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SEM study of pyrophyllite high-temperature transformations

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The changes taking place during the dynamic heating of pyrophyllite up to 1430° C are investigated by means of scanning electron microscopy. X-ray diffraction was used as a complementary technique for phase identification, being pyrophyllite and its dehydroxylate, mullite and cristobalite. The different morphologies developed when pyrophyllite is progressively transformed by heating into new phases such as mullite and cristobalite are revealed and presented in this study. It is established that pyrophyllite dehydroxylate shows the same shape as the unheated material. However, upon further heating, the formation of mullite and later cristobalite, as well as the increase of the glassy phase, contribute to the observed microstructures.

1. Introduction

The hydrous silicate of aluminium pyrophyllite, $Al_4Si_8O_{20}(OH)_4$ is used as a ceramic raw material in refractory compositions such as insulating, firebrick or foundry specialities, and also in various whiteware bodies. It is generally associated with kaolinite, mica and others silicates, but it resembles talc in its softness and structure [1–4].

Some authors have studied the thermal reactions of pyrophyllite by several thermo-analytical methods [5–7] and new techniques such as nuclear magnetic resonance – magic angle spinning (NMR–MAS) [8]. Others such as Nakahira and Kato [9], and more recently Salvadori and Sousa Santos [10] have studied the thermal reactions of pyrophyllite by transmission electron microscopy (TEM) and X-ray methods. However, the application of scanning electron microscopy (SEM) to the study of this silicate is very scarce and very little information about its thermal transformations has been published. In contrast, other silicates such as kaolinite and illite have been studied by SEM when they are thermally treated over a range of temperatures [11–13].

It is interesting to note the suggestion of Schüller and Kromer when SEM is applied to fired kaolinite [13]. These authors indicated that TEM requires replica techniques. As a consequence, this technique gives good results only when the material has become completely rigid during firing. However, when using SEM, the structure of the unfired material can be examined as well as that of the fired material even when it is fired at low temperatures and so not yet consolidated.

In a previous paper on thermal transformations of pyrophyllite [14], samples of this silicate were thermally treated up to 1430° C. The present paper completes this information with the aid of SEM for a more detailed study of the processes involved, microstructures produced by dynamic heating and for describing the morphological changes at high temperatures. X-ray diffraction is used for phase identification.

2. Experimental details

A pyrophyllite sample from Hillsboro, North Carolina, USA (supplied by Ward's, Rochester, New York) was used as starting material. The mineralogy obtained by X-ray diffraction (XRD) (Fig. 1) revealed $\sim 90\%$ pyrophyllite accompanied by other related minerals in low proportion (5% kaolinite and 5% muscovite). The material was crushed and ground to a particle size less than 50 μm. Portions of this powdered material ($\sim$ 33 mg) were gently packed in platinum crucibles and subjected to thermal treatment in a platinum resistance furnace of the differential thermal analysis (DTA) apparatus (Rigaku, PTC-10 A model) with Pt/Pt–Rh 13% thermocouples at a heating rate of 12° C min^{-1}. The heating was stopped at several temperatures up to 1430° C by using fresh samples each time.

The DTA of this material indicated a very broad endothermic effect centred at 760° C due to elimination of structural water, and three weak exothermic peaks at higher temperatures [14]. The first peak ($\sim$ 1000° C) is associated with kaolinite present as an impurity because it is well-known that this effect is characteristic of kaolinitic samples alone, and is not in pyrophyllites [7, 14–16]. The second weak exothermic effect is produced at 1215° C and another appears at 1325° C (Fig. 2).

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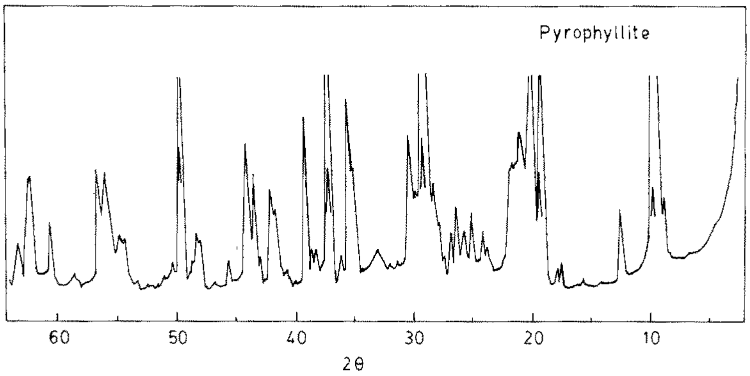

Figure 1 X-ray diffraction powder diagram of original pyrophyllite (Cu$K\alpha$ radiation).

