

THERMAL ANALYSIS OF PYROPHYLLITE TRANSFORMATIONS

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ABSTRACT

The thermochemical behaviour of pyrophyllite from Hillsboro (NC, U.S.A.) was studied by DTA–TG up to 1430 °C. The phases formed were identified in thermally treated samples by X-ray diffraction (XRD) analysis. The DTA curve shows a broad endothermic dehydration peak centred at 760 °C and a shoulder effect at 840 °C, the latter being associated with a residual loss of hydroxyl groups. Thus pyrophyllite dehydroxylate is produced gradually, with a weight loss caused by structural dehydroxylation to a maximum of 5.0%. This phase retains a well-organized structure according to XRD results and persists over a large temperature range.

On further heating, two exothermic DTA effects appear due to pyrophyllite decomposition, centred at 1215 °C and 1325 °C. They are related to mullite and cristobalite crystallization at the expense of the dehydroxylate. However, the formation of these phases is initiated at lower temperatures.

INTRODUCTION

It is well known that pyrophyllite is a hydrous silicate of aluminium with the formula $\text{Al}_4\text{Si}_8\text{O}_{20}(\text{OH})_4$. It resembles talc in its softness and structure [1,2], but it occurs less commonly in nature associated with kaolinite, sericite, quartz and other silicates [3,4]. Commercial deposits of pyrophyllite have been found principally in Japan, U.S.A., Canada, Australia and Brazil. Economic information on pyrophyllite has been compiled in a previous review [3]. The U.S.A. deposits in North Carolina and California have been used as a ceramic raw material in refractory compositions such as insulating, firebrick or foundry specialities and also in various whiteware bodies. This is because pyrophyllite has good technological properties which are produced by thermal treatment [3–7].

Several authors [8–16] have studied the thermal reaction of pyrophyllite. Various thermoanalytical methods have been applied in pyrophyllite studies.

For example, Kristóf et al. [17] used simultaneous TG, DTG, DTA and a continuous water detector to study the progressive thermal decomposition. In a recent paper, Schomburg [15] reported results on thermal investigations on pyrophyllites from Shokozan (Japan) and Robbins (U.S.A.) using DTA, TG and dilatometric analysis. The samples were heated to only 1100°C and the thermal decomposition process was not supported by X-ray diffraction (XRD) analysis. MacKenzie et al. [14] studied the thermal reactions of pyrophyllite from Coromandel (New Zealand) using high-resolution solid-state nuclear magnetic resonance (NMR) techniques with magic-angle spinning (MAS). This is a new method of studying the atomic environment of both Si and Al in minerals. The results were obtained using evolved gas analysis, XRD and DTA-TG techniques up to 1350°C. These workers also suggested that weak recrystallization exotherms may be present through heating at high temperatures but they are very diffuse and difficult to distinguish. Salvadori and Sousa Santos [16] studied crystallographic and morphological transformations in pyrophyllite from Diamantina (Brazil) by heating up to 1300°C.

The results obtained by the workers mentioned above suggest that the transformations of pyrophyllite on heating need further research. Thus, the aim of this paper is to analyze the thermal transformations of pyrophyllite using DTA-TG and X-ray diffraction to provide more information about the behaviour of this silicate after thermal treatment.

EXPERIMENTAL

A sample of pyrophyllite from Hillsboro (NC, U.S.A.), supplied by Ward's Establishment Inc., Rochester NY, was used as a starting material. It was crushed and lightly ground to pass 50 μm .

The characterization of the sample has been reported previously [18,19]. Briefly, the mineralogical composition from XRD analysis is ca. 90% pyrophyllite with minor quantities of kaolinite (5%) and mica (5%). Chemical analysis by atomic absorption revealed the high purity of this sample. The most relevant quantity is K_2O (0.24%), which is associated with the mica present.

Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were carried out simultaneously in static air with an automatic thermal analyzer system (Rigaku, PTC-10 model). The data processing system (DPS-1) and the Watanabe Plotter Miplot were fitted to the DTA-TG apparatus. Pyrophyllite samples of about 40 mg were packed loosely into a platinum holder and were thermally treated from 20°C to a maximum of 1430°C, at a heating rate of 12°C min^{-1} (Pt/Pt-Rh 13% thermocouple). Calcined alumina was used as a reference material. The sensitivity range in DTA was $\pm 25 \mu\text{V}$ and was 5 mg in TG. The chart speed was 2.5 mm min^{-1} . The

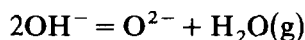
temperatures of the exothermic and endothermic peaks were estimated from the position of the top or bottom of the peak on the chart record.

X-ray powder diffraction diagrams were obtained using a Siemens Kristalloflex D-500 diffractometer at 26 mA and 36 kV with Ni-filtered Cu $K\alpha$ radiation at a goniometer speed of $1^\circ 2\theta \text{ min}^{-1}$ and a chart speed of 1 cm min^{-1} . Thermally treated samples lightly ground in an agate mortar were mounted as oriented aggregates on glass slides with silicone standard paste. The relative intensities as peak areas were also calculated from the X-ray diagrams.

RESULTS AND DISCUSSION

Figure 1 shows the DTA-TG curves obtained up to 1350°C . Thermogravimetric analysis of pyrophyllite indicates a gradual weight loss up to 1050°C . The weight loss data were calculated from the TG diagram and are shown in Table 1. The weight loss begins at 500°C ; it gradually increases with heating, and becomes very important in the range $700\text{--}800^\circ\text{C}$. After and before this range, the weight loss values are very similar as is shown in Table 1. The minimum weight losses are obtained above 900°C .

The weight loss is assumed to be due entirely to loss of structural water by dehydroxylation and is associated with a continuous expansion behaviour [8,15] according to the reaction scheme [11,13,20]



During this process, a dehydroxylated phase is produced.

Several factors influence the thermal stability with dynamic conditions of heating, as pointed out by Hórváth [20] for dehydroxylation in clay miner-

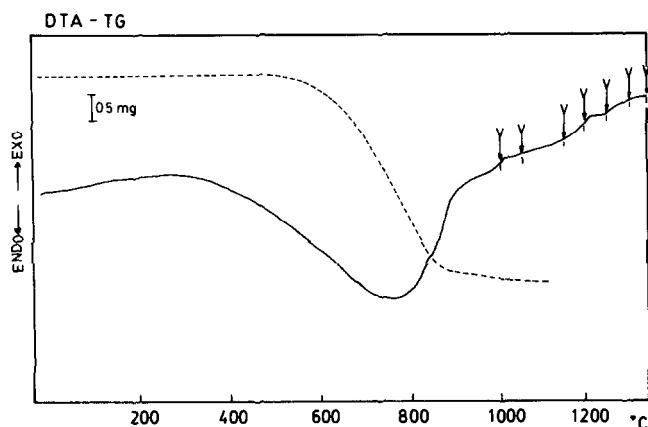


Fig. 1. DTA-TG curves of pyrophyllite from Hillsboro.

TABLE 1

Calculated weight losses (%) at different temperatures from TG diagram ($\beta = 12^\circ\text{C min}^{-1}$)

500–600 °C	600–700 °C	700–800 °C	800–900 °C	900–1000 °C	1000–1050 °C
0.35	1.20	1.95	1.25	0.20	0.05

Total weight loss = 5.0%.

als. According to his suggestion, higher temperatures are necessary in pyrophyllite than in kaolinite due to the bonding energy of the OH groups in the structure. The process of dehydroxylation is considered to be a homogeneous reaction [21]. Kristóf et al. [17] observed very closely overlapping complex decomposition stages in the dehydroxylation of the related clay minerals, illite and muscovite.

On further heating, the remaining structural water molecule is removed and this is the origin of the low weight losses obtained (Table 1). The total weight loss agrees closely with that of ideal pyrophyllite.

