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## THE FUSION RELATIONS OF IRON-ORTHOCLASE

WITH A DISCUSSION OF THE  
EVIDENCE FOR THE EXISTENCE OF AN  
IRON-ORTHOCLASE MOLECULE IN FELDSPARS\*

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### ABSTRACT

An examination of the equilibrium relations existing along the section  $K_2O \cdot 6SiO_2$  (glass)†- $Fe_2O_3$  of the ternary system  $K_2O$ - $Fe_2O_3$ - $SiO_2$  has shown that the compounds iron-orthoclase ( $KFeSi_3O_8$ ) and iron-leucite ( $KFeSi_2O_6$ ) exist, and that they can be prepared from dry melts. On heating, the iron-orthoclase dissociates into iron-leucite and a liquid, and the iron-leucite in turn dissociates into hematite and a liquid. Hematite is the stable phase at the liquidus  $1265^\circ C$ . The difficulty in the synthesis of iron-orthoclase can be traced, in part, to these complex incongruent melting relations. Powder  $x$ -ray diffraction patterns indicate the similarity of the two potash-iron-silicates with the corresponding aluminum compounds. The question of the ferric feldspars and the entry of the iron-orthoclase molecule into the feldspars proper has been critically reviewed.

### TABLE OF CONTENTS

- I. Introduction
- II. Historical
- III. Methods of studying phase relations in silicate melts
- IV. Preparation of the mixtures
  - $SiO_2$  component
  - $K_2O$  component
  - $Fe_2O_3$  component
- V. The furnaces and measurement of temperatures
  - Crystallizing furnace
  - Quenching furnace
  - Accuracy of temperature control
  - Thermometric measurements
- VI. Refractive indices and the ferrous oxide content of the glasses

\* A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

† This designation does not signify a compound of  $K_2O$  and  $SiO_2$  in the ratio of 1:6, but is a convenient method of expressing the molecular composition of the mixture.

## VII. Quenching experiments

- Field of hematite
- Field of iron-orthoclase
- Field of iron-leucite
- Field of the silica minerals

## VIII. Properties of the crystalline phases

- Iron-orthoclase
- Iron-leucite
- Hematite
- Silica minerals

## IX. Discussion of the evidence for the existence of an iron-orthoclase molecule in feldspars

- Chemical and physical data
- Occurrence of ferriferous feldspars
  - The occurrence of a ferriferous-orthoclase
  - The occurrence of other iron-bearing feldspars
- Evidence from synthetic studies
  - Experiments of Hautefeuille and Perrey
  - Evidence from the present studies
- Interpretations

## X. Acknowledgments

## I. INTRODUCTION

The ternary system  $K_2O-Fe_2O_3-SiO_2$  is seemingly unimportant in petrology, owing to the lack of any indication of its compounds occurring alone in nature. It is, nevertheless, of interest in the explanation of their significant absence in igneous rocks. In this paper the relations obtaining along the  $K_2O \cdot 6SiO_2(\text{glass})-Fe_2O_3$  section will be considered in so far as they permit interpretation. Experimental study of the system  $K_2O \cdot 4SiO_2-Fe_2O_3-SiO_2$  is in progress.

This investigation was undertaken to determine the existence or non-existence of certain compounds thought to form in the ternary system here considered. The compound  $K_2O \cdot Fe_2O_3 \cdot 6SiO_2$ , which for the purpose of mineralogical analogy may be termed iron-orthoclase, has been prepared by French mineralogical chemists. They, however, prepared it by using catalytic or mineralizing substances and not from the simple ternary components.

Although up to the present no conclusive evidence of the existence of iron-orthoclase as a distinct mineral species has been reported, its manifestation in nature may be masked by isomorphism with the analogous aluminum compound orthoclase,  $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ , and some credence is given to this belief through the discovery of a yellow iron-bearing orthoclase from the area near Fianarantsoa, Madagascar.

For this and other reasons it was considered very desirable to investi-

gate and compare the phasal relations obtaining in this system with those in the analogous system  $\text{Na}_2\text{O}-\text{Fe}_2\text{O}_3-\text{SiO}_2$ , and these results will be published later when the work is completed.

In addition, when the principal portion of the system is worked out, the phasal relations as deduced from the liquidus curves may be of use in helping to determine the course of crystallization of the residual liquids rich in iron, which are believed to exist in the later stages of the cooling of some rock magmas.

Moreover, the results of the present study may also be of some value to the glass industry, for the section studied contains the  $\text{K}_2\text{O}:\text{SiO}_2$  ratio present in many hard glasses; and the effects of the oxides of iron on the refractive index and the liquidus, will be more accurately known.

## II. HISTORICAL

Various investigators in mineral synthesis have attempted the preparation of certain compounds in this system. Thus, Hautefeuille<sup>1</sup> as early as 1880 prepared what he terms "leucite ferrique,"  $\text{K}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 4\text{SiO}_2$ , by pouring into molten potassium metavanadate, stoichiometric proportions of potassium nitrate, silica, and ferric oxide, and obtained a product consisting of yellow-green, icositetrahedral crystals showing the characteristic polysynthetic twinning of the mineral leucite. In 1888 Hautefeuille and Perrey<sup>2</sup> succeeded in isolating what they called "orthoclase ferrique,"  $\text{K}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 6\text{SiO}_2$ , as amber-yellow crystals possessing similar crystallographic and optical properties, including the characteristic Karlsbad, Manebach and Baveno twins, of the mineral orthoclase. Niggli<sup>3</sup> obtained by the methods of hydrothermal synthesis "Kaliägrin," crystallizing as long slender prisms or clusters, and possessing a light yellow-green color. This compound possesses the same chemical formula as the "leucite ferrique" of Hautefeuille; and, Niggli attempts to explain this in the following manner:

Through the preparation of the potassium-aegerite there is now produced a connection between the leucite form and the amphibole-pyroxene form of the silicate  $\text{R}'\text{R}''\text{Si}_2\text{O}_6$ . The compound  $\text{KFeSi}_2\text{O}_6$  crystallizes out of vanadate-bearing melts as iron-leucite, which under ordinary hydrothermal conditions forms as potassium-aegerite.

In this connection it would be well to recall the actual observations of Larsen and Hunt<sup>4</sup> who investigated two vanadiferous soda-aegerites from Libby, Montana, and gave analyses from which the following data in Table 1 are taken:

<sup>1</sup> Hautefeuille, P., *Compt. rendus*, vol. 90, pp. 378-380, 1880.

<sup>2</sup> Hautefeuille, P., and Perrey, A., *Compt. rendus*, vol. 107, pp. 1150-1152, 1888.

<sup>3</sup> Niggli, P., *Zeit. anorg. Chem.*, vol. 84, pp. 31-55, 1914.

<sup>4</sup> Larsen, E. S., and Hunt, W. F., *Am. Jour. Sci.*, vol. 36, pp. 289-296, 1913.

	Vanadiferous- Aegerite	Vanadiferous-Aegerite- Augite
Na <sub>2</sub> O	10.46%	6.26%
K <sub>2</sub> O	0.22	0.26
V <sub>2</sub> O <sub>5</sub>	3.98	2.86

They state further:

These two pyroxenes occur together in veins that were probably formed under deep-seated conditions and at a high temperature. Indeed they have some resemblance to pegmatites.

Thus the discovery of a vanadiferous soda-aegerite does not substantiate the generalization regarding the phase of R'R''Si<sub>2</sub>O<sub>6</sub> to be expected according to Niggli's interpretation. Furthermore, iron-leucite was prepared from dry melts in this present study.

In addition, Duboin<sup>5</sup> using molten potassium fluoride as a bath has also prepared an iron-leucite of the composition K<sub>2</sub>O · Fe<sub>2</sub>O<sub>3</sub> · 4SiO<sub>2</sub>.

### III. THE METHOD OF STUDYING PHASAL RELATIONS IN SILICATE MELTS

Silicate melts possess great viscosity and hence offer resistance to the attempt of molecules, or atomic groups, to arrange themselves in an orderly fashion to form crystals.

