Discussion of "A Re-Assessment of Phase Equilibria Involving Two Liquids in the System K_2O-Al_2O_3-FeO-SiO_2," by G.M. Biggar

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Introduction

Dr. Biggar and I have corresponded extensively over the last 6 years concerning the difficult experimental problems posed by the system K_2O-FeO-Al_2O_3-SiO_2. We had planned a joint paper, but have been unable to reach agreement on its contents. Thus, I welcome the opportunity to comment on the present paper (Biggar 1983). The first half of his paper is an exercise in model quaternary phase-diagram topology to which I have no objection; my comments refer solely to his discussion of the experimental data.

Twenty-one studies of parts of this system, as well as of closely related systems, have been published, only 7 of which are referred to by Biggar (1983). Where the data from these various studies overlap, there are many small and some large differences in the extent and temperature limits of the field of immiscibility. The main differences, however, involve the K-Al ratio[1] of coexisting melts from bulk compositions starting in the plane leucite-fayalite-silica (i.e., starting with K/Al=1). Dr. Biggar and I differ on the possible significance of these discrepancies. He explains the discrepancies by the assumption that immiscible high-iron and high-silica melts separating from bulk compositions in this plane are not ternary but have K/Al <1 and >1, respectively. I hold that most of the data he uses are from bulk compositions that have lost alkali and hence are no longer in the plane. Although I suspect that the immiscibility field in the system leucite-fayalite-silica may be ternary (except for the effects of ferric iron), the existing experimental studies, and particularly the accuracy of existing electron microprobe data on the results of these experiments, are inadequate to resolve these problems.

Biggar's Interpretation of Roedder's Data in the System K_2O-FeO-Al_2O_3-SiO_2

I do not claim that my (1978) data are complete, correct, or even concordant, and I made many caveats in that paper. However, Biggar (1983) has made a series of statements about my data that simply do not agree with the facts; I address here only some of his points.

"...one has no idea how tightly controlled Roedder's [1978] provisional phase diagram was." Phase equilibria in the immiscibility volume are such that very tight control is needed, both in terms of compositions and run temperatures. Roedder (1978, p. 1603, and Tables 1 and 2) reported

5631 quench runs on 519 compositions. Seventy-seven compositions were in the 1:1 K/Al plane, and 442 others in a series of other planes, 5 of which differed from the 1:1 plane in the vicinity of the immiscibility volume by a maximum of 2 wt.% K_2O or Al_2O_3 (my Fig. 4). Of the 77 compositions in the plane, 43 showed immiscibility. Out in the quaternary adjacent to the 1:1 plane, 60 other compositions intersected the immiscibility volume. Therefore, I believe that the reader does have at least an "idea" how closely controlled my diagram is.

In contrast, Biggar (1978) presents a total of 39 electron microprobe analyses of his quench run results on 9 compositions. It is very difficult to tell from his Table 24 just which of these analyses represent actual observed immiscible pairs, as this important point is not stated, but from the table it is apparent that 2-liquid pairs were analyzed for only 2 compositions: on composition S15 run at 1,213° C, and a series of 6 analyses for composition 1:15, all run at 1,174° C. The remainder of the analyses in his table seem to be of runs that had only 1 liquid.

"Roedder's data (show) the existence of Fa + Tr + 2 Lq over...1,158° to 1,138° C..." This is a point of interpretation rather than of fact. If the system leucite-fayalite-silica were ternary, this isobaric assemblage should be invariant, but I note in several places that this system cannot be truly ternary, because ferric iron (up to 2.3 wt.% Fe_2O_3) is present in all such melts. When the data from my Table 2 on the 12 compositions in the 1:1 plane that show this 4-phase assemblage are considered in light of the various stated observational difficulties, the temperature range is much less than Biggar states. Nine of these 12 compositions show an average of 6° C for this range (actual values, in °C: 8, 9, 5, 10, 6, 4, 4, 5, 6). I believe that this 6° range is mainly due to the presence of ferric iron, and various experimental laboratory problems as detailed by Roedder (1978) are responsible for the greater spreads shown by the other 3 samples (14, 20, and 50° C).

