding vessels used were hard porcelain and agate, containing 10 and 5 balls respectively, assumed to be of the same materials, 20 mm in diameter.

The maximum amount of MgO found in the material using the hard porcelain device was 2·78 wt% after 325 min grinding, as determined by atomic absorption.

The grinding treatment produces an increase in surface area from 0·63 m^2/g to 60 m^2/g at 30 min grinding, with a drastic diminution of average particle size from 3·40 μm to 0·03 μm. After 30 min, there is a slight variation of particle size, and the material becomes more agglomerated. At 325 min the surface area was 7 m^2/g and the average particle size 0·30 μm.

To obtain worn fragments of the mill components, 10 ml hexane (analytical grade) was poured into the vessel with balls without sample. It was ground for 30 min, and a white solid was obtained. X-Ray diffraction of this solid showed the presence of mullite, cristobalite, enstatite and clinoenstatite (Fig. 1(e)). The above experiment was repeated using the same pot as before and new balls, and also using a new pot and used balls. The X-ray results yielded similar features. The chemical analysis (wt%) of the solid showed Al_2O_3 (21·27), SiO_2 (58) and MgO (13·85). Evidently, the manufacturer of the mill and balls had added MgO to reach a lower sintering temperature.

Original and ground samples were heated in an electric furnace unit (maximum 1600°C, Pt/Pt–Rh 13% thermocouple), in static air atmosphere at a heating rate of 12°C/min.

The ground, unground and heated samples were examined by X-ray diffraction (Kristalloflex D-500 diffractometer, Siemens Aktiengesellschaft, Karlsruhe, FRG), using Ni-filtered CuK_α radiation.

3 Results and Discussion

Table 1 shows the phases detected by X-ray diffraction of original pyrophyllite and heated at 1050, 1300 and 1450°C. After heating at 1300°C (Fig. 1(c)) mullite appears, and an amorphous phase is detected by XRD (see Fig. 1(b)) which gives cristobalite at higher temperatures (1450°C). These findings were consistent with those reported by other authors.[1–4]

Although the formation of mullite solid solutions with andalusite is possible, the latter aluminium silicate persists after heating at 1050, 1300 and 1450°C because it is decomposed at higher temperatures (1500°C), giving more mullite, but andalusite is still detected by X-ray diffraction.

After grinding the pyrophyllite sample in an agate mill for periods of 270 min quartz appears (see Table 1). This crystalline phase was not initially present, and is attributed to contamination coming from the pot and balls of the mill. Andalusite persists in a low proportion. After grinding and heating at 1050°C, the changes are significant as compared to those of unground heated samples because mullite clearly appears. The formation of mullite in ground pyrophyllite at lower temperatures than in the original sample has been described previously.[15] It is suggested that the mechanical treatment could be yielding a specially degraded structure. When this material is submitted to thermal treatments, possible segregation of amorphous silica takes place: consequently mullite formation is rapid at relatively lower temperatures than in unground material. After heating at 1300°C, mullite is well detected by XRD and cristobalite starts to appear. Cristobalite is completely formed in the sample heated at 1450°C. The results obtained after heating at 1300°C and 1450°C in ground pyrophyllite using an agate mill are analogous to those obtained in the unground sample.

Table 1. Major[a] crystalline phases detected by X-ray diffraction after thermal treatment of ground pyrophyllite

Grinding time (min)	*Room temperature*	*1050°C*	*1300°C*	*1450°C*
0	Py (K, And)	DPy (And)	Mu (Cr, And)	Mu, Cr (And)
270 (agate mortar)	And (Q, Py)	And, Mu (Q)	And, Mu (Q, Cr)	Mu, Cr (And, Q)
270 (hard porcelain mortar)	And (Mu, Cr, En, Cl)	And, Mu (Cr, En, Cl)	Mu, Cr (Cd)	Mu, Cd, Cr

Py = Pyrophyllite; DPy = dehydroxylated pyrophyllite; And = andalusite; Ru = rutile; Q = quartz; Mu = mullite; Cr = cristobalite; Cd = cordierite; En = enstatite; Cl = clinoenstatite.

[a] Minor detected crystalline phases in parentheses.

Changes are detected by XRD when the grinding time in the hard porcelain mill was increased. The sample ground for a period of 270 min and heated at 1050°C (Table 1) is constituted by a vitreous or amorphous phase (as deduced from the X-ray background), appearing clearly as mullite. This phase may be produced by milling contamination or as a new phase formed after milling and heating. Taking into account the composition of the balls (see Section 2), it is clear that a proportion of mullite is produced by contamination. Nevertheless, considering the results summarized in Table 1, using an agate mill where mullite contamination is not possible, mullite is formed after milling and heating pyrophyllite. After this result, it can be concluded that the mullite present after milling pyrophyllite in hard porcelain mills and heating is produced by contamination and neoformation.