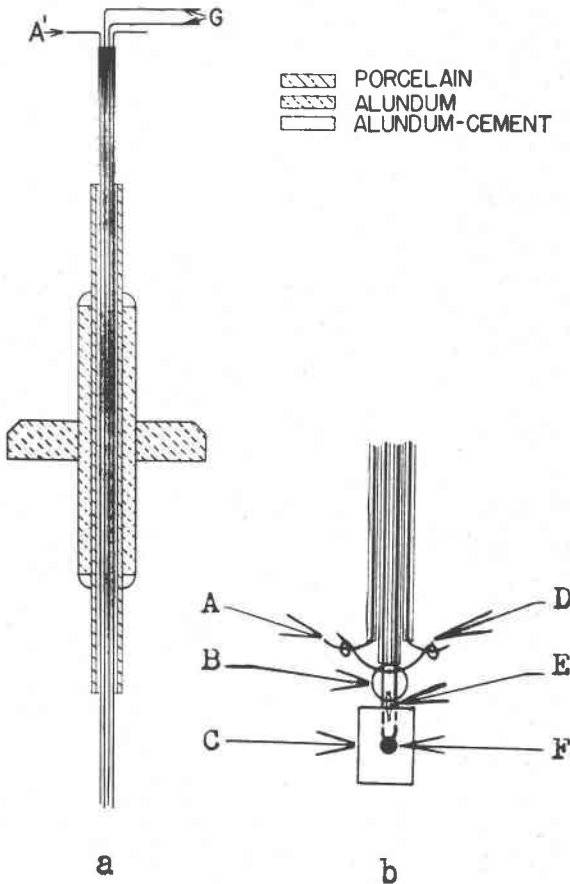
Since the silicate melts, in general, exhibit heating curves which do not give evidence of a sharp break, but rather show a melting interval, the determination of the liquidus must be investigated by some other method. The method used to investigate silicates, which exhibit sluggish tendencies to crystallize, is known as the "quenching-method" and was originally described by Shepherd, Rankin and Wright<sup>6</sup> in 1909.

In this method a small quantity of the charge is placed in a tiny platinum envelope which is suspended in the furnace and left there for a period judged to be sufficient to ensure the attainment of equilibrium conditions. After measuring the temperature at equilibrium, the charge is immediately removed from the furnace by an electrical device<sup>6</sup> which fuses a small platinum wire suspending the charge and causes the envelope with its contents to be dropped out of the furnace into a mercury well where it is quenched to room temperature. See Fig. 1.

By this method of quenching it is possible to bring the charge down to room temperature rapidly enough so that the phase or phases which are present in the furnace at the temperature of equilibrium are preserved.

<sup>5</sup> Duboin, A., *Compt. rendus*, vol. 185, pp. 416-417, 1927.

<sup>6</sup> Shepherd, E. S., Rankin, G. A., and Wright, F. E., *Am. Jour. Sci.*, vol. 28, p. 293, 1909.



FIGS. 1 (a and b). The "quenching rig." (Fig. 1b represents a more highly magnified portion of the lower part of the apparatus.)

The wires making up the thermoelement and heavy platinum lead wires are encased in porcelain capillary tubes.

AA' = Heavy platinum lead wires.

B = Refractory (porcelain) ring.

C = Envelope made of platinum foil.

D = Fine platinum wire connecting the refractory ring to the heavy platinum lead wires AA'. Note:—it is this wire that is fused when the charge is dropped out of the furnace.

E = Fine platinum wire connecting the platinum envelope to the refractory ring.

F = The tip of the thermocouple.

G = The thermocouple wires before entering the capillary tubes.

The charge is removed from the platinum envelope by placing it in an agate mortar and crushing it with the pestle to loosen the charge from the foil. A brass collar may be used to surround the charge to prevent

loss of material. A sample is then placed on a microscope slide and examined by the liquid immersion method for determining the optical constants of mineral fragments.

If the previously crystallized charge when quenched and examined under the petrographic microscope consists only of glass, obviously the temperature at which the charge was held is above that at which those crystals (which constitute the primary phase for that portion of the system) can exist in equilibrium with the liquid—namely, the liquidus temperature. Lower temperatures are next tried until the crystals are found to be stable, and the limit between glass, and glass plus crystals, is narrowed down to a very short temperature interval. This point then represents the liquidus temperatures for that particular composition.

Concerning the accuracy of the liquidus temperature determinations, one can do no better than to quote from the excellent, critical discussion of Kracek.<sup>7</sup> The italics are mine.

Thus, if the liquidus temperature is given as 764°, interval +3 -2, it is meant that the preparation when quenched from 767° was all glass, and when quenched from 762° contained crystals. *Since the thermostatic control of the furnace is accurate to 0.5°, the limits 767° and 762° are intended to denote that these temperatures are known to the nearest 0.5° of the values given; the interval then denotes the limit within which the transformation was determined, and not the uncertainty of the temperature measurement.*

#### IV. PREPARATION OF THE MIXTURES

In order to obtain accurate determinations of the position of the liquidus temperature it is necessary to use very pure materials in the experimental work, for small amounts of impurities may have a decided effect upon it.

##### SiO<sub>2</sub> COMPONENT

This was prepared from Sylvania sandstone, which is weakly bound with calcite as cementing material. A preliminary examination made in 1930 by Professor W. F. Hunt<sup>8</sup> showed the presence of small quantities of celestite, garnet, pyrite, tourmaline, magnetite, and zircon as the heavy residues. The sandstone was crushed, sieved, and the heavy minerals separated by means of bromoform. The sand was then boiled with dilute acids until the acid extractions no longer yielded a test for iron. The resulting material was then washed free of acid, dried, and heated in a platinum crucible to approximately 1450°C. for a period of ten to twelve hours. This heating inverts most of the quartz and owing to the consequent volume changes a white powder is produced which is very easy to crush. The break-down of the grains exposes the small cracks

<sup>7</sup> Kracek, F. C., *Jour. Phys. Chem.*, vol. 36, pp. 2529-2542, 1932.

<sup>8</sup> Hunt, W. F., Oral communication.

in which adsorbed oxides of iron cling tenaciously. After again crushing, the material was placed in a casserole and digested with the acid mixture; and the iron oxide, together with any platinum crystals which may have volatilized and deposited on the sand while in the furnace, were removed. After washing, the material was dried and stored over  $P_2O_5$  in a desiccator. Analysis of two samples by evaporation with HF and  $H_2SO_4$  and ignition with  $(NH_4)_2CO_3$  gave values of 99.94 and 99.93%  $SiO_2$ , corrections being made for the blank.

#### $K_2O$ COMPONENT

The potash component was supplied by an especially pure  $KHCO_3$  analytical reagent (Mallinckrodt) which was analyzed and found to meet the minimum requirements of standard works on the purity of reagents.<sup>9,10</sup> Several samples upon titration yielded the theoretical factor.

#### $Fe_2O_3$ COMPONENT

The iron oxide was prepared by starting with an exceptionally pure ferric ammonium sulphate. The salt was placed in a platinum casserole and dissolved in distilled water; a few drops of nitric acid were added to ensure the ferric state of the iron, and ammonia gas was bubbled into the solution until a decidedly basic reaction was observed. The precipitate was then transferred to a filter paper and while still warm, was washed with a hot solution containing one per cent of ammonium nitrate, until no further tests for sulphate could be detected. This precipitate was carefully dried, placed in a crucible (porcelain) and heated, slowly at first and then the temperature was gradually raised to below  $1000^\circ C$ . The material thus obtained was examined under the microscope and also by means of the x-ray powder method to ensure the absence of magnetite.

To check the accuracy of the quantitative determinations, Dr. Kenneth B. Thomson,<sup>11</sup> Research Spectroscopist in the Department of Physics in the University of Michigan, very kindly investigated the purity of samples of the three components by an examination of their spectra of which he states:

The quartz shows no strong lines other than those of silicon and two or three weak lines which are probably silicon lines but were not listed in the tables at hand.

There is no evidence of any titanium in the ferric oxide preparation and only an exceedingly small amount of aluminum and silicon. The presence of the aluminum is however, not definitely established.

<sup>9</sup> *Chemical Reagents; Their Purity and Tests*. Merck & Co., 1914.

<sup>10</sup> Murray, B. L., *Tests for Reagent Chemicals*, 2nd Ed., New York, 1927.

<sup>11</sup> I desire at this time to thank Dr. Thomson for his willingness to analyze these preparations.

For the analysis of the  $\text{KHCO}_3$ , a solution (prepared) containing 3 grams of  $\text{KHCO}_3$ , 5 c.c. of  $\text{HCl}$  and distilled water to make up to 100 c.c. This solution was run against a blank containing 5 c.c. of  $\text{HCl}$  and 95 c.c. of water and a known solution containing 0.05%  $\text{Na}$ , and in addition 0.01%  $\text{Mg}$ , 0.01%  $\text{Mn}$ , 0.005%  $\text{Cu}$ , 0.05%  $\text{Ca}$ , 0.3%  $\text{K}$ , all present as chlorides. The sodium in the  $\text{KHCO}_3$  if any is exceedingly small and judging by comparison with the standard solution containing 0.05%  $\text{Na}$ , the amount would be probably less than 0.01% of this value. Further,  $\text{Mg}$ ,  $\text{Ca}$ ,  $\text{Fe}$ , and  $\text{Al}$  lines were all absent.