"Roedder's maximum temperature for two liquids... (1,270° C) ... is higher than anyone else's. The evidence for this in his data table is slender ..." Biggar then reinterprets "... Roedder's maximum as being 1,242° C (one run) and 1,226° C (many runs)."

As the intersection of the 1:1 plane with the immiscibility volume may include a maximum temperature for such immiscibility in the quaternary system, the temperature of this point may have considerable significance. In contrast with the above quotation, the actual data, all from my Ta-
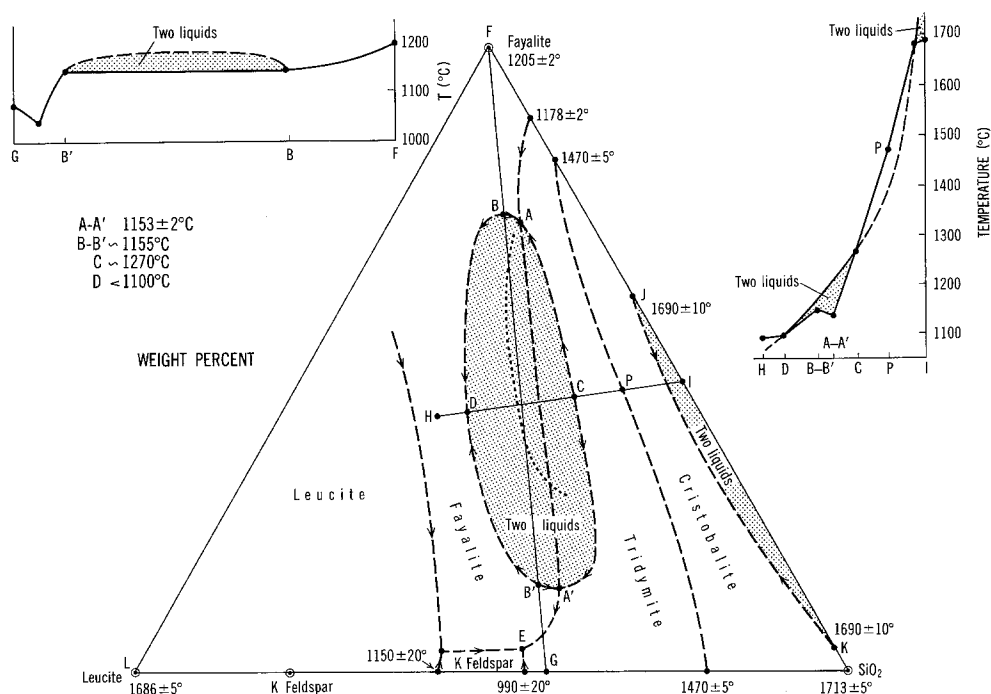
Fig. 1. Preliminary diagram of the system leucite-fayalite-SiO_2 (adapted from Roedder 1951), showing field of immiscibility (shaded) at high temperature (along J-K), and at low temperature (A-B-D-B'-A'-C-A). All compositions run in metallic iron under one atm N_2. Dotted line is the 1,180° C isotherm on upper surface of two-liquid solvus (Watson 1976). The inset figures are T-X sections along the lines G-F and H-I

ble 2, are as follows: In the 1:1 plane, there are 10 compositions on which quench runs bracket immiscibility starting at 1,225° ± 5° C, 6 compositions at 1,242°–1,248° C, 1 at 1,260° C, and 1 at 1,267 ± 3° C. (Note also that these are all *compositions*, on each of which numerous *quench runs* bracket the onset of immiscibility; they are not simply "runs" as termed by Biggar 1983.) The composition yielding 1,267° ± 3° C has an obviously erroneous iron analysis, as stated, but this does not negate the 2-liquid temperature. Even so, I have no reason to believe I hit the maximum with these compositions. Out in the quaternary, on both sides of the 1:1 plane, 22 of the 34 compositions showing 2 liquids plus silica do so at >1,200° C. The "1,270° C was established on the basis of a *combination* of all these data points, plus extrapolation downward on the liquidus field of silica and upward on the 2-liquid solvus, using my own data and those of Watson (1976), plus several established points on the metastable subliquidus extensions of the solvus (e.g., that of Irvine 1976). These all met at 1,270° ± 10° C (*one* such extrapolation was shown on my Fig. 2, reproduced here as Fig. 1).

