EFFECTS OF DRY GRINDING ON PYROPHYLLITE

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ABSTRACT: Dry grinding of pyrophyllite (Hillsboro, USA) has been studied by X-ray diffraction (XRD), specific surface area measurements (BET) and scanning electron microscopy (SEM). At the beginning of the grinding process, some effects such as delamination, gliding and folding of the layers, and decrease in particle size were detected by SEM and XRD, resulting in a large increase in specific surface area, up to a maximum of $\sim 60 \, m^2 . g^{-1}$. Marked changes in the structure take place between 30 and 32 mins grinding. Longer grinding times increase the degree of disorder and SEM and specific surface area data suggest that aggregation occurs. XRD results indicate that some residual order persists in the degraded structure.

Pyrophyllite is a relatively rare mineral and has scarcely been studied until quite recently. For this reason, it has generally been overlooked in commercial circles, but its high alumina content and physico-chemical properties make it useful in many industries, principally in refractories, ceramics and sundry uses (Harben, 1981). Much research is being carried out to obtain a better knowledge of its properties. Pérez-Rodríguez *et al.* (1985) have studied its determination in mineral mixtures, and more recently, Maqueda *et al.* (1986, 1987) have discussed some analytical problems related to its incomplete dissolution in acids.

Fine mineral particles are obtained principally by grinding (wet or dry), the nature of which plays an important role in determining the physico-chemical properties of the powdered material (Grim, 1968; Somasundaran, 1978).

Levine & Joffe (1947) described some grinding experiments with pyrophyllite, and Hayashi *et al.* (1962) studied the continued grinding of pyrophyllite and its effect on toxicity of the cell. Juhász (1977) suggested that destruction of this mineral during mechanochemical activation (intensive dry grinding) may be accelerated by cations and adsorbed water. Pyrophyllite solid solutions have been synthesized by Rosenberg & Cliff (1980) from a gel and from lightly ground and milled natural materials. They indicated that "pyrophyllite structure is rapidly degraded by milling and its X-ray reflections completely disappear after 60 minutes", but no data were shown. Nemecz (1984) found that pyrophyllite 1 *Tc* is transformed into a monoclinic modification as a result of grinding for up to 60 mins. Other researchers, *e.g.* Okuda *et al.* (1969) have studied the density of charges on the edge and basal surfaces of dry- and wet-ground pyrophyllite. Industrial grinding of pyrophyllite materials has also been studied to determine the efficiency of the method (Kuwahara, 1971; Stanczyk & Feld, 1980) and to separate the pyrophyllite from other minerals (Hayashi *et al.*, 1979).

These published results suggest that further research is needed on the grinding of

pyrophyllite and the aim of this paper is to study the effects of intensive dry grinding of a natural pyrophyllite.

EXPERIMENTAL

Material

A commercial sample of pyrophyllite from Hillsboro (North Carolina, USA) supplied by Ward's N.S. Establishment Inc., Rochester N.Y. was used as starting material. The geological description of the area and the genesis of this mineral have been given by various authors (Zen, 1961; Sykes & Moody, 1978). The natural material was crushed, lightly ground and sieved to 50 μm before being used.

Methods

Grinding. The pyrophyllite was ground in 2·2 g quantities in a Retsch S-1 ball mill at a rate of 250 r.p.m. for 5 to 325 mins using a grinding vessel made of hard porcelain containing ten balls of 20 mm diameter made of the same material.

X-ray powder diffraction. XRD patterns were obtained using a Siemens Kristalloflex D-500 diffractometer with Ni-filtered Cu-$K\alpha$ radiation, a goniometer speed of 1° 2θ/min, a chart speed of 1 cm/min at 2×10^3 cps and time constant 2. Randomly oriented samples were prepared using a side-packed holder and tapping the holder gently to consolidate the powder (Niskanen, 1964). The best results were obtained using the side-packed holder with the window covered by a piece of filter paper between the sample and the glass slide (Miller & Oulton, 1970; Pérez-Rodríguez et al., 1985).

Specific surface areas. The specific surface areas (S_{BET}) were determined with an automatic system Micromeritics, 2200 A model, using nitrogen gas as adsorbate at liquid nitrogen temperature.

Scanning electron microscopy. Samples dispersed with acetone were coated with Au to make them conducting and examined under a scanning electron microscope ISI model SS-40 fitted with a Kevex model 8000 energy dispersive X-ray analyzer.