The general characteristics of the DTA curve (Fig. 1) agree with previously published results [22]. The principal endothermic peak is very broad and is centred at 760 °C. Schomburg [15] reported DTA peaks at 670 °C and 690 °C in two samples of pyrophyllite from Shokozan (Japan) and Robbins (U.S.A.), respectively.

As has previously been indicated by Zelazny and Calhoun [2], considerable variability has been observed in published DTA curves for pyrophyllites. Mackenzie [22] separates the published DTA curves into distinct categories according to whether one or two endothermic peaks are present. The first category contains DTA curves with one peak in the 600–800 °C region; the second category contains DTA curves with two peaks at 600–800 °C and 750–850 °C. In this work, the DTA curve appears in the first category; a single broad endothermic peak is observed in the 600–800 °C region.

Nemecz [23] has suggested a triple endothermic system at 540, 655 and 845 °C; however the first and third are similar and give shoulders. Figure 1 indicates that the pyrophyllite sample studied presents a shoulder effect at 840 °C in the DTA curve. This may be due to the loss of the last of the hydroxyl groups which are very strongly retained in the pyrophyllite structure. At higher temperatures (Fig. 1) weak exothermic peaks are produced. The processed data permit us to amplify the high temperature zone of this curve ($> 1000^\circ\text{C}$). These results are indicated in Fig. 2. The first peak ($\sim 1000^\circ\text{C}$) is associated with the kaolinite impurity present (5%). This effect is characteristic of kaolinitic samples as has been shown previously [22], but not of pyrophyllites. The second exothermic effect is produced at 1215 °C and another exothermic peak appears at 1325 °C.

Previous results obtained by Bradley and Grim [9] have shown an exothermic peak at high temperatures which represents recrystallization to

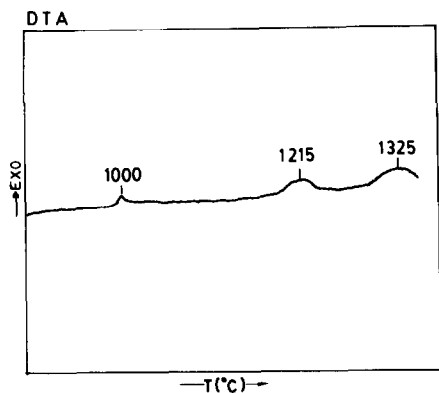


Fig. 2. High temperature zone of DTA curve.

mullite. Ivanova [24] has also suggested one S-shaped endothermic-exothermic system in the DTA curve at 1100–1200°C.

The X-ray diffraction results clearly indicate the processes which occur on thermal treatment. The arrows marked in Fig. 1 indicate the temperatures at

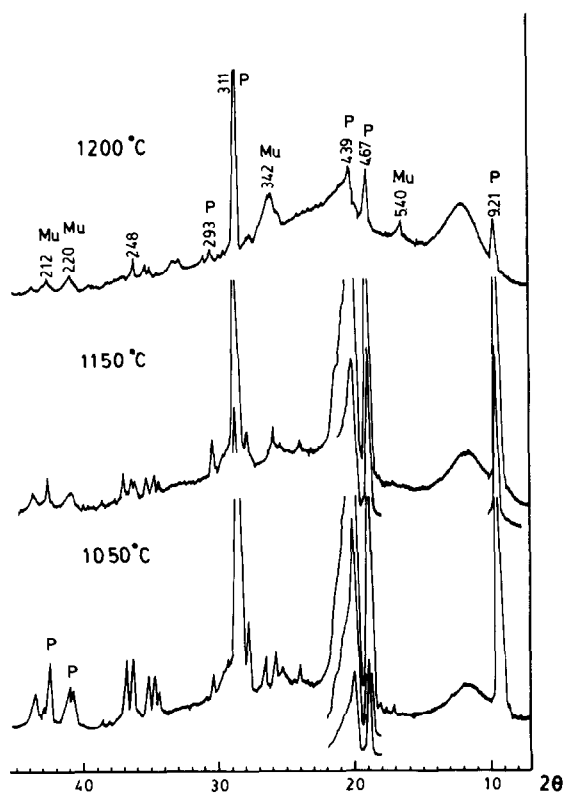


Fig. 3. X-ray diagrams of samples heated at 1050, 1150 and 1200°C (P = pyrophyllite dehydroxylate; Mu = mullite).

