

## SOLID STATE FORMATION OF ANORTHITE FROM SOME CLAY MINERAL-CALCIUM MINERAL MIXTURES

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### ABSTRACT

This investigation is concerned with the formation of anorthite in the solid state. Anorthite was synthesized from kaolinite and halloysite each successively mixed with fluorite, gypsum and calcite. In addition, an oxide mixture of anorthite composition was prepared by mixing calcium hydroxide, gamma alumina and synthetic cristobalite. The clay mineral-calcium mineral mixtures were treated with ethylene glycol to observe the effect upon the formation of anorthite. Phosphorus pentoxide was added to the kaolinite-fluorite mixture to observe its effect upon formation of high temperature phases.

The mixtures were examined by means of continuous high-temperature x-ray diffraction, making possible observations of phase changes and intensity changes during heating at a constant rate.

The following conclusions are reached: 1. Anorthite forms directly from oxide mixtures of appropriate composition. 2. Fluorite and anhydrite react directly with metakaolin to form anorthite. 3. Calcite decomposes to calcium oxide before reacting with metakaolin to form anorthite. 4. Ethylene glycol affects kaolinite reactions by exerting a stress upon kaolinite particles, causing the temperature of appearance of anorthite to be raised. This effect is not observed in halloysite mixtures. 5. The presence of phosphorus pentoxide favors the formation of cristobalite rather than anorthite because of similarities in crystal structure. 6. Metakaolins formed from halloysite and kaolinite are identical in structure because differences in reactivity are very small. 7. Presence of trace minerals can affect both mineralogy and texture in metamorphic rocks.

### INTRODUCTION

The development of continuous high-temperature x-ray diffraction (Grim and Kulbicki, 1957) has provided a useful tool in the study of solid state reactions. By using this method it is possible to scan solid state reaction mixtures during heating at various rates.

In this investigation, continuous high-temperature x-ray diffraction was used to study some reactions which result in the formation of anorthite in the solid state. One objective of the investigation was to compare temperatures and rates of reaction of an oxide mixture with temperatures and rates of reaction of more complex substances. To this end, a mixture of oxides of theoretical anorthite composition and mixtures of kaolinite and halloysite with calcite, gypsum, and fluorite were prepared. A second objective was to compare reaction rates and temperatures of kaolinite mixtures with halloysite mixtures. The mixtures of kaolinite and halloysite with calcite, gypsum and fluorite previously mentioned provide this comparison. A third objective was to examine the effect of an organic compound, ethylene glycol, upon clay mineral-

calcium mineral mixtures. Because ethylene glycol causes an expansion of the halloysite structure but does not show similar effects upon kaolinite, some differences in temperature and reaction rates were expected. Byrne (1953) has shown that addition of ethylene glycol and other organic compounds to montmorillonites influences the phases formed at high temperature. A final objective of this investigation was to examine the effect of phosphorus pentoxide upon one of the clay mineral-calcium mineral mixtures. The kaolinite-fluorite mixture was chosen for convenience. Because of the similarity of phosphate and silicate structures, some differences in the formation of high temperature phases were expected.

#### PREVIOUS SYNTHESSES OF ANORTHITE

Many investigators have been concerned with the crystallization of silicate melts. Anorthite has been encountered as a phase in many of these systems. In contrast, only a few investigations have dealt with the formation of anorthite in the solid state.

Jander and Petri (1938) prepared anorthite by heating oxides and mixtures of calcium silicates and aluminates (with appropriate simpler compounds) in a gas muffle furnace at 1050°–1100° C. X-ray powder photographs revealed the formation of anorthite and gehlenite. These investigators concluded that gehlenite was formed as an intermediate step in the formation of anorthite but suggested that anorthite could form directly from kaolinite mixtures.

Michel-Lévy and Wyart (1939a) obtained anorthite by mixing precipitates of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{CaCO}_3$  with hexogene and detonating in a closed vessel. Following detonation, an argon atmosphere and temperatures of 510°–560° C. were maintained in the vessel for from four to seven days. Optical and x-ray analyses of spherulites obtained indicate the presence of anorthite and calcite.

