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CHEMICAL REACTIVITY IN AN A12O3-GLASS COMPOSITE

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Stett, Mark A.

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CHEMICAL REACTIVITY IN AN  $Al_2O_3$ -GLASS COMPOSITE

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Special Thesis

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UNIVERSITY OF CALIFORNIA

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Berkeley, California

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Mark A. Stett  
(M. S. Thesis)

May 25, 1966

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CHEMICAL REACTIVITY IN AN  $\text{Al}_2\text{O}_3$ -GLASS COMPOSITE

Mark Alexander Stett

Inorganic Materials Research Division, Lawrence Radiation Laboratory,  
and Department of Mineral Technology, College of Engineering,  
University of California, Berkeley, California

May 25, 1966

ABSTRACT

In order to better understand the hot-pressing process, a study of the effect of hot pressing variables upon chemical reactions within a two-phase system was undertaken. The reaction between alumina and sodium disilicate glass to form nephelite ( $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) was chosen as a model. This reaction was studied using x-ray, electron microprobe, and petrographic techniques.

Dissolution of the alumina and its migration into the glass matrix was found to be the controlling step in the reaction to form nephelite. Pressure, temperature, and holding time were found to have little or no effect. The nephelite nucleates at the surface of the alumina and grows into the glass matrix.

## I. INTRODUCTION

In recent years considerable work has been done on the mechanical properties of two-phase systems and the effect of the dispersed phase upon the mechanical properties of the composite. Physical aspects, such as volume fraction, particle geometry, and thermal expansion have been studied in an effort to enhance these mechanical properties. Little work has been done, however, on improving these mechanical properties by chemical techniques such as interfacial bonding or chemical reactions.

Several studies have shown that some physical properties, such as compressive strength, can be enhanced by hot pressing during a chemical reaction.<sup>1-6</sup> Chemical reactions can occur during the normal process of hot pressing of a two-phase composite, resulting in the possible improvement of some physical or chemical properties. In order to better understand hot pressing, it must be determined if and how temperature and pressure affect a reaction that can occur between the two phases of a composite. The system alumina ( $\text{Al}_2\text{O}_3$ )-sodium disilicate ( $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ ) glass was chosen as a model system to investigate these effects. In this system the phases react at high temperatures to form nephelite ( $\text{Na}_2\text{O}\cdot \text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ ).

## II. LITERATURE

Reactive hot pressing has been defined as the hot pressing of a material during a chemical reaction. While a chemical reaction is in progress, the reactivity of a solid is high. This increased reactivity may be employed to produce better microstructures and thus enhance mechanical properties in the hot-pressed body. Chaklader and McKenzie<sup>2</sup> showed that by hot pressing clays while dehydroxylation reactions were occurring, the compressive strength of the resulting body was increased almost tenfold over those hot pressed after dehydroxylation had occurred. Bulk densities were also improved by this technique. Chaklader and Baker<sup>3</sup> applied this process to the phase transition in zirconia. Reactive hot pressing produced strong, dense zirconia that did not fracture while undergoing the phase transition. They reasoned that strong interparticle bonds were produced by this technique. With normal hot-pressing techniques the zirconia fractured as a result of the 9% volume change during the phase transition. Reactive hot pressing during a decomposition reaction was also used to increase compressive strengths. The decomposition of boehmite into alumina was used by Chaklader and Shetty<sup>1</sup> to produce strong cermets of alumina and several metals. Morgan and Scala<sup>4</sup> used a reactive hot-pressing technique in order to obtain nearly fully dense MgO and Al<sub>2</sub>O<sub>3</sub> from brucite and gibbsite, respectively. They used the dehydration reaction in each case as their hot pressing reaction. Chaklader<sup>5</sup> also used the decomposition of a carbonate to hot press strong and nearly fully dense MgO. Fulrath<sup>10</sup> has investigated the internal stresses in a glass-ceramic composite, using powdered alumina and sodium disilicate glass. At hot



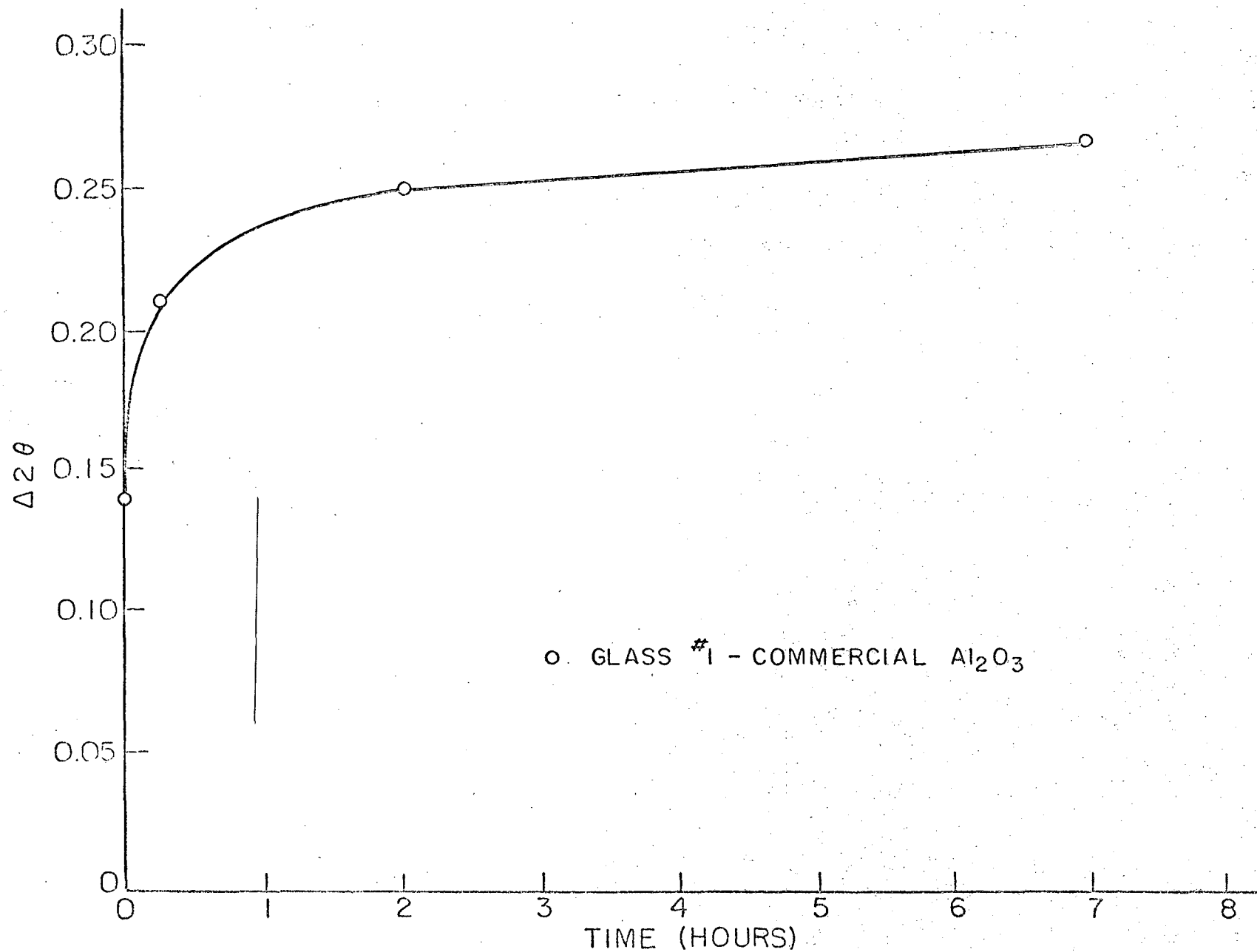
pressing temperatures of 850°C and higher it was found that a second crystalline phase, nephelite, was formed. The nephelite formation was found to directly influence the internal stress and was proposed as a possible mechanism of stress transfer. The relationship between the x-ray strain and the time at temperature for the hot-pressed samples is shown in Fig. 1.

Studt and Fulrath<sup>11</sup> used mullite-glass systems to examine the effect of chemical composition, crystal shape, and crystal size on mechanical properties. The formation of nephelite at several hot-pressing temperatures was observed. No attempt was made to further investigate the phenomenon. A diffusion-controlled mechanism was the assumed explanation. The formation of  $\alpha$ -cristobalite was observed at hot-pressing temperatures of from 600 to 650°C. This phenomenon was explained as the nucleation of  $\alpha$ -cristobalite by a diffusion-controlled mechanism.

Pask<sup>12</sup> studied the sintering of alumina-sodium disilicate compositions. The formation of bridges between the alumina particles which stiffened the structure was observed. This stiffening was attributed to the formation of nephelite on the surface of the alumina which helped to hold the alumina particles together. These bridges would collapse at the carnegieite-alumina eutectic temperature of 1475°C. It was postulated that hot pressing would break the bonds in these bridges and yield nearly theoretically dense bodies.

Nephelite,  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , is a colorless crystal that is commonly found as a glass stone. It crystallizes as laths, needles, feathers, or irregular filmy patches in glass matrices. Nephelite

Fig. 1. X-ray strain vs. time at 849°C for hot compacted samples  
(after Fulrath<sup>10</sup>)



has a low birefringence and a refractive index of 1.533-1.537 which is slightly higher than normal glasses.<sup>7-8</sup>

Sodium disilicate crystals and their nucleation and growth from the glass were studied by Scott and Pask,<sup>9</sup> using a high temperature microscope. Only heterogeneous nucleation, both bulk nucleation at high temperatures and surface nucleation at low temperatures, was found. The high temperature nucleation occurred between 450°C and the melting point of crystalline sodium disilicate at 874°C. The maximum rate was found to occur at approximately 600°C. When the glass was exposed to the air at temperatures of from 25 to 375°C and then heated to about 800°C, surface nucleation occurred. Both the alpha and beta forms of sodium disilicate were observed as crystallization products. Growth occurred between 600 and 870°C for both forms. The maximum growth rates were observed at 800°C.