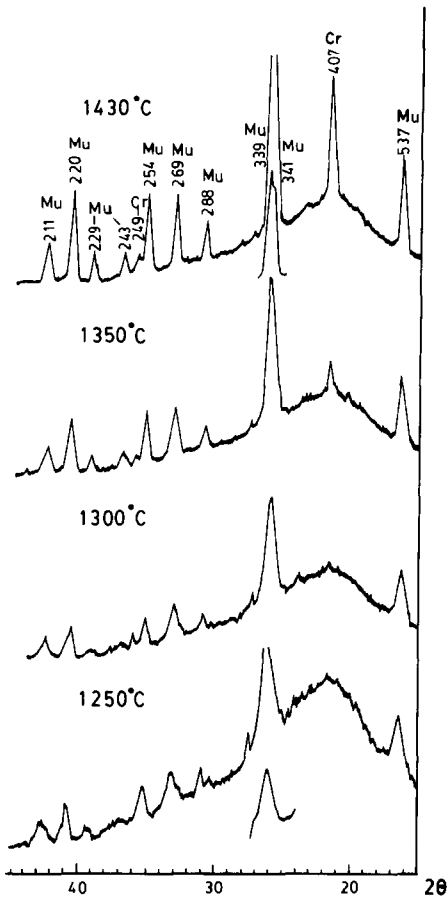


Fig. 4. X-ray diagrams of samples heated at 1250, 1300, 1350 and 1430 °C (Mu = mullite; Cr = cristobalite).

which heating was stopped, allowing the sample to reach room temperature. Fresh samples were used for each heat treatment. The X-ray diffraction diagrams obtained are shown in Figs. 3 and 4. The samples heated to 1000 and 1050 °C show the characteristic X-ray patterns of pyrophyllite dehydroxylate. This phase retains a well-organized structure, as reported by several workers [10,21,25]. Wardle and Brindley [21] have also claimed that this phase presents aluminium in coordination number five in an approximately trigonal bipyramidal configuration. Evidence supporting this suggestion has been reported by Rozenson and Heller-Kallai [26], Kristóf et al. [17] and MacKenzie et al. [14], the latter using NMR–MAS techniques.

According to Wardle and Brindley [21] the dehydroxylated phase is stable over a large temperature range. Schomburg [15] indicates up to 1150 °C and MacKenzie et al. [14] up to 1100 °C. In this study the X-ray diffraction patterns of the pyrophyllite dehydroxylate sample decrease very quickly

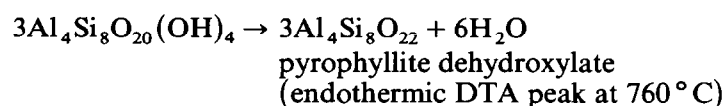
from 1150 to 1200 °C. Very weak lines of this phase survive on heating up to 1250 °C, principally 3.11 and 2.94 Å. This is probably due to the dynamic conditions of heating.

After heating to 1150 °C and before the following exothermic DTA effect (see Fig. 1), very weak X-ray diffraction patterns of mullite are detected. At 1200 °C, immediately before the DTA effect, gradual crystallization of mullite occurs at the expense of the dehydroxylate phase. The mullite is well characterized by XRD in the sample heated at 1250 °C; this temperature is slightly higher than the temperature of the exothermic effect (1215 °C), when destruction of the dehydroxylate phase takes place. Mullite appears and an amorphous phase is separated as is indicated by the XRD background (Fig. 4, 1250 °C). The development of mullite increases with heating. The double-peak system characteristic of mullite (3.39–3.42 Å) is clearly present at 1430 °C (Fig. 4).