Michel-Lévy and Wyart (1939b) obtained anorthite and amphibole from a fine grained calcareous schist. Using a bomb with an explosive, pressures of 3000–4000 kilograms per square centimeter were obtained. The mixture was not acted upon by gases produced in detonation. A temperature of 600° C. was maintained for ten days. Anorthite and amphibole appeared as coatings on the wall of the bomb.

Anorthite has also been formed during ceramic processes. Hugell (1944) reported anorthite as a product of attack of slags upon fire clay and sillimanite refractories. Anorthite with corundum has formed during reduction smelting of bauxite in an electric arc furnace (Filonenko, 1945).

Yoder (1950) obtained anorthite with gehlenite and wollastonite at

900°–1000° C. from mixtures of calcite, alumina, quartz and kaolinite or wollastonite of grossularite composition sintered into briquettes. Hydrothermal treatment of glass of the same composition at 2000 atmospheres and above 850° C. also produced anorthite, gehlenite, and wollastonite.

Ehlers (1953) found that zoisite was transformed to anorthite and hydrogrossularite above 400° C. under hydrous conditions. Between 200° C. and 400° C., the hexagonal polymorph of anorthite was formed. Anorthite and gehlenite formed from epidote at 810° in dry melts.

Davis and Tuttle (1952), Goldsmith and Ehlers (1952), and Ehlers (1953) have reported orthorhombic and hexagonal polymorphs of anorthite at elevated temperatures and water vapor pressures. Sorrell (1962) reported analogous hexagonal phases during the formation of barium, strontium, and lead feldspars from dry mixes of halloysite and kaolinite with appropriate sulfates. These hexagonal phases formed in the solid state at 800° C.–1100° C. in an open furnace.

#### EXPERIMENTAL PROCEDURE

##### *Selection of starting materials*

###### (a) Oxides

Chemical grade calcium hydroxide and gamma alumina were used as sources of lime and alumina in the oxide experiments. Synthetic cristobalite, produced by firing silicic acid at 1350° C. for 24 hours, was used as a source of silica.

###### (b) Clay materials

To compare effects of crystal structure of kaolinite and halloysite upon the formation of anorthite, two clay materials were selected:

1. Missouri flint clay, composed of extremely small particles of well crystallized kaolinite and containing traces of mica and anatase, was used as the source of kaolinite.
2. Halloysite from Muswellbrook, New South Wales, described by Loughnan and Craig (1960) as being in the fully hydrated form, was used as the source of halloysite. This material contains traces of quartz and anatase. Although electron micrographs (K. M. Towe, personal communication) show no elongate or tube-like fragments, ethylene glycol causes an expansion of (001). Thus, *x*-ray diffraction confirms the identification.

###### (c) Calcium compounds

The calcium compounds (calcium fluoride, calcium sulfate dihydrate, and calcium carbonate) are of reagent grade, and have been determined to have the structures of fluorite, gypsum, and calcite by means of *x*-ray powder diffraction procedures.

*Preparation of reactants.* Large amounts of each reactant were ground

to pass through a 200 mesh sieve. After grinding and screening, each reactant was remixed to provide the same particle size distribution in all runs with which the particular reactant was involved. After remixing, each reactant was dried for several hours at 60° C. and stored in air tight containers.

One to one mole ratio mixtures of calcium minerals and each clay mineral were prepared. After weighing to the nearest milligram on an analytical balance, each preparation was mixed (dry) for 20 minutes in a mortar. Each batch weighed approximately eight grams. The six clay mineral-calcium mineral mixtures were stored in air tight containers until used.

Thick pastes of each clay mineral-calcium mineral mixture with ethylene glycol were prepared to investigate the effect of that organic liquid upon the formation of anorthite from these mixtures. The pastes were stored in a desiccator with ethylene glycol until studied.

In order to determine the effect of phosphorus pentoxide upon the kaolinite fluorite reaction, a portion of the kaolinite-fluorite mixture with 20 per cent by weight phosphorus pentoxide was prepared.

*Method of analysis.* The method of analysis used in the investigation, continuous high temperature  $x$ -ray diffraction, has been described in detail in several publications (Grim and Kulbicki, 1957; Sorrell, 1962). The furnace used in this investigation had a heating rate of approximately five degrees Centigrade per minute and a maximum temperature of 1400° C.