### III. EXPERIMENTAL PROCEDURE

#### A. Glass

The sodium disilicate glass used in this investigation was made in the laboratory from silica flour and reagent grade sodium carbonate. The materials were dry mixed and then melted and refined in platinum crucibles at 1300°C in an electric furnace. Automatic rotation of the crucible on an inclined plane was used to increase the fining action. The cast glass was crushed and dry ground to -325 mesh in an alumina-lined ball mill with alumina pebbles. The density of the glass, measured by an Archimedes technique, was found to be 2.57. Methyl alcohol was used as the liquid phase and all measurements were made on a Mettler balance.

#### B. Alumina

Commercial sapphire boules were used as the source of alumina. The boules were thermally shocked into coarse size fractions by heating to 1000°C and then quenching into cold water. The resulting particles measured a few millimeters in diameter. This procedure also eliminated any possibility of contamination of the alumina by iron from a crusher. Final reduction was performed by using an alumina-lined ball mill with alumina pebbles. The ground particles were separated into several size fractions and then introduced into a commercial d-c plasma jet in order to spheroidize the particles.<sup>13</sup> Argon was used as the carrier gas and a moderate quenching rate was employed.<sup>14</sup> The settings used on the plasma jet can be seen in Table I. A density separation was made on the material coming from the plasma jet to eliminate foreign materials, and the particles were placed on an incline to separate out the spherical particles. The spherical alumina that was obtained was x-rayed and

found to be almost entirely  $\alpha\text{-Al}_2\text{O}_3$ .

Table I. Plasma jet settings for the spheroidization of alumina

Operating voltage	25 v.
Amperage	450 amps
Line gas flow	85 s.c.f.h.
Carrier gas flow	11 s.c.f.h

### C. Hot Pressing

The glass and alumina spheres were weighed into the proper volume fractions, thoroughly mixed with isopropyl alcohol, and dried. The use of isopropyl alcohol instead of water prevented the attack of both the glass and the alumina by water. The measured densities of 3.97 and 2.57 for the alumina and sodium disilicate glass, respectively, were used in calculating the required volume fractions.

The hot-pressing arrangement is shown in Fig. 2. The mixed powders were loaded into a tungsten carbide die body and graphite plungers were inserted. The extreme fluidity of the glass at the hot-pressing temperatures made a tungsten carbide die body necessary. Because of the fluidity, a nearly hydrostatic force was present within the composite and the resulting tangential force on the walls of the die body exceeded the maximum strength of the grade of graphite which was the original die body material. The viscosity of sodium disilicate glass as a function of temperature can be represented by the equation<sup>9,15-17</sup>

$$\log_{10}\eta = -0.38 + \frac{5.61 \times 10^6}{T^2}$$

From this equation it can be seen that the viscosity of the sodium

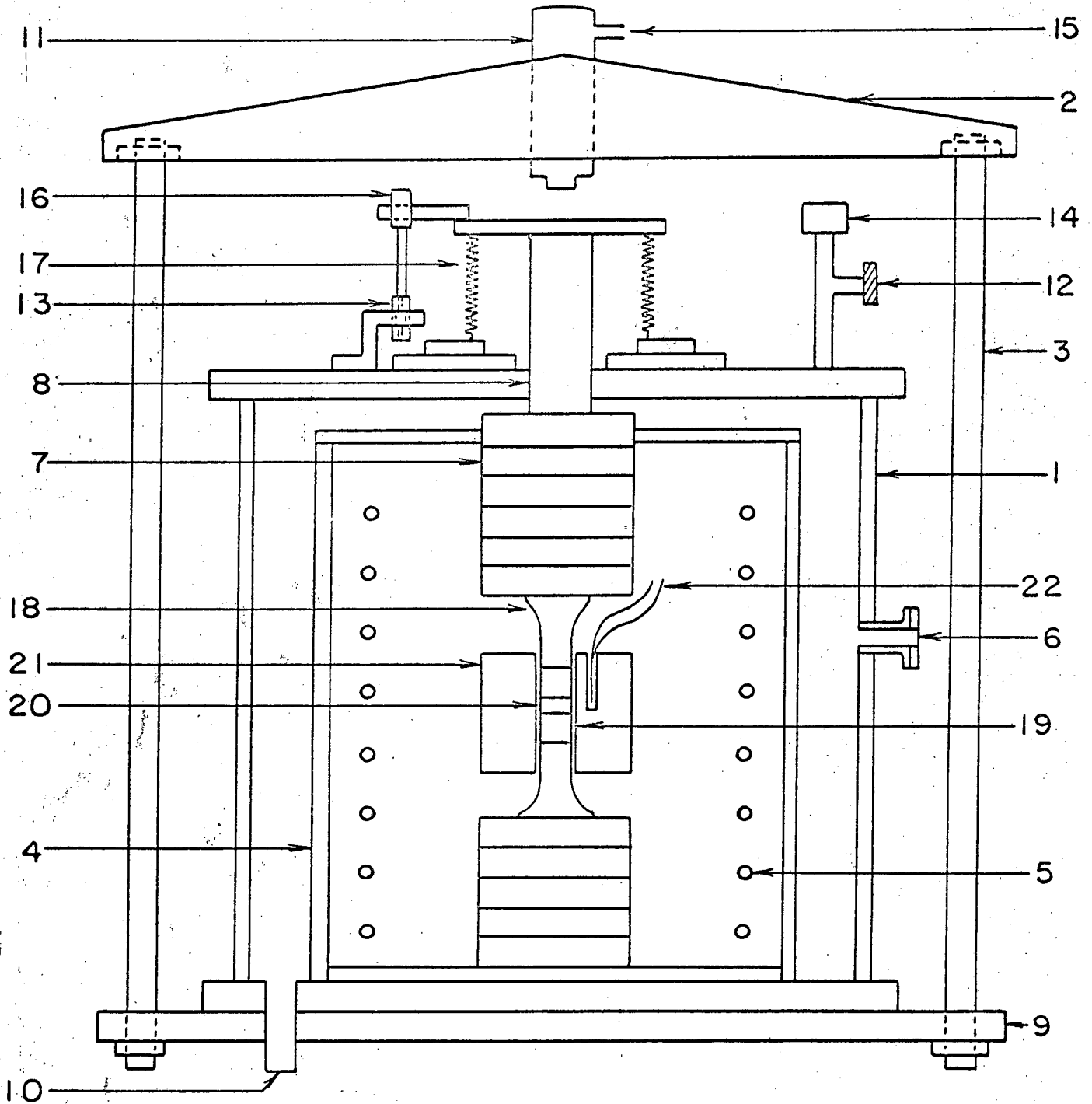


Fig. 2. Schematic diagram of hot press.

KEY

1. Vacuum cover
2. Top yoke
3. Load bearing column
4. Radiation shield
5. Mo heating coil
6. Sight window
7. Insulating spacers
8. Plunger
9. Bottom support plate
10. Vacuum port
11. Hydraulic ram
12. Air inlet
13. Linear variable differential transformer
14. Vacuum gauge
15. Pressure inlet
16. Micrometer head
17. Bellows
18. Graphite plunger
19. Graphite plug
20. Sample
21. Tungsten carbide die body
22. Thermocouple

disilicate glass in this investigation ranged from  $5.34 \times 10^4$  at the lowest temperature of  $775^\circ\text{C}$  to  $1.17 \times 10^4$  at the highest temperature of  $850^\circ\text{C}$ . After loading, the die body was positioned in the vacuum chamber. A Pt-Pt 10% Rh thermocouple was inserted in the die body and the system was evacuated to less than a micron pressure.

Resistance heating was employed using a 115 mil molybdenum heating coil. Pressures varying from 1500 to 3000 psi and temperatures of  $775$  to  $850^\circ\text{C}$  were used. The length of time at temperature and pressure ranged from ten minutes to four hours. Rates of cooling from maximum temperature were controlled by the furnace's free cooling rate.

Preliminary pressings were made to determine the softening characteristics of the glass. A linear differential transformer attached to the bellows was used as a measure of the compaction of the sample in the die. It was found that a pure glass sample, heated at a rate of  $10^\circ\text{C}$  per minute under a 500 psi holding pressure, softened over a temperature range from  $430$  to  $480^\circ\text{C}$ .

Hot pressing of the composite samples was done at  $775$ ,  $800$ ,  $825$ , and  $850^\circ\text{C}$  in order to obtain the nephelite phase while preventing crystallization of either the alpha or beta sodium disilicate. Preliminary investigations showed that the nephelite first appeared at  $750^\circ\text{C}$  while under the minimum pressure used.

The hot-pressed samples were sectioned and mounted in a clear casting resin. All samples were polished with a set of silicon carbide papers (240, 400, and 600 grit) and then finished on a series of diamond paste laps (6, 2, and  $1/2$  micron diamond). Carbon was vapor deposited on the finished samples to provide a conductive surface



suitable for electron microprobe analysis.

D. Electron Microprobe

The electron microprobe yields essentially a fluorescent analysis of an area on a micro scale. The sample is used as the target which is bombarded with a beam of electrons producing fluorescent x-rays. A Model 400 Electron Microprobe Analyzer manufactured by the Materials Analysis Company was used in this investigation. The characteristic radiation emitted by the elements in the specimen was resolved by properly positioned potassium acid phthalate (KAP) crystals and the intensities were measured with proportional detectors. A motor-driven gear mechanism moved the sample in a stepwise fashion relative to the electron beam. Operating conditions for the electron microprobe are listed in Table II.

Table II. Operating conditions for the electron microprobe.

