

EFFECT OF RADIATION DAMAGE ON MULLITE FORMATION IN KAOLINITE

by

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ABSTRACT

Kaolin was irradiated with 0.67 meV gamma-rays from a Cs¹³⁷ source. Irradiation dosages of more than 10¹⁹ eV/g retarded mullite formation whereas smaller dosages appeared to have enhanced mullite formation slightly. It appears that preferentially oriented mullite formation from kaolinite is energetically favored and is adversely affected by radiation-produced $nb/3$ shifting of the Al ions. A possible mechanism for the effects of the radiation on mullite formation is suggested.

INTRODUCTION

The purpose of this investigation was to determine the effect which disordering of the aluminum ions in the kaolinite crystalline structure had on the kaolinite-to-mullite transformation.

The degree of structural order of kaolinite may be altered by the shifting either of ions or of whole kaolinite layers. The term $nb/3$ -crystallinity¹ is here applied to a specific type of order; destruction of which occurs by either of two crystallographically equivalent mechanisms; (1) shifts of entire kaolinite layers by intervals of magnitude of $nb/3$ or (2) similar shifts of individual aluminum ions either along b or 120° on either side. The second mechanism is possible because only two-thirds of the possible nearly equivalent Al sites are filled at any time in a stoichiometric crystal. Previous work by Corbett *et al.* (this Volume) had indicated that radiation damage produced by gamma-rays is manifested by variations in the degree of $nb/3$ -crystallinity. While these variations may be caused by whole kaolinite layer shifts in the a - b plane, random movement of the aluminum ions themselves (by units of $nb/3$ into vacant sites) is more likely and is probably caused by Compton electrons.² Therefore, gamma-ray damage appeared to be a promising method

¹This rather cumbersome term is advanced to avoid the ambiguities which arise from the common practice of using the non-specific expression, "crystallinity" for the same purpose.

²For 0.67 meV gamma-rays incident on aluminum ions, the cross-section for the Compton process is more than 400 times that for the photoelectric process.

for changing the $nb/3$ -crystallinity without significantly changing other variables such as impurities.

PROCEDURE

Three samples of kaolinite of poor, medium and excellent $nb/3$ -crystallinity were obtained from Twiggs County, Georgia. Each was electrodialed and X-ray fluorescence analyses were made of the impurity contents (Table 1).

TABLE 1.—X-RAY FLUORESCENCE ANALYSIS FOR METAL IMPURITIES IN KAOLINITE (AFTER ELECTRODIALYSIS)

Impurities	Percent present in sample		
	Excellent $nb/3$ -crystallinity	Medium $nb/3$ -crystallinity	Poor $nb/3$ -crystallinity
Zr	0.2	0.2	0.25
Fe	0.7	0.8	0.8
Zn	0.05	0.1	0.15
K	none	trace	trace
Ti	1.1	1.25	1.0
Total	2.05	2.35	2.20

1. Poor $nb/3$ -crystallinity kaolinite—CWF grade processed clay obtained from Huber Corporation, Twiggs County, Georgia, 25 to 40 percent less than 2μ .

2. Medium $nb/3$ -crystallinity kaolinite—Degrittied crude grade processed clay obtained from Huber Corporation, Twiggs County, Georgia, 60 to 68 percent less than 2μ .

3. Excellent $nb/3$ -crystallinity kaolinite—unprocessed lump kaolin from Georgia Kaolin Company, Twiggs County, Georgia.

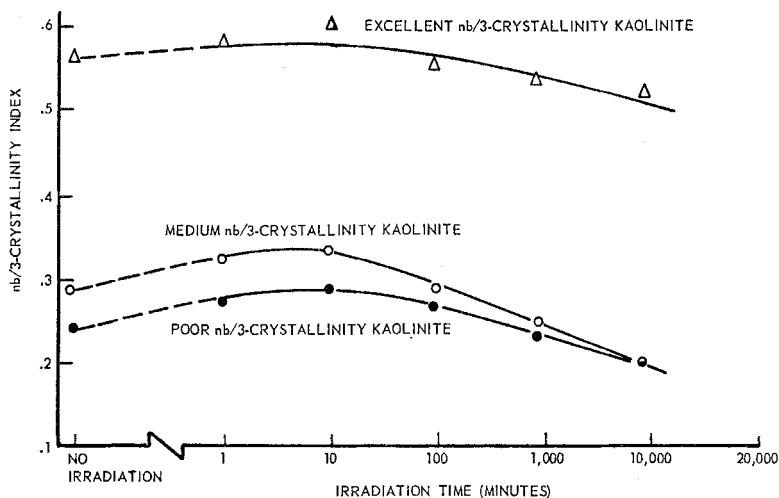
The samples of clay were screened through a 325 mesh screen. An $nb/3$ -crystallinity index¹ was determined by the X-ray diffraction method of Johns and Murray (1959) for each clay sample before and after irradiation with 0.67 meV gamma-rays from Cs¹³⁷. The gamma-ray dosages are given in Table 2, and the $nb/3$ -crystallinity indices are shown in Fig. 1. No change was found when the $nb/3$ -crystallinity indices of several samples were redetermined several weeks later. The X-radiation used in the X-ray diffraction examinations had no detectable effect on the $nb/3$ -crystallinity index.