Two runs of each mixture were made to check reproducibility. In the first run, scans over wide  $2\theta$  ranges were made to determine temperature of appearance and disappearance of phases. During reruns, scans over narrow  $2\theta$  ranges were made to determine temperatures more precisely. Because the same furnace was used for all runs, heating rates in all runs was approximately the same.

Under the experimental conditions used in the present investigation, neither mixtures of oxides nor calcium mineral-clay mineral mixtures produced orthorhombic nor hexagonal polymorphs of anorthite that could be detected with  $x$ -ray powder diffraction; only the triclinic polymorph of anorthite was formed.

*Oxide mixtures.* The development of peak intensities with increase in temperature in the oxide mixture of anorthite composition is shown in Fig. 1. The intensity for gamma alumina gradually decreases until a temperature of 500° C. is reached. Above this temperature, there is no evidence for the presence of alumina on the diffractogram. Alumina has probably gone into a state amorphous to  $x$ -rays. At 400° C., calcium

carbonate in the form of calcite begins to form from calcium hydroxide. Its peak intensity is greatest at about 500° C., and disappears at 600° C. Calcium oxide begins to form at 400° C. Its formation is retarded by the formation of calcite to a temperature of 500° C.; above 500° C. calcium oxide forms rapidly up to 650° C. and then begins to disappear. At 1200° C., calcium oxide disappears from the diffractogram. Anorthite begins to form at 625° C., but its peak intensity (Fig. 1) does not in-

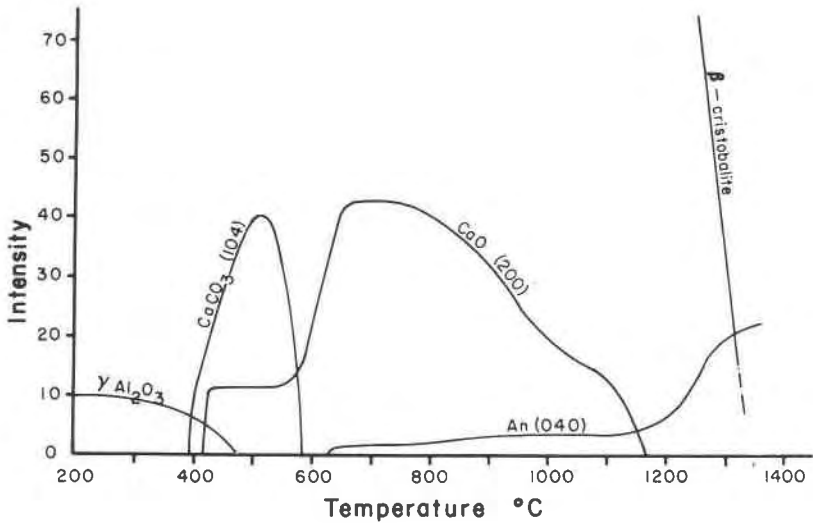


FIG. 1. Development of peak intensities in oxide mixture of anorthite composition.

crease substantially until a temperature of 1150° C. is reached. Above 1150° C., the intensity of the (040) peak of anorthite increases rapidly. Although not included here, integrated intensities of the anorthite (040) peak in this mixture and all clay mineral-calcium mineral mixtures were plotted. Their developments in all cases was the same as for peak intensities.

*Kaolinite-fluorite mixtures.* In kaolinite-fluorite mixtures, metakaolin is formed at about 550° C. at the heating rate used. There is no evidence of an effect upon fluorite during the transformation of kaolinite to metakaolin. A sharp decrease in peak intensity (Fig. 2) of the (111) peak of fluorite occurs at about 900° C. This is accompanied by the appearance of anorthite, indicating that a simple reaction between metakaolin and fluorite has taken place.

Peak intensities (Fig. 2) of the anorthite (040) reflection show a

stepwise development. Relatively small increase in intensity takes place up to a temperature of about 1150° C. Above this temperature intensities increase abruptly.