RESULTS AND DISCUSSION

The mineralogical composition, specific surface area and chemical analysis of the original material are shown in Table 1.

This material is composed of *ca.* 90% pyrophyllite, 5% kaolinite and 5% mica (Pérez-Rodríguez et al., 1985). The contents of CaO (0·09%), MgO (0·01%), TiO_2(0·1%) and Fe_2O_3 (0·2%) are not significant, as expected for a material containing a high proportion of pyrophyllite. The K_2O content (0·24%) is due to the mica component, and the loss-on-ignition (5·41%) agrees with that calculated for an ideal pyrophyllite. The specific surface area is very low (0·52 $m^2 \cdot g^{-1}$) compared to that for other clay minerals.

The SEM study (selected micrograph in Fig. 1) showed large flat crystals, some book-like structures and also smaller amounts of a fibrous phase, and microanalysis revealed Si and Al in proportions corresponding to pyrophyllite.

TABLE 1. Characteristics of the sample studied.

Chemical composition	Mineralogy	
SiO$_2$ 66·42%	Pyrophyllite	90%
Al$_2$O$_3$ 27·31%		
Fe$_2$O$_3$ 0·20%	Mica	5%
TiO$_2$ 0·10%		
CaO 0·09%	Kaolinite	5%
MgO 0·01%		
Na$_2$O 0·10%	Specific surface area	
K$_2$O 0·24%		
L.O.I. 5·41%	S$_{BET}$ 0·52 m^2.g^{-1}	
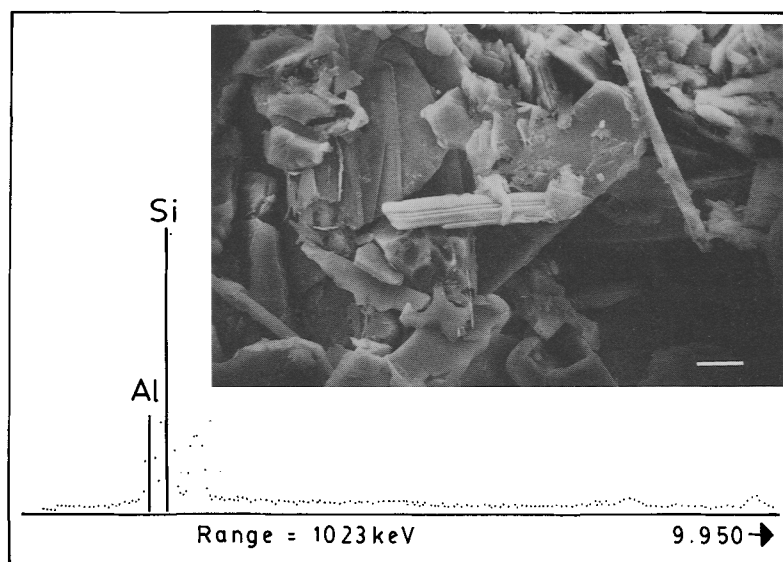
FIG. 1. SEM-EDX of pyrophyllite (scale marker 10 μm).

The XRD patterns (Figs. 2 and 3) indicated increasing disorder as the grinding time increased. The particle size diminution, defects and microstrains in the crystal structure produced during the mechanical treatments cause an increase in the background and broadening of the diffraction bands, with their final disappearance after very long grinding times, indicating a gradual breaking down of the structure. For montmorillonite, it is assumed that degradation by percussive grinding results in complete breakdown of the structure producing a matrix which consists mainly of the residue of tetrahedral sheets and deformed incomplete tetrahedra and octahedra, or consists of individual atoms held together in clumps either by Van der Waals forces or possibly, in some cases, by newly-formed chemical bonds (Cicel & Kranz, 1981).