Sixty of the 103 compositions showing immiscibility fall off the 1:1 plane on both sides; of these, only 2 had 2 liquids come in at temperatures higher than 1,240° C, but 6 of the 43 compositions in the plane had 2 liquids higher than 1,240° C. This suggests that the maximum may lie in the 1:1 plane, and explains the lower values found by Biggar (and others) for compositions that had lost alkali and hence were no longer in the plane.

In addition to the thermal evidence, other facts suggest that the 1:1 plane has some real significance. Thus, the immiscibility field lies astride and is greatly elongated in the 1:1 K/Al plane (Roedder 1978, Fig. 5). In view of the curvature of the isofracts and the very great increase in

the viscosity of melts on approaching the 1:1 plane in the system K_2O-Al_2O_3-SiO_2 (Schairer and Bowen 1955), this ratio apparently has a special significance in melt structure. This is also suggested by 2 other studies. Dickenson and Hess (1980) showed that the 1:1 ratio affected the Fe^{+++}/Fe^{++} ratio in K_2O-Al_2O_3-SiO_2 melts containing iron, and Freestone (1978) showed that when he varied the K/Al ratio of a composition lying in the field of immiscibility, the upper critical mixing temperature (the maximum temperature for 2 liquids) and the compositional separation of the 2 immiscible melts were at a maximum as the ratio approached 1:1.

Biggar's Figs. 9 to 13 are "a representation of the data tabulated by Roedder." Throughout Biggar's replotting of my data on these diagrams, errors and omissions are too numerous to detail completely. Thus, his Fig. 8 has 11 of my data points misplotted, some seriously, 7 points missing, and 1 wrong point plotted. His Fig. 13 has 8 points plotted as my data for 2 liquids " <1,135° C," but there are 11 such in my Table 2. In discussing this figure in the text, where he refers to Fig. 13 as giving data points " <1,140°'" (of which there are 16 in my Table 2 rather than 8), he says that I quote "a minimum of 1,090° C," but my Table 2 shows a minimum of <1,030° C.

Biggar's Re-Interpretation of Data of Biggar (1978) in the System K_2O-FeO-Al_2O_3-SiO_2

"Phases" Without Phase Boundaries (i.e., "Graded Glasses")

Biggar indicates that his "Fig. 14C is a very substantial re-interpretation of the original [i.e., Biggar 1978] data at 1,162° C." This re-interpretation is based on his revised in-

terpretation of "graded glasses" as being valid examples of immiscibility (i.e., they constitute two "phases"). I suggest several more mundane explanations that do not invalidate the phase rule: 1) Variable charge composition due to local inhomogeneities. Such inhomogeneities occurred in my own runs when experimental failure caused oxidation of an iron container, and could similarly occur if the container extracted iron from the melt (as Mo and Pt will do). 2) Change from immiscible to homogeneous melt during a run. Thus, a charge might split (stably or metastably) during run heatup or during a temporary excursion to slightly lower temperatures (or higher pO_2) and then not have adequate time subsequently to level out the rather gross local inhomogeneities caused by the immiscibility.

Loss of Alkali from Melts in the System

Loss of alkali, causing change in bulk composition, has been a constant source of ambiguity in the interpretation of high-temperature phase-equilibrium data on alkali-bearing systems. Its magnitude is not simply a result of the time-temperature combination, because alkalies volatilize much more readily in the presence of a partial pressure of water and/or carbon dioxide, even if this pressure is very low (Kracek 1932). I used the standard Geophysical Laboratory procedure involving preparation of stoichiometric crystalline potassium silicates as the source of alkali for the batches, and made the runs in tightly folded and sealed iron foil capsules. Biggar used the gel technique to prepare his batches and made his runs in open molybdenum capsules. I believe that the possibility of loss of potassium from the final run sample is much greater in this latter procedure.

Hamilton and Henderson (1968) reported *no* detectable loss of K_2O in their tests of melt synthesis by the gel technique, but Biggar shows that his 14 glasses had K/Al that averaged 0.93. This means that 7% of the alkali has gone, and 1 analysis shows 14% loss, placing the bulk compositions well *off* the 1:1 plane, in a part of the diagram where large changes in the phase behavior take place as a result of small compositional shifts, particularly in K:Al ratio (e.g., Roedder 1978, Fig. 5). Even greater losses have been reported by others using gels; Visser and Koster van Groos (1979a) reported loss of *as much as half the starting* K_2O, and their average loss was $\sim 1/4$.