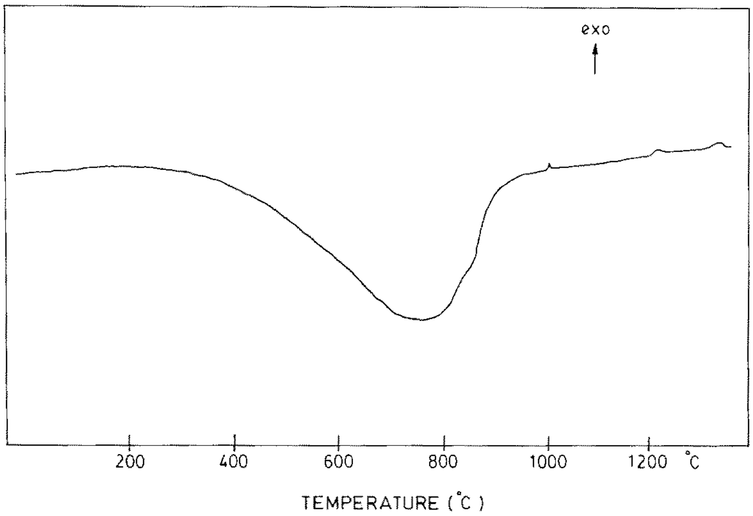

Figure 2 Differential thermal analysis of pyrophyllite.

After cooling to room temperature, the heat-treated samples were investigated by X-ray diffraction (Siemens Kristalloflex D-500 diffractometer) for determining the phases produced, in relation to the DTA effects.

Finally, with their surfaces made conductive by the sputtering of thin gold films, these samples were examined by scanning electron microscopy (SEM ISI apparatus, SS-40 model). Selected scanning electron micrographs of many visual fields studied are reported here. An energy dispersive X-ray analyser Kevex (model 8000) was fitted to this SEM system.

3. Results and discussion

The original sample of pyrophyllite shows large flat crystals, some book-like structures and also fibrous forms in lower proportions, in the SEM examination (Fig. 3). Analysis by energy dispersive X-rays shows a proportion or silicon and aluminium corresponding to a typical pyrophyllite mineral.

SEM examination of samples heated up to 1150° C (Fig. 4) indicates no differences compared with the untreated material (see Fig. 3), showing the same shape of stacks. No visible changes in plate structures caused by the heat treatment are apparent.

According to Wardle and Brindley [6], pyrophyllite dehydroxylate is produced after total dehydroxylation. This phase retains a well-organized structure similar to hydroxylate and is stable over a large range of temperatures: Heller [5] and Schomburg [7] indicated up to 1150° C and MacKenzie *et al.* [8] up to 1100° C. Our results indicated that pyrophyllite dehydroxylate

