LOW TEMPERATURE LIQUID IMMISCIBILITY IN THE SYSTEM K_2O-FeO-Al_2O_3-SiO_2

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ABSTRACT

Liquid immiscibility has been found in anhydrous silicate melts at temperatures as low as 1100° C and in compositions containing as much as 16% alumina plus alkalies in the system K_2O-FeO-Al_2O_3-SiO_2. A preliminary equilibrium diagram is presented for the system leucite-fayalite-silica, a plane through the more general system, which cuts the new region of immiscibility.

Some students of petrology have considered the occurrence of certain rock pairs in the field to indicate splitting of rock magmas due to liquid immiscibility. Such an association, however, may be explained with equal facility by other processes. In 1927 Greig* published the results of his experimental equilibrium studies on a number of silicate systems showing that liquid immiscibility does indeed occur in some instances, but that the high temperatures and limited compositions involved were such that the occurrence of the process in nature was unlikely. During the course of phase equilibrium studies on the quaternary system K_2O-FeO-Al_2O_3-SiO_2, the writer has found an entirely unexpected area of liquid immiscibility (completely surrounded by miscibility), at much lower temperatures and less restricted compositions. This discovery lightens somewhat the burden of proof for the advocate of magma splitting, but does not affect the main objection which Bowen (1928) raises, that the mechanism of liquid immiscibility is such that evidence of its occurrence in nature should be visible in the glassy rocks; this evidence has not been found.

Work is still in progress on the system, but as the discovery of this new area is of considerable interest, and as it will be some time before sufficient data can be obtained to present a completed equilibrium diagram for this part of the system, a preliminary diagram will be given here, based on available data. Figure 1 represents the ternary subsystem leucite ($K_2O \cdot Al_2O_3 \cdot 4SiO_2$)-fayalite ($2FeO \cdot SiO_2$)-$SiO_2$. It can be considered as a plane through the tetrahedron representing the more general quaternary system K_2O-FeO-Al_2O_3-SiO_2. The data were obtained by the method of quenching, using essentially the techniques of Bowen and Schairer (1932). All melts were run in intimate contact with pure metallic iron, thus containing only that amount of Fe_2O_3 which represents equilibrium with metallic iron at the liquidus temperature for the individual melt composition. Each melt was analyzed for ferrous and ferric iron after such treatment, and the ferric iron content recalculated to ferrous in

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* References are given at the end of the paper.

order to plot the diagram. The variation of the equilibrium constant $[Fe_2O_3]/[FeO]$ with temperature and composition of the liquid phase is such as to yield from 0.5 to 2.5 weight per cent Fe_2O_3 in most of the compositions studied. The diagram is based on approximately 500 quenching runs made on 26 compositions; considerably more data are needed, and when these are obtained a more detailed paper will be presented, giving composition and quench data as well as experimental technique. The data on the sidelines fayalite-silica and leucite-silica (Fig. 1) are from the published works of Bowen and Schairer (1932) and Schairer and Bowen (1947).

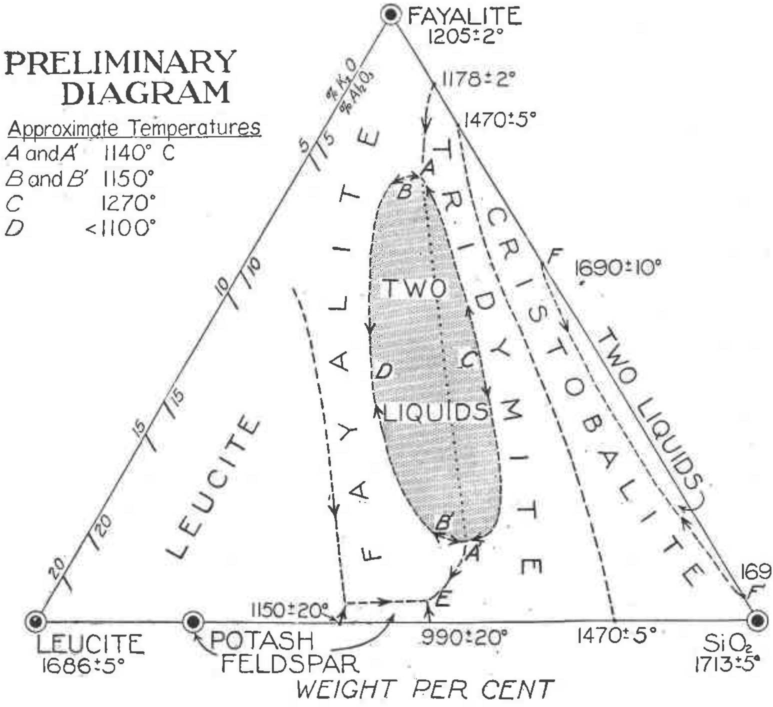

FIG. 1. Preliminary equilibrium diagram for the system leucite-fayalite-silica, showing the fields of the several crystalline phases and the intersection of the new area of immiscibility with the liquidus surface (shaded). In the area *AA'CA* two liquids are in equilibrium with silica crystals, and in the area *AA'B'DBA* two liquids are in equilibrium with fayalite crystals. Along the line *AA'* two liquids (*A* and *A'*) are in equilibrium with each other and with crystals of both silica and fayalite. All melts contain Fe_2O_3 in amounts representing equilibrium with pure metallic iron.

