

## SEM studies on micro structure of fired kaoline - illite - quartz bodies

### *Kaolinit - illit - kuvars bünyelerde mikro-yapının SEM ile incelenmesi*

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#### ABSTRACT

SEM observations were undertaken from the etched fresh surfaces of kaolinite-illite-quartz bodies after coating with Jeol JSM 6400 scanning electron microscope equipped with link energy dispersive spectrometer. The fractured fresh surfaces were treated with a hot and cold HF. Scanning electron micrographs and the chemical compositions of the selected areas and points on the fresh etched surfaces show that primary mullite arises mainly from clay zones while growth of secondary mullite occurs essentially within the feldspathic glassy zones or, relict feldspar grains. SEM micrographs also show actual pore sizes developed in the fired bodies. The bodies have three kinds of pore sizes. But according to the spatial distribution of the porosity observed in the micrographs, porosity can be divided into intragranular and intergranular porosities.

- The intragranular pores refer to the pores within the original grains; they are small and are produced by bubbling and blistering. They can be divided into two groups ranging from 5-10 $\mu$  to 1 $\mu$ .

- The intergranular porosity consists of elongated shrinkage pores; they are large and are formed between the grains and their size change between 20 -50  $\mu$ .

**Key Words :** Amorphous/ glassy phase, Porosity, Primary mullite, Secondary mullite, Smullite

#### ÖZ

*Kaolinit-illit-kuvars bünyelerden kırılmış taze yüzeyler altınla kaplandıktan sonra Jeol-JSM-6400 taramalı elektron mikroskopuyla gözlenmiştir. Taze kırılmış yüzeyler sıcak ve soğuk hidroflorik asitle dağlanmış. SEM görüntüleri ve örnek yüzeylerinden yapılan kimyasal analiz sonuçları; birincil müllitlerin kil alanlarından (kil taneleri), ikincil müllitlerin ise feldispatlı cam alanları ve kalıntı feldispat tanelerinin içinde büyüdüklarini göstermiştir. Bu görüntüler aynı zamanda gerçek gözenek boyutlarını da göstermektedir. Bünyelerde üç çeşit büyüklükte gözenek bulunmaktadır. Gözenekler, görüntülerdeki uzaysal dağılımlarına göre tane içi ve tanelerarası şeklinde ikiye ayrılabilir.*

- *Tane içi gözenekler, orijinal tanelerin içindekiler; bu gözeneklerden küçük ve gaz çıkışları ile oluşan kabarcıklardır, boyutları iki grupta, 1 $\mu$  ve 5 $\mu$ -10 $\mu$  arasında değişmektedir.*

- *Tanelerarasında uzunlamasına büzülme ve küçülme ile oluşmuş gözenekler; taneler arasında 20 $\mu$  - 50 $\mu$  boyutlarında büyük gözeneklerdir.*

**Anahtar kelimeler:** Amorf/camsı faz, Birincil müllit, Gözeneklilik, İkincil müllit

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## INTRODUCTION

X-Ray diffraction, petrographic microscopy and SEM analysis are used together to obtain qualitative and quantitative information on the microstructure of kaolinite-illite-quartz bodies. The petrographic microscope is used to analyse of the microstructure and mineralogy of the fired products. But the results have not been entirely satisfactory because of the inability to detect crystalline particles of submicrometer mullite, cristobalite and pores. The body consists of mullite cristobalite and quartz (crystalline phases) in a composite structure where crystals and porosity are embedded in the matrix of amorphous/glassy phase. Both glass and amorphous phases appear in more or less significant amounts in all the studied fired clay bodies. The presence of quartz, detrital mica and Ca-Na feldspar indicate bodies being usually fired under nonequilibrium conditions and that many chemical reactions do not go to completion because of the lack of sufficient heat treatment and of intimate contact of the constituents. If the reactions were allowed to go to completion this would result in a large glassy phase that would endanger the desirable properties of the clay based ceramic bodies.