¹The ratio of the areas of the $02\bar{1}$ and 060 reflection intensities is accepted as the crystallinity index. The $02\bar{1}$ reflection is affected by $nb/3$ -shifting of the Al ions; the 060 is not. This index is directly related to, but is not necessarily a linear function of, the $nb/3$ -crystallinity. It may take on values ranging from zero (for random distribution of the aluminum ions among the nearly equivalent aluminum sites) to slightly more than one.

TABLE 2.—IRRADIATION DOSAGES

Time in irradiator	Nominal dosage received* (eV/g)
1 min	1.5×10^{18}
10 min	1.5×10^{19}
100 min	1.5×10^{20}
1000 min	1.5×10^{21}
10,000 min	1.5×10^{22}

* Assuming the absorption of kaolinite to be the same as that of a ferrous ion dosimetry solution (Carter and Palmer, 1960). This assumption is probably valid within an order of magnitude.

FIGURE 1.— $nb/3$ crystallinity changes.

An attempt was made to detect any annealing effect due to the temperature, less than 100°C , of the specimens in the Cs^{137} irradiator. None was found.

A high temperature X-ray diffractometer was used to investigate the kaolinite-to-mullite transformation in both gamma irradiated and unirradiated specimens. Special care was taken to minimize alignment errors "at temperature". The rate of mullite formation from each clay sample was observed at three temperatures: 1095°C , 1150°C , and 1205°C . A typical series of growth curves, obtained in this case for medium $nb/3$ -crystallinity kaolinite, are shown in Fig. 2. Except for a scale factor, which varied slightly from run to run, the amount of mullite present at any time was assumed to