The  $\text{K}_2\text{O} \cdot 6\text{SiO}_2$  glass<sup>12</sup> was prepared by weighing directly into a platinum crucible the stoichiometric proportion of  $\text{SiO}_2$  required by the molecular composition of the glass. The correct proportion of  $\text{KHCO}_3$  necessary to yield the theoretical quantity of  $\text{K}_2\text{O}$  required was weighed out on a watch glass and added to the silica. The two were carefully mixed on a piece of glazed paper and returned to the crucible, which was then placed over a bunsen flame and heated *gently* for two hours. The crucible containing the charge was removed and placed in a Hoskins furnace at approximately  $800^\circ$  to  $900^\circ\text{C}$ . and left for twelve hours, after which it was transferred to the crystallizing furnace and held at  $1100^\circ\text{C}$ . for a short period of time. The temperature of the crystallizing furnace was then raised to  $1400^\circ\text{C}$ . and the charge kept in it for five hours. The charge was finally removed from the furnace, cooled quickly, and placed in a desiccator over  $\text{P}_2\text{O}_5$ .

This method of heating was followed for several reasons. In the first place,  $\text{CO}_2$  is expelled from the melt and in order to minimize losses of  $\text{K}_2\text{O}$  and silica from the melt due to mechanical causes it is necessary to reduce frothing. Secondly, Kracek<sup>7</sup> has shown that glasses free of  $\text{CO}_2$  lose very little  $\text{K}_2\text{O}$  by direct volatilization, even at high temperatures; thus, the careful heating tends to expel the  $\text{CO}_2$  with the minimum loss of  $\text{K}_2\text{O}$ . Even with all these precautions, some  $\text{K}_2\text{O}$  is unavoidably lost. In order to compensate for this loss, the cooled crucible of  $\text{K}_2\text{O} \cdot 6\text{SiO}_2$  glass was weighed and the loss in weight was taken as due entirely to the volatilization of  $\text{K}_2\text{O}$ ; for Sosman<sup>13</sup> states that:

The direct volatilization of silica at temperatures below  $1600^\circ\text{C}$ . has not been proved.

A quantity of potassium bicarbonate sufficient to supply the amount of  $\text{K}_2\text{O}$  lost was therefore added to the powdered glass and the mass refused three times with fine crushing between fusions, until homogeneity was obtained.

The glasses on the section were made by adding weighed quantities of  $\text{Fe}_2\text{O}_3$ , corresponding to definite compositions, to the homogeneous  $\text{K}_2\text{O} \cdot 6\text{SiO}_2$  glass, mixing thoroughly and heating. The resulting glass

<sup>12</sup> This designation does not signify a compound of  $\text{K}_2\text{O}$  and  $\text{SiO}_2$  in the ratio of 1:6, but is a convenient method of expressing the molecular composition of the mixture.

<sup>13</sup> Sosman, R. B., *The Properties of Silica*, New York, p. 109, 1927.



was crushed and reheated until optical examination showed the absence of undissolved iron oxide and the new glasses appeared homogeneous. This usually requires as many as six fusions with intervening grindings. The glasses thus obtained were placed in the crystallizing furnace.

#### V. THE FURNACES AND MEASUREMENT OF TEMPERATURES

The furnaces and the thermometric equipment which were used in this investigation were modelled after those of the Geophysical Laboratory and the Lime and Gypsum section of the National Bureau of Standards.

##### CRYSTALLIZING FURNACE

The crystallizing furnace was connected in series with three resistances having the values of 2, 2.75, and 6 ohms, respectively. The furnace-coil, consists of 100 grams of 0.8 mm. diameter iridium-free platinum wire containing 10% rhodium, and having a resistance of 3.28 ohms at zero degrees and 7.54 ohms at 1000°C.

##### QUENCHING FURNACE<sup>14</sup>

This furnace and its attendant regulator employed in this study was patterned largely after a modification of the "Geophysical Thermostat" used by the National Bureau of Standards in phase rule problems. (Fig. 2.)

In the investigation of the stability of a phase at any one temperature it is necessary to provide a suitable means for the control of this temperature within the furnace and over an area of sufficient size to contain the charge. The workers at the Geophysical Laboratory have diligently experimented with all types of thermoregulating devices until they have developed, within the last ten years, extremely accurate and very sensitive controls for regulating furnace-temperatures.<sup>15</sup>

The essential features of the thermoregulator consist of a Wheatstone bridge, one arm of which consists of the heating-coil of the furnace, and a suitable arrangement of a galvanometer-relay with some type of a switching device to function under conditions of unbalance. See Fig. 3.

<sup>14</sup> I am indebted to Mr. F. F. Barry, Technician in the Geophysical Laboratory, for sketches from which the drawings of the furnaces were made.

<sup>15</sup> White, W. P., and Adams, L. H., *Phys. Rev.*, vol. 14, pp. 44-48, 1919.

Roberts, H. S., *Jour. Wash. Acad. Sci.*, vol. 11, pp. 401-409, 1921.

Roberts, H. S., *Jour. Opt. Soc. Am. & R. S. I.*, vol. 6, pp. 965-977, 1922.

Adams, L. H., *Jour. Opt. Soc. Am. & R. S. I.*, vol. 9, pp. 599-603, 1924.

Roberts, H. S., *Jour. Opt. Soc. Am. & R. S. I.*, vol. 11, pp. 171-186, 1925.

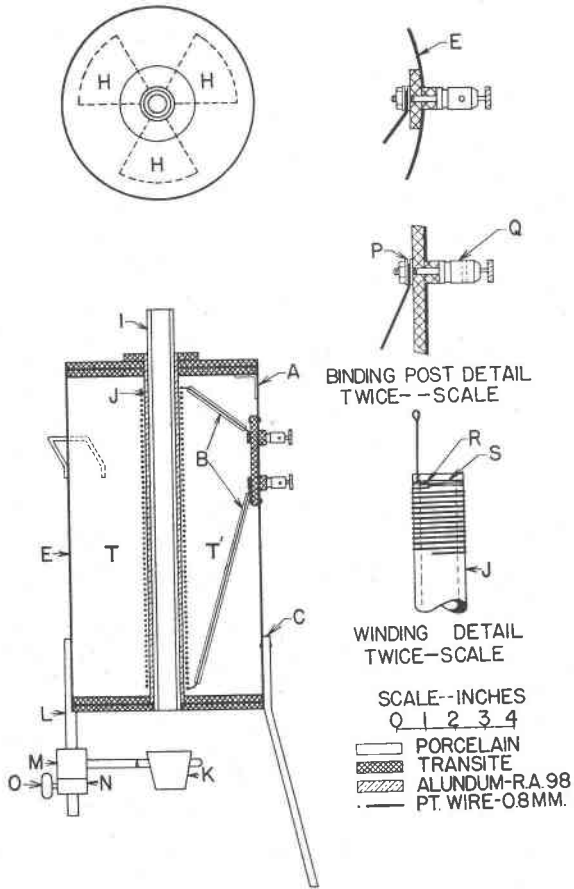


FIG. 2. The Geophysical Quenching Furnace.

- A = Brass support.  
 B = Porcelain capillary tubes protecting the heating element.  
 C = Brass leg.  
 E = Sheet Brass.  
 H = Slots in transite cover.  
 I = Porcelain tube. (Not gas tight.)  
 J = Norton Alundum tube, special design.  
 K = Iron crucible containing mercury.  
 L = Brass rod.  
 M = Brass collar holding arm and crucible.  
 N = Brass clamp holding M in place.  
 O = Brass screw.  
 P = Heating element connection.  
 Q = Binding Post.  
 R = Loop in platinum winding about which string is wound to hold wire in place. Winding is painted with refractory cement and the string is burned away.

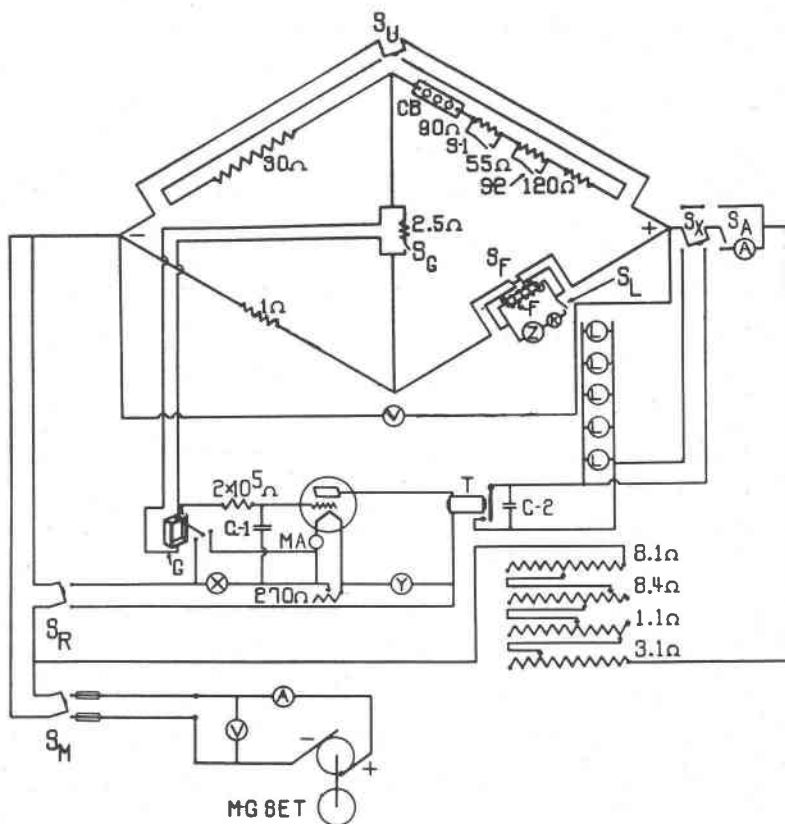


FIG. 3. Wiring diagram of the furnace and the thermoregulator.