---

Takeoff angle	40.29°
Voltage	15 KV
Specimen current	0.020 $\mu$ amps
Oscilloscope magnification	$\sim$ 350X
Al counter setting	1.2645 $\text{\AA}$
Si counter setting	1.0805 $\text{\AA}$

---

Analyses were made simultaneously of aluminum and silicon K-alpha radiation. Radiation intensities were registered on scalers as total counts per ten seconds. Integrated counts were taken at various intervals along the radius of an alumina sphere sufficient to give a smooth curve of concentration as a function of distance. This system

of glass and alumina spheres was ideal for electron microprobe analysis in that the necessary standards for the glass and alumina are built into the sample. With only 10v/o spheres the matrix has a negligible concentration of aluminum and can be used as the glass standard. The center of an alumina sphere can be used as the alumina standard.

All data obtained from the proportional counters must be corrected for background, absorption, counter dead time and non-linearity, fluorescence, and atomic number. In this case the counter dead time, fluorescence, and atomic number corrections are negligible and the background can be accounted for by a simple subtraction. The absorption, however, requires more careful consideration. Corrections were made for several compositions ranging from pure glass to pure alumina for aluminum and silicon radiation. Detailed procedure and mass absorption coefficients were taken from Smith.<sup>18</sup> Results of the absorption corrections are shown in Fig. 3 and Fig. 4 where K is the uncorrected concentration and C is the corrected concentration.

The electron microprobe was equipped to take photomicrographs of the sample and to take photographs of the x-ray image for any element from an oscilloscope. Magnification with the photomicrographs was limited by the equipment to about 200X only, but the magnification of the x-ray image could be varied from about 225X to about 4000X with the voltage used in this investigation. The voltage that will give the most accurate measurements depends upon the atomic number of the elements in question. For the low atomic number elements a low voltage yields the best results and in this case 15KV was used.

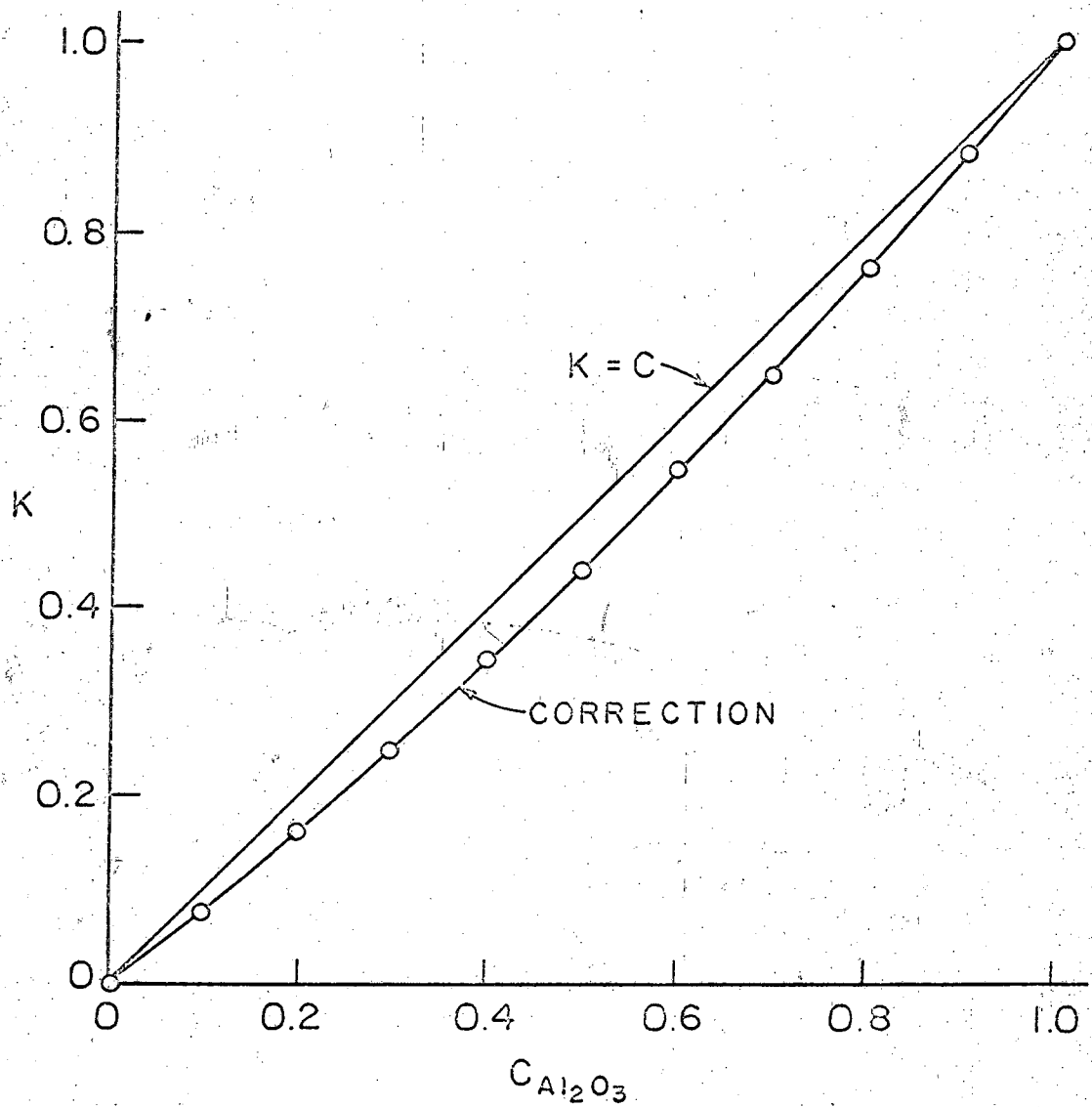


Fig. 3. Measured concentration (K) vs. corrected concentration (C) for Al radiation.  $K=C$  for no absorption.

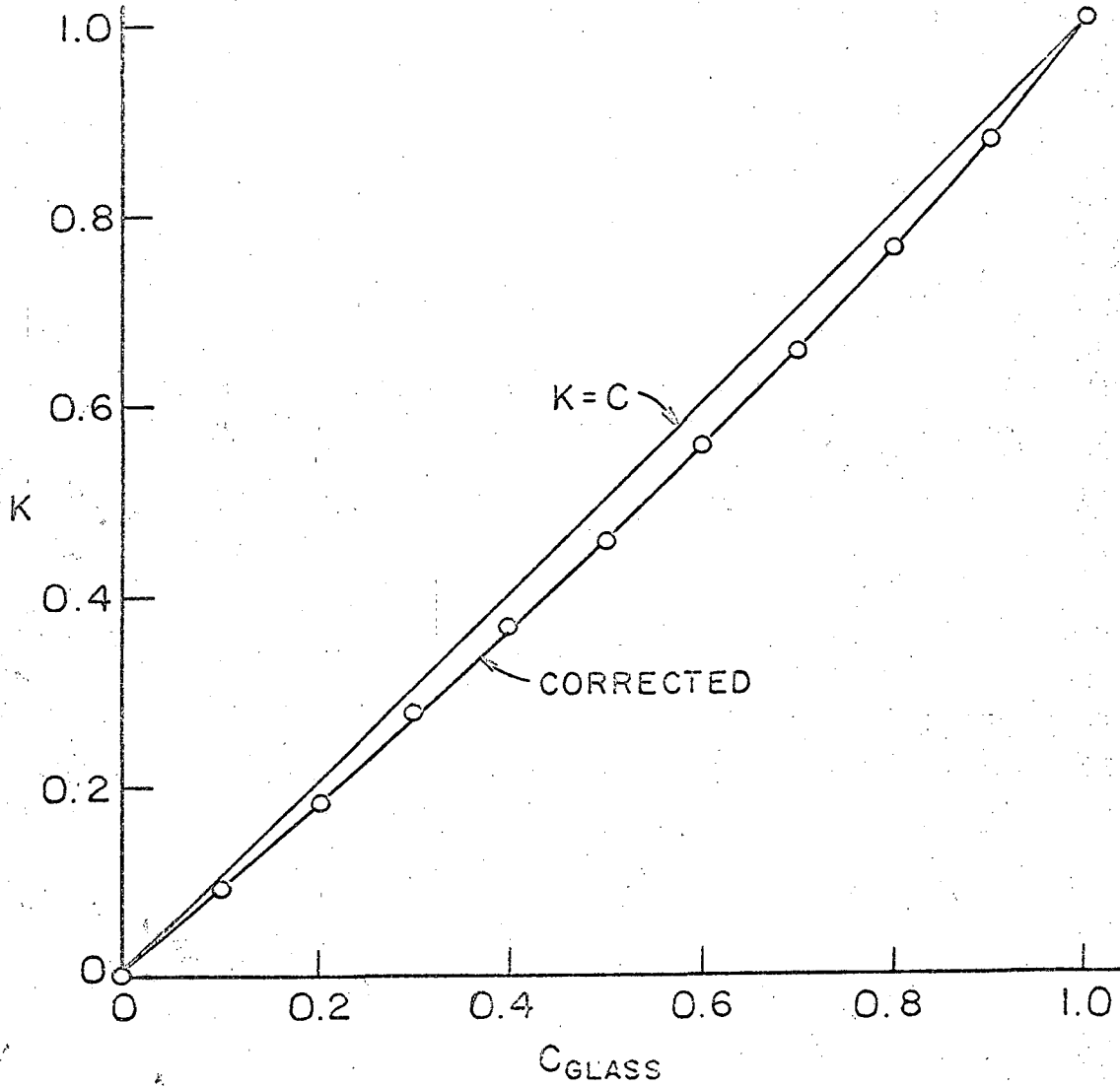


Fig. 4. Measured concentration (K) vs. corrected concentration (C) for Si radiation.  $K=C$  for no absorption.

