

# THE EFFECTS OF ALUMINIUM FLUORIDE ON THE THERMAL BEHAVIOUR OF KAOLIN

By A. BIEN\* and W. L. DE KEYSER  
Université Libre de Bruxelles, Belgium.

[Read 12th April, 1962]

## ABSTRACT

A systematic study has been made of the effects of aluminium fluoride on the thermal behaviour of kaolin, using differential thermal, thermogravimetric, X-ray and electron microscope techniques. It is shown that mullite can be formed at a temperature as low as 600°C; that in the presence of aluminium fluoride the exothermic reaction occurs at a lower temperature and is reduced in size; that the size of the mullite crystals is increased as a result of pretreatment with aluminium fluoride.

## INTRODUCTION

The formation of mullite from kaolinite generally occurs above 1000°C, but the authors have been able to obtain it at a temperature as low as 600°C (*i.e.*, immediately after the dehydroxylation of the kaolinite) through the action of aluminium fluoride. In addition to the interest of obtaining mullite, which is the stable high-temperature phase of the silica-alumina system, at a relatively low temperature and before the collapse of the metakaolinite lattice, the action of aluminium fluoride contributes new information on the thermal decomposition of kaolinite.

## EXPERIMENTAL

*Methods.* A North American Philips X-ray diffractometer with a Geiger counter was used with Cu K $\alpha$  radiation.

In the differential thermal apparatus all samples were heated at a rate of 13-15°C/min. up to 1200°C. The thermogravimetric and differential thermogravimetric curves were obtained by the method of De Keyser (1953*a*; 1953*b*). The heating rate was 3°C/min. and a constant temperature difference of 8°C was maintained between the two samples in the differential thermobalance.

An R.C.A. electron microscope, Model EMU 2 B, was used.

*Materials.* The kaolinite employed was Zettlitz kaolin with the composition SiO<sub>2</sub> 46.27, Al<sub>2</sub>O<sub>3</sub> 39.36, Fe<sub>2</sub>O<sub>3</sub> 0.74, K<sub>2</sub>O 0.20, H<sub>2</sub>O 13.31, total 99.88. The thermal behaviour of this material has been studied in several earlier papers. All reagents were of A.R. grade, and hydrated aluminium fluoride was prepared from alumina and hydrofluoric acid. Chemical analysis and X-ray examination of this material shows it to have the formula 2AlF<sub>3</sub>.6H<sub>2</sub>O. Differential thermogravimetric analysis (Fig. 1) shows that it dehydrates between

\*Died 21st December, 1961.

95°C and 268°C; above this temperature, and up to 687°C, it consists of anhydrous  $\text{AlF}_3$ . Between the latter temperature and 1000°C a slow endothermic reaction occurs and X-ray examination of the sample heated to 1000°C demonstrated the presence of  $\text{AlF}_3$  and  $\alpha\text{-Al}_2\text{O}_3$ . Several relatively intense diffraction lines, which have not yet been identified, also occur on these X-ray patterns.

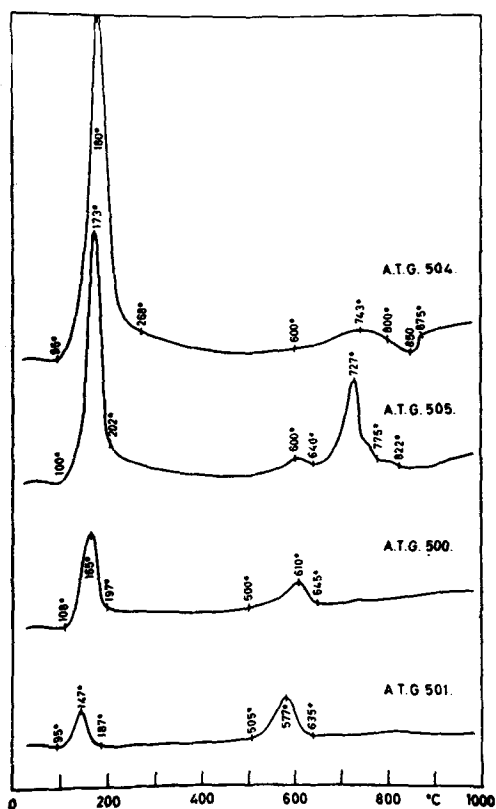


FIG. 1—Differential thermogravimetric curves for: A.T.G. 504—hydrated aluminium fluoride; A.T.G. 505—kaolin with 69.5 per cent. aluminium fluoride; A.T.G. 500—kaolin with 30 per cent. aluminium fluoride; A.T.G. 501—kaolin with 10 per cent. aluminium fluoride.