## MATERIALS AND METHOD

The changes in the crystalline and glassy phases were studied with the aid of SEM micrographs obtained from the fired bodies of kaolinite rich HB, mixed HK (%50HB+%50KW), illite rich KW and the ir feldspar mixed bodies on which tests of XRD, as well as thin section studies and physical properties had been made. SEM observations were undertaken on etched fresh broken surfaces of the above mentioned bodies after coating with gold. They were examined at 20-30 kV accelerating voltage with a Jeol JSM 6400 equipped with a Link energy dispersive spectrometer for qualitative analysis of chemical composition of the selected points or areas. The peak heights for the same element of different spectrums were used as a measure for the individual element concentration.

The fractured fresh surfaces were treated during 1,2 minute or 3 minute with hot and cold HF. Figure 1-a, b, c, d, e and f were taken from a fractured surface of wet mixed HK body fired at 1200°C. The specimen was etched with hot HF for 1 min and coated with gold. Treatment with hot HF produces much more solution cavities and pits in amorphous/glassy phase. These small rounded and tiny elongated etch pits tended to develop in size and depth with increasing leaching time. The micrographs of Figure 2 was taken from kaolinite rich (d, e, f) and feldspar mixed bodies (a, b, c). HF treatment also resulted in the formation of new crystalline phases that were precipitated from leaching solutions (Figure 3-a, b, c, d, e, f). The immediate washing with water after etching eliminated the new formed crystals on etched surfaces. They are all fired also at 1200°C.

## RESULTS OF SEM OBSERVATIONS

As shown in Figure 1 a, b and c the quartz grains have been rounded by partial dissolution. The crack patterns are severe and numerous around the larger quartz grains as well as within the glassy matrix. In the microphotograph a, it is difficult to differentiate the porosity and the solution pits of the glassy phase. This dissolution pattern shows that the amorphous/glassy phase has not a homogeneous composition and structure. The difference between the etched amorphous/glassy surface, the original quartz and the fresh cracked surface are clearly seen on the micrographs of Figure 1 b. As shown in the same micrograph, the new formed crystal on the fresh cracked surface of quartz confirmed the curved structure on the original quartz surface (Figure c) which is not produced by HF treatment. This curved structure may indicate cristobalite formation. Tuttle and Cook (1949) have confirmed its presence by X Ray identification.

SEM micrographs also show actual pore sizes developed in the fired bodies. In Figures 1- d, e it is seen that at 1250°C, the bodies have three kinds of pore size dimensions. But according to the spatial distribution of porosity observed in SEM, the poro-



sity in the fired body can be divided into intragranular and intergranular.

-The intragranular pores refer to pores within the original grains; they are small and produced by bubbling and blistering. They can be subdivided into 5-10 $\mu$ m and 1 $\mu$ m- $<$ 1 $\mu$ m. (Figure 1-d)

-The intergranular porosity consists of elongated shrinkage pores; they are large and formed among the grains (quartz and clay grains) and its size changes between 20-50 $\mu$ m (Figure 1-e).

In the Figures 1 e, f coarser grains of K feldspar have glass in which the best development of mullite occurred but nearby grains that contain more bubbles and blebs have not mullite. The long needles of mullite were more developed in the less viscous K-feldspar glass than in the more viscous K-feldspar glass. Therefore the absence of mullite in some of the K-feldspar-glass was assumed to be indicative of relatively higher viscosity than that of nearby grains, filled with mullite. The presence of blebs in this mullite-free feldspar glass supported this assumption the gas was retained by grains of higher viscosity but escaped easily from those of lower viscosity. Local impurities in feldspar may have caused differences in viscosity of the individual grains. On the other hand, many authors pointed out that the amount of mullite, formed in the feldspar glass, should depend not only on the viscosity but also on the time afforded for molecular diffusion from the clay glass. Bubbling and blistering in the glassy phase depends not only on the viscosity but also on the heating rate. Bubbles in the feldspar glass are caused by the evolution of dissolved gases. The gradual escape of some of these gases during a slow temperature rise accounted for the scarcity of bubbles. In rapidly heated specimen, insufficient time for the gradual escape of gas resulted in the production of numerous bubbles.