#### IV. RESULTS AND DISCUSSION

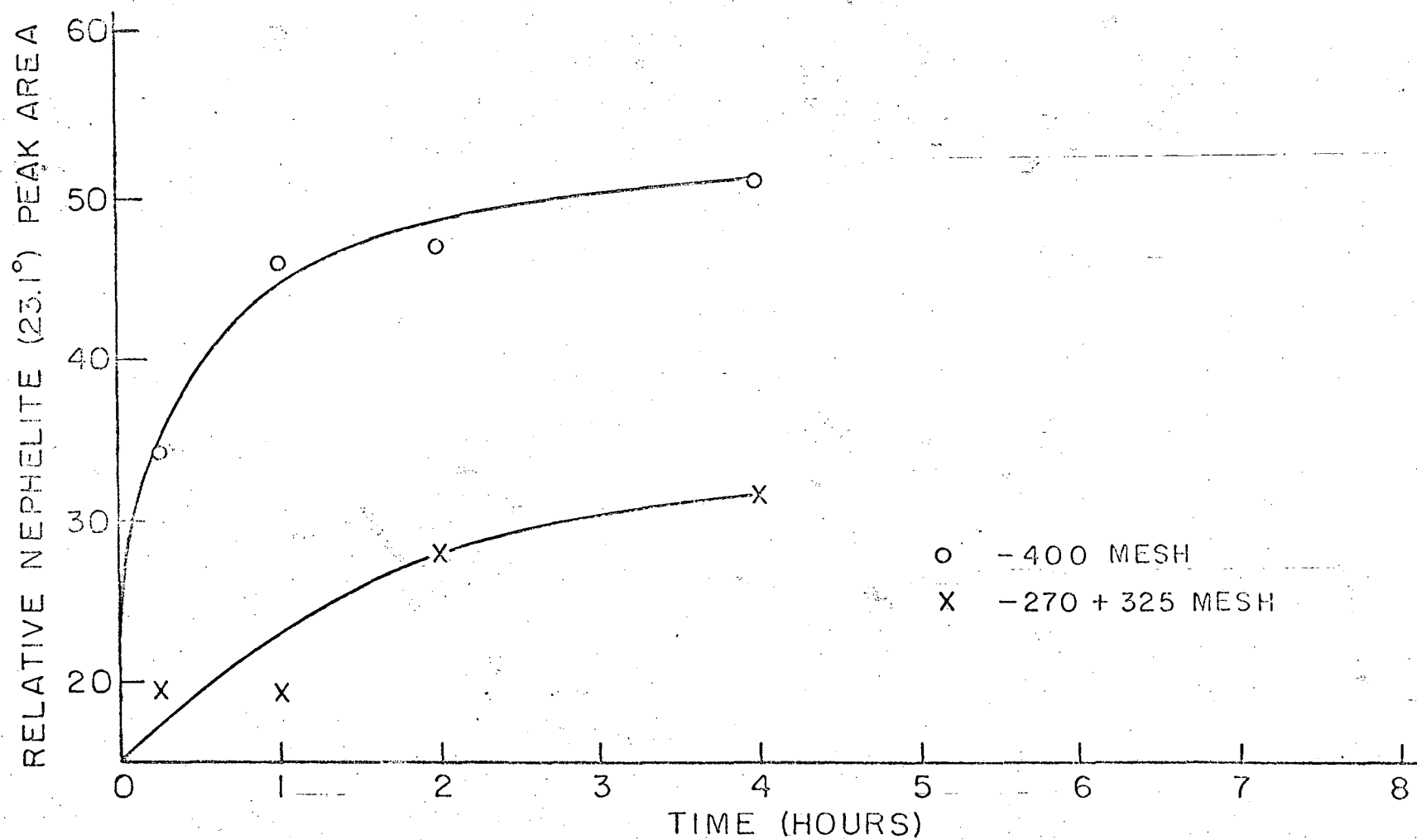
##### A. X-Ray

Samples of 40v/o alumina spheres and 60v/o glass were pressed at 800°C and 2000 psi for various holding times. These samples were then x-rayed to determine the extent of nephelite formation. A sample spinner was used in order to insure that the x-ray beam covered a representative portion of the sample face. The patterns obtained in this manner were then measured at both an alumina ( $2\theta=25.5^\circ$ ) peak and a nephelite ( $2\theta=23.1^\circ$ ) peak and the peak area was estimated. Care was taken to avoid samples that showed any crystallization of either form of sodium disilicate. The peak area was then plotted as a function of holding time as seen in Fig. 5. The curve rose sharply and leveled off at a maximum peak area indicating that the reaction of the alumina with the glass is rapid. The similarity between this curve and the internal strain curve in Fig. 1 should be noted. A second set of samples was hot pressed under the same conditions, except that a particle size of -400 mesh was used, rather than -270+325 mesh, and peak area measurements were made in the same manner. The resulting curve had the same shape as the -270+325 curve, but the -400 mesh samples contained about twice as much nephelite formed at each corresponding holding time, indicating that surface area plays an important part in the alumina-glass reaction.

##### B. Microprobe

In order to determine the effect of temperature, pressure, and holding time upon this reaction, sets of 10v/o alumina samples were made with two of these variables constant in each set. The samples

Fig. 5. Effect of holding time and particle size upon nephelite formation.



in each set were probed from the center of a sphere outward and the silicon and aluminum concentrations were measured at selected spots. The values obtained for concentration were then plotted as a function of distance from the center. There was no indication of any step in the curve which would imply the formation of the compound nephelite at the alumina-glass surface. The concentration values formed a smooth diffusion couple in every case.

The slopes of these curves were then measured and plotted as a function of the variable parameter in each instance. Two sets of samples were made to investigate the effect of pressure. In the first set a temperature of 775°C and a holding time of 10 minutes were used. Pressures of 1500, 2000, 2500, and 3000 psi were applied. The results of the slope measurements in this set can be seen in Fig. 6. These data show that there is little or no effect of pressure upon the migration of alumina from the sphere into the glass. The two values for the slope in each case represent the results of probing each sphere in two different directions at right angles to each other in order to account for the anisotropy of alumina, which will be discussed in a later section. The second set of samples was pressed at 800°C for 10 minutes at pressures of 1500, 2000, 2500, and 3000 psi. The results of the slope measurements can be seen in Fig. 7. Once again there is little effect of pressure upon the nephelite reaction. The values for the slopes of all the samples investigated were quite steep and did not differ from each other by a large degree. This result is to be expected since the effect of pressure on the solubility of solids in liquids is generally quite small.

The third set of samples was pressed at 2000 psi for 10 minutes

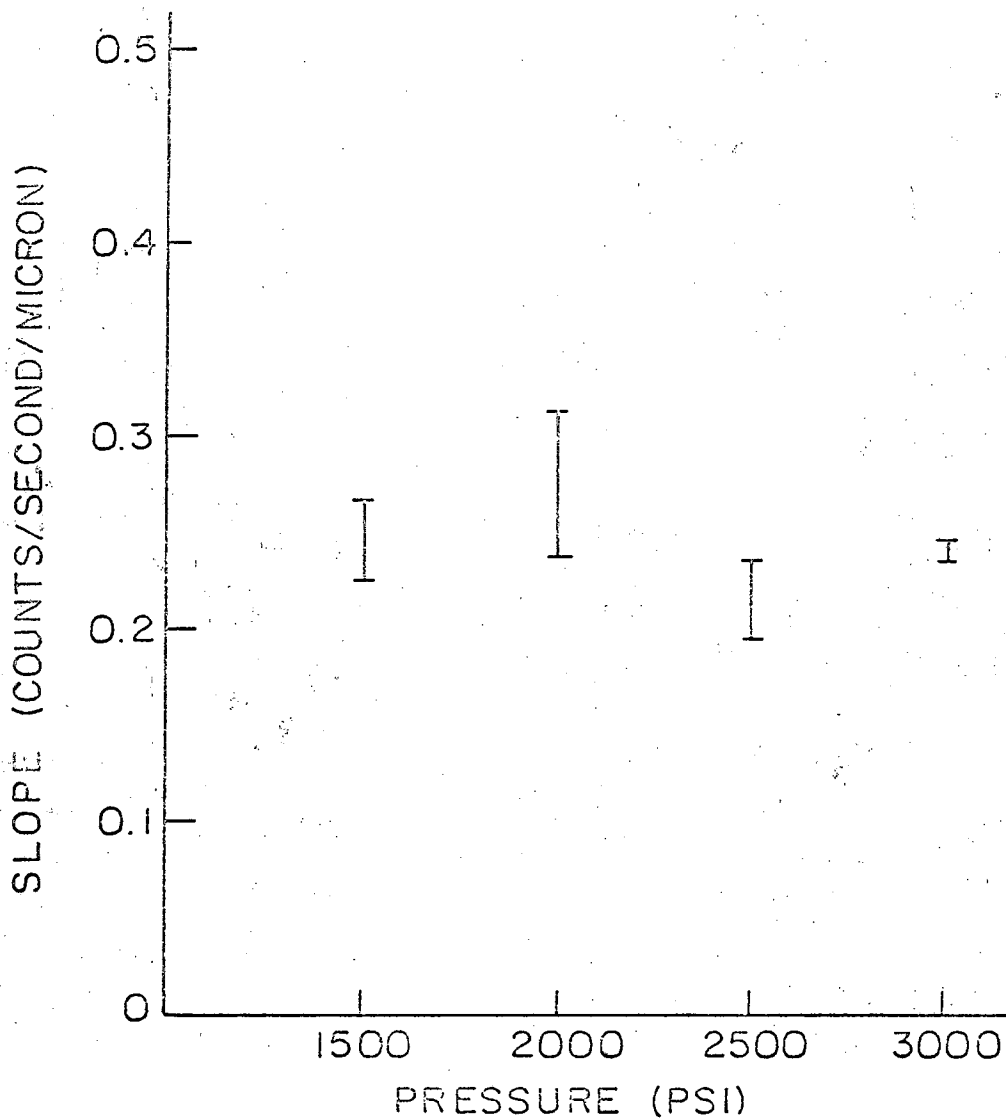


Fig. 6. Effect of pressure at 775°C upon solution of alumina.