Kaolin samples were treated with hydrofluoric acid by dispersing 40 g kaolin in 100 ml distilled water in a polythene container, adding various amounts of hydrofluoric acid and evaporating to dryness at 110°C. Six samples were obtained in this way using different amounts of hydrofluoric acid (Table 1).

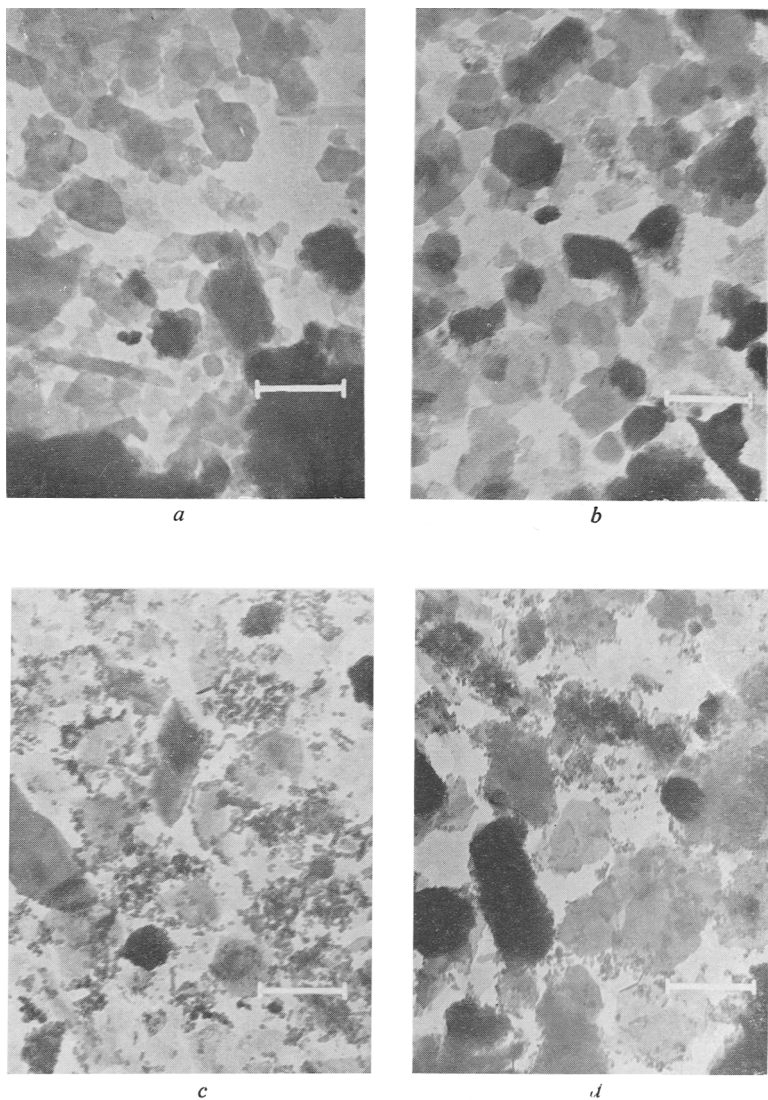


FIG. 2—Electron micrographs showing the formation of aluminium fluoride by the reaction of HF with kaolin: *a*—Zettlitz kaolin, untreated; *b*, *c* and *d*—treated with 2.5 ml, 7.5 ml, and 15 ml HF.

TABLE 1—Samples treated with hydrofluoric acid.