However, after long grinding times, some structural order persists in pyrophyllite, and in general, the non-basal reflections are less affected than the basal reflections (Figs. 2 and
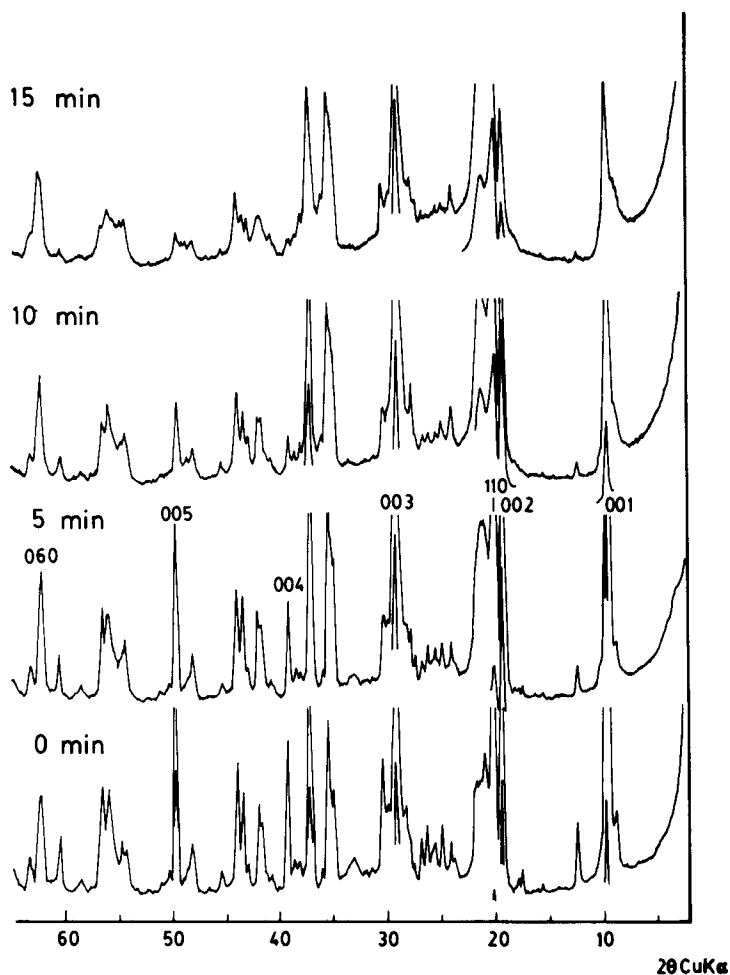
FIG. 2. XRD patterns of pyrophyllite ground for 0–15 mins.

3). Similar results have been reported by Miller & Oulton (1970) and Hlavay *et al.* (1977) for kaolinite.

During the firsts stages of grinding, delamination effects are likely to be produced and particle orientation occurs in samples prepared for X-ray examination and, consequently, basal reflections seem to increase. This phenomenon has been reported by several authors when grinding other clay minerals (Miller & Oulton, 1970; Hlavay *et al.*, 1977; Cicel & Kranz, 1981; Juhász & Somogyi, 1984), but not pyrophyllite.

It is interesting to note the dramatic change in the XRD patterns when the grinding time increases beyond 30 mins, producing the greatest degree of broadening as indicated in Fig. 3. Having noted after 60 mins grinding that there was a great qualitative difference in the XRD pattern compared to that at 30 mins grinding, it was decided to establish precisely the time at which the change occurred. It is clearly shown in Fig. 3 that the change occurred between 30 and 32 mins grinding.
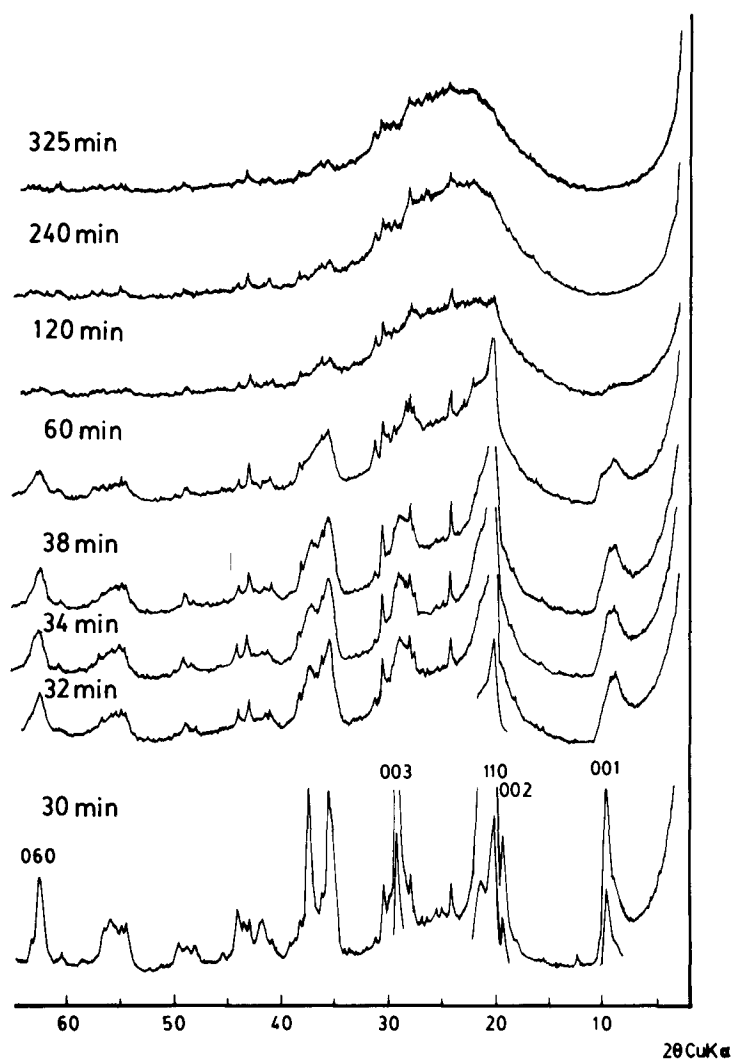
FIG. 3. XRD patterns of pyrophyllite ground for 30–325 mins.