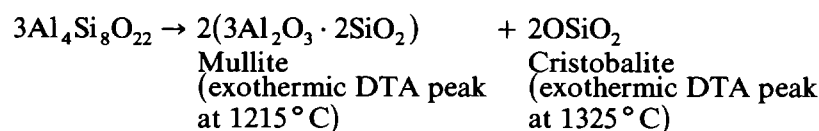
Cristobalite X-ray patterns start to appear at 1300 °C and crystallization occurs at 1350 °C, after the DTA exothermic effect at 1325 °C. Its amount increases from 1350 °C to 1430 °C. MacKenzie et al. [14] indicate a cristobalite formation temperature of 1150 °C, lower than the present results. This is probably due to the variation in the nature, amount and type of impurities present and in the crystallite size of the different samples studied.

The thermal processes in pyrophyllite can be represented by the following scheme.

(i) Dehydroxylation (≤ 1050 °C)



(ii) Structural decomposition (> 1050 °C)



As Bradley and Grim [9] have shown previously, these processes take place in a crystallographically ordered form. Heller [10] and Nakahira and Kato [12] found evidence of mullite and cristobalite formation using a topotactic reaction. The latter suggest that an aluminium ion migrates into the mullite and liberates the excess silica, which crystallizes as cristobalite at higher temperatures. The equilibrium diagram for the SiO_2 – Al_2O_3 system also indicates that heating pyrophyllite compositions at high temperatures yields a mixture of mullite and cristobalite [27].

In Fig. 5 the relative intensities of the X-ray diffraction characteristics on the different phases obtained are shown as a function of temperature. All the results are shown in this graph. The proportion of the dehydroxylated phase of pyrophyllite decreases slowly until 1150 °C. It disappears very

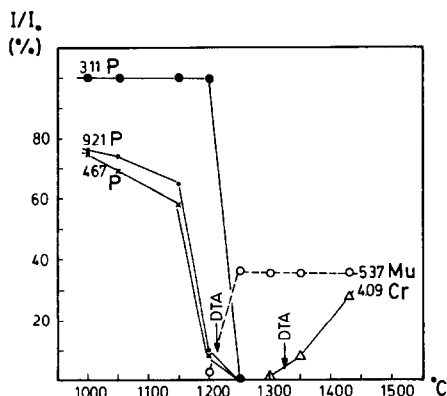


Fig. 5. Plot of the relative intensities of the X-ray diffraction characteristics of the different phases as a function of temperature (temperatures of the DTA peaks are indicated).

rapidly from 1150 °C to 1200 °C and is hardly detected at all at 1250 °C, where the intensity of the 3.11 Å diffraction is very weak.

Mullite formation takes place at 1200 °C and its intensity becomes almost constant after crystallization occurs, as detected by DTA (Fig. 2) and X-ray diffraction (Fig. 3).

Cristobalite formation begins at 1300 °C, followed by crystallization at 1325 °C. Its concentration increases on further heating up to 1400 °C. At this point the development of the high temperature phases is complete.

CONCLUSIONS

(1) The homogeneous dehydroxylation reaction of pyrophyllite is gradual and slow, beginning at 500 °C. The maximum structural water loss occurs in the range 700–800 °C. On further heating the remaining water is eliminated; this is complete at 1050 °C.

(2) The dehydroxylate phase produced is detected by XRD, showing a well-organized structure, in agreement with previous investigations [14,15,25]. It remains unchanged over a large temperature range.

(3) The DTA curve shows a broad endothermic effect due to structural water loss, with a maximum at 760 °C. The last hydroxyl groups require higher temperatures for their complete removal. This is associated with the shoulder effect at 840 °C.

(4) Two exothermic DTA effects are detected due to pyrophyllite decomposition. The first is at 1215 °C, corresponding to mullite crystallization with a simultaneous disappearance of pyrophyllite dehydroxylate. An amorphous phase is also produced in this process. The second effect is at 1325 °C and is associated with cristobalite crystallization. Some disagreement with previous investigations is due to the different nature of the starting materials. Mullite

and cristobalite phases are well crystallized at 1430 °C. It is remarkable that the energetic exothermic changes associated with pyrophyllite transformations on heating are very small compared with kaolinitic materials.

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