EFFECT OF RADIATION DAMAGE ON MULLITE FORMATION IN KAOLINITE 359

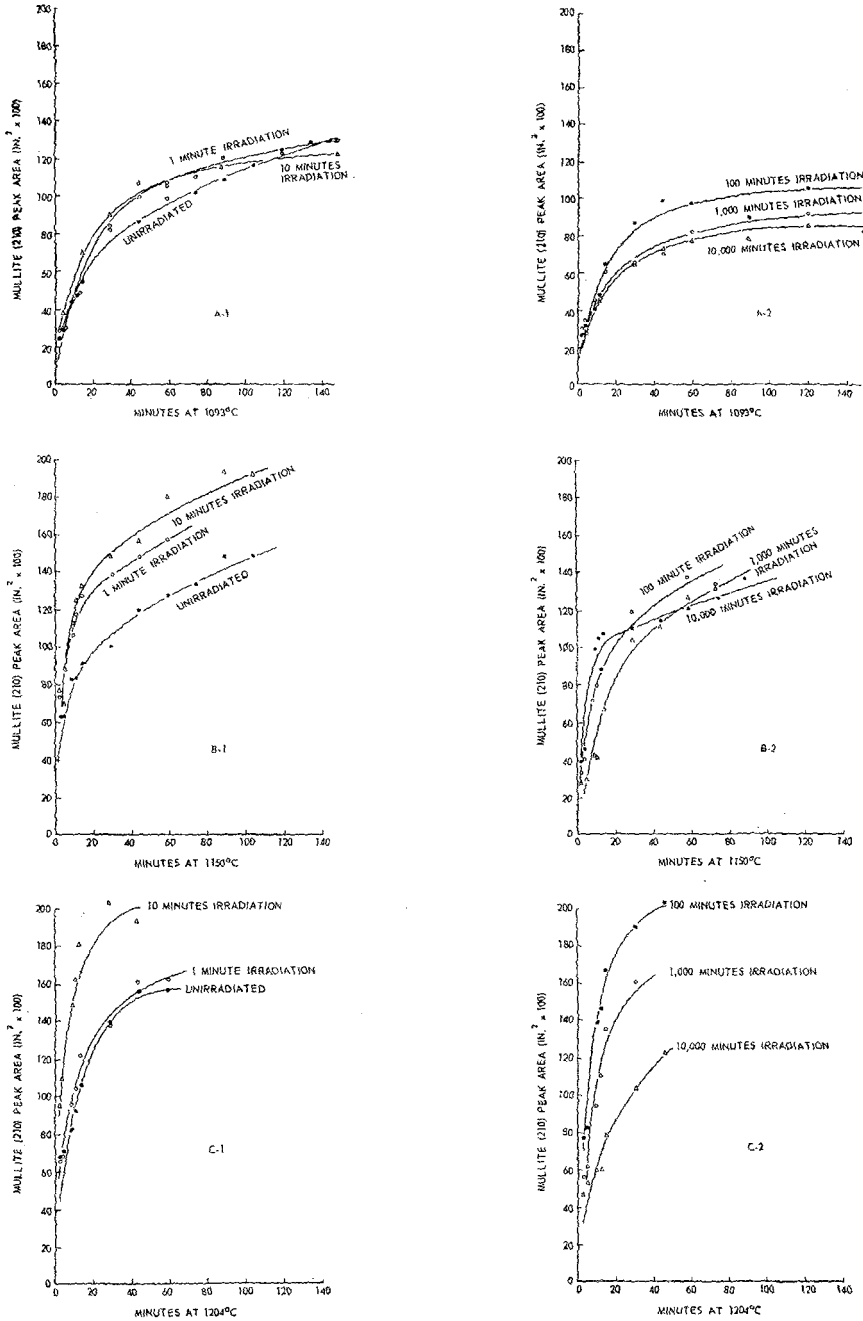


FIGURE 2.—Mullite growth from medium $nb/3$ crystallinity kaolinite.

be proportional to the area of the mullite 210 peak on the recorder chart. The scale factor, obtained by comparison with a standard 63.6 percent mullite-36.4 percent cristobalite sample, for the series of formation curves in Fig. 2 was approximately 1 percent mullite per 0.2 in².

Fired samples of each kaolinite (heated to 1200°C during a 20-hr cycle) were examined with an electron microscope and standard preshadowed replica techniques. Little mullite was observed. No attempt was made to obtain quantitative results from the micrographs.

Owing to the magnitude of the errors involved, no conclusive information was obtained from studies of diffraction peak breadth changes.

RESULTS

Kaolinite Radiation Damage

Exposure of kaolinite to 0.67 meV gamma-rays produced observable radiation damage. A small increase appeared to be produced in the *nb/3*-crystallinity index by irradiation for times of 10 min (a dosage of approximately 10¹⁹ eV/g of ferrous ion dosimetry solution) or less. Irradiation for substantially longer times caused progressive lowering of the *nb/3*-crystallinity index. Similar damage trends occurred in each of the three kaolinites used.

X-ray fluorescence analysis gave no indication of a change in impurity content due to irradiation. The gamma-ray irradiation appeared to produce no obvious changes in the other variables such as particle size, color, etc. However, no direct experimental measurements were made of these other variables.

Mullite Formation Kinetics

In the present preliminary work the experimental errors were too large, and the time-at-temperature too short, to permit meaningful calculations of activation energies. Therefore, it is not possible at this time to discuss the observed effects in the quantitative detail which is ultimately obtainable with the methods used. However, it is possible to make meaningful qualitative comparisons among the mullite formation curves obtained and exemplified by Fig. 2.

Several observations can be made which apply to all three clays at all three temperatures:

1. Heavy irradiation inhibits mullite formation.
2. Light irradiation (up to 10 min or 10¹⁸ to 10¹⁹ eV/g of ferrous ion dosimetry solution) probably slightly enhances mullite formation in most cases and never inhibits it.
3. The total mullite formation and the crystallinity index show a similar qualitative dependence on radiation dose.
4. For all clays and all radiation dosages used, the mullite formation rates in the later stages of heating are roughly the same at a given temperature; the demonstrable differences in mullite formation all occur in the early portions of the heating periods.

5. In no case does the total mullite formed during the observation period approach the theoretical maximum (63.6 percent) nor does the total amount show any real indication that it would become as much as one-third of that maximum if held at temperature indefinitely.