Primary mullite arises mainly from the clay areas, while growth of secondary mullite occurs essentially within the feldspathic glassy zone or relict feldspar grains (Figures. 2 a, b, c). During firing, the K-feldspar grains start to melt above 1000°C. There is no change in the shape, because of the high viscosity.

Smaller grains disappear by reaction with the surrounding clay and the larger ones interact with the clay (alkali diffuse out of the feldspar and mullite crystals are formed in a glass). Therefore, the outlines of glass-mullite areas correspond with the original feldspar grains (Figures 2- b, c). The lath-shaped mullite crystals have well-defined outlines and their dimensions are rather constant (thickness less than 1 $\mu$ m and length larger than 2 $\mu$ m) in the relicts of feldspar (Figure 2 c). The primary mullite developed in clay has dimensions in the magnitude of nanometer and the outlines of crystals are not well defined because of a diffuse image at higher magnification (Figure 2 f). The crystals have continuous development in the clay/amorphous matrix. Therefore mullite is the crystalline phase in both the original feldspar/glassy grains and in the clay amorphous/glassy matrix. (Figure 2- d, e, f) The crystal size and development are quite different larger mullite needles growing into the feldspar relicts from the surface as the composition changes by alkali diffusion. The formation of mullite within the clay would not be observed on the thin sections even not at 1250°C firing. But SEM studies provide important contributions to the understanding of the differences in primary and secondary mullite formations.

#### Energy dispersive X Ray analysis (EDX)

The presence of phases determined by X-Ray diffraction analysis is confirmed by means of energy dispersive X-Ray analysis (EDX). The phases are:

- primary and secondary mullite,
- clay and feldspar amorphous/glassy phase,
- Fe and Ti rich impurities

and there is a new formation of calcium or potassium aluminosilicate crystals which are formed with different morphology on etched surfaces. EDX data were also obtained from this new formation.

In general EDX data were obtained in

- scan mode with the beam rastered over areas as

large as  $3000\text{\AA} \times 4000\text{\AA}$  (corresponding higher magnification ( $\times 300000$ )) and

-stationary point beam analysis mode.

The scan mode analysis for primary and secondary mullite analysis include also glassy materials, because the above-mentioned minimum area is larger than the observed mullite crystal size. The stationary point mode analysis diagram (Figure 4 a, b) is obtained on the secondary mullite crystal and the matrix, displays only a strong peak of Al and a relatively small peak of Si. On the amorphous glassy matrix the reverse is observed a with strong peak of Si and relatively small peak of Al (Figure 4 c). But the scan mode analysis diagram of the same secondary mullite displays Al, Si and weak K, Ca, Ti and Fe peaks because the analyzed area is not homogenous. The obtained image of primary mullite at higher the magnification measured in nanometer is not used for point analysis because the detector position or the low working distance (7,6 mm) hindered EDX analysis. For this reason EDX diagrams of selected areas with primary mullite include amorphous/glassy phase resulting in lower Al/Si ratio and higher K, Ca, Ti, Fe peaks.

The HF etching developed new crystals on the leached surfaces of the SEM samples. The EDX spectrum of this new crystals displayed strong K and Ca and relatively weak of Si and Al indicating that these aluminosilicates were rich in K and Ca (Figure 4 e, f). It is widely accepted that dissolution of glasses is incongruent. The chemical composition of new crystals indicate selective leaching of alkali ions from the amorphous/glassy matrix; therefore leaching also produces a dealcalized layer. In Figure 3 A, B the etching developed as gel-like grains exhibiting spherical humps on the surface of Ca-Na feldspar mixed bodies. The EDX diagram of this material displays a strong peak of Ca and relatively small peaks of Si and Al (Figure 4- e). The SEM microphotograph of figure 3 d, e, f show the different K and Na-rich crystals appearing as hexagonal platy, lath and cubic-shaped and twinned crystals. The EDX spectrum of the hexagonal platy crystals shows strong K and Si and

small peaks of Al, Ti and Na (Figure 4 d). The EDX diagram of the twinned crystals show strong Si and relatively low Na and Al (Figure 4 f). The EDX diagrams of lath and small cubic shaped crystals are given in the same chemical composition. The variation in chemical composition of these new crystals precipitated from leaching solutions of glasses indicate different chemical composition and incongruent leaching of amorphous/glassy phase.