Addition of ethylene glycol to mixtures of kaolinite and fluorite causes an increase of 100° C. in the temperature at which anorthite begins to form. There is no evidence for the presence of any organic material at the temperature at which anorthite begins to form.

Addition of 20% by weight phosphorus pentoxide to the kaolinite-fluorite mixture radically changes the nature of high temperature phases formed. The only high temperature crystalline phase obtained from the

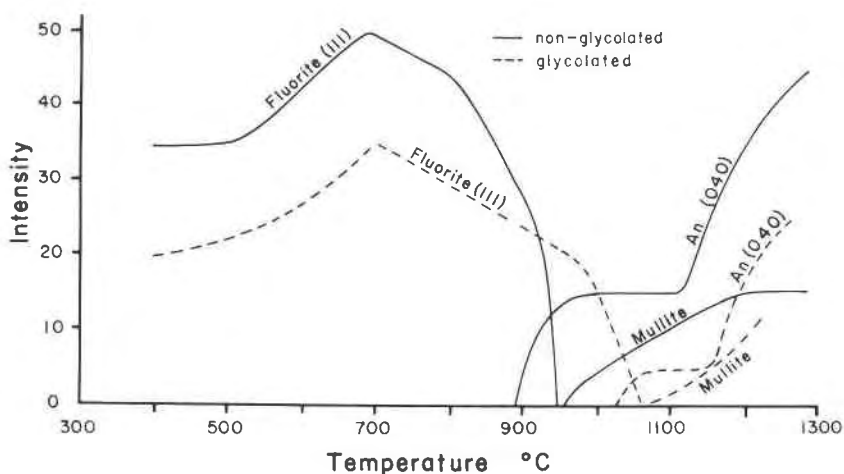


FIG. 2. Development of peak intensities in glycolated and non-glycolated kaolinite-fluorite mixtures.

kaolinite-fluorite-phosphorus pentoxide mixtures is cristobalite, which begins to form at approximately 1025° C.

*Kaolinite-gypsum mixtures.* Development of peak intensities in glycolated and non-glycolated gypsum mixtures is shown in Fig. 3. In non-glycolated mixtures, anhydrite formed from dehydration of gypsum begins to react with metakaolin to form anorthite at approximately 1000° C. Glycolated mixtures begin to react at approximately 1080° C. The development of peak intensities of the anorthite (040) reflection are not step-wise as in the case of oxide and kaolinite-fluorite mixtures; instead, intensities increase rapidly from the beginning of reaction.

*Kaolinite-calcite mixtures.* The development of peak intensities in glycolated and non-glycolated kaolinite-calcite mixtures is shown in Fig. 4.

Calcium oxide begins to form from decomposition of calcite at 600° C. In non-glycolated mixtures, anorthite begins to form from reaction between calcium oxide and metakaolin at approximately 1050° C. In glycolated mixtures, anorthite begins to form at approximately 1075° C. Peak intensities (Fig. 4) of the anorthite (040) reflection do not show a step-wise development; instead, there is rapid increase from the beginning of the reaction.

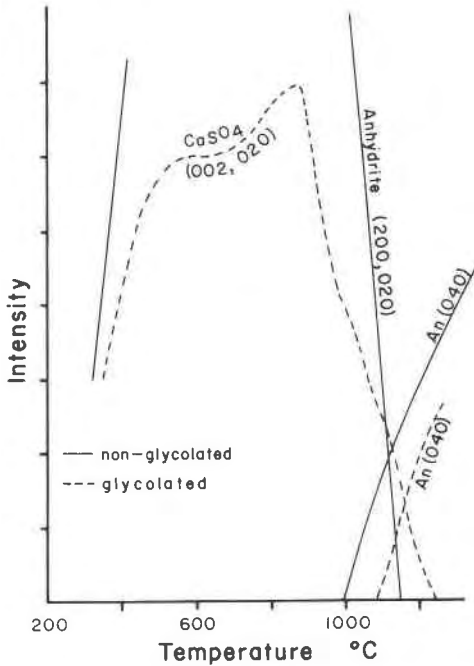


FIG. 3. Development of peak intensities in glycolated and non-glycolated kaolinite-gypsum mixtures.

