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THE SYSTEM
 $K_2O-FeO-Al_2O_3-SiO_2$

by

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FINAL REPORT
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CONTRACT N onr 195(00)

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PHASE EQUILIBRIUM RELATIONSHIPS IN
THE SYSTEM $K_2O - FeO - Al_2O_3 - SiO_2$

Final Report on Contract Nonr - 195(00)
January 1954

Introduction

Research on this system is not complete at present and negotiations are underway for the issuance of an equipment loan contract to complete the work done under Contract Nonr - 195(00) which expired November 30, 1953. As a result, this report must be more in the nature of a progress report than a final report. The following publications have come from this contract:

Low Temperature Liquid Immiscibility in the System
 $K_2O-FeO-Al_2O_3-SiO_2$, American Mineralogist 36, 282-286, (1951).

Composition and Significance of Fluid Inclusions in Minerals,
(Abst.), Bull. Geol. Soc. Am. 62, 1472, (1951).

Progress Report on Liquidus Relations in the System
 $MgSiO_3-FeSiO_3-CaSiO_3$, (Abst.), Bull. Geol. Soc. Am. 63, 1370,
(1952).

A Reconnaissance of Liquidus Relations in the System
 $K_2O \cdot 2SiO_2-FeO-SiO_2$. Bowen Memorial Volume of American
Journal of Science, 435-456, (1952).

High-Silica Portion of the System $K_2O-FeO-Al_2O_3-SiO_2$,
(Abst.), Bull. Geol. Soc. Am. 64, 1554, (1953).

Liquid Immiscibility in the System $K_2O-FeO-Al_2O_3-SiO_2$,
(Abst.), Bull. Geol. Soc. Am. 64, 1466, (1953).

The following manuscript is being planned as a conclusion to the research: "Liquidus Equilibria in the High Silica Portion of the System $K_2O-FeO-Al_2O_3-SiO_2$ ". The manuscript will probably be submitted to the American Journal of Science. In addition, a publication is planned on the compounds $K_2O \cdot FeO \cdot 3SiO_2$ and $K_2O \cdot FeO \cdot 5SiO_2$.

Personnel

Since the inception of this contract December 1, 1950, Dr. Edwin Roedder has been Project Director and Senior Investigator. Mr. K. F. Marquardson did a master's thesis in mineralogy on a portion of the system $K_2O-FeO-SiO_2$, and numerous students have worked part time on the project. All optical phase identifications, except for Mr. Marquardson's runs, were performed by the Senior Investigator, and most of the latter were also checked by him.

Summary of Available Data on the System

All mixtures studied so far (416 made, 35 in progress) have fallen within the following compositional limits: $K_2O < 44$ wt.%; $FeO < 80\%$; $Al_2O_3 < 36\%$; balance SiO_2 . All mixtures had $K_2O:Al_2O_3$ (molecular ratio) equal to or greater than 1:4, and most had $FeO < 50$ wt.%. These limitations are imposed in part by the melting point of the pure iron containers used ($1520^\circ C$) and in part by other experimental difficulties and a lack of specific geologic significance to the remainder of the diagram.

The procedure and technique used has been described previously (Roedder, 1952) but can be summarized as follows: The calculated amounts of carefully prepared, stoichiometrically correct raw materials

(crystalline K-silicates, Fe_3O_4 solid solution, Al_2O_3 , and SiO_2 glass) for a 10 gram batch are weighed into a pure iron crucible, mixed, a large excess of pure iron chips added, and these are heated to 1450-1475°C in pure N_2 at atmospheric pressure for one hour. The batch is then quenched in mercury, the silicate melt crushed to less than 0.030 mm grain size, and refused, this process being repeated until a perfectly homogeneous glass is obtained. Phase equilibrium determinations at various temperatures ("quench runs") are then run on small portions of this glass to determine the temperature of the liquidus and other phase changes. After this a larger portion is run at the liquidus temperature to provide a sample for analysis for FeO and Fe_2O_3 , the latter being present in the amounts representing equilibrium with the metallic iron containers for that particular composition at that particular temperature. Nearly 4000 such quench runs have been made on the 416 prepared compositions, and the petrographic data on these are adequate to delineate fairly well the liquidus phase relations in the portion of the system studied, as indicated in the last three papers listed above.

This high silica portion of the system is considerably complicated by the existence of 13 binary and ternary compounds, of which at least 6 show two or more crystal modifications each; and by the existence of two separate fields or phase volumes, each representing two immiscible liquids in equilibrium with one or more crystalline phases. No quaternary compounds as such have been found, but evidence does point toward at least partial quaternary solid solution with rapidly lowering liquidus temperatures from $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$.

2SiO_2 , (Kalsilite and K-nepheline) to $\text{K}_2\text{O}\cdot\text{FeO}\cdot 3\text{SiO}_2$, and from $\text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2$ (Leucite) to $\text{K}_2\text{O}\cdot\text{FeO}\cdot 5\text{SiO}_2$.

The existing data indicate that the lowest temperature quaternary invariant points are close to $\text{K}_2\text{O}\cdot 4\text{SiO}_2$, and all of the low temperature portions in the liquidus diagram are close to the $\text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ side. The phase volume of fayalite occupies a large part of the center of the portion of the diagram studied, coming very close to the $\text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ side, particularly over the field of K feldspar. Within this fayalite phase volume and extending into the adjoining phase volume for tridymite lies the region of liquid immiscibility described in the last paper listed above. The phase volume for the silica minerals tridymite and cristobalite is surprisingly small, with a considerable concavity in the boundaries and isothermal surfaces toward the $\text{FeO}\cdot\text{SiO}_2$ edge. The isothermal surfaces in the fayalite field are severely warped in the vicinity of the immiscibility field, and as a consequence, many compositions in this region show a number of phase changes and large amounts of crystallization upon being cooled just the 10 degrees from 1150° to 1140° .

Equilibrium is obtained in one hour in all batches except those low in iron oxide and the very low liquidus compositions in the system $\text{K}_2\text{O}\cdot\text{FeO}\cdot\text{SiO}_2$ (approximately 700°C), where pre-crystallization and long duration runs are required.

Plans for Future Work

Work is still in progress and it is hoped that the data will be essentially complete and ready for the publication of a general

article on the system sometime in 1955. Future work will be concentrated on the details of the phase relationships in and around the low temperature immiscibility volume, on the crystal chemistry of the compounds $K_2O \cdot FeO \cdot 3SiO_2$ and $K_2O \cdot FeO \cdot 5SiO_2$, and the experimentally more difficult low-iron region. Application has been made for a National Science Foundation grant to carry on this work, aided perhaps by the issuance of an equipment loan contract from the Office of Naval Research.