The XRD peaks in the range 19 to 21° 2θ (Fig. 2) require to be studied in more detail. Pyrophyllite exists in three polytypic forms: a two-layer monoclinic ($2M$), a one-layer triclinic ($1Tc$) and a disordered form (Brindley & Wardle, 1970). Brindley & Wardle (1970) have recognized the $1Tc$ and $2M$ structures in natural pyrophyllites, and also mixtures of the two forms in some samples. Identification of pyrophyllite polymorphs is difficult because of interference by coexisting phases and because of the weakness of diagnostic X-ray reflections due to orientation effects and poor crystallinity of many samples (Rosenberg, 1974). Brindley (1980) has indicated that talc and pyrophyllite are easily distorted by mechanical treatment, and distortion-free crystals suitable for single crystal analysis are not easily obtained. In addition, Weiss & Durovic (1984) have pointed out that the identification of polytypes using X-ray powder diagrams is complicated.

Nemecz (1984), using X-ray powder patterns, suggested that pyrophyllite $1Tc$ is transformed into the monoclinic modification as a result of intense grinding or oriented stress. The patterns for the sample used in the present work do not clearly show the transformation of $1Tc$ into $2M$, but disordered structures appear progressively as the grinding time increases (Wiewiora, 1987, personal communication).

As shown above, between 30 and 32 mins grinding, drastic changes occur in the XRD patterns. In the 2θ range 19 to $21°$, only the (110) reflection persists, and this disappears completely after 240 mins grinding. These changes show a more disordered structure with profound distortion of the crystal lattice.

Rosenberg & Cliff (1980) have indicated that the pyrophyllite structure is rapidly degraded by milling, X-ray reflections beginning to deteriorate almost immediately, and disappearing completely after 60 mins. These findings do not agree with the results reported here, but the discrepancy may be due to different experimental conditions.

The effect of prolonged grinding on the structure and properties of clay minerals has been studied by many authors (Grim, 1968; Juhász, 1980), but there is little data on the changes in specific surface area provided by mechanical treatments. The plot of BET surface area *vs.* grinding time (Fig. 4) shows an initial large increase from 0·52 to ~ 60 m^2.g^{-1} during the first 30 min, followed by a decrease to 7 m^2.g^{-1} after 325 mins grinding. This behaviour is similar to that observed for other materials undergoing mechanical treatments (Gregg, 1968; Somasundaran, 1978; Papirer & Roland, 1981; Henmi & Yoshinaga, 1981). The existence of a practical limit to grinding has been demonstrated, determined mainly by the tendency of the particles produced to reaggregate and establish a physical equilibrium between fragmentation and reduction in size with an increase in specific surface area, and aggregation resulting in a decrease in specific surface area. Also, the solid residues from grinding became
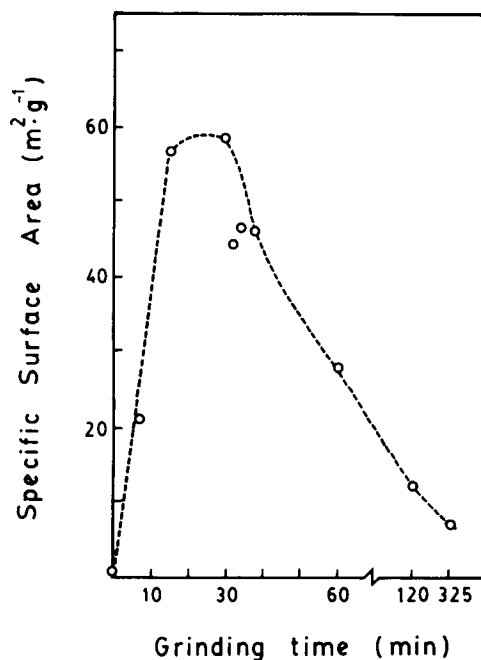