## DISCUSSION AND CONCLUSIONS

-The characteristic needle-like habit of mullite crystals is not observed in the amorphous/glassy matrix under the optical microscope since the primary mullite crystals, developed directly from amorphous clay are not large enough; however they are identified by the SEM studies.

-K-feldspar relicts consist of glass and mullite ( $<1\mu$  thickness,  $10-5\mu$  length). The outlines of glass-mullite areas correspond to the original feldspar grains and the unresolved matrix correspond to the amorphous/glassy grains of clay.

-SEM observations show the difference of the primary and secondary mullite formations. The larger mullite needles grow in the K feldspar relicts (thickness less than  $1\mu\text{m}$  and length larger than  $2\mu\text{m}$ ) (crystallized in the melt) but the elliptic shaped primary mullite in the clay amorphous/glassy phase has dimensions in the magnitude of nanometers (formed by a reaction in the solid state)

-A study of the amorphous and glassy phase remains one of the most important problems in the consideration of the fired bodies. Finally two types of amorphous material may exist together, i.e. a phase where the crystal structure has been destroyed, (so that no characteristic X Ray peaks can be observed). The composition and structure of the amorphous and glassy phase are constantly undergoing changes during the heat treatment and the glassy component increases. On the other hand the transformation in the crystalline state takes place very gradually and under high viscosity conditions so that the true glassy state



is not immediately established because equilibrium conditions are not attained during the firing time at 1150-1250°C. Amorphous material and glass are not determined qualitatively because of the ambiguity in distinguishing different phases in samples fired 1150-1250°C. Inclusions, blebs and bubbles in the glassy grains and their shapes helped in the process of identification of the glasses.

Microscopical examination of thin sections and SEM observations show only

-shrinkage pores at the peripheries of segregated clay aggregates (Intergranular)

-flaw patterns in the peripheries and inside of the quartz (Intergranular)

-sealed pores in the amorphous/glassy matrix (Intragranular)

During firing at 1150°C, elongated shrinkage pores firstly become maximal, then are partly healed, and the amount of sealed porosity increases. The quartz flaws occur at cooling. The initial small micropores disappeared, and the larger shrinkage pores grew. All these observations showed that as the porosity decreases, the distribution of the pore size shifted to a larger size with increasing temperature.

## REFERENCE

- Tuttle, M.A., Cook, R.L., 1949 Fundamental study of crystalline and glassy phases in whiteware bodies J.Amer.Ceram. Soc. 32. 9 279-294