Designation	Amount HF added to 40 g. clay (ml)
KHF(a)	0.1
KHF(b)	2.5
KHF(c)	5.0
KHF(d)	7.5
KHF(e)	10.0
KHF(f)	15.0

Each of these samples was examined under the electron microscope and by X-ray diffraction. The latter showed that treatment with hydrofluoric acid at 110°C does not greatly affect the crystal structure of the kaolinite; however, a decrease in intensity of the diffraction lines is observed, mainly of the 7.1 Å and 3.58 Å lines which correspond to the 001 and 002 reflections. The electron microscope, however, showed the presence of small spherical particles dispersed among the kaolinite hexagons (Fig. 2). The amount of these particles increases with increasing amount of hydrofluoric acid and the authors believe that this substance is hydrated aluminium fluoride resulting from chemical attack on the kaolinite. Three mixtures of kaolinite with hydrated aluminium fluoride were prepared having 10 per cent., 30 per cent., and 69.5 per cent.  $2\text{AlF}_3 \cdot 6\text{H}_2\text{O}$ , respectively. These powders were homogenized in the dry state. The mixture containing 30 per cent. aluminium fluoride would give a material with

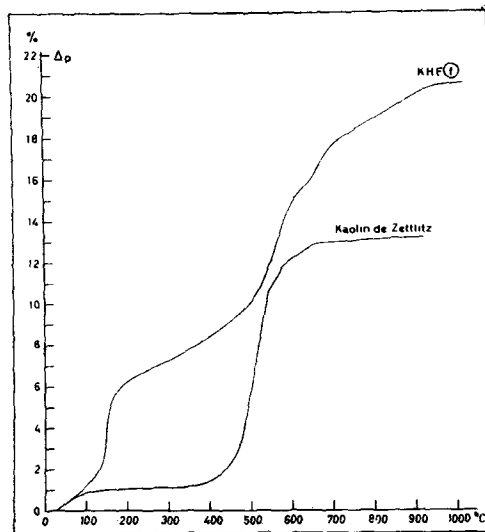


FIG. 3—Thermogravimetric curves for pure Zettlitz kaolin and for the same kaolin with added  $\text{AlF}_3$ .

the formula  $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$  if all the fluorine initially introduced were eliminated by a chemical reaction with silica to give  $\text{SiF}_4$ . The mixture containing 69.5 per cent. aluminium fluoride would give rise

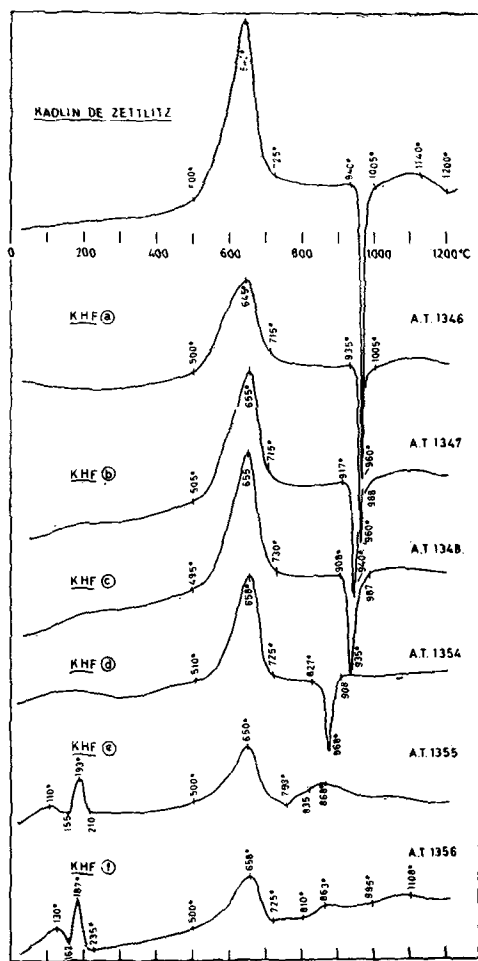


FIG. 4—Differential thermal curves for kaolin treated with increasing amounts of HF. For sample treatment see Table 1.

to a material with the formula  $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$  if, on the other hand, the fluorine were to react quantitatively with water to produce HF.