*Halloysite-fluorite mixtures.* The development of peak intensities in glycolated and non-glycolated halloysite-fluorite mixtures is shown in Fig. 5. Reaction between metakaolin formed from halloysite and fluorite begins at 900° C. in both glycolated and non-glycolated mixtures. Peak intensities (Fig. 5) of the anorthite (040) reflection show a step-wise development, increasing gradually from 1000° C. to 1200° C. and increasing rapidly above 1200° C.

*Halloysite-gypsum mixtures.* Development of peak intensities in glycolated and non-glycolated halloysite-gypsum mixtures is shown in Fig. 6.

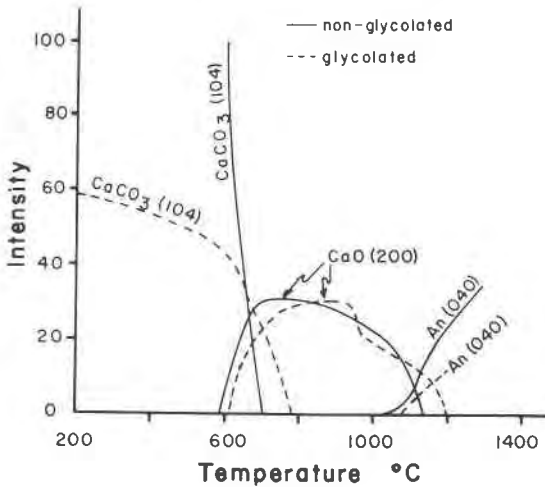


FIG. 4. Development of peak intensities in glycolated and non-glycolated kaolinite-calcite mixtures.

Anorthite begins to form from reaction between anhydrite and metakaolin at approximately  $1040^\circ\text{C}$ . in both glycolated and non-glycolated mixtures. Peak intensities (Fig. 6) of both glycolated and non-glycolated mixtures increase rapidly from the beginning of reaction.

*Halloysite-calcite mixtures.* The development of peak intensities in glycolated and non-glycolated halloysite-calcite mixtures is shown in Fig. 7. Calcium oxide begins to form from decomposition of calcite at approximately  $630^\circ\text{C}$ . Reaction between calcium oxide and metakaolin to form

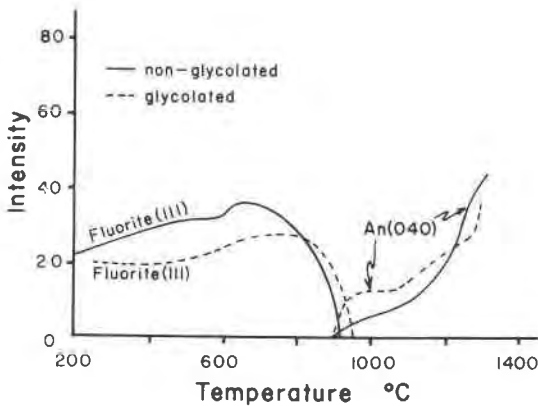


FIG. 5. Development of peak intensities in glycolated and non-glycolated halloysite-fluorite mixtures.



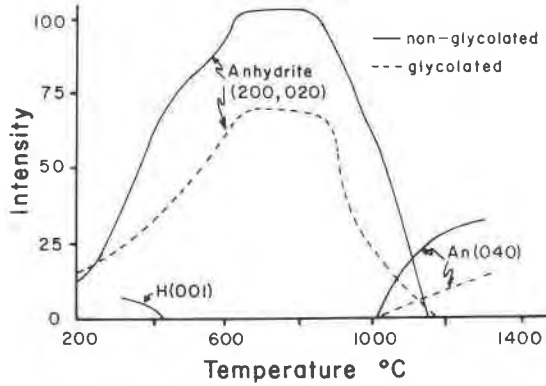


FIG. 6. Development of peak intensities in glycolated and non-glycolated halloysite-gypsum mixtures.

anorthite begins at 1065° C. in both glycolated and non-glycolated mixtures. Peak intensities (Fig. 7) of the anorthite (040) peak increase rapidly from the beginning of the reaction.