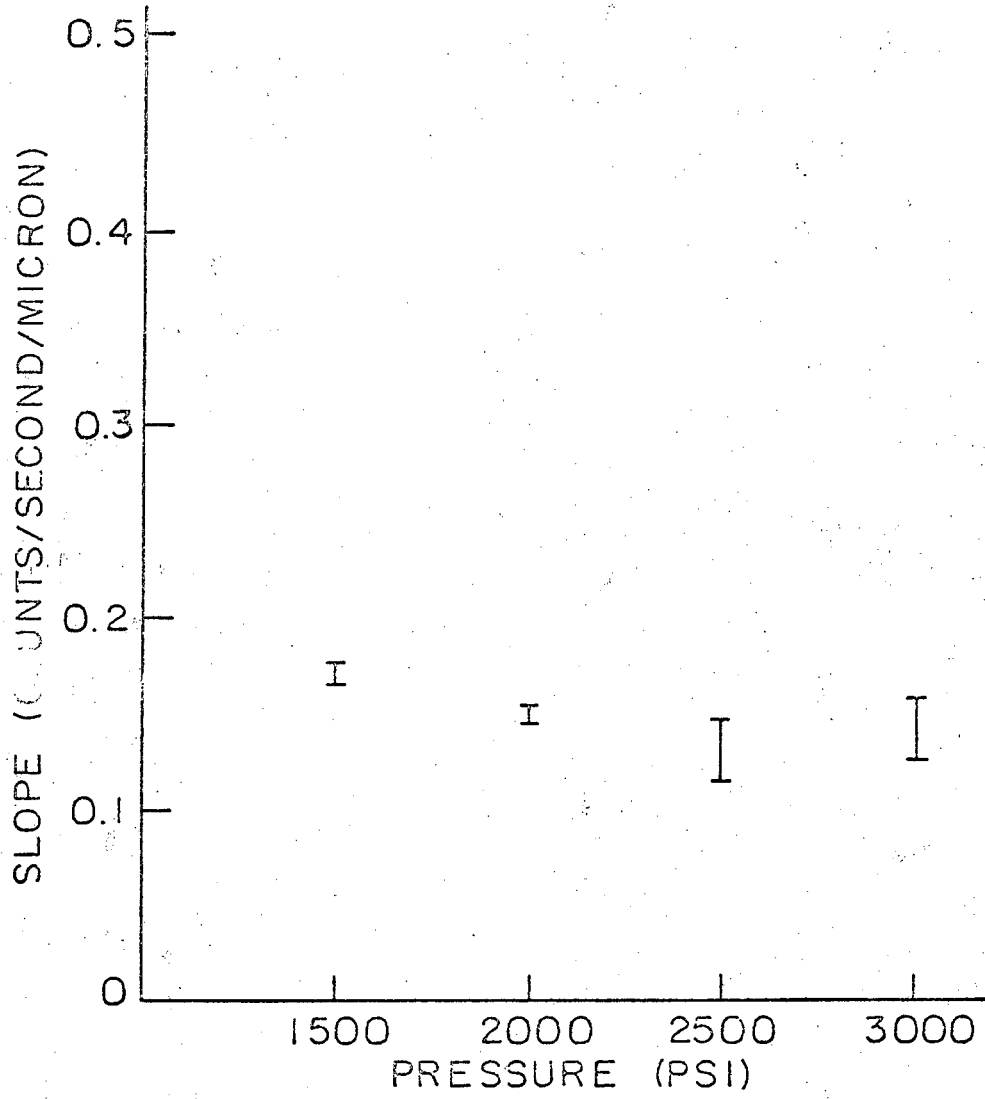


Fig. 7. Effect of pressure at 800°C upon solution of alumina.

and at temperatures of 775, 800, 825, and 850°C. The results of these slope measurements can be seen in Fig. 8. As with the second set of pressure-varied samples, the slopes are nearly the same and there is little effect of temperature upon this reaction. The influence of temperature on the solubility of solids in liquids can vary markedly. Most substances absorb heat on solution and tend to become more soluble at higher temperatures. When the process is exothermic, however, a decrease in solubility accompanies a temperature increase.

A fourth set of samples was pressed at 775°C, 2000 psi, and for holding times of 10 minutes, 1 hour, 2 hours, and 4 hours. Once again there is little or no dependence upon the variable, in this case the holding time. This can be seen in Fig. 9 where the slope of the curve once again is nearly zero. As long as there is a concentration gradient away from the alumina spheres the solubility rate will remain constant with time.

In order to investigate the effect of the anisotropy of alumina upon the measured slopes, a sample pressed at 800°C and 3000 psi for 10 minutes was probed at intervals of 30° and the slopes of the resulting curves were measured. These slopes, plotted as a function of angle, can be seen in Fig. 10. The anisotropy of alumina can be seen in the maxima and minima that occur at 120° intervals for this hexagonal crystal. By taking any 90° interval it can be seen that the spread in the two values for the slope calculated for each sample is to be expected.

Each of these samples made with 10v/o spheres was x-rayed to attempt to verify the formation of the nephelite phase. One of the

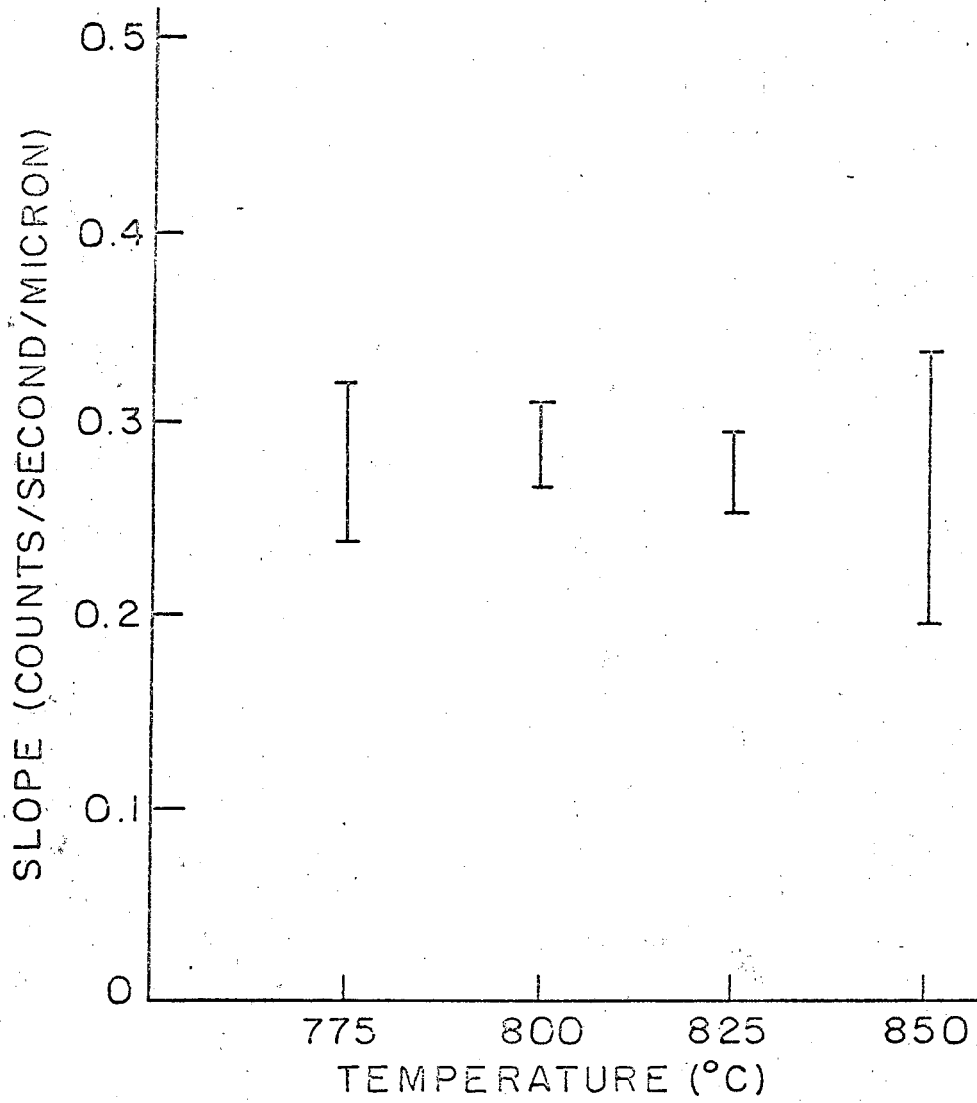


Fig. 8. Effect of temperature upon solution of alumina.