The new area of liquid immiscibility has been indicated in Fig. 1 by shading (the area *ACA'DA*). Greig (1927) found liquid immiscibility at high temperatures in the system FeO-SiO_2 (of which the binary system fayalite-silica is a portion), and there must be an extension of this region of liquid immiscibility into the quaternary system K_2O-FeO-Al_2O_3-SiO_2. In the plane studied, this extension is evidently small, as indicated by the dashed line between F and F', and the newly discovered area of two liquid formation appears to be entirely separate from it. The new area may be divided into two portions. In the area $AA'CA$ two liquids are in equilibrium with tridymite crystals (in part metastably with cristobalite in place of tridymite), and in the area $AA'B'DBA$ two liquids are in equilibrium with fayalite crystals. Liquids A and A' are in equilibrium with each other and with both tridymite and fayalite crystals, and hence represent invariant conditions (neglecting the effect of the Fe_2O_3 as another component). AA' is the only line connecting conjugate liquids that can be drawn at present with any degree of certainty, although it appears that the other conjugation lines will be roughly parallel to it. Present data would seem to indicate that there are also a pair of maximum points B and B', somewhere along the line ADA', joining conjugate liquids in equilibrium with fayalite crystals, with temperatures dropping away toward D and AA' on both sides of these maximum points; the true positions of these two maximum points B and B' on the line ADA' are not known. The true positions of point C, representing the maximum temperature for the existence of two liquids in equilibrium with crystals of silica, and point D, representing the minimum temperature for the existence of two liquids in equilibrium with crystals of fayalite (and the minimum temperature for the existence of two liquids), are also unknown at present.

Liquid A, when quenched to a glass, is dark greenish brown, with an index of refraction of approximately 1.70, and liquid A' is colorless, with an index of 1.51. Microscopic observation of such samples, showing two liquids (two glasses), each embedded in and containing globules of the other, is striking but is not the only evidence for liquid immiscibility. More significant perhaps is the thermal evidence of two liquids of grossly different composition (A and A') both in equilibrium with fayalite and tridymite crystals, at the *same* temperature, within the limits of variation imposed by the presence of the small, equilibrium amounts of ferric iron and the experimental error in measurement. High viscosities and difficulties inherent in the experimental technique necessary for silicate equilibrium studies involving ferrous oxide have precluded obtaining samples of individual liquids for analysis, but experiments with that objective are in progress. None of the points or lines on Fig. 1 are sufficiently well established in composition to be located definitely, but the shape of the diagram is not expected to be changed radically by further data. Present data establish the position of *ACA′* with far better definition than *ADA′*.

This area of immiscibility as shown on Fig. 1 actually represents only the intersection of a liquid immiscibility "dome" with the liquidus surface, i.e., two liquids in equilibrium with crystals of fayalite or silica or both. At higher temperatures, batches having gross compositions falling in the area *ACA′DA* will consist of two liquids alone. Insufficient data are available to draw isotherms on the surface bounding this region of two liquids, but they are adequate to show that immiscibility is eliminated by a comparatively small increase in temperature in the compositions studied, none of them exhibiting two liquid formation above approximately 1260° C.

Compositions showing immiscibility are not confined to this plane section through the tetrahedron representing the more general system K_2O-FeO-Al_2O_3-SiO_2, as adjacent compositions have been made and they also show it. The plane of Fig. 1 thus represents only a section through an immiscibility volume. The system FeO-Al_2O_3-SiO_2 (one side of the tetrahedron) shows no such region of low temperature immiscibility, thus indicating that the presence of K_2O is necessary in this case, but the effect of the addition of other materials such as Na_2O or H_2O on the extent of immiscibility is unknown. For this reason it is impossible at present to apply these results directly to the problem of the origin of those special rock types that approach most closely the compositions studied. Liquid *A′* can be considered to be equivalent to a fayalite bearing potash-granite, although the eutectic point *E* (the exact composition of which has not been determined) would represent a closer approach to the composition of some natural fayalite granites, neglecting the fact that these tend to be soda-rich rather than potash-rich. This does not require, however, that these rocks originated through the process of liquid immiscibility. More significant perhaps for the proponent of immiscibility is the fact that it can occur at temperatures as low as 1100° C in dry silicate systems containing as much as 16% alumina plus alkali,* but the problem of satisfactory evidence for it in the rocks looms as large as ever.

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* Point *B′* (Fig. 1) as drawn could be represented in the following terms:

K_2O	7.8%	Leucite	36%	Potash Feldspar	46%
Al_2O_3	8.4%	SiO_2	50%	SiO_2	40%
FeO	9.9%	Fayalite	14%	Fayalite	14%
SiO_2	73.9%				

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