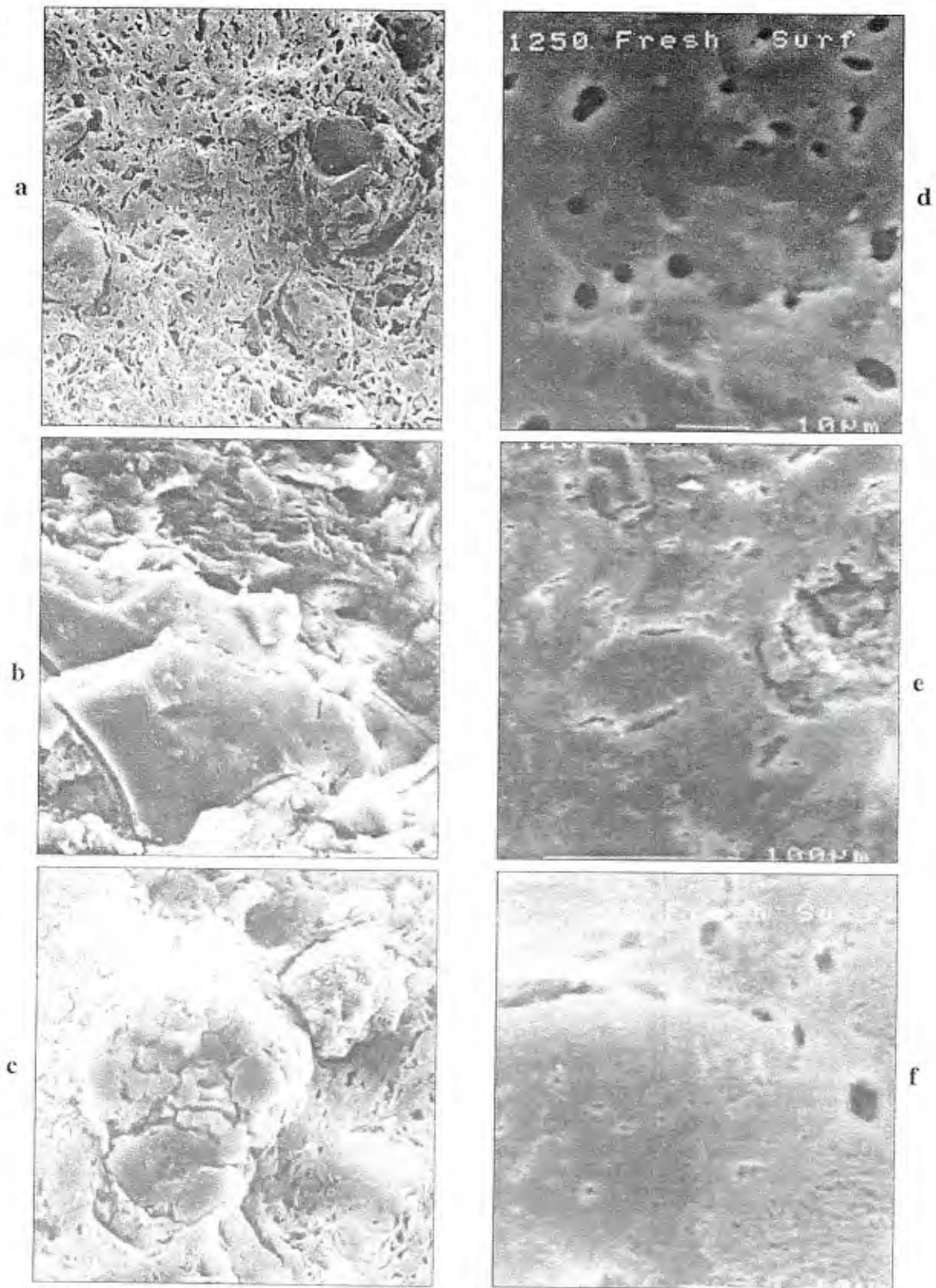


Figure 1. Scanning electron micrographs of etched fresh surface of kaolinite-illite-quartz bodies fired at 1250°C illustrate the overall microstructure, solution rim of quartz grains (a, b, c), K feldspar grains and porosity (d, e, f). Scale bar a, b, c = 10µm, d, e, f = 10µm, 100µm, 10µm