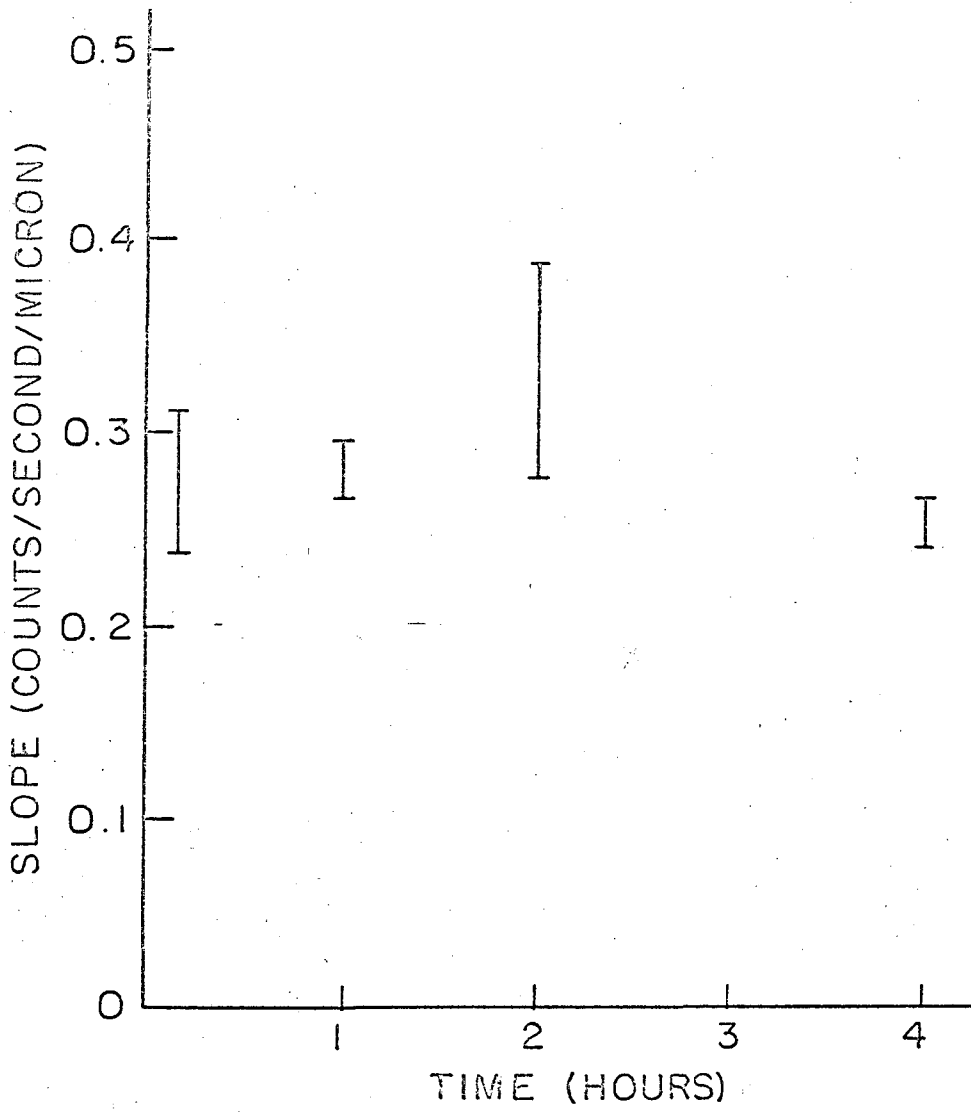


Fig. 9. Effect of holding time upon solution of alumina.

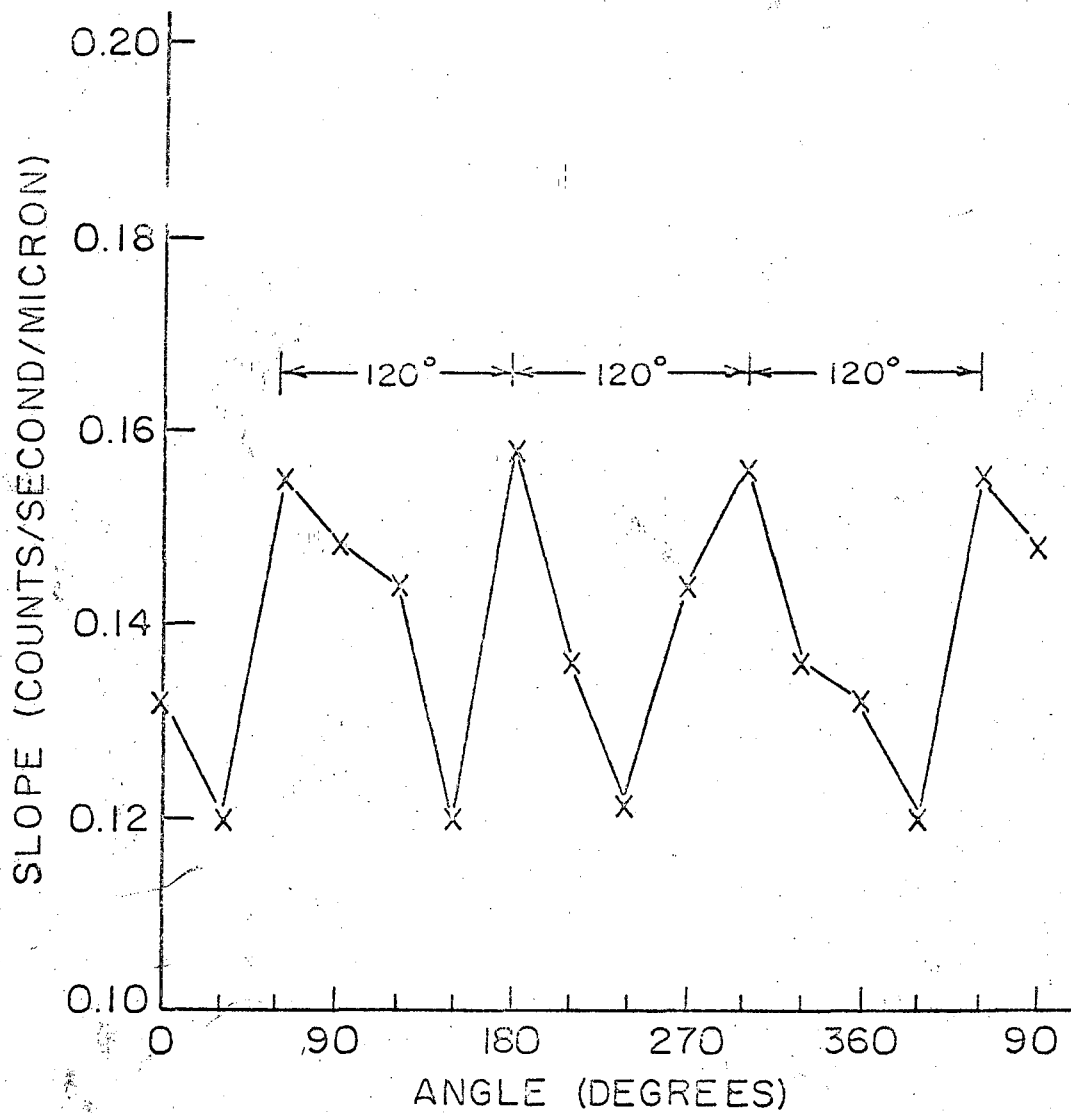
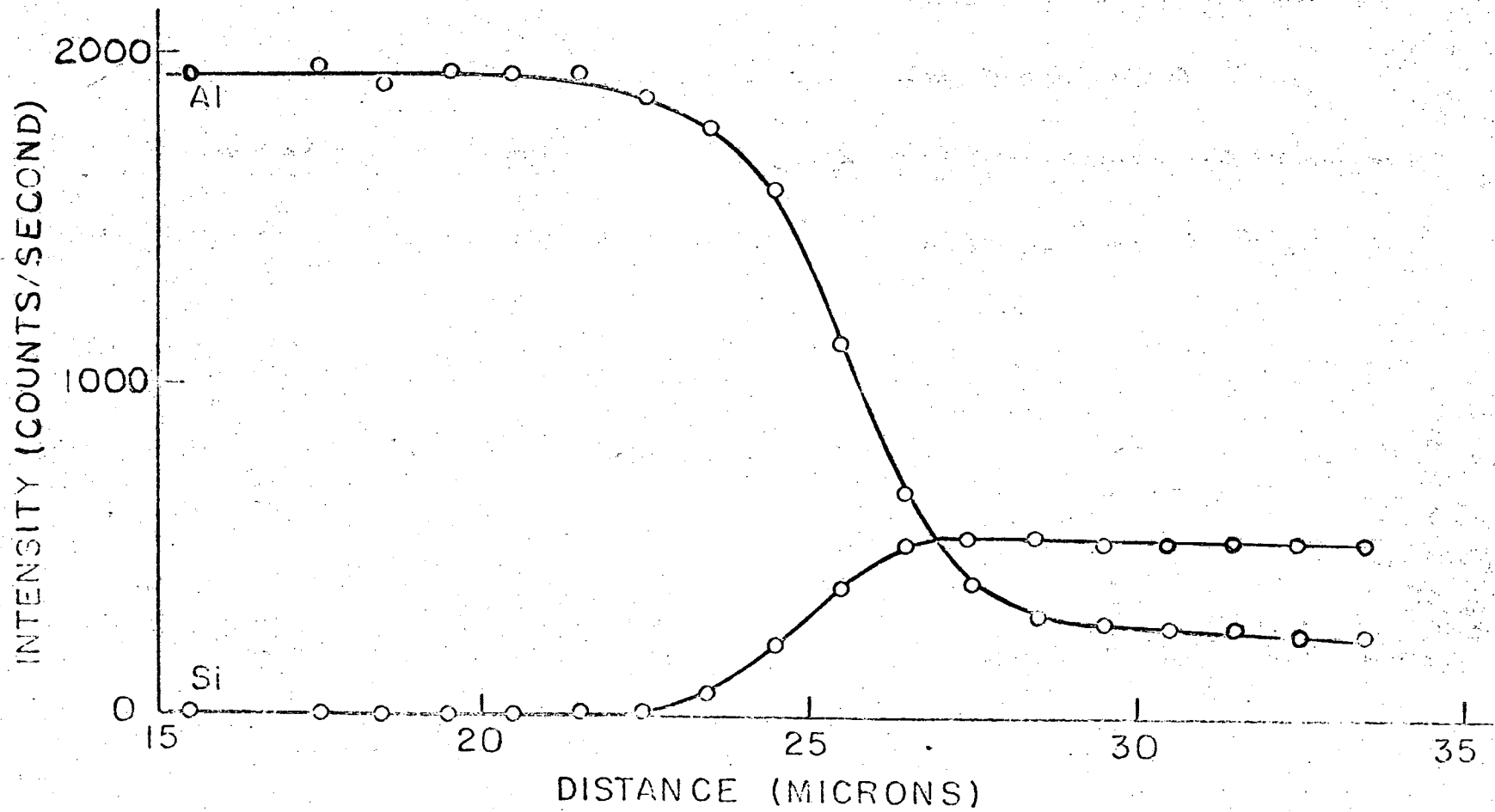
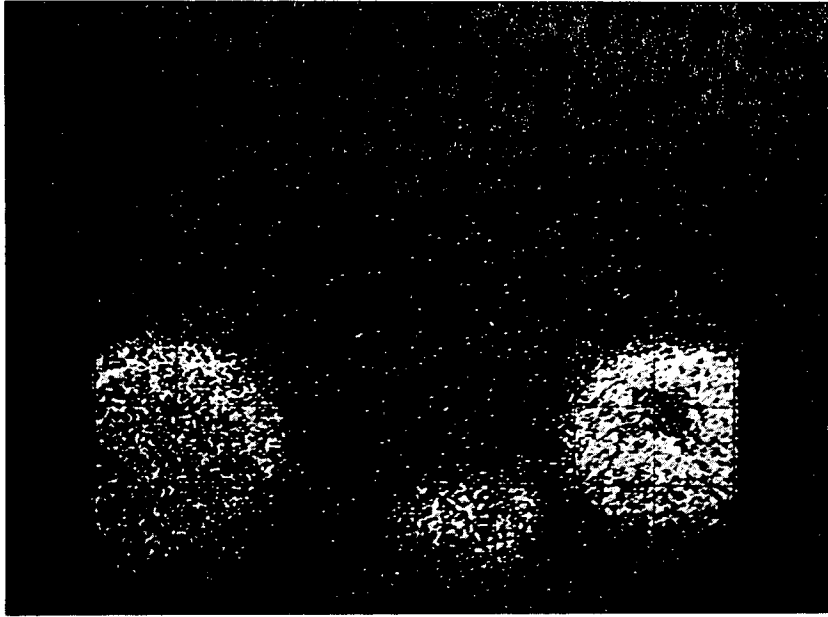