$S_A$  = single-pole, double-throw switch.

$S_M$  = main switch, fused at 15 amperes.

$S_R$  = switch throwing regulator into the circuit.

$S_U$  = switch throwing in the upper arm of the bridge.

$S_L$  = switch throwing tungsten filament bulb into the furnace circuit.

$S_F$  = switch throwing the furnace into the circuit.

$S_G$  = switch throwing galvanometer shunt in galvanometer circuit.

$S_X$  = switch, when in the "up" position heats furnace independent of the upper bridge arm.

switch, when in the "down" completes the regulator circuit.

L = 75 watt, 32 volt, Mazda "C" lamp.

X = 60 watt, 120 volt, lamp.

Y = 40 watt, 120 volt, lamp.

Z = 50 watt, 32 volt, Mazda "C" lamp.

T = telegraphic relay. A = ammeter. V = voltmeter.

S-1, S-2 are shunting switches. MA = milliammeter.

F = platinum-wound furnace. K = 6 amperes, 120 v. fuse.

C-1 = condenser 0.01 mfd. G = galvanometer relay.

C-2 = condenser 0.1 mfd. Electron tube = CX-71 A.

M-G set = GE motor-generator set, 5 kw, 110 volt.

C B = continuous circuit click-box resistance of 999 ohms, used to change the temperature of the furnace.

#### ACCURACY OF THE TEMPERATURE CONTROL

The accuracy is dependent largely on the sensitivity of the regulating instruments and the insulation of the furnace. It is possible to control the "hot spot," a cavity of sufficient size to contain the charge, to within a maximum variation of 0.2°C. over a period of a day in the temperature range of 800–1200°C.

#### THERMOMETRIC MEASUREMENTS

Measurements were made with platinum: platinum-rhodium thermocouples calibrated at the following three fixed points:

NaCl	melting-point	800.4°C.
Au	melting-point	1062.6°C.
CaMgSi <sub>2</sub> O <sub>6</sub> (Diopside)	melting-point	1391.5°C.

The NaCl and diopside were very kindly furnished by the Geophysical Laboratory. The gold was of very high purity made especially for thermometric calibrations. The microvoltages developed by the thermocouple were measured with a Wolff potentiometer and a very sensitive galvanometer. These measurements were all corrected with the use of a standard deviation curve constructed for the particular couple used.

The accuracy of the temperature determinations is within the usual limit for this type of work, namely 0.2°C. and their reliability is based on the frequent calibration. Although the temperature may be determined to within 0.2°C. the transformations are very sluggish and are only known to within 2°C. for most compositions. Thus the range within which the transformation occurs is accurately known to within  $\pm 0.2^\circ\text{C}$ . on either side.

#### VI. REFRACTIVE INDICES AND THE FERROUS OXIDE CONTENT OF THE GLASSES

Petrographic-microscopic examination of the glasses for homogeneity may be accomplished by immersion of some of the powdered glass in a liquid of known refractive index, searching for reddish-brown patches of undissolved ferric oxide, hematite. After the thermal treatment had been sufficient to dissolve all of the ferric oxide and give a glass of uniform color, the refractive index was measured by the liquid immersion method. The accuracy of these measurements is  $\pm 0.002$ , each liquid immediately after use being checked on an Abbe total reflectometer.

Fig. 4 shows the relation between the refractive index and the ferric oxide content of the  $K_2O \cdot 6SiO_2$  glasses. This relation is apparently linear along the  $K_2O \cdot 6SiO_2 - Fe_2O_3$  section.<sup>16</sup>

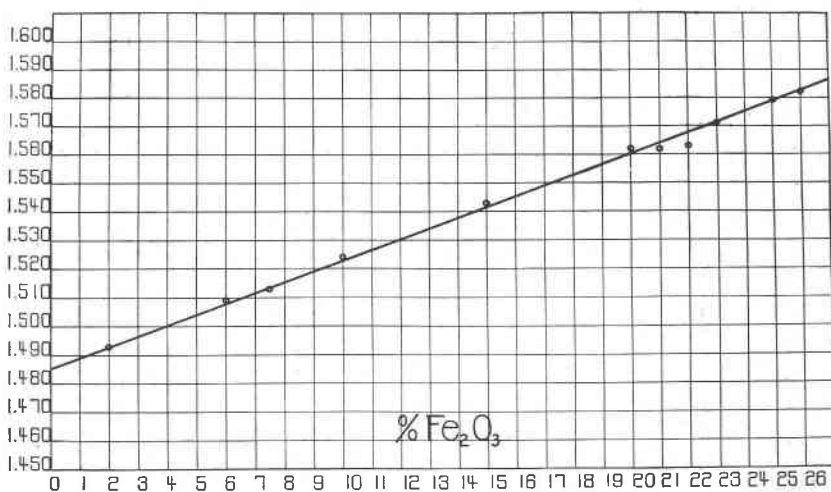


FIG. 4. The relation between the index of refraction and the iron content of the glasses. Total iron content expressed as  $Fe_2O_3$ .

It is to be remembered that these glasses contain small amounts of ferrous oxide ( $FeO$ ). Studies by Hostetter and Roberts<sup>17</sup> indicate that the amount of dissociation of ferric oxide into ferrous oxide and oxygen in silicate melts, is relatively small, especially if the temperature of heating lies below  $1200^\circ C$ . Furthermore in the somewhat analogous system  $Na_2O - Fe_2O_3 - SiO_2$ , Bowen, Schairer, and Willems<sup>18</sup> made a careful study of the state of oxidation of the iron in the melts and found that the  $FeO$  reaches a maximum of 1.09% in a melt containing 35%  $Fe_2O_3$  held at  $1175^\circ C$ . At 26%  $Fe_2O_3$  a charge held at  $838^\circ C$ . contained 0.39%  $FeO$ .

For the ferrous iron determinations of some of the glasses along this section, a 0.5 gram sample was placed in a platinum foil envelope and held approximately at the liquidus temperature for that composition, and for a length of time equivalent to that which was necessary in the quenching experiments. Since platinum has some effect on the state of

<sup>16</sup> In the ternary system the isofracts are curved lines.

<sup>17</sup> Hostetter, J. C., and Roberts, H. S., *Jour. Am. Cer. Soc.*, vol. 4, pp. 927-938, 1921.

<sup>18</sup> Bowen, N. L., Schairer, J. F., and Willems, H. W. V., *Am. Jour. Sci.*, vol. 20, p. 418, 1931.

oxidation of the iron,<sup>19</sup> the samples to be analyzed were subjected to the same conditions as those employed for the liquidus determinations. The analysis of the ferrous oxide content was made by the modified Pratt Method using a fused quartz flask. As this procedure has been adequately described elsewhere<sup>20</sup> it will not be repeated here.

TABLE 2. FERROUS IRON CONTENT OF REPRESENTATIVE GLASSES

Composition of the glass				% FeO	°C. Temperature
K <sub>2</sub> O·6SiO <sub>2</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O		
79.00%	62.63%	21.00%	16.37%	0.31±0.03	928.4
78.00	61.84	22.00	16.16	0.29±0.03	987.4
77.00	61.05	23.00	15.95	0.18±0.01	1,011.2
75.00	59.46	25.00	15.54	0.33±0.01	1,097.5

## FERROUS IRON CONTENT OF REPRESENTATIVE GLASSES

Table 2 shows that the dissociation of Fe<sub>2</sub>O<sub>3</sub> into FeO and oxygen, in silicate melts under laboratory investigation is of the order of magnitude indicated by the work of others.<sup>12,13</sup> The dissociation is, however, quite small, indicating that the departure in the more general quarternary system K<sub>2</sub>O-Fe<sub>2</sub>O<sub>3</sub>-FeO-SiO<sub>2</sub> is not very great. We may therefore neglect its presence in our discussion without destroying the validity of the generalization, although it should be remembered that some FeO is present.