#### SUMMARY AND CONCLUSIONS

Anorthite forms directly from an oxide mixture of appropriate composition. No intermediate gehlenite phase, as suggested by Jander and Petri (1938), was found during continuous high temperature *x*-ray diffraction. The temperature of appearance of anorthite is considerably lower than in clay mineral-calcium mineral mixtures investigated, and can undoubtedly be attributed to the high reactivity of synthetic cristobalite and  $\gamma$ -alumina.

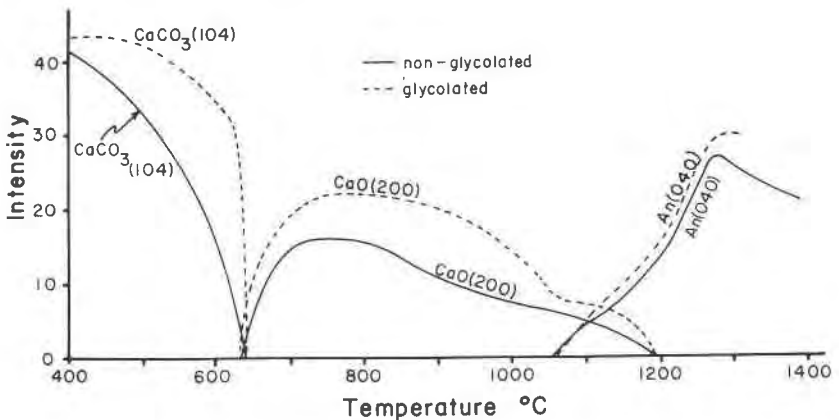


FIG. 7. Development of peak intensities in glycolated and non-glycolated halloysite-calcite mixtures.

Anorthite forms by direct reaction between metakaolin and fluorite or anhydrite. In reactions involving calcite, decomposition of calcite to calcium oxide takes place before the formation of anorthite.

The appearance and disappearance of calcite in the oxide mixture is an interesting phenomenon. No doubt the formation of calcite represents a reaction of calcium hydroxide and atmospheric carbon dioxide. The disappearance of the calcite formed in oxide mixtures (Fig. 1) is considerably lower than in pure, well-crystallized calcium carbonate. Peak intensities in halloysite-calcite (Fig. 7) and kaolinite-calcite (Fig. 4) mixtures begin to decrease at temperatures below 400° C. The explanation for this is not immediately obvious to the writer. Decrease in peak intensity may not necessarily indicate a decrease in total amount of calcium carbonate in kaolinite-calcite and halloysite-calcite mixtures. A decrease in peak height with increase in peak width would indicate decrease in crystallite size. Even if this is taken into account, however, there does seem to be some lowering of decomposition temperature of calcite in mixtures. Further investigation into this phenomenon is clearly indicated.

Addition of ethylene glycol to kaolinite mixtures causes a rise in the temperature of appearance of anorthite. Halloysite mixtures are not affected in such a way. There is no evidence for the presence of ethylene glycol or high temperature products in the kaolinite mixtures at the temperatures at which anorthite begins to form. Therefore, any effect that ethylene glycol has upon kaolinite-calcium mineral mixtures must be exerted at low temperatures. The writer believes these effects to result from stresses exerted upon kaolinite particles by ethylene glycol, causing a breakdown into smaller particles. Although smaller particle size would ordinarily be expected to favor lowering reaction temperature, it may be that the physical breakdown is such that particle shape is radically changed. This could inhibit nucleation of anorthite by changing surface characteristics. In some kaolinite mixtures, there is evidence for smaller particle size making up amorphous metakaolin in glycolated mixtures. The amorphous band for metakaolin in these mixtures has a greater half-height width.

In halloysite mixtures, the temperature of appearance of anorthite is about 10°–15° C. higher than in kaolinite mixtures. This suggests that the structure of metakaolin formed from either kaolinite or halloysite is essentially the same.