DISCUSSION

The results suggest that an energetically preferred orientation relationship exists between the mullite and the original kaolinite, that this relationship is disrupted by the heavier irradiation, and that the propagation of this preferred orientation information from the kaolinite to the mullite phase somehow depends on the ordered positioning of the Al atoms. In the absence of an energetically favored orientation relationship, one might expect the poorly crystallized material to transform most readily as the free energy of the disturbed lattice would be expected to be larger than that of the undisturbed lattice.

While the present work was in progress, definite electron-microscope observations of mullite growth in preferred orientation on kaolinite particles were reported by Comer (1960). The degree of orientation appeared to be greater if the kaolinite was well crystallized. Johns (1955) had previously suggested that mullite formed more readily from well-crystallized than from poorly crystallized kaolinite.

It is perhaps surprising, however, that the orientation information appears to be propagated from the initial kaolinite crystals through two intermediate phases (metakaolin and a spinel phase) to the mullite phase. Brindley and Nakahira (1959) have suggested a mechanism based on an orderly arrangement of alumina octahedra which is maintained throughout the several phase transformations. Very recently Comer (1961) has strongly corroborated the BN (Brindley and Nakahira) mechanism by showing that the spinel phase is preferentially oriented in the manner predicted by the BN mechanism. Comer also notes that the spinel-phase crystallite sizes all seemed to be in the range 75 Å to 125 Å.

In terms of the BN mechanism it is to be expected that disordering of the Al ions, which would upset the orderly arrangement of alumina octahedra, would inhibit mullite growth as additional thermal energy would be required to allow the octahedra to form in the mullite phase positions they would have occupied anyway if the original kaolinite had not been disordered. The observed correlation of mullite formation with $nb/3$ -crystallinity index (within a series of samples of a given clay) is therefore explained by the BN mechanism.

In view of the foregoing, present results suggest that two competing radiation damage effects may be identified; (1) energy stored in the lattice, by the formation of various point defects, is available to enhance nucleation and growth and, (2) the formation of particular point defects, especially those consisting of movement of the Al ions into nearly equivalent sites,

disrupts the orderly arrangement of alumina octahedra and thereby inhibits mullite formation.

It would appear that in this study the stored lattice energy attained its equilibrium (maximum) value with about 10 min of irradiation (which corresponds to approximately 10^{19} eV/g of ferrous ion dosimetry solution). Continued irradiation then had primarily the effect of redistributing the Al atoms among initial and nearly equivalent sites with attendant reduction of the $nb/3$ crystallinity index. A possible mechanism for these effects is presented in Appendix A. It has not been established here whether the $nb/3$ shifting of Al ions (presumed measured by the $nb/3$ -crystallinity index) is actually the most important process of nucleation-center destruction or merely correlates with it. In either event, it would be expected that the number of nuclei of "normal" activation energy would decrease with increasing irradiation and that the observed correlations of inhibited mullite formation and decreased $nb/3$ -crystallinity with heavy irradiation, and with each other, would be found.

It has been pointed out that, for all the clays and irradiations, the mullite formation curves at a given temperature appear to have roughly the same slope, rather than the same percent increase with time, in the later stages of heating. This result may be related to the small size and separation of the spinel-phase crystallites (Johns, 1955) and to the fact that none of the reactions approached theoretical completion.

Since the differences among the various mullite formation curves occur in the first few minutes "at temperature", it appears that the differences brought about either by irradiation or by initial $nb/3$ -crystallinity variations are primarily differences in nucleation. Such is just what would be predicted from the preceding arguments: the number of nucleation centers is not materially affected by low radiation dosages and the additional lattice energy thereby provided causes activation of more than enough additional centers to compensate for any reduction in number of centers.

In some cases the "medium-crystallinity" kaolinite seemed to yield more mullite than did the "excellent-crystallinity" kaolinite. It is presumed that the nature and manner of incorporation of the impurities may be responsible for this effect. It is known, for example, that iron catalyzes the kaolinite-to-mullite transformation (Parmelee, 1942). If the iron were to enter preferentially at the "nearly equivalent" and ideally vacant Al sites, its presence would be expected to reduce the $nb/3$ -crystallinity index used here. This specially placed iron would both enhance the 060 and diminish the 02I intensities. By its presence, the iron might be expected to add to the lattice energy, thus helping to activate nucleation centers without having any particular effect toward either destroying or raising the activation energy of any of them. Strict comparisons among clays should not be attempted except where either (1) the role of the impurities is clearly understood, or (2) the impurity contents are identical.