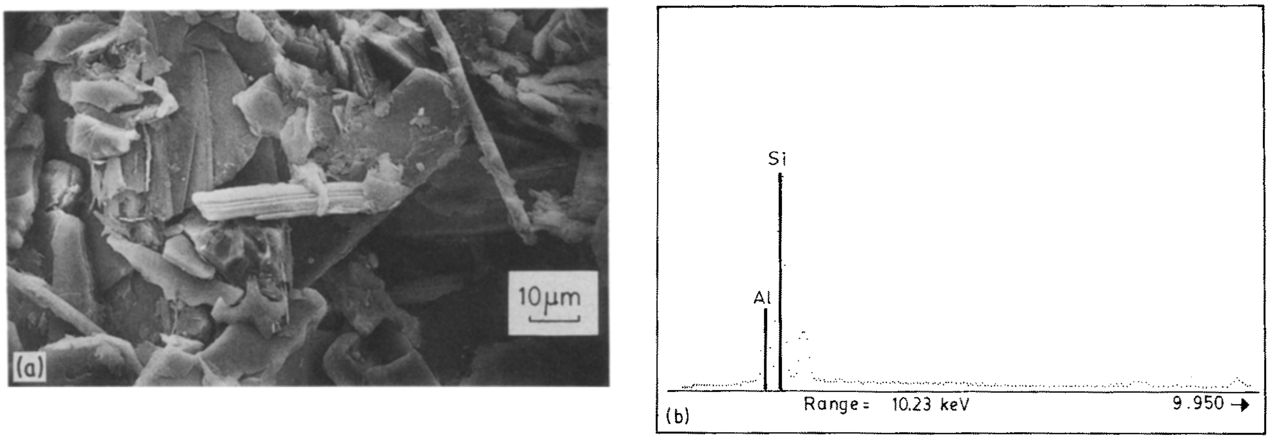

Figure 3 (a) Scanning electron micrograph and (b) corresponding analysis by EDXRA of original pyrophyllite.

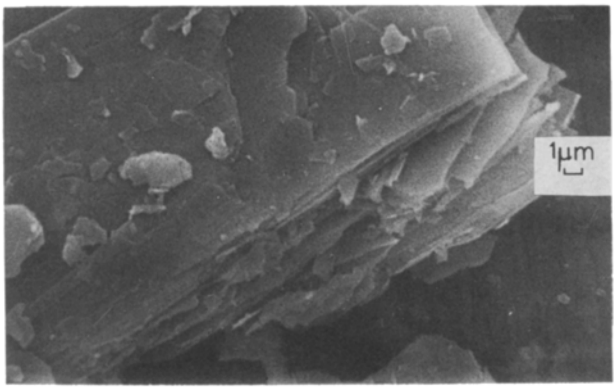

Figure 4 Scanning electron micrograph of pyrophyllite thermally treated at 1150° C.

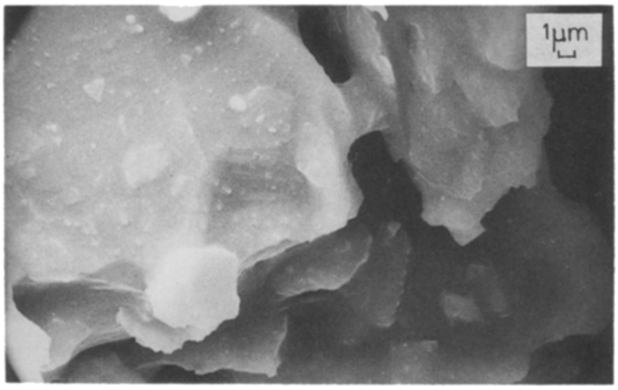

Figure 6 Scanning electron micrograph of pyrophyllite thermally treated at 1200° C.

X-ray patterns decrease very quickly from 1150 to 1200° C (Fig. 5). However, the shape of the original and heated samples is the same, as SEM results suggest. In the case of kaolinite, Schüller and Kromer [13] have claimed that the shape of this silicate is preserved during firing to high temperatures, although it is completely converted to mullite.

Very weak X-ray patterns of mullite begin to be detected at 1150 and 1200° C from the progressive disappearance of pyrophyllite dehydroxylate indicated in Fig. 5. Mullite undergoes a sudden increase at 1250° C, after the DTA exothermic effect at 1215° C. Thus, it has been previously established that this weak exothermic effect is associated with mullite crystallization [14], as occurs in kaolinite [15]. At the same time, an amorphous phase is produced, as the background of the X-ray diagram suggests.