Detection by XRD of cristobalite and enstatite besides mullite in samples only ground in a hard porcelain mill is most likely due to contamination coming from the grinding equipment. Samples ground and heated at 1300°C show that after 32 min grinding (Fig. 1(c)), cristobalite begins to appear. After 60 min grinding and heating the sample at 1300°C (Fig. 1(d)), this phase is well-developed according to the X-ray results. The most interesting phenomenon in ground and heated pyrophyllite at 1300°C is that formation of a new phase occurs only after contamination of the ground powder has taken place. This new crystalline phase is cordierite, and its proportion increases as grinding time increases (Fig. 1(d)). After 270 min grinding and heating at 1300°C, this phase is completely developed, as shown in Table 1. The increase of cordierite proportion as grinding times increase suggests a relation with the contamination produced by the grinding equipment.

The X-ray diffractogram of the wear fragments from both the pot and balls is shown in Fig. 1(e). The X-ray diffractogram of the fragments obtained from the pot (Fig. 1(f)) corresponds to mullite. In accordance with these results, enstatite and clinoenstatite, first found in the residue (see Section 2) as shown in Fig. 1(e), indubitably came from the balls. A similar composition of the balls was found by Gammage & Glasson in their grinding study.[12]

According to Sarver & Hummel's pressure–temperature phase diagram,[16] a transformation occurs between enstatite polymorphs at high temperatures and pressures. Consequently, the appearance of clinoenstatite and enstatite (and possibly protoenstatite) found in the residue from the grinding experiment using hexane (Fig. 1(e)) was not unexpected. Enstatite or clinoenstatite might also be partially decomposed by grinding in a mixture of SiO_2 and MgO, as has been suggested by Gammage & Glasson.[12]

Cordierite can be produced by a solid-state reaction occurring between mullite, cristobalite and protoenstatite at 1100–1275°C, as was proposed by de Aza & Espinosa de los Monteros:[17]

$$\underset{\text{mullite}}{2(3Al_2O_3.2SiO_2)} + \underset{\text{protoenstatite}}{6MgSiO_3} + \underset{\text{cristobalite}}{5SiO_2} = \underset{\text{cordierite}}{3(2Al_2O_3.2MgO.5SiO_2)}$$

The formation of cordierite may also be produced by a solid-state reaction involving MgO. The formation of a liquid phase (at room temperature, a vitreous or glassy phase), however, is also involved according to the phase diagram and the sintering mechanism.[17,18] After cooling, more cordierite is produced by devitrification of that glassy phase.

Cristobalite formation at lower temperature in ground samples as compared with unground is produced by amorphous silica crystallization.[19] Amorphous silica is possibly segregated by combined mechanical and thermal treatments. The presence of MgO as contaminant in the ground pyrophyllite as opposed to unground samples may be also responsible for cristobalite formation at low temperatures. Various authors have studied the effects of adding MgO and other oxides as impurities to clay minerals.[15,20] These compounds have a strong impact on the temperatures at which mullite and cristobalite are formed.

According to the results shown in Table 1, cristobalite formation at lower temperatures after milling in hard porcelain is not ascribed to the grinding process in the present experimental conditions. Similar results have been obtained grinding kaolinite.[14]

Finally, another experiment was conducted. Ground and unground pyrophyllite samples in an agate mortar were mixed with 10 wt% of material obtained after grinding in a hard porcelain mill with hexane and no powder sample, as previously described. These mixtures were heated at 1300°C. The X-ray diagrams obtained may be found in Fig. 1(g) and (h). They show the presence of cristobalite, which did not appear in the agate milling experiment. These data confirmed that cristobalite formation results mainly from contamination coming from the porcelain grinding experiment.

4 Conclusions

In this paper, it has been shown that mullite formation after grinding pyrophyllite is not influenced by contamination produced during grinding treatment.

The appearance of cordierite phase after grinding in a porcelain mortar, and heating at 1300°C, is due to the reaction between magnesium-containing phases, such as enstatite coming from the balls used, and the new phases mullite and cristobalite formed by pyrophyllite decomposition during heating.

The formation of cristobalite at lower temperatures in ground as opposed to unground pyrophyllite is ascribed mainly to the effects of contamination coming from the hard porcelain mill.

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