FIG. 4. Plot of specific surface area of pyrophyllite *vs.* grinding time.

cemented together by highly reactive amorphous material that acted as a coating as grinding progressed (Papirer & Roland, 1981). Hayashi *et al.* (1962) also reported the formation of an aggregated amorphous product on grinding pyrophyllite.

At the beginning of the grinding, delamination of the pyrophyllite layer and a decrease in particle size occur, and at the same time, structural distortion takes place and microstrain must increase. These phenomena result in an increase in the specific surface area. Later, as a consequence of the interaction of active broken edges following grinding, the particles become agglomerated and, therefore, the specific surface area (nitrogen adsorption) begins to decrease to 7 $m^2.g^{-1}$. These active surface groups are very important in the processes of mechanochemical agglomeration (Mendelovici *et al.*, 1984).

Henmi & Yoshinaga (1981) reported a rapid decrease in specific surface area when grinding time increased for imogolite, and at the same time, the particle morphology changed from fibres to coarse aggregates. These authors claimed that the decrease in the measured surface area was caused by collapse of the micropores which account for the large specific surface area of imogolite.

The processes of agglomeration occur naturally in powders because of adhesion forces that always act between the fine particles produced by grinding. The bonding mechanisms have been discussed in detail by Rumpf & Schubert (1978).

Juhász (1982) has indicated that during grinding of solid matter it is useful to distinguish primary and secondary mechanochemical processes. The first generate the increase in the free energy of the system and increase the chemical reaction capacity and activity of the matter. These processes are the mechanochemical dispersion accompanied by surface structural transformations, and the mechanochemical activation affecting the internal structure and the chemical bonds, respectively. The energy needed for the primary processes is supplied by the absorption of mechanical energy. The second take place spontaneously in the activated systems and are accompanied by a decrease in free energy. These processes are aggregation, which can be deduced from the activity of adhesive forces, agglomeration derived from the chemical reactions of grain surfaces, and adsorption and chemisorption, surface reactions, and recrystallization.

In general, the changes in specific surface area are strongly influenced by experimental grinding conditions. Okuda *et al.* (1969) studied dry- and wet-ground pyrophyllite, and Hayashi *et al.* (1979) used additives for industrial grinding of pyrophyllite to prevent agglomeration of particles so that pyrophyllite could be separated from other minerals. The values of specific surface area in both papers are lower than those obtained in the present work. The use of solvents, chemisorbed on the surfaces of the ground materials, reduces the surface energy of the fracture surface and, therefore, prevents aggregation (Somasundaran, 1978; Papirer & Roland, 1981).

Grinding also increases the weight loss of pyrophyllite on heating at <200°C *i.e.* an increase in "free moisture" of the samples, suggesting that some extremely weakly bound hydroxyl groups of an amorphous phase are being lost in this temperature range (TG data not shown). The high initial increase in specific surface area indicates that probably some hydroxylation processes take place by adsorption with atmospheric water molecules. Both adsorbed water molecules and extremely weakly bound OH groups are eliminated at lower temperatures.