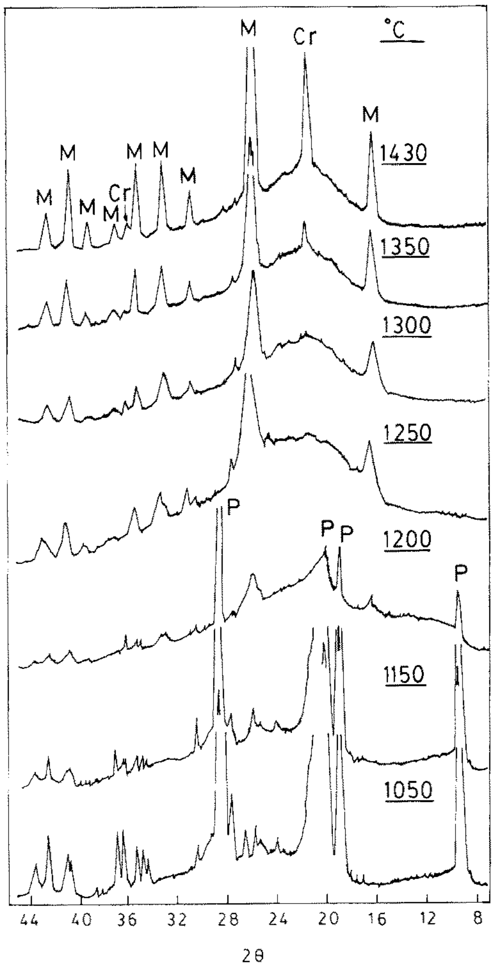

Figure 5 X-ray diagrams of pyrophyllite samples heated at different temperatures. (P = pyrophyllite dehydroxylate; M = mullite; Cr = Cristobalite.)

Nucleation of mullite is also detected in the SEM study of samples heated at 1200° C (Fig. 6). At this point, some small crystals appear distributed on the plates leading to a slight roughening of the surfaces examined, indicating an initial formation. Upon further heating at 1250° C, when mullite is present as detected by XRD (Fig. 5) and after the weak DTA exothermic effect, SEM micrographs (Fig. 7a) show a greater development of mullite crystals but flat forms are also still present and they are easily identified.

A higher magnification of selected samples heated at this temperature clearly shows the surfaces containing large numbers of mullite crystallites (Fig. 7b) as small needles outside the large flat crystals and plates, even over themselves. The same micrograph indicated that the book-like structures are revealed on magnification, but they are more consolidated than in the unheated material.

At 1300° C, just before the second DTA exothermic effect, mullite crystals appear distributed over all the surfaces and no additional information about the microstructural changes can be expected (Fig. 8).

Cristobalite X-ray patterns begin to be detected at 1300° C and especially at 1350° C (see Fig. 5) after another weak DTA exothermic effect at 1325° C takes place. Therefore, it is associated with cristoballite crystallization from an amorphous phase separated when the thermal treatment is carried out progressively.

SEM examination of samples heated at this temperature are presented in Fig. 9. At low magnification (Fig. 9a, b) results similar to those described above are found, but a larger degree of sintering can be observed due to an increase by progressive heating of the glassy phase formed. Fig. 9c shows rounded plates and their granulated aspect. At higher magnification (Figs 9d, f), mullite crystals appear growing from the fibrous forms especially as shown in Fig. 9d. The glassy phase is detailed in Fig. 9e. However, the highest magnification (Fig. 9f) showed the formation or nucleation of small crystallites, possibly due to cristobalite detected by XRD, although it is difficult to distinguish the mullite matrix, according to energy dispersive X-ray (EDX) results (data not shown).

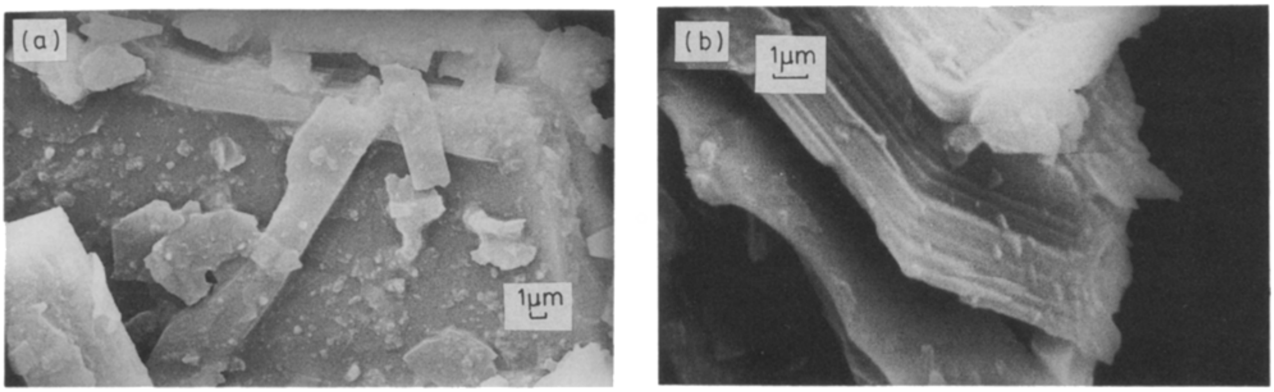

Figure 7 Scanning electron micrographs of pyrophyllite thermally treated at 1250° C. (a) low magnification; (b) higher magnification.