Phosphorus pentoxide radically changes the high temperature phases formed in kaolinite-fluorite mixtures. Anorthite and a small amount of mullite form in the kaolinite-fluorite mixtures. The usual high temperature phases for pure kaolinite are gamma alumina, mullite, and cristobalite. Cristobalite appears at about 1300° C. In kaolinite-fluorite-

phosphorus pentoxide mixtures, cristobalite, which appeared at 1025° C., was the only crystalline phase observed at high temperatures. Although it is not possible to state definitely that the total amount of cristobalite formed is greater than that normally forming from dissociation of kaolinite, the fact that no gamma alumina and very little mullite appeared suggests that this is the case. Further, the temperature of appearance of cristobalite in kaolinite-fluorite-phosphorus pentoxide mixtures is significantly lower than the temperature of appearance from kaolinite. The similarity of phosphate and cristobalite structures probably favors the nucleation of cristobalite and inhibits the formation of anorthite. It is possible that mineralogy of metamorphic rocks can be radically changed by small amounts of impurities such as phosphates.

It is possible that textures of metamorphic rocks as well as their mineralogy can be affected by the presence of trace minerals. This is suggested by the stepwise development of peak and integrated intensities in kaolinite-fluorite, halloysite-fluorite, and oxide mixtures. In these mixtures, anorthite begins to form at comparatively low temperatures. Intensities increase only slightly up to a temperature of about 1150° C. and then increase rapidly. In contrast, peak and integrated intensities in kaolinite-gypsum, halloysite-gypsum, kaolinite-calcite, and halloysite-calcite mixtures increase rapidly from the beginning of reaction. Presence of small amounts of fluorite in a rock of appropriate composition would provide a few centers of nucleation in the temperature range 900°–1150° C. at the heating rate used. Further crystal growth would most easily take place about these centers of nucleation, forming a rock with relatively few large anorthite crystals. In contrast, many nuclei would form in pure clay-mineral-gypsum or clay-mineral-calcite mixtures. This would result in a mass of comparatively small crystals.

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#### REFERENCES

- BYRNE, P. S. B. (1953) The effect of variations in montmorillonites upon the nature of montmorillonite-organic complexes. Ph.D. dissertation, Univ. of Illinois.
- DAVIS, G. L. AND O. F. TUTTLE (1952) Two new crystalline phases of anorthite composition. *Am. Jour. Sci.*, *Bowen Vol.* 107–114.

- EHLERS, E. G. (1953) An investigation of the stability relations of the Al-Fe members of the epidote group. *Jour. Geol.* **61**, 231-251.
- FILONENKO, N. E. (1945) On some high alumina minerals in a block of electrocorundum. *Dokl. Acad. Nauk SSSR*, **48**, 430-433.
- GOLDSMITH, J. R. AND E. G. EHLERS (1952) Stability relations of anorthite and its hexagonal polymorph. *Jour. Geol.* **60**, 386-397.
- GRIM, R. E. AND G. KULBICKI (1957) Études aux rayons x des réactions des minéraux argileux a haute température. *Bull. Soc. Franc. Ceram.* 21-27.
- HUGILL, W. (1944) The spherulitic crystallization of anorthite. *Brit. Ceram. Soc. Trans.* **43**, 90-92.
- JANDER, W. AND J. PETRI (1938) Die Bildung von Anorthit und Gehlenit durch Reaktion in festen Zustände. *Zeit. Electrochemie*, **44**, 747-754.
- LOUGHNAN, F. C. AND D. C. CRAIG (1960) Occurrence of fully-hydrated halloysite at Muswellbrook, New South Wales. *Am. Mineral.* **45**, 783-790.
- MICHEL-LÉVY, A. AND J. WYART (1939a) Synthèse de l'anorthite par pneumatolyse à l'aide l'explosifs brisants. *Compte Rendu, Acad. Sci. Paris*, **208**, 1030-1033.
- (1939b) Néogenese de minéraux au coeur des roches par recuit dans gas et vapeur d'eau sous haute pressons. Production de phénomènes de métamorphisme artificiel. *Compte Rendu, Acad. Sci. Paris*, **209**, 175-177.
- SORRELL, C. A. (1962) Solid state formation of barium, strontium, and lead feldspars in clay-sulfate mixtures. *Am. Mineral.* **58**, 221-253.
- YODER, H. S., JR. (1950) Stability relations of grossularite. *Jour. Geol.* **58**, 221-253.

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