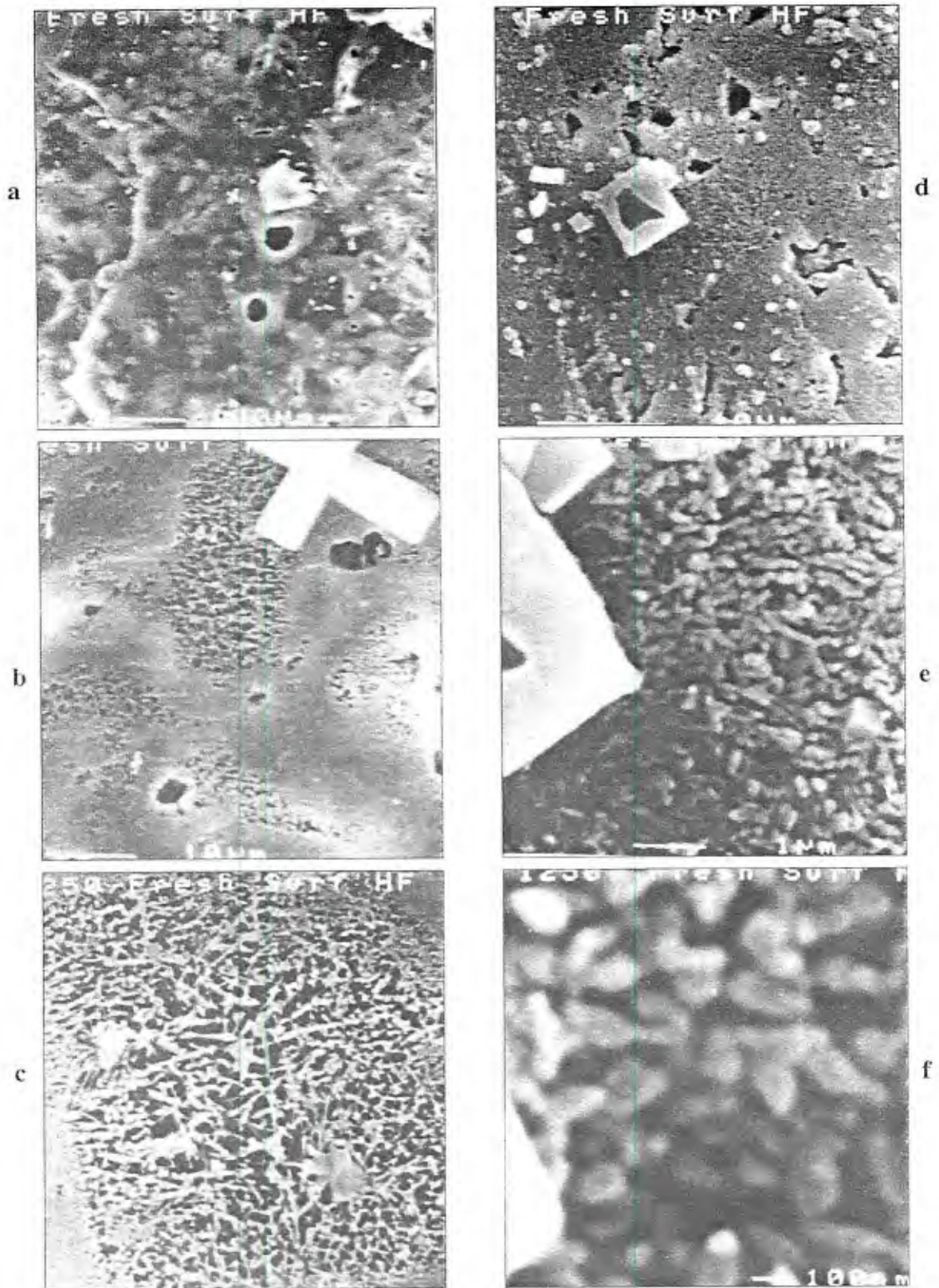


Figure 2. Scanning electron micrographs of etched fresh surface of kaolinite-illite-quartz bodies fired at 1250°C. Illustrate the existence of primary (a, b, c) and secondary (d, e, f) mullite within amorphous /glassy matrix. Scale bar a, b, c = 100µm, 10µm, 10µm, d, e, f = 10µm, 1µm, 100nm