#### WEIGHT LOSSES DURING HEATING

Both mixtures of kaolin with aluminium fluoride and kaolin treated with HF show two weight losses in the region up to 700°C—

namely, the dehydration of the fluoride between 100°C and 200°C and the dehydroxylation of the kaolinite starting at 500°C. On heating these samples above 600°C a weight loss is observed up to 1000°C, whereas pure kaolin shows no weight loss between 750°C and 1000°C (Fig. 3). The most likely explanation is that silicon fluoride resulting from reaction between  $\text{AlF}_3$  and kaolinite is volatilized at these temperatures. The size of the first dehydration peak on both the differential thermogravimetric and differential

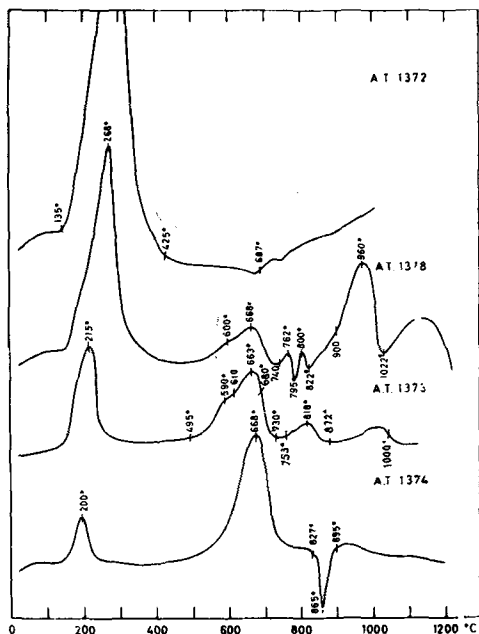


FIG. 5—Differential thermal curves for: A.T. 1372—hydrated aluminium fluoride; A.T. 1378—kaolin with 69.5 per cent. aluminium fluoride; A.T. 1373—kaolin with 30 per cent. aluminium fluoride; A.T. 1374—kaolin with 10 per cent. aluminium fluoride.

thermal curves (Fig. 4) depends on the amount of hydrated aluminium fluoride present in the sample.

#### THE EXOTHERMIC REACTION: MULLITE FORMATION ABOVE 600°C

The presence of aluminium fluoride markedly affects both the temperature and height of the kaolinite exothermic peak. This is well shown by the differential thermal curves in Figs. 4 and 5, obtained for samples treated with hydrofluoric acid and for samples mixed with aluminium fluoride. Addition of 10 per cent. aluminium fluoride, indeed, causes the peak temperature of the exothermic peak to drop by about 100°C.

In order to determine the crystallographic significance of the exothermic peak, samples were heated in the differential thermal apparatus to just before and just after the peak and quenched in air. These were then examined by X-ray diffraction. For the material giving curve A.T. 1374, Fig. 5, diffraction lines corresponding to mullite were identified at temperatures as low as 820°C—*i.e.*, before the beginning of the exothermic reaction. At 890°C, after the exothermic reaction, the mullite lines increase in intensity and a small amount of a spinel phase appears. Addition of small amounts, *e.g.*, 10 per cent., of aluminium fluoride, markedly reduces the size of the

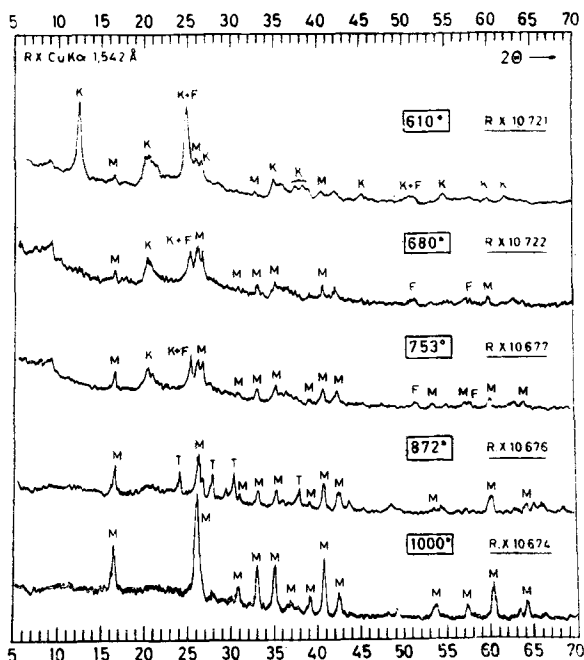


FIG. 6—Development of the mullite as a function of temperature, as shown by X-ray diffractometer tracings: M—mullite, K—kaolinite, F—aluminium fluoride, T—topaz. Sample containing 30 per cent. aluminium fluoride, fast heating.

exothermic peak and increase in the amount of aluminium fluoride up to 30 per cent. causes its complete disappearance.