Among the possibly important "other variables" which must be considered in the interpretation of the present observations are crystalline imperfections other than the specialized type accounted for by $nb/3$ -crystallinity. As an

example, the possibility that the slight increase in the $nb/3$ -crystallinity index for the poorly $nb/3$ -crystallized kaolinite was due to a preferential reduction of the 060 intensity, occasioned by a more general type of lattice distortion, could not be eliminated. Also, there were some changes in the ratio of the 001/002 reflection intensities which could be indicative of additional disordering of the lattice.

ACKNOWLEDGMENT

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APPENDIX A

PROPOSED RADIATION DAMAGE MECHANISM

It is patently impossible to store indefinite amounts of energy in the lattice without destroying the lattice and, hence, the order which its existence implies. Consideration of possible relaxation processes which take place continuously during the irradiation¹ is therefore appropriate. In the following discussion, thermally- and impurity-produced defects and all unduly complicating features of radiation-induced defect formation, stabilization, and relaxation are neglected.

Since all possible anion sites are occupied in an ideal kaolinite crystal, it is expected that radiation-displaced anions could relax only to sites occupied by anions initially, i.e. before irradiation was begun. The net change in the statistically averaged occupancy of a given anion site, therefore, is expected to be small if the lattice is to remain recognizable as such. That is to say, if n anions are displaced, only n relaxation sites are available to them, and the average occupancy of a given site is $(N-n)/N$, where N is the total number of anions in the specimen. Energy equilibrium during irradiation is obtained when the rate of displacement equals the rate of relaxation. Unless the displacement rate is high or the temperature low, it is clear that an equilibrium will be established in which the lattice structure will be maintained and the energy stored in the lattice will not be increased by further irradiation. Therefore, the statistically averaged distribution of anions among structural sites and interstitial positions will not undergo further change with continued irradiation.

Excepting for the possibility that some Si ions might relax to Al sites, essentially the same reasoning applies to the average occupancy of the Si ion sites.

For the Al sites, however, the situation is quite different because of the availability of the initially-vacant "nearly equivalent" Al ion sites. Let n' be the number of radiation displaced and unrelaxed (i.e. mainly interstitial) Al ions at any time. Let N' be the total number of Al ions in the specimen, and hence the number of initially occupied Al sites. There are also $N'/2$ ideally vacant sites which are so nearly equivalent in energy to the initial "correct" sites that at ordinary temperatures any relaxation of Al ions from these "nearly equivalent" sites to the "correct" sites may be neglected. The n' displaced Al ions have both the n' initially occupied sites and also these $N'/2$ nearly equivalent sites into which they may relax essentially completely.

Suppose first, for illustrative purposes only, that in analogy to the situation with the anions, the displaced Al ions were allowed to relax only into the N' initially occupied sites. Let n' be the number of displaced Al ions at dynamic equilibrium. In this case, the

¹ It is presumed that the relaxation processes that take place on cessation of irradiation do not depend critically on the irradiation period.

average occupancy of these initially occupied sites would be $(N'-n')/N'$ and that of the $N'/2$ nearly equivalent and initially unoccupied sites would remain zero.

When the $N'/2$ "nearly equivalent" sites are then introduced into the relaxation process, two new results are noted. (1) The equilibrium number, n' , of displaced atoms (in a given radiation field at a given temperature) is reduced. (2) The average occupancy of all $3N'/2$ sites is $2(N'-n')/3N'$. Let a_0 be the average occupancy of the initially filled sites, considered alone, and let a_u be that of the initially unoccupied sites at any time. It is to be expected that, when dynamic equilibrium is first established, a_0 will be nearly equal to $(N'-n')/N'$ and a_u will be nearly equal to zero. Only as the process continues at "equilibrium" will both a_u and a_0 , separately and from opposite directions, approach their final value of $2(N'-n')/3N'$.

The overall result, considering all ions, is that once a dynamic equilibrium is established no further change in lattice energy is produced by continued irradiation. However, the redistribution of the Al ions does continue, without significant change in lattice energy, until the average occupancies of both the initially filled and the initially unfilled Al sites have become equal. Thus, it may be expected that, with mild irradiation, the destruction of nucleation centers by relaxation of Al ions and perhaps some Si ions to the "nearly equivalent" sites (related to the "correct" sites by $nb/3$ shifts) will continue long after the energy stored in the lattice has reached its constant maximum value.

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