Fig. 10. The anisotropy of alumina.

samples showed any trace of the main nephelite peak. Samples pressed under the same conditions, but with 40v/o spheres, did show a marked nephelite peak with the x-ray pattern. One of these 40v/o sphere samples was probed in an effort to identify the nephelite phase with the microprobe. This probe profile can be seen in Fig. 11 and there is no evidence of any step to indicate the formation of nephelite at the sphere-glass interface. This profile, along with Fig. 5 and the x-ray results, indicate that the reaction is not controlled by diffusion as was thought by Studt and Fulrath.<sup>11</sup> Instead, the reaction appears to be controlled by the rate of solution of the alumina sphere and hence is highly dependent upon the particle size and therefore the surface area. When the particle size of the saturating phase becomes very small the solubility of a solid in a liquid is usually increased. Photographs of the x-ray image generated by aluminum as displayed on the oscilloscope were taken of samples pressed at 850°C and 2000 psi for 10 minutes. These are shown in Fig. 12 and Fig. 13. The aluminum content in the matrix increases with an increase in the volume fraction of alumina in the composite. With the higher aluminum content in the matrix the nephelite phase was identified by x-ray techniques. Since all other parameters--pressure, temperature, particle size, and holding time--were the same for each of these two samples, the factor responsible for the presence of the nephelite must be the level of alumina in the glass matrix. Thus the reaction between the alumina and the glass is controlled by the solution of the alumina sphere and the migration of this alumina into the glass. Once a certain alumina level is reached, the reaction can proceed and the nephelite is formed in the glass and

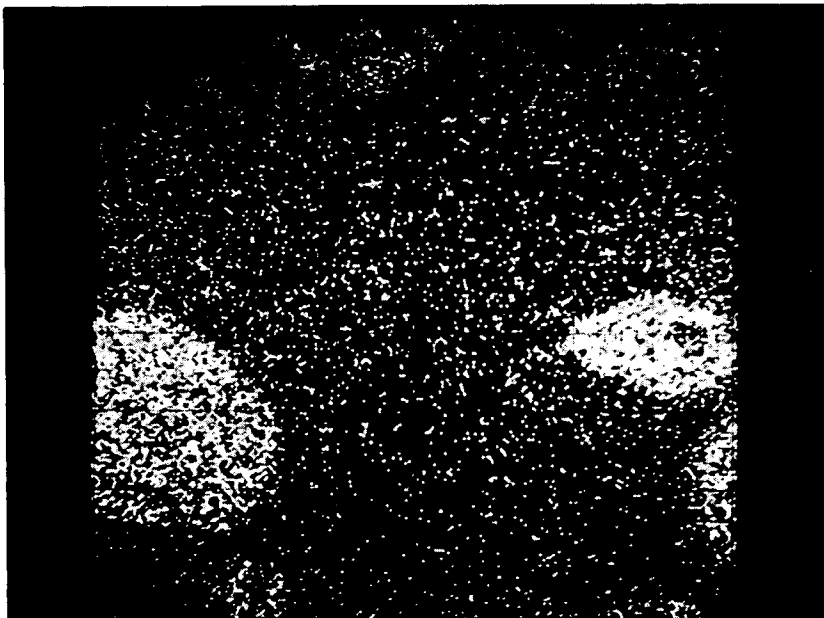
Fig. 11. Electron microprobe profile of 40v/o spheres composite.





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Fig. 12. Oscilloscope photograph of 10v/o spheres composite (Al radiation and about 350X).



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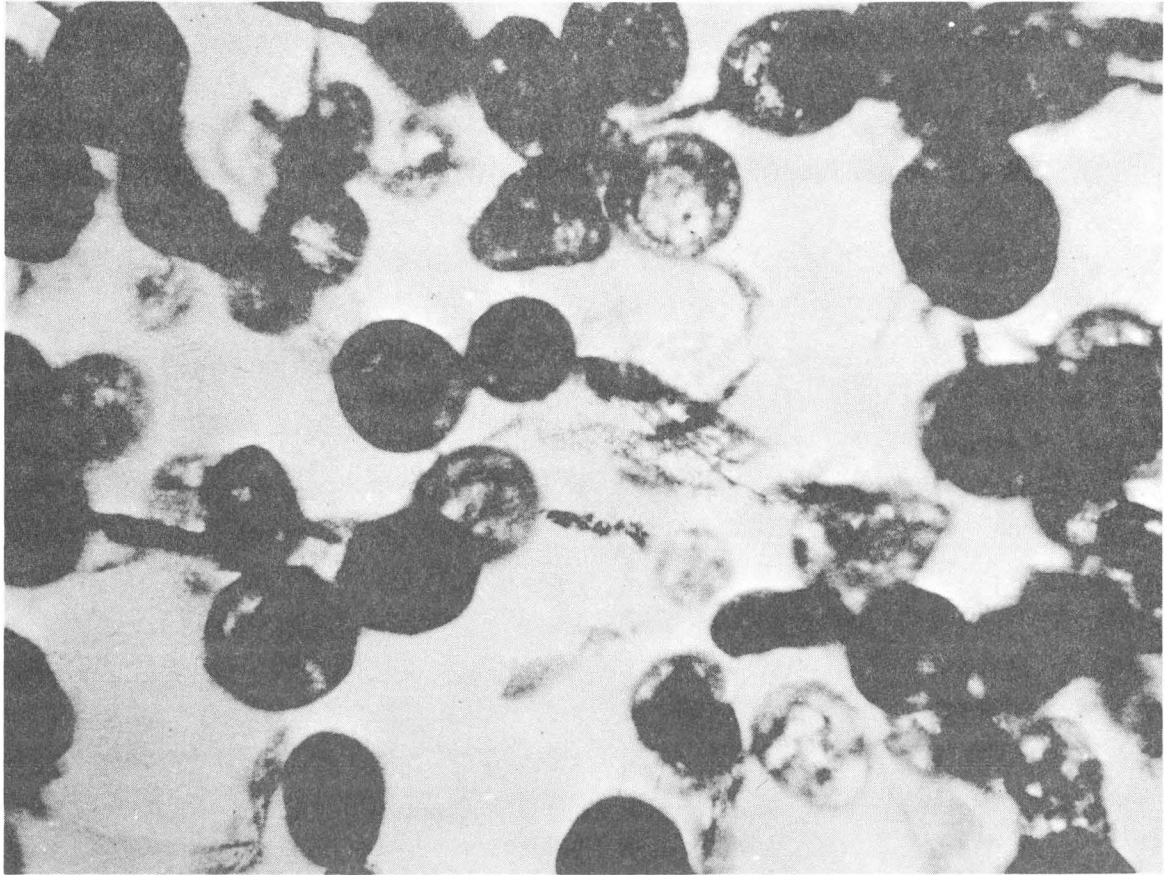
Fig. 13. Oscilloscope photograph of 40v/o spheres composite (Al radiation and about 350X).



not as a shell around the alumina particle.