## VII. QUENCHING EXPERIMENTS

The data presented in Table 3 represent, in general, only those critical quenches which establish the position of the liquidus and this group constitutes but a small portion of the numerous quenching experiments carried out in the laboratory.

<sup>19</sup> Sosman, R. B., and Hostetter, J. C., *Jour. Wash. Acad. Sci.*, vol. 5, pp. 293-303, 1915.

<sup>20</sup> Soule, B. A., *Jour. Am. Chem. Soc.*, vol. 50, p. 1691, 1928. Bowen, N. L., and Schairer, J. F., *Am. Jour. Sci.*, vol. 24, pp. 178-213, 1932. *The procedure on page 185, was the one followed in this work.*

TABLE 3

Composition (weight per cent)			Time hrs.	Tempera- ture °C.	Final condition of the initially crystalline charge
K <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>			
20.72	—	79.28		1133	Liquidus <sup>21</sup>
20.31	2.00	77.69	3½	1056	Glass
			1¾	1052	Glass plus very rare needles of tridymite
			3	1050	Glass plus tridymite
			3½	1009	Glass plus tridymite and pine-tree crystals of cristobalite
19.48	6.00	74.52	3	941	Glass
			3¾	939	Glass plus extremely rare tridymite
			4	931	Glass plus rare tridymite
19.17	7.50	73.33	15	904	Glass plus extremely rare cristobalite
			12½	900	Glass plus rare cristobalite, poorly distributed
18.65	10.00	71.35	5¾	838	Glass
			14	829	Glass plus extremely rare tridymite
17.61	15.00	67.39	21	836	Glass
			19	835	Glass plus extremely rare iron-orthoclase
17.09	17.50	65.41	33	920	Glass
			10	906	Glass plus rare iron-orthoclase
16.58	20.00	63.42	47	921	Glass
			23	920	Glass plus extremely rare iron-orthoclase
			22	917	Glass plus rare iron-orthoclase
16.47	20.50	63.03	74	933	Glass
			12	920	Glass plus exceedingly rare iron-orthoclase
			8½	917	Glass plus rare iron-orthoclase
16.37	21.00	62.63	3½	926	Glass
			5	921	Glass plus extremely rare iron-leucite
			4½	913	Glass plus iron-leucite, plus rare iron-orthoclase
16.16	22.00	61.84	9	992	Glass
			4	984	Glass plus extremely rare iron-leucite
			3½	926	Glass plus iron-leucite
			5	921	Glass plus iron-leucite, plus iron-orthoclase melting to iron-leucite

<sup>21</sup> Kracek, F. C., Bowen, N. L., and Morey, G. W., *Jour. Phys. Chem.*, vol. 33, pp. 1857-1879, 1929.

TABLE 3.—Continued.

Composition (weight per cent)			Time hrs.	Tempera- ture °C.	Final condition of the initially crystalline charge
K <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>			
15.95	23.00	61.05	4	1013	Glass
			6	1007	Glass plus iron-leucite
			3	1004	Glass plus iron-leucite
15.54	25.00	59.46	3	1091	Glass plus extremely rare hematite, very close to liquidus
			4½	1052	Hematite plates common in glass
			3	1050	Glass plus fair amounts of hematite, iron-leucite rare
15.33	26.00	58.67	3	1037	Glass plus abundant iron-leucite
			1½	1265	Very rare hematite in glass, very close to the liquidus
			1½	1260	Rare hematite in glass
			2½	1051	Much hematite in glass
			1½	1020	Numerous plates of hematite in glass

*Discussion of the Results.* The charges containing 2, 6, 7.5, 20, 20.5, 21, 22, 23, 25, and 26.00% Fe<sub>2</sub>O<sub>3</sub> were all crystallized from dry melts. The portion of the liquidus determined by these charges is indicated in Fig. 5, in heavy full lines.

The charges having 10, 15, and 17.5% Fe<sub>2</sub>O<sub>3</sub> presented great difficulties in crystallization. Repeated trials extending over many months and at various temperatures failed to yield crystals, the glasses possessing little tendency to crystallize. It was necessary to resort to hydrothermal methods in order to bring about crystallization. This was accomplished by placing a small portion of the charge in a platinum thimble which, in turn, was placed into a fused quartz tube, about three-quarters of an inch in diameter and 12 inches long. A few drops of water were introduced along the side of the tube and the whole system sealed by fusing the end of the fused quartz tube. This was then placed in the crystallizing furnace and its temperature raised to some point below the liquidus. The resulting mass contained an abundance of small crystals but, owing to their great number, liquidus determinations proved difficult because of the greater uncertainty in the decision as to whether or not the charge had actually attained the equilibrium state. Runs, as long as 50 hours and more, were made in an attempt to attain equilibrium. Hence the liquidus temperatures, obtained on samples hydrothermally crystallized, are not as accurate as those obtained by the use



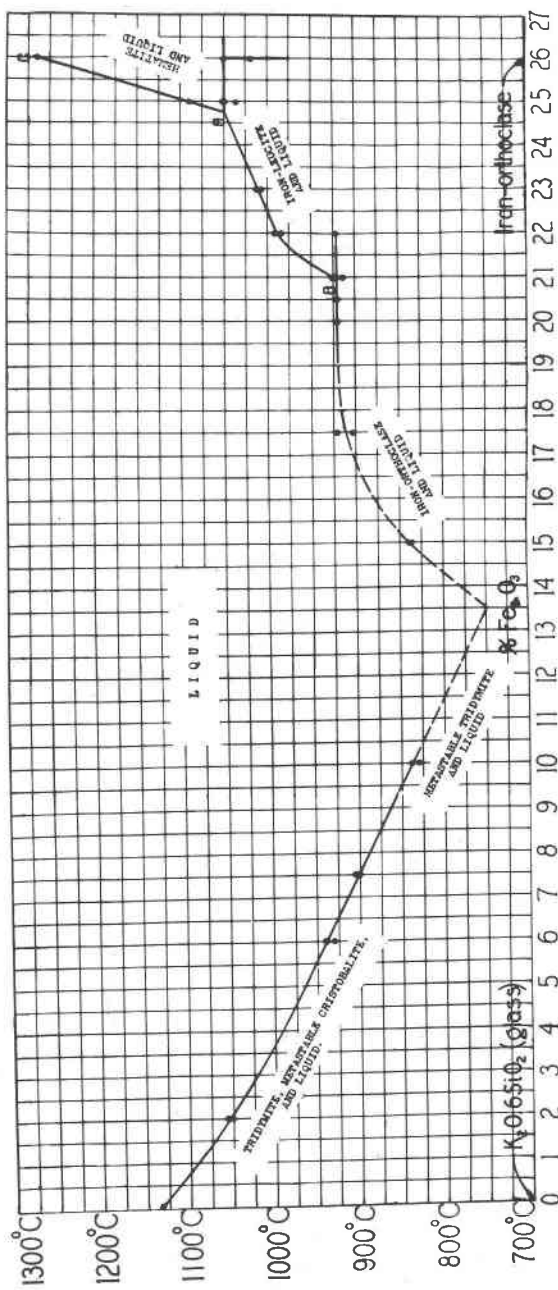


FIG. 5.

of materials crystallized from dry melts, and this is indicated in Fig. 5, by the heavy dashed lines.

The  $K_2O \cdot 6SiO_2 - Fe_2O_3$  section now being considered is not a binary system in itself, but only a straight line section through the ternary system  $K_2O - Fe_2O_3 - SiO_2$ , shown as the line  $X - Fe_2O_3$  in Fig. 6. Therefore, the course of crystallization, for compositions located on the section, cannot be completely foretold without having recourse to a portion of the ternary system.

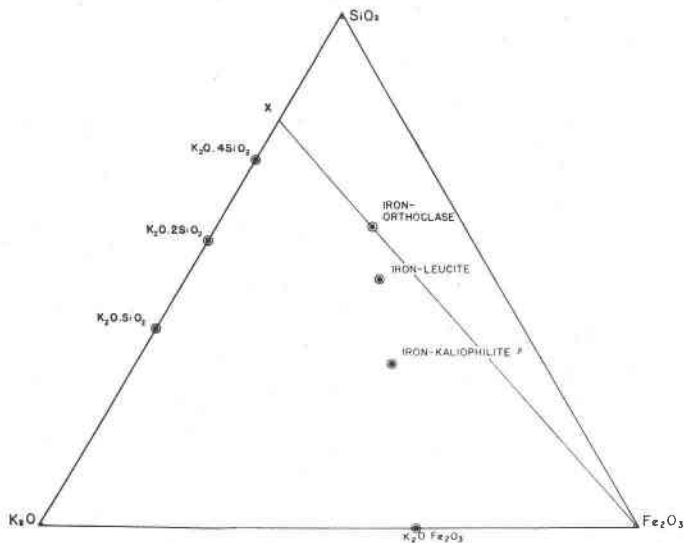


FIG. 6.