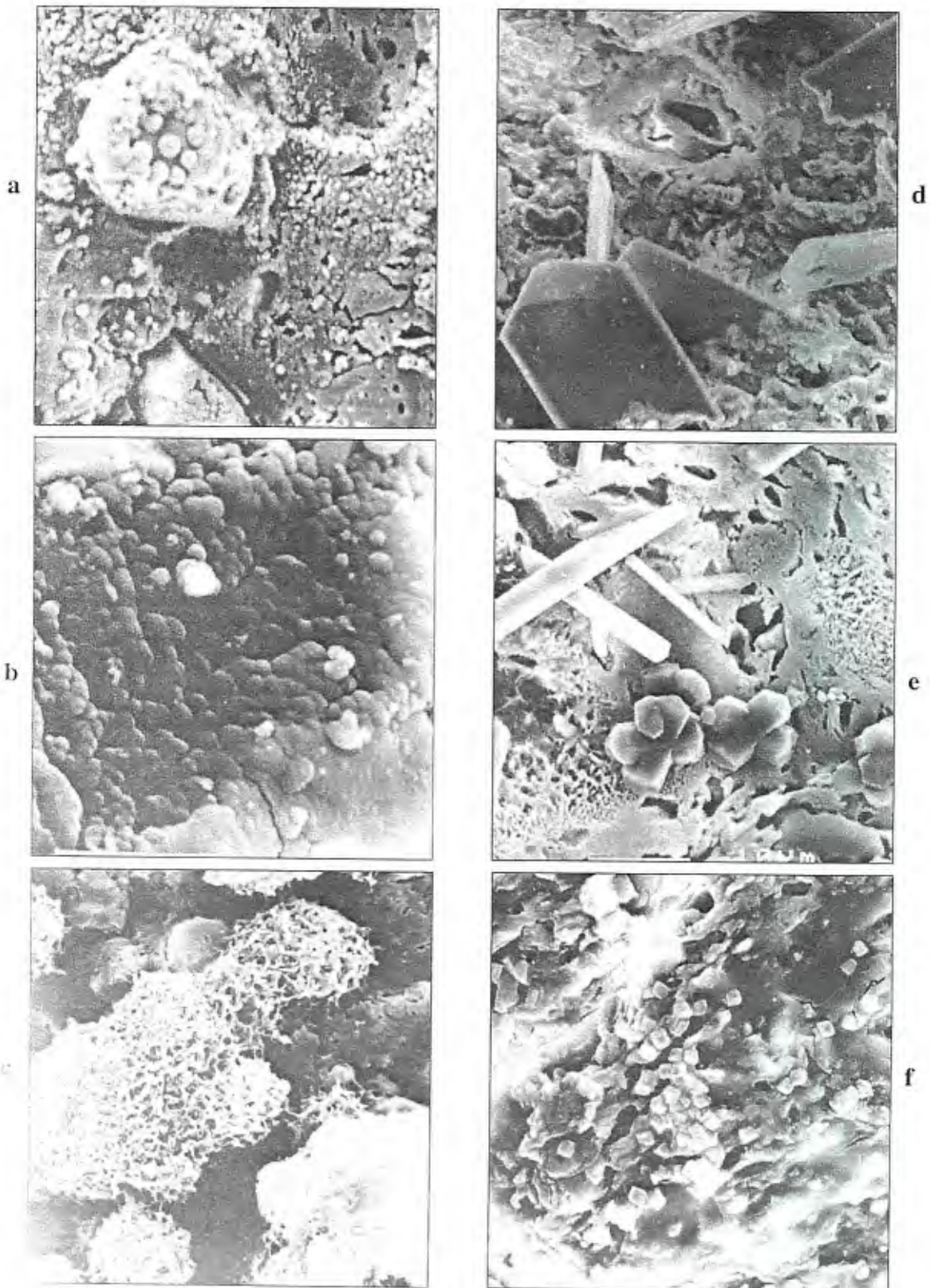


Figure 3. Scanning electron micrographs of etched fresh surface of Ca-Na and K feldspar bodies fired at 1250°C illustrate the existence of Ca rich spherical humps (a, b, c) and K rich crystals of new formation (d, e, f). Scale bar a, b, c = 10µm, d, e, f = 10µm