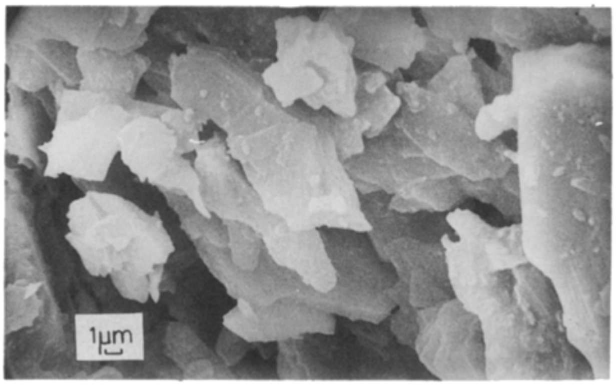

Figure 8 Scanning electron micrograph of pyrophyllite thermally treated at 1300° C.

Upon further heating up to 1430° C, mullite and cristobalite X-ray diffraction patterns become larger (see Fig. 5). SEM study of samples treated at this temperature shows larger areas of contact and consolidation of the material due to a greater degree of sintering combined with grain growth of mullite and cristobalite crystals (Fig. 10). Thus, the plates of the original or unheated pyrophyllite cannot be recognised.

In conclusion, the changes in the mineralogical constitution found by X-ray diffraction in samples of pyrophyllite heated to 1430° C manifest themselves in a changed form and microstructure of the material, according to this SEM study.

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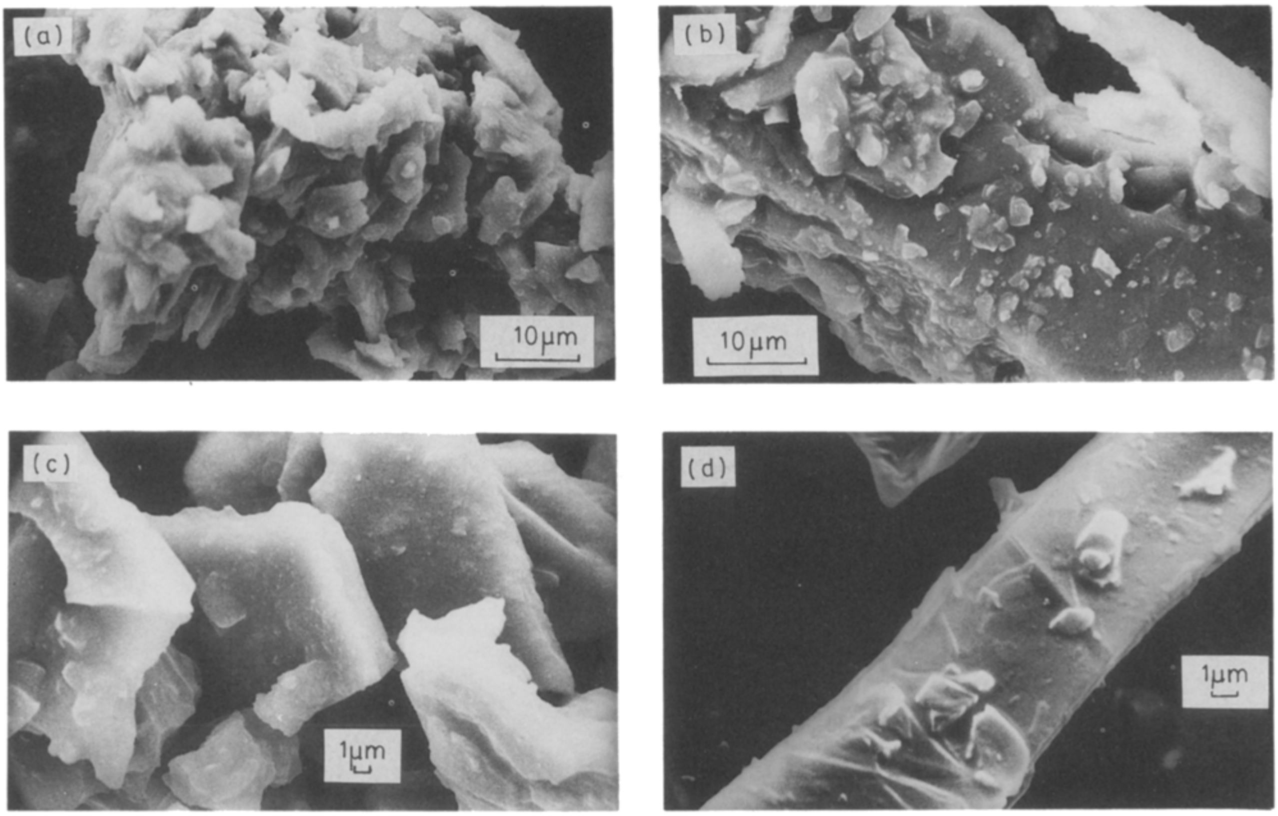