Comparison of the differential thermal curves for mixtures containing 30 per cent. aluminium fluoride (Curve A.T. 1373, Fig. 5) and 69.5 per cent. aluminium fluoride (Curve A.T. 1378, Fig. 5) shows that they are similar up to 730°C; in this region only the endothermic peaks due to the dehydration of the hydrated aluminium fluoride and to the dehydroxylation of the kaolinite are observed.

With the sample containing 69.5 per cent. aluminium fluoride, however, the latter part of the curve is rather complex. Between 740°C and 822°C there is an endothermic reaction probably due to the volatilization of SiF<sub>4</sub> and superposed on it a stronger exothermic reaction with a peak at 795°C. The latter probably corresponds to the formation of topaz, (AlF)<sub>2</sub>SiO<sub>4</sub>. Above 900°C there is a large endothermic reaction which is probably due to volatilization of SiF<sub>4</sub> formed by the reaction of topaz with AlF<sub>3</sub>. The last endothermic peak commencing at about 1022°C is caused by sublimation of the aluminium fluoride, and at 1200°C only α-Al<sub>2</sub>O<sub>3</sub> is left. Samples of the mixture giving curve A.T. 1373, Fig. 5, were examined by X-rays after heating to 610°C, 680°C, 753°C, 872°C and 1000°C. Fig. 6 shows that mullite can be observed at 610°C—i.e., immediately the kaolinite is dehydroxylated—and that the mullite lines increase markedly in intensity at 680°C and at 753°C—i.e., after complete dehydroxylation. The endothermic reaction in the 753–872°C region is attributed to the volatilization of SiF<sub>4</sub>. At 872°C topaz is clearly observed, although there is no corresponding exothermic reaction; this is probably due to the smaller amount of aluminium fluoride. The endothermic reaction at about 1000°C is attributed to the decomposition of topaz, since above this temperature topaz is no longer observed. At 1000°C one finally obtains mullite which is better crystallized than the mullite obtained on heating the same kaolinite at 1100°C for 24 hours without the addition of aluminium fluoride.

#### MECHANISM OF REACTION BETWEEN KAOLINITE AND ALUMINIUM FLUORIDE

In view of the properties of aluminium fluoride, two types of reaction have been considered:

(a) Because of the similarity of the ionic radii of OH<sup>-</sup> and F<sup>-</sup> (1.30Å and 1.33Å respectively), the F<sup>-</sup> can, partially at least, replace the OH<sup>-</sup> in the kaolinite structure.

(b) Because of the presence of fluoride and silica in the mixtures the silica sheets in the metakaolinite can undergo a reaction of the type



a reaction which could result in premature collapse of the metakaolinite structure.

In order to distinguish between the two possible mechanisms, it is sufficient to employ experimental conditions where substitution of F<sup>-</sup> for OH<sup>-</sup> is not possible. This is so when mixtures of metakaolinite (kaolinite dehydroxylated by heating at 800°C for one hour) and anhydrous aluminium fluoride (dehydrated at 650°C) are employed. The differential thermal curves for such mixtures (Fig. 7) show that the exothermic reaction is displaced in exactly the same manner as that previously observed for the original mixtures. It is clear therefore that only mechanism (b) is operative.



On the basis of earlier work it is believed that the exothermic reaction is due to rearrangement within the lattice which occurs without the formation of any crystalline phase detectable by X-ray diffraction (De Keyser, 1959). The reduction in peak temperature and in size of the exothermic peak on the addition of  $\text{Na}_2\text{O}$  or  $\text{K}_2\text{O}$  has previously been explained by a reaction occurring between the metakaolinite and the alkali. This reaction both accelerates the collapse of the lattice and reduces the size of the exothermic peak through the introduction of  $\text{Na}_2\text{O}$  into the lattice at the site left vacant by the removal of  $\text{H}_2\text{O}$ . The authors believe that the action of aluminium fluoride is analogous: the partial attack on  $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$  and volatilization of the  $\text{SiF}_4$  liberates  $\text{Al}_2\text{O}_3$  which combines with unreacted  $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$  to form mullite.