### C. Photomicrograph

The formation of nephelite can be seen when the composite is viewed with transmitted light. The 40v/o spheres sample was cut and a thin section was made. When viewed under transmitted light, laths and feathers of nephelite can be seen in the vicinity of the alumina spheres. Another portion of the same sample was powdered and a refractive index of between 1.52 and 1.55 for discrete particles of nephelite was measured with calibrated oils. The particles showed the pleochroism that is characteristic of nephelite, changing from yellow to green under polarized light. A representative photomicrograph showing the nephelite particles can be seen in Fig. 14. The nephelite grows radially from the sphere into the glass. Occasionally a particle of nephelite will be seen entirely surrounded by glass. Microprobe data show the alumina concentrations in the matrix for this 40v/o sphere sample to vary from 12.0 to 19.5v/o  $\text{Al}_2\text{O}_3$ . With this level of  $\text{Al}_2\text{O}_3$  in the glass matrix the primary phase upon crystallization for the temperatures used in this work would be nephelite.<sup>19</sup> This can be seen in Fig. 15 and Fig. 16. The alumina spheres serve as nucleation sites for the nephelite crystallization and the crystals grow into the glass phase. Occasional nephelite crystals will be seen isolated in the matrix, but these are a result of the sectioning process.



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Fig. 14. Photomicrograph of thin section of 40v/o spheres composite (128X).

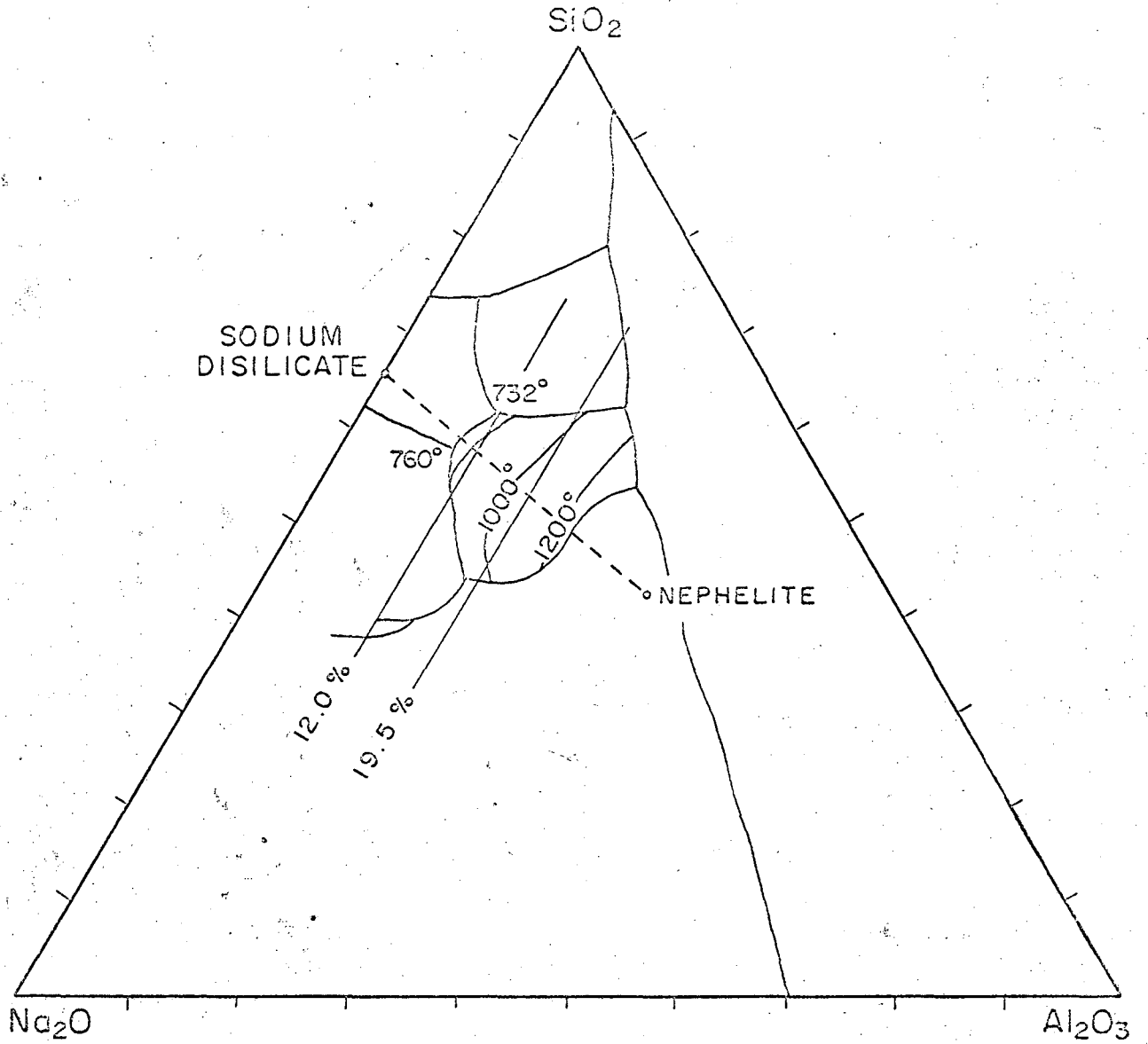


Fig. 15. Portion of Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system under study.

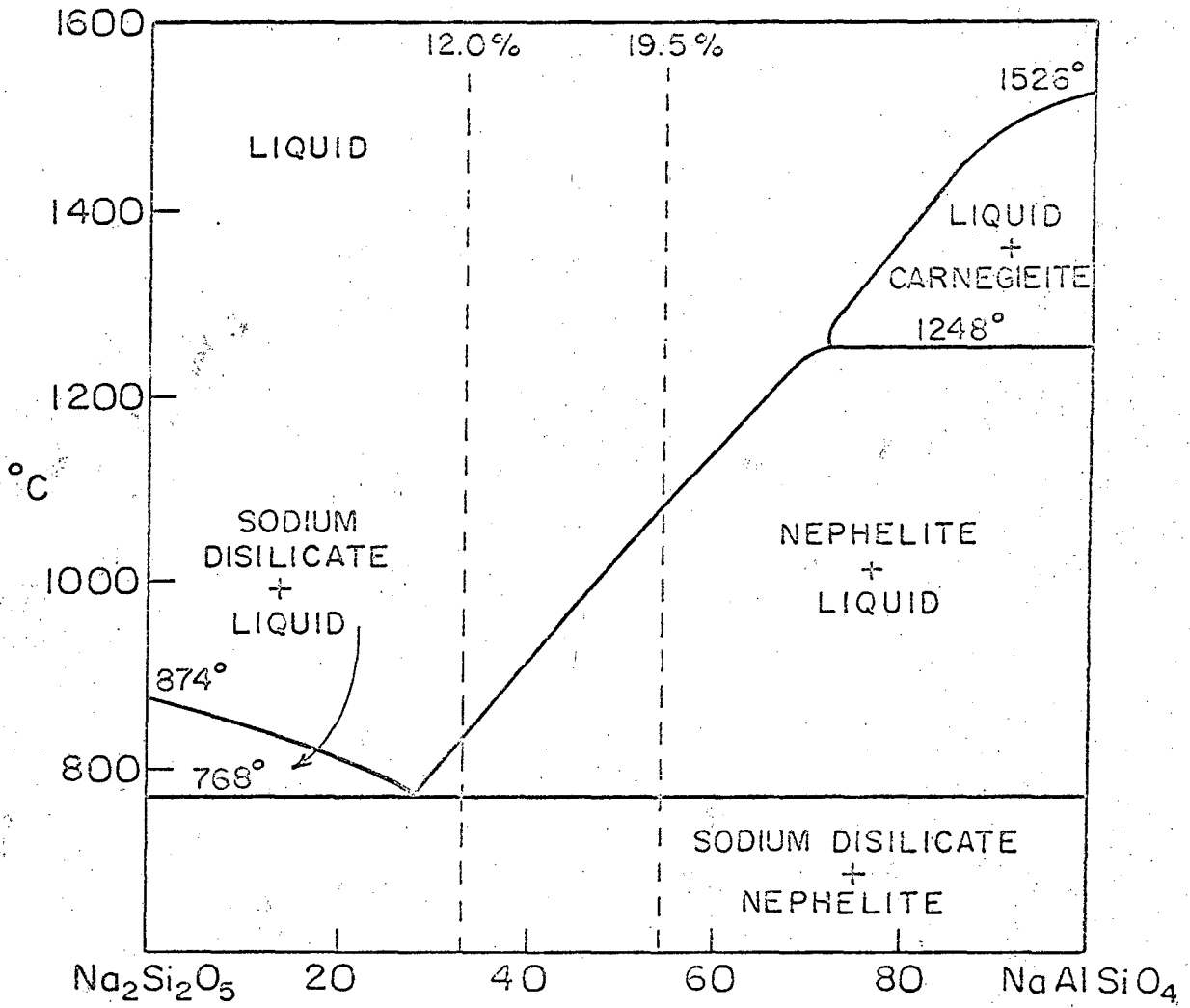


Fig. 16. Portion of  $\text{Na}_2\text{Si}_2\text{O}_5$ - $\text{NaAlSiO}_4$  system under study.

## V. SUMMARY

Chemical reactions can occur in a two-phase composite during normal hot-pressing processes. The reaction between alumina and sodium disilicate glass to form nephelite has been found to occur at hot-pressing temperatures of 750°C and higher.

Electron microprobe analysis of composites of alumina spheres and sodium disilicate glass does not show the distinct step at the sphere interface which would indicate a diffusion-controlled reaction. Rather the reaction has been found to depend upon the concentration of alumina in the glass matrix. An increase in the  $\text{Al}_2\text{O}_3$  concentration in the matrix was found to accompany an increase in the amount of nephelite formed, indicating that the reaction is controlled by the dissolution of the alumina sphere. The maximum rates of solution in different directions about each sphere occur at 120° intervals for this hexagonal crystal. Pressure, temperature, and holding time have little or no effect upon this dissolution. The nephelite has been found to nucleate at the surface of the alumina sphere and grow into the glass phase.

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