#### FIELD OF HEMATITE

The liquidus for the stability of hematite rises abruptly from point A (Fig. 5) and theoretically extends to the melting point of  $Fe_2O_3$ . In this connection Sosman and Merwin<sup>22</sup> state:

The melting point of pure  $Fe_2O_3$  is unknown, as it dissociates under atmospheric pressure of oxygen before the melting point is reached into oxygen and a solid solution of  $Fe_3O_4$  in  $Fe_2O_3$ .

The curve was not investigated beyond 26%  $Fe_2O_3$  or at temperatures exceeding  $1265^\circ C$ . because of the increase in the rate of the dissociation of ferric oxide and the consequent entry into the quaternary system,  $Fe_2O_3 - FeO - K_2O - SiO_2$ . The field thus extends from 24.75%  $Fe_2O_3$  to 100%  $Fe_2O_3$ .

<sup>22</sup> Sosman, R. B., and Merwin, H. E., *Jour. Wash. Acad. Sci.*, vol. 6, pp. 532-537, 1916.

## FIELD OF IRON-ORTHOCLASE

The stability boundaries for this phase extend from about 13.5%  $\text{Fe}_2\text{O}_3$  over to 21%  $\text{Fe}_2\text{O}_3$ . Iron-orthoclase was not found to be metastable at temperatures exceeding 921°C. It must be emphasized at this point that the crystallization of iron-orthoclase has proved to be a rather difficult task. Experience has shown that in melts in which it is stable, particular attention must be paid to the constancy of the furnace temperature, and long periods of time, extending from three weeks to several months, are often necessary to merely induce the iron-orthoclase to crystallize. After the first nuclei are formed careful heating is very essential to the growth of the crystals.

At this time the actual fusion relations of iron-orthoclase cannot be given entirely. The present data indicate that iron-orthoclase melts incongruently to yield iron-leucite and a liquid at 920°C. Iron-leucite, in turn, decomposes to form hematite and a liquid. Hematite is the primary phase at the liquidus, disappearing at 1265°C.

## FIELD OF IRON-LEUCITE

The field of stability for iron-leucite extends from 21%  $\text{Fe}_2\text{O}_3$  over to 24.75%  $\text{Fe}_2\text{O}_3$ . Iron-leucite does not exist as a metastable phase at temperatures above 1050°C. on this section. In the melts, crystallized at temperatures at which iron-orthoclase is the stable phase, however, it was found that iron-leucite formed and further, it usually was the first of the two phases to form.

## FIELD OF THE SILICA MINERALS

This field extends from 0.0 to 13.5%  $\text{Fe}_2\text{O}_3$  along the composition coordinate and from 750°C. to 1130°C. along the temperature coordinate. The stable phase between 870°C. and 1130°C. is tridymite and this phase was observed in all melts. Between 870°C. and 750°C. the stable phase should be quartz but no signs of it were noticed, the liquidus being determined from the metastable tridymite present. In some charges, dendritic octahedra of metastable cristobalite were observed.

## VIII. PROPERTIES OF THE CRYSTALLINE PHASES

## IRON-ORTHOCLASE

The optical properties of the iron-orthoclase prepared by Hautefeuille and Perrey have been measured by Hautefeuille and Perrey,<sup>2</sup> Niggli,<sup>3</sup> and Gaubert<sup>23</sup> and found to be as follows:  $\alpha = 1.601$ ,  $\beta = ?$ ,  $\gamma = 1.609$ ;  $\gamma - \alpha$

<sup>23</sup> Gaubert, R., *Compt. rendu du congrès des Sociétés Savantes de Paris et des Départements*. Sections des Sciences, pp. 402-408, 1925.

=0.008. The compound is monoclinic and occurs in crystals resembling those of ordinary orthoclase. Its color is yellow. The optic plane is parallel to (010) and the extinction in (010) is  $7^\circ$  to  $8^\circ$  to the  $a$  axis. These indices are decidedly greater than the values for ordinary orthoclase. Thus we may assume that the refractive indices of orthoclase containing iron-orthoclase in solid solution should be raised somewhat.

In the routine determination of iron-orthoclase, as it occurs in the melts, its characteristic appearance as lath-shaped crystals was used to identify it. In melting, iron-orthoclase crystals are corroded more rapidly perpendicular to the length, and in such a manner as to produce an hour-glass structure.

The identification of this compound was made by comparison of the  $x$ -ray diffraction patterns of powders of iron-orthoclase and ordinary orthoclase. The replacement of aluminum ( $\text{Al } 3^+$ ) by iron ( $\text{Fe } 3^+$ ) should cause a decrease in the spreading of the lines on the powder photograph of iron-orthoclase. That is, the lines should move progressively in toward the zero beam, indicating an increase in the size of the lattice. This follows from a consideration of the ionic radii,<sup>24</sup> ( $\text{Al } 3^+$ ) = 0.57, ( $\text{Fe } 3^+$ ) = 0.67. The actual powder photographs verify this.

#### IRON-LEUCITE

Iron-leucite occurs as small subhedral to rounded grains which are yellow in color. The grains exhibit low grey interference colors, and this double refraction can be detected more easily by the use of the gypsum test plate. The optical properties measured on Hautefeuille's original material by Gaubert<sup>23</sup> are as follows:

$n = 1.619$ . Birefringence greater than the  
aluminous variety.

The identity of this compound with the ordinary leucite with reference to the molecular ratios of the constituent oxides, 1:1:4, and similarity of crystalline structure is made very evident by a comparison of their respective  $x$ -ray powder diffraction patterns. Except for the progressive movement of the lines toward the zero beam, the patterns are in good agreement. As was stated in connection with the  $x$ -ray studies of iron-orthoclase, the lattice spacing is larger as would be expected from a consideration of the ionic radii. Along this section, the iron-leucite crystals developed as subhedral grains which have a strong tendency to arrange themselves in star-like or ray-like patterns.

Optical measurements on a well crystallized preparation of the composition of iron-leucite showed the grains to possess an intricate poly-

<sup>24</sup> Hassel, O., *Kristallchemie*, p. 12, Leipzig, 1934.

synthetic twinning, resembling very closely the twinning of ordinary leucite. The interference colors are predominantly low greys, although in large fragments straw-yellow appears. The double refraction is weak. The index of refraction of this material is 1.619 in agreement with Gaubert's measurement.

#### HEMATITE

The hematite observed was in the form of typical crystals, consisting of translucent hexagonal plates usually having a reddish color, but in very thin sheets they were quite often yellow. Since the properties are so characteristic and cannot be confused with those of other compounds, and since the index is so high as to be very difficult of measurement, the value of its optical constants was not determined.

#### SILICA MINERALS

The tridymite crystals exhibit the characteristic hexagonal platy structure. Plates standing on end, so as to give a needle-like appearance, are easily observed because of the birefringence. Cristobalite occurs usually in characteristic dendritic growths.

#### IX. DISCUSSION OF THE EVIDENCE FOR THE EXISTENCE OF AN IRON-ORTHOCLASE MOLECULE IN FELDSPARS.

The feldspars as a group constitute about sixty per cent of the earth's crust. As a result of their great abundance and development as crystals there naturally has accumulated a vast amount of physical and chemical data concerning them.

The major constituents of the feldspars, silica, lime, soda, potash, and alumina, have been carefully investigated from an experimental standpoint. Tschermak's classic interpretation of the isomorphic relations of the plagioclase feldspars has been experimentally verified by the work of Day and Allen,<sup>25</sup> and later by Bowen.<sup>26</sup> The Geophysical Laboratory is extending its experimental work in the systems involving the three fundamental molecules, orthoclase, albite, and anorthite.

With the exception of the work by Pentti Eskola<sup>27</sup> on the barium and strontium feldspars little has been done with the minor constituents, viz., lithium, ferric iron, and cesium and rubidium.

In the light of the preceding investigation it was considered appro-

<sup>25</sup> Day, A. L., and Allen, E. T., Isomorphism and the thermal properties of the feldspars: *Carnegie Inst. of Wash., Pub. No. 31*, 1905.

<sup>26</sup> Bowen, N. L., The melting phenomena of the plagioclase feldspars: *Am. Jour. Sci.*, vol. 35, pp. 577-599, 1913.

<sup>27</sup> Eskola, Pentti, The silicates of strontium and barium: *Am. Jour. Sci.*, vol. 4, pp. 331-375, 1922.

priate to review the literature concerning the existence of ferric feldspars and this has been done, but with no attempt at completeness.