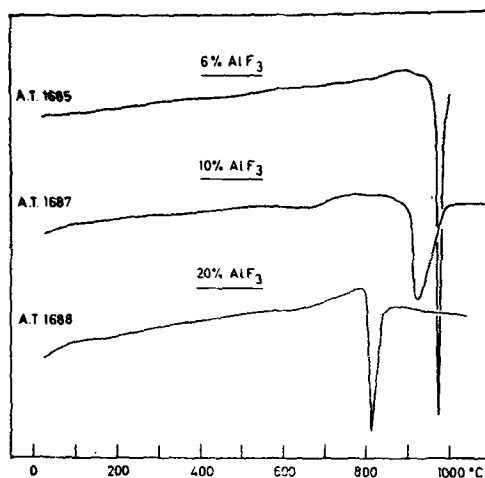


FIG. 7—Differential thermal curves for metakaolin with added  $\text{AlF}_3$ .

#### FORMATION AND GROWTH OF MULLITE CRYSTALS

On the basis of the above argument, samples containing aluminium fluoride produce mullite above  $600^\circ\text{C}$  by the reaction of unaffected  $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$  with  $\text{Al}_2\text{O}_3$  formed by aluminium fluoride attack. It should also be noted that by mixing colloidal silica and hydrated aluminium hydroxyfluoride in the ratio  $\text{SiO}_2 : \text{Al}_2\text{O}_3 = 1$  mullite can be obtained below  $700^\circ\text{C}$ .

Comparison of X-ray diffraction patterns of mullite obtained at low temperatures shows that growth of the mullite crystals is slow below  $1050^\circ\text{C}$ . This temperature appears to be a threshold, since above it growth of mullite crystals becomes more rapid.

The aluminium fluoride, by inducing the formation of mullite at low temperatures, ensures a slow but regular growth of the crystals,

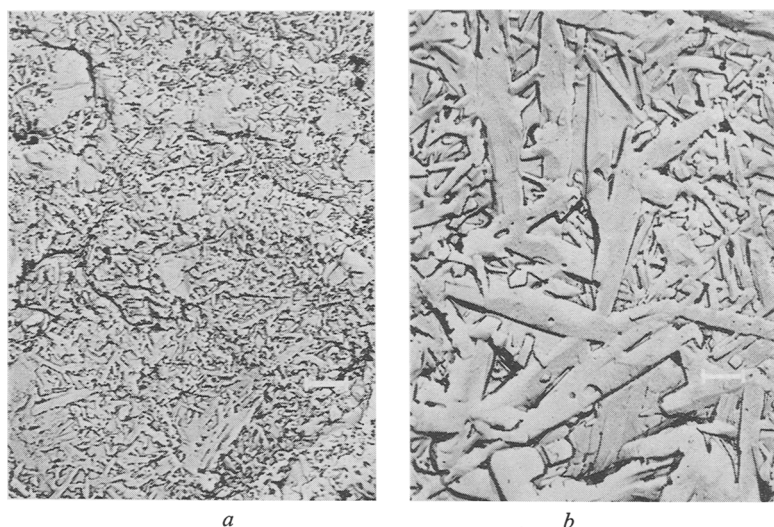


FIG. 8—Electron micrographs of Zettlitz kaolin heated at 1300°C for 24 hours in the absence (a) and in the presence (b) of  $\text{AlF}_3$ .

an interpretation that is confirmed by the density of samples of kaolin with and without additions of aluminium fluoride (Table 2) after heating at 1300°C. It is clear that the greater the initial amount of fluoride the higher the density of the samples.

TABLE 2—Density of samples heated for 24 hours at 1300°C.

Sample	Density
Kaolin	2.688 g/cm <sup>3</sup>
Kaolin+10% a.f.*	2.745 g/cm <sup>3</sup>
Kaolin+30% a.f.*	2.835 g/cm <sup>3</sup>

\*Aluminium fluoride.

The favourable action of aluminium fluoride on the growth of mullite crystals can be directly observed from electron micrographs using the replica technique. This is clearly demonstrated in Fig. 8 where the size of mullite crystals obtained from pure kaolinite at 1300°C is compared with that obtained by heating kaolinite with 10 per cent. aluminium fluoride at the same temperature for the same time.

#### REFERENCES

- DE KEYSER, W. L., 1953a. *Nature, Lond.*, **172**, 364.  
 DE KEYSER, W. L., 1953b. *Bull. Soc. franc. Céram.*, No. 20.  
 DE KEYSER, W. L., 1959. *Silicates Industr.*, **24**, 117, 190.