Figure 9 Scanning electron micrographs of pyrophyllite thermally treated at 1350° C. (a, b, c) Low magnification; (d, e, f) higher magnification.

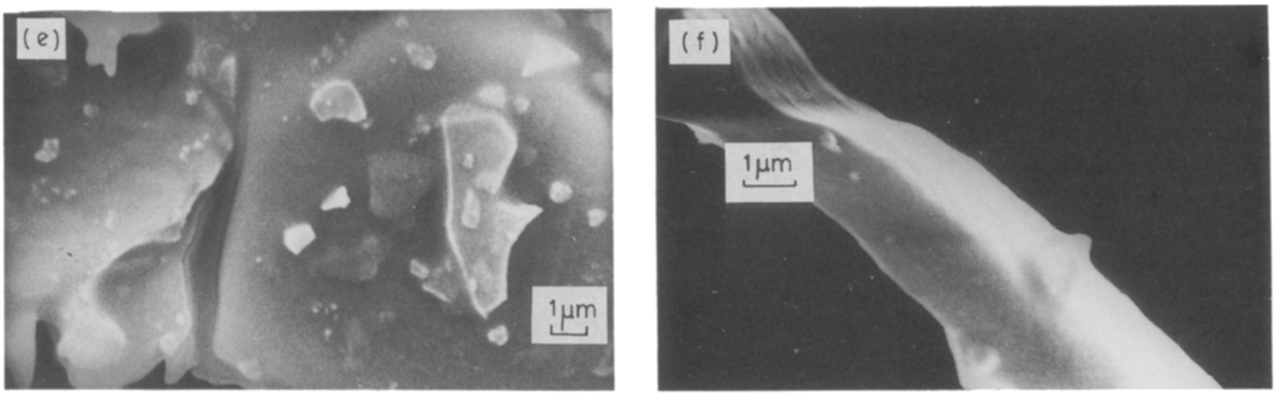

Figure 9 Continued

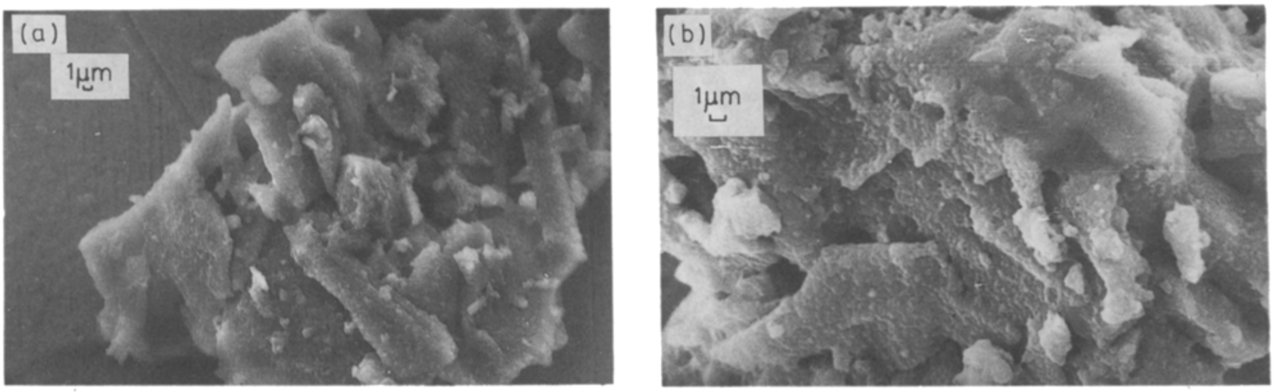

Figure 10 Scanning electron micrographs of pyrophyllite thermally treated at 1430° C. (a) lower magnification; (b) higher magnification.

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