#### CHEMICAL AND PHYSICAL DATA

The analyses of feldspars, both of the alkali and plagioclase varieties, have in most cases yielded oxides of iron in determinable amounts. Some mineralogists have considered all of this iron to be due to contamination of the feldspars by foreign inclusions, and consequently not essential to the composition of the mineral. In many cases this is probably true to some extent. Others have attributed the presence of the iron oxides to weathering phenomena.

On the other hand, this is not always the case, for many writers have noticed that in the sunstone variety of feldspars there is an abundance of hematite crystals and they have demonstrated that the definite orientation of the plates, which give to these minerals their attractive chromatic effects, is due to an exsolution process.

The most outstanding example of a ferriferous orthoclase is the yellow, homogeneous orthoclase from Madagascar. A series of analyses given by Lacroix<sup>28</sup> and Seto<sup>29</sup> are listed in Table 4.

TABLE 4. ANALYSES OF FERRIFEROUS-ORTHOCLASE

	1	2	3	4	5	6
SiO <sub>2</sub>	64.25	64.21	64.26	64.19	63.99	64.76
Al <sub>2</sub> O <sub>3</sub>	16.06	17.78	17.23	16.62	18.02	17.98
Fe <sub>2</sub> O <sub>3</sub>	2.93	1.15	2.16	2.88	0.97	1.18
FeO	0.25	0.09	0.18	0.18	—	0.09
MgO	none	none	none	—	—	0.08
CaO	tr.	0.07	0.05	—	0.50	0.16
BaO	—	—	—	n.d.	0.06	n.d.
K <sub>2</sub> O	16.15	15.21	15.55	15.81	14.32	15.39
Na <sub>2</sub> O	0.44	0.42	0.38	0.34	1.86	1.07
H <sub>2</sub> O+	—	—	—	—	0.51	0.20
Sum	100.08	98.93	99.81	100.02	100.23	100.91

<i>Analysis</i>	<i>Analyst</i>	<i>Comments</i>
1	K. Seto	Optically examined by Kozu.
2	K. Seto	Lighter in color. The analysis 2, either contains a typographical error, or was incorrectly summed, the total given being 99.63.
3	K. Seto	Color intermediate between 1 and 2.
4	Boiteau	Original analysis, for Lacroix.

<sup>28</sup> Lacroix, A., *Minéralogie de Madagascar*, Paris, vol. 1, pp. 557-562, 1922.

<sup>29</sup> Seto, K., *Science reports, Univ. Tohoku*, (III), vol. 1, pp. 221-223, 1923.

- 5 Boiteau Colorless adularia associated with yellow orthoclase in the pegmatite.
- 6 Analyzed specimen in the collection of the University of Rochester.

In Table 5 these analyses of the ferriferous orthoclase have been calculated into their component molecules, assuming all of the iron to be present in the ferric state. Actually, the amount of ferrous iron in the analyses is small and would not cause a great change in the final results. Theoretically these sums should total to 100%, but incompleteness in analysis, or inaccuracies in methods, etc., cause slight deviations.

TABLE 5. CALCULATION OF THE ANALYSES INTO THE VARIOUS COMPONENT FELDSPARS

	1	2	3	4	6
Orthoclase	84.20	85.44	83.62	82.60	86.74
Albite	3.72	3.55	3.21	2.87	9.05
Anorthite	—	0.35	0.25	—	0.79
Iron-orthoclase	12.35	4.81	9.08	11.85	4.93
Totals	100.27	94.15	96.16	97.32	101.51
Analyses Totals	100.08	98.93	99.81	100.02	100.91

These data offer support to the view that orthoclase and iron-orthoclase are isomorphous. The maximum concentration of the iron-orthoclase so far reported is about 12%.

The physical properties which have been determined on this Madagascar feldspar include optical and spectrographic studies.

The indices of refraction of the specimens whose analyses are given in Table 5 are listed below:

- Analysis 1  $\alpha=1.5216, \beta=1.5259, \gamma=1.5261,$   
 2  $\alpha=1.5185, \beta=1.5225, \gamma=1.5239,$   
 4  $\alpha=1.5197, \beta=1.5248, \gamma=1.5253, 2V_{Na}=34^{\circ}06'.$

These values show slight increases over pure orthoclase, which would be expected in the substitution of iron for aluminum.

*The Transmission of Light through Yellow Orthoclase.* Some unpublished notes by Dr. E. F. Holden<sup>30</sup> on the ferriferous feldspar from Madagascar are given with the permission of Professor W. F. Hunt. The data are given in Table 6 and Plotted in Fig. 7.

This spectrographic data by Holden demonstrates that the iron is in the ferric state and as such must proxy for aluminum.

<sup>30</sup> Mineralogical Laboratory, University of Michigan.

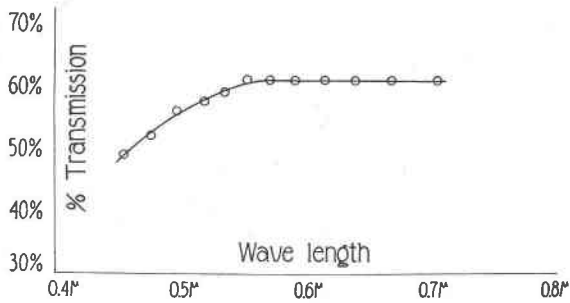


FIG. 7.

This unusual variety of orthoclase from Madagascar, is yellow and transparent. It has been described by Lacroix who published an analysis by Boiteau, indicating 2.88% Ferric oxide. The curve in Fig. 7, from data obtained on a cleavage plate one cm. in thickness, shows that the absorption of light by this mineral is like that of ferric compounds,<sup>31</sup> which exhibit no bands but simply show a general absorption of the light in the blue end of the spectrum. The color may be ascribed to large amounts of ferric iron.

TABLE 6

Wave length	Percentage of Transmission
.704	61%
.668	61
.639	61
.615	61
.592	61
.572	61
.554	61
.537	59
.520	57.5
.498	56
.478	52
.457	49

#### OCURRENCE OF FERRIFEROUS FELDSPARS

*The Occurrence of a Ferriferous-Orthoclase.* The only field occurrence of what may be termed an iron-orthoclase: orthoclase mineral is the one reported by Lacroix.<sup>28</sup> At d'Itrongay, Fianarantsoa, Madagascar, a gem-like yellow to yellow-gold orthoclase occurs in a pegmatite associated with adularia, transparent zircon, and *diopside*. This group of minerals, occurring in fairly large crystals in a pegmatite, is distinctly unique. Further studies should lead to some interesting conclusions concerning the physico-chemical environment at the time of injection. It is to be noted that the associates include just those with which we should expect to find iron-orthoclase compatible, *especially the diopside*. Washington<sup>32</sup>

<sup>31</sup> Holden, E. F., *Am. Mineral.*, vol. 10, pp. 127-128, 1925.

<sup>32</sup> Washington, H. S., *Jour. Franklin Inst.*, vol. 190, p. 792, 1920.



has pointed out from a graphical study of numerous analyses of igneous rocks that "magnesia and the iron oxides tend to go together."

*Occurrence of Other Iron-Bearing Feldspars.* The classic examples of feldspars containing, at the time of their separation, iron oxides in solid solution are the aventurine feldspars. Andersen<sup>33</sup> in particular has made a rather extensive study of aventurine feldspars and his conclusions concerning the hematite are very instructive (Note: the words in italics are the writer's):

The formation of aventurine feldspars by unmixing in the solid state may be conceived as follows: the feldspar crystals were, at the time of their separation, wholly, or in part homogeneous and contained small amounts of  $\text{Fe}_2\text{O}_3$  in solid solution, either as hematite or as a constituent of a ferric compound. By a change in the exterior conditions prevailing at the time of formation, e.g. change in temperature, the equilibrium of the solid solution may be disturbed in such a way that  $\text{Fe}_2\text{O}_3$  can no longer be held in solution, but must separate in individual crystals . . . (and) in such a manner that the hematite lamellae have separated along structural planes (translation planes) of the feldspar.

Some peculiar distributions of iron oxides in feldspars have been described in the literature. Thus Schairer<sup>34</sup> in an analysis of brown feldspar from Portland, Connecticut, points out that small red flakes of iron oxide occur *only* in the *microcline* of a microcline-albite microperthite, and that their distribution is irregular. Further, Lacroix<sup>35</sup> describes a violet colored orthoclase occurring in a syenite pegmatite from Sabotsy (to the west of Fianarantsoa), Madagascar, and states that its color is due to fine inclusions of magnetite. He makes no statement regarding their origin in the orthoclase. The results of Andersen's experiments (p. 376) may, however, apply here.

(1) Cleavage piece with numerous transparent hematite lamellae heated for one hour at 1260°: The feldspar remained birefringent throughout with outlines sharp as before the heating; colorless; transparent, but somewhat dim. All hematite inclusions disappeared.