The gradual size reduction and associated morphological changes which occur during the grinding of pyrophyllite are revealed by the SEM study and some selected micrographs are shown in Fig. 5. At the beginning of the grinding, some gliding (Alcover & Giese, 1986),
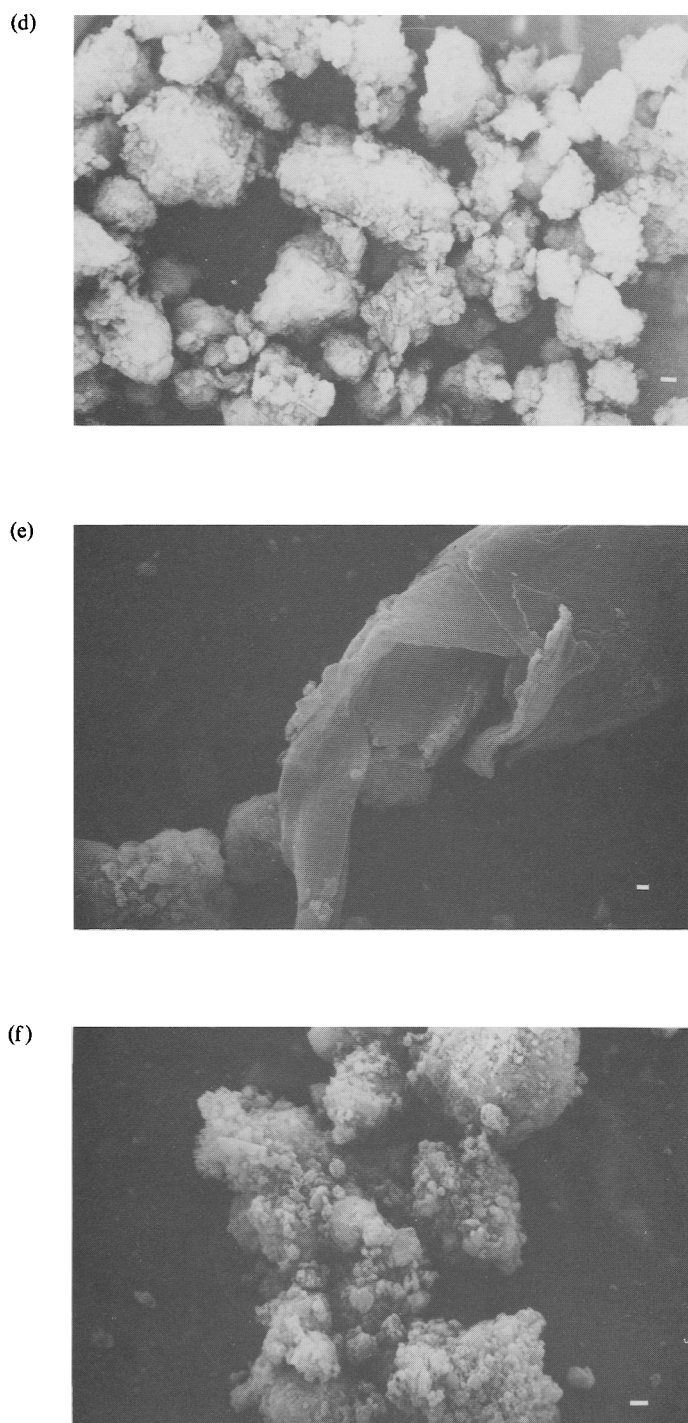
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(a)

(b)

(c)

(d)

(e)