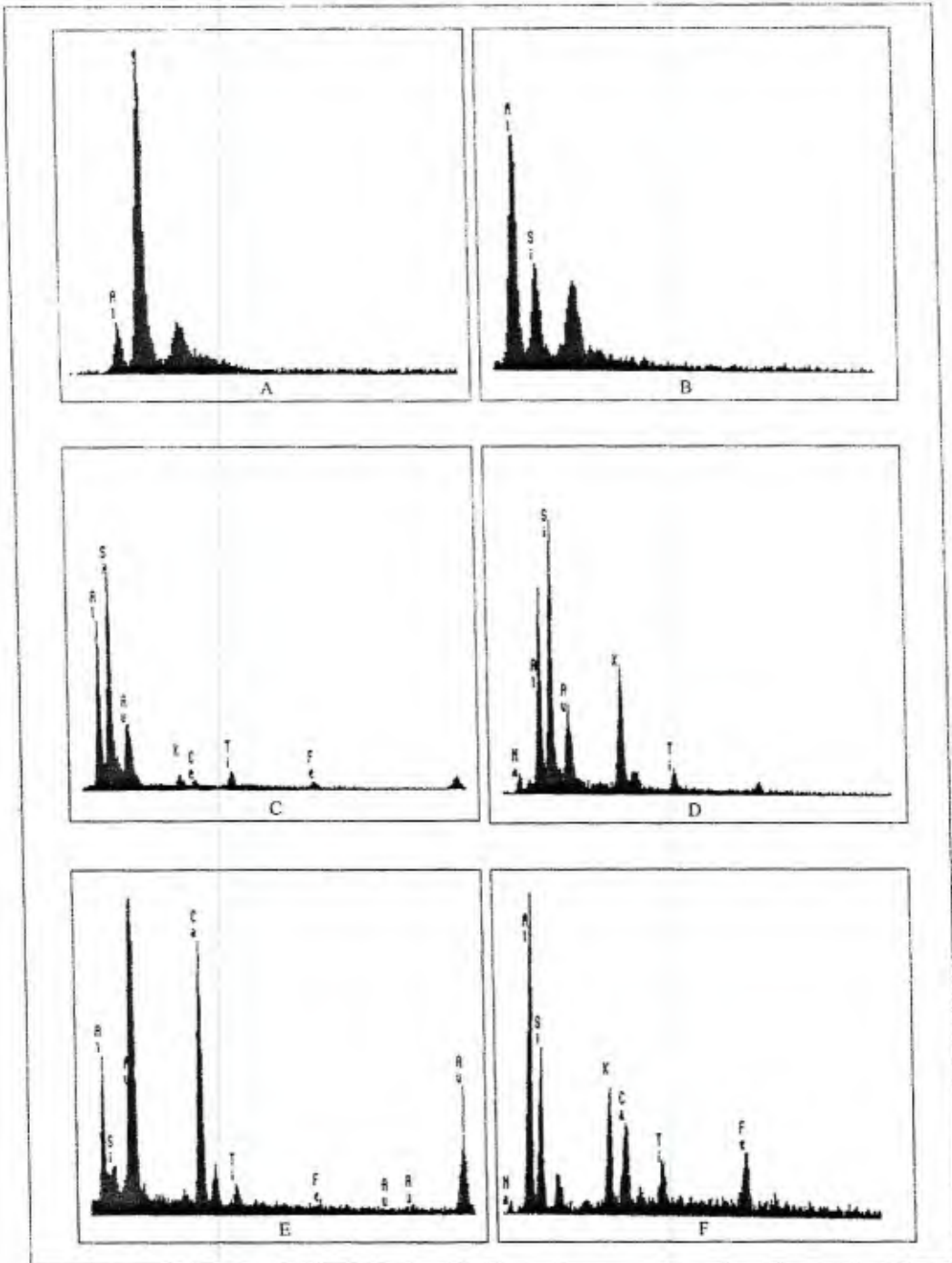


Figure 4. Scanning and stationary beam mode of EDX analysis spectras of secondary mullite primary mullite, amorphous /glassy phase and new formation crystals