(5) Piece from exp. (1) heated for twenty-four hours at about 1050°: Feldspar milk white, dull, full of very fine black dust.

(6) Cleavage piece with numerous hematite lamellae heated for one-half hour at 1235°: Feldspar birefringent; colorless; somewhat dim, but still transparent. All hematite disappeared.

In pegmatites no such temperatures prevail but long continuous heatings at much lower temperatures may be able to bring about the same reactions.

#### EVIDENCE FROM SYNTHETIC STUDIES

*Experiments of Hautefeuille and Perrey.* As early as 1888, Hautefeuille and Perrey<sup>2</sup> attempted to prepare an analogous iron-orthoclase molecule

<sup>33</sup> Andersen, Olaf, *Am. Jour. Sci.*, vol. 40, pp. 351-399, 1915.

<sup>34</sup> Schairer, J. F., *Proc. Yale Min. Sc.*, vol. 2, pp. 20-21, 1924-1925.

<sup>35</sup> Lacroix, A., *Minéralogie de la France*, vol. 5, p. 28, Paris, 1913.

from dry melts and failed. They then resorted to the use of mineralizing agents and succeeded in producing iron-orthoclase, iron-leucite, and hematite at will, by merely controlling the proportions of the components employed. Their comments are worthy of repetition:

The exclusive production of iron-leucite characterizes the primary phase of the mineralization. But the nature of the products which arise subsequently, is essentially dependent upon the proportions of the materials used and this amount can ensure the stability of the leucite, or determine, on the other hand, the appearance of hematite crystals or of feldspar crystals.

*Evidence from the Present Studies.* From the experiments conducted in this laboratory, we may conclude that the existence of the iron-orthoclase molecule has been definitely confirmed. Its fusion relations are quite complicated, originating in the incongruent melting of iron-orthoclase to iron-leucite and a liquid, followed by the subsequent incongruent melting of iron-leucite into hematite and a liquid.

From a study of Fig. 5, it is quite apparent that iron-leucite would probably be the primary phase of mineralization in the attempts of Hautefeuille and Perrey to produce iron-orthoclase. The diagram also explains their statements regarding the appearance of hematite or iron-orthoclase depending upon the adjustment of the composition.

It is not surprising that these early investigators failed to discover the phenomenon of the incongruent melting of iron-orthoclase; since the recently developed quenching method, employed in this study for the examination of the phasal relations, is the only method available at present to indicate incongruent melting.

In this investigation iron-orthoclase was prepared for the first time from a dry melt, namely, without the use of mineralizing agents.

#### INTERPRETATIONS

##### (A) *The Ferriferous Plagioclases.*

Andersen<sup>33</sup> has suggested that the feldspars contain small amounts of  $\text{Fe}_2\text{O}_3$  in solid solution either as hematite, or as a constituent of a ferric compound.

Niggli<sup>3</sup> writes concerning these hematite inclusions as follows:

It does not appear to me to be a simple weathering phenomenon but rather an unmixing of the  $\text{Fe}_2\text{O}_3$  originally existing in isomorphic replacement of the  $\text{Al}_2\text{O}_3$ , and we can suppose that this unmixing can begin on cooling at approximately 450°C.

Wherry<sup>36</sup> does not consider the replaceability of iron in the feldspars practicable, and uses it as one of the criteria for choosing a system to explain the isomorphism of the feldspars. He states:

<sup>36</sup> Wherry, E. T., *Am. Mineral.*, vol. 7, pp. 113-121, 1922.

No explanation of the isomorphism in question (atomic isomorphism) can be accepted if it does not account for the molecular volume relations, *the practical non-replaceability of aluminum by iron*, and very limited isomorphism of orthoclase and carnegieite with anorthite . . . .

Holden<sup>30</sup> commenting on the work of Andersen noted that all the aventurines examined were either plagioclase or microcline, and suggested that the solid solution of the iron component, in the case of the aventurine, was insoluble at low temperatures, whereas in orthoclase it could remain in a stable state, as in the Madagascar orthoclase.

(B) *The Ferriferous Orthoclase.*

Lacroix considered  $\text{Fe}_2\text{O}_3$  as replacing  $\text{Al}_2\text{O}_3$  in the yellow orthoclase from Madagascar and attributed the attendant change in properties to this substitution. Recently, in a review of the life and works of Hautefeuille, Lacroix<sup>37</sup> writes concerning the compounds prepared by him (Hautefeuille) as follows:

. . . a leucite and a yellow orthoclase in which the aluminum oxide is replaced by ferric oxide, since he has produced this special feldspar, I have discovered from Madagascar, a yellow-gold orthoclase which contains several per cent of it.

Seto<sup>29</sup> has carried out some interesting thermal experiments with the Madagascar ferriferous orthoclase and his results are pertinent to this discussion. He heated a crystal for one hour at  $1200^\circ\text{C}$ ., which is higher than the temperature applied by Lacroix,<sup>38</sup> and observed no change in color. Upon heating perthite, this temperature proved sufficient to easily oxidize the iron, and he concludes that the iron in perthites is a "subordinate ingredient." On the basis of these experiments he concludes:

that the iron in the yellow feldspar is combined in a stable form with other essential components of the minerals. So far as our investigation goes, it is uncertain at present in what position the iron atom is situated in the space lattice of the feldspar. But it appears most likely that the ferric iron is replaceable for alumina.

The conclusion thus drawn by Seto from his thermal experiments seems to strengthen the views of Holden regarding the possibility of a greater stability of the iron in orthoclase solution relations than in plagioclases and microcline.

Barth<sup>39</sup> also believes in the existence of an iron orthoclase. Unfortunately, in this discussion there is a misprint and he has corrected this in a written communication to the writer.<sup>40</sup>

<sup>37</sup> Lacroix, A., *Figures de Savants*, vol. 1, p. 85, (Paris), 1932.

<sup>38</sup> Lacroix, A., *Compt. rendus*, vol. 155, p. 672, 1912.

<sup>39</sup> Barth, T. W. F., *Norsk. Geol. Tidsskrift*, vol. 12, pp. 57-72, 1931.

<sup>40</sup> Written communication, dated January 9, 1935.

. . . I see that there is a peculiar misprint in the formula of the iron feldspar p. 59. Of course  $\text{Fe}^{+++}$  should proxy for  $\text{Al}^{+++}$  so that the formula becomes  $\text{KFeSi}_3\text{O}_8$ . I do not know how the misprint happened, for I have never had any other idea about the replacement in feldspar. Also in Seto's paper (which is quoted by me) only the substitution of  $\text{Fe}^{+++}$  for  $\text{Al}^{+++}$  is considered.

The views of recent workers thus indicate that for the most part they are in agreement with the idea that at least partial isomorphism exists between the ferric feldspars and the alkalic and plagioclase varieties. It is not likely to be of the same extent in each type, but probably is more pronounced in the case of orthoclase. In the plagioclases and microcline, the isomorphic replacement becomes unstable at lower temperatures and exsolution occurs with hematite separating out as a new phase. The term ferric feldspar suggests several possibilities: iron-orthoclase, iron-albite (?), iron-anorthite (?), and iron-microcline (?).

*Iron-albite* (?)  $\text{Na}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 6\text{SiO}_2$ . An examination of the ternary system,  $\text{Na}_2\text{SiO}_3$ - $\text{Fe}_2\text{O}_3$ - $\text{SiO}_2$ ,<sup>18</sup> shows that a compound corresponding to that composition has no place on the liquidus of the system, and its synthesis with fluxes has not been reported. This does not preclude the possibility of its existence, for catalysts and pressure might induce its formation, but its existence is very doubtful.

*Iron-anorthite* (?)  $\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 2\text{SiO}_2$ . So far no synthesis of this compound has been reported. The only suggestion of its existence is contained in the work of Day and Allen.<sup>25</sup>

*Iron-microcline* (?)  $\text{K}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 6\text{SiO}_2$ . Hautefeuille and Perrey<sup>2</sup> believed that they had synthesized an iron-microcline (?).

*Iron-orthoclase*  $\text{K}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 6\text{SiO}_2$ . This compound has been definitely shown to exist. Field occurrences support the isomorphism of iron-orthoclase with ordinary orthoclase to the extent of about 12% iron-orthoclase.

Thus the chemical, physical, and synthetic data establish the existence of an iron-orthoclase molecule and substantiate the view that in the case of the Madagascar feldspar we are dealing with a solid-solution of iron-orthoclase in orthoclase. Just what the composition of the ferric feldspar, which was present before exsolution, in the aventurines may have been, we do not know. It seems that it is not unreasonable to suppose that the hematite in the aventurines was originally present, in part, as a solid-solution of iron-orthoclase in plagioclase. Alling<sup>41</sup> has expressed a similar view.

<sup>41</sup> Alling, H. L., *Jour. Geol.*, vol. 31, p. 368, 1923.

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