(f)
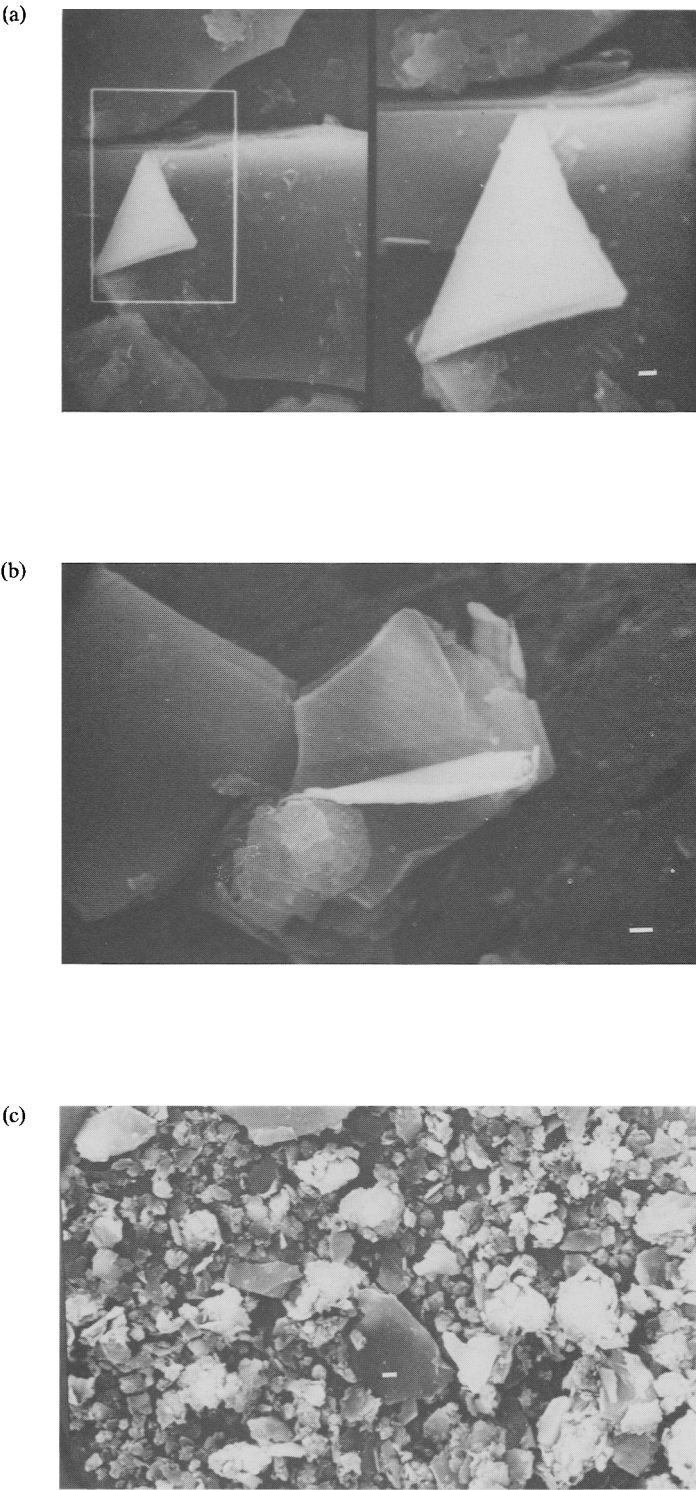
FIG. 5. SEM photographs of pyrophyllite ground for different times: a—7 min; b—10 min; c—30 min; d—32 min; e—45 min; f—120 min. Scale marker 1 μm.

delamination and folding of the layers are observed, together with a decrease in particle size (Fig. 5a,b). These observations agree with the increase in specific surface area described above. After 30 mins grinding, a decrease in particle size occurs as shown in Fig. 5c. Agglomeration of the particles starts after 32 mins (Fig. 5d), at the same time as dramatic changes occur in the XRD patterns (Fig. 3). The agglomeration process increases with grinding time, although cracks in some degraded particles are observed (Fig. 5e), reflecting the highly strained and defective crystalline structure. Agglomeration is clearly very important after long grinding times (Fig. 5f). The SEM study lends support to the results obtained by XRD and nitrogen adsorption.

Other materials such as imogolite and chrysotile also become agglomerated during grinding according to electron microscopy results (Henmi & Yoshinaga, 1981; Papirer & Roland, 1981), although the grinding medium strongly affects the morphology of the ground material, as indicated by Papirer & Roland (1981) for chrysotile.

CONCLUSIONS

The XRD patterns and specific surface area measurements (nitrogen adsorption) of pyrophyllite dry ground for different times show a high degree of degradation of the original crystalline sample. During the first 30 mins, the material is delaminated and a decrease in particle size causes a large increase in specific surface area up to a maximum value *ca.* 60 $m^2 . g^{-1}$.

In the experimental conditions used, a dramatic change is observed in the XRD patterns after 30–32 mins grinding with an increase in the background, broadening of the diffraction bands and an increase in the degree of disorder. Longer grinding times seem to increase the disorder further, and decrease the specific surface area due to particle aggregation and agglomeration. After long grinding times, some residual order still persists.

The X-ray results do not clearly show a transformation of triclinic pyrophyllite into monoclinic, as claimed by Nemecz (1984). It is likely that the mechanical treatment produces high structural disorder, but the triclinic-monoclinic transformation is difficult to observe by X-ray powder diffraction (Weiss & Durovic, 1984).

The SEM study confirms the alteration of pyrophyllite during dry grinding suggested by the results of the other techniques, providing additional information on folding, gliding of layers (Alcover & Giese, 1986), particle size diminution and aggregation. However, the influence of the grinding medium in the grinding operation is very important and needs further experimental work.

The remarkable contrast between the high chemical stability of pyrophyllite (Pérez-Rodríguez *et al.*, 1985) and its mechanical instability should be noted.

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