At Biggar's suggestion, in 1979 I had 6 of my original glass compositions analyzed for K_2O and Al_2O_3 by several methods to test the Geophysical Laboratory synthesis procedure. These were all compositions in the immiscibility volume, synthesized to be on the 1:1 plane, but quenched from temperatures just above the immiscible liquid solvus, so that each was a homogeneous glass. The K_2O determination was by flame atomic absorption and posed no problems. The determination of small amounts of Al_2O_3 in the presence of large and variable amounts of iron was not routine, and several methods had to be tried. Thus, the colorimetric method for Al_2O_3 used in the standard rapid-rock method (Shapiro 1975) gave results that averaged 0.22% Al_2O_3 high in 4 samples, which were also run by the atomic-absorption method (here presumed to be the most accurate). The specific amounts of K_2O and Al_2O_3 found by analysis are affected by variation in the iron content, but K/Al should be independent of iron. Table 1 shows that this ratio, by analysis, is very close to that calculated by synthesis. The average of K/Al for all 6 batches is 0.989, and most of the deviation from the expected 1.000 is a result of 1 analysis (18–40).

From the above tests, it appears that little, if any, detectable alkali loss takes place during batch preparation when the modified Geophysical Laboratory procedure is used, but the sample mass here (10 g) is large and the exposed surface is small. As the mass of a quench run (2–3 mg) is much smaller, the possibilities of loss of alkali during quench runs should also be checked, but the amount of material is far too small for wet-chemical analysis. I suspect, however, that volatilization at this stage is also at a minimum, as it requires exposure of the liquid melt to a gas phase (or vacuum). In a typical quench run made in an iron foil envelope, once the charge melts and wets the folded seams, the "exposure" is almost completely eliminated.

Validity of Electron Microprobe Analyses of Immiscible Melts

Biggar and I differ greatly in our evaluations of the accuracy of electron microprobe analyses of these immiscible melts. I question whether microprobe analysis can produce reliable numbers on these samples, on the basis of a series of tests made at the U.S. Geological Survey, some of which are shown in Table 1. Apparently, two main problems exist:

Table 1. Comparison of chemical composition of synthetic glasses in the system leucite-faylite-silica by several methods

Batch[a]	Synthesis				Wet chem. anal.			Elec. microprobe[e]		
	FeO (%)	K_2O (%)	Al_2O_3 (%)	K/Al	K_2O[b] (%)	Al_2O_3[c] (%)	K/Al	K_2O (%)	Al_2O_3 (%)	K/Al
ER3-20A	29.95	4.53	4.90	1.000	4.6	4.92	1.012	4.03	5.15	0.847
ER3-30B	35.93	4.15	4.49	1.000	4.2	4.69	0.962	3.83	4.71	0.880
ER8-10A	10.66	7.71	8.34	1.000	7.5	(8.08)[d]	1.005	6.89	9.01	0.828
ER18-10A	10.59	6.74	7.31	1.000	6.7	(7.18)[d]	1.010	6.22	7.93	0.849
ER18-25	26.10	5.57	6.03	1.000	5.7	6.24	0.989	5.07	6.37	0.861
ER18-40	39.84	4.54	4.91	1.000	4.4	4.99	0.954	3.99	5.06	0.853

[a] Roedder (1978, Table 2)
[b] Flame photometer. F.W. Brown and P.J. Aruscavage, U.S. Geological Survey
[c] Atomic absorption. F.W. Brown and P.J. Aruscavage, U.S. Geological Survey
[d] Calculated from colorimetric determination, which was assumed to be high by 0.22% Al_2O_3
[e] J. Hedenquist and L.B. Wiggins, U.S. Geological Survey (see text)

1) mobility of alkali under the beam, and 2) correction routines. *First,* alkali in such glasses is still mobile, even when the electron beam is defocussed to the maximum extent permitted by the finely intergrown phases in such samples and still hit only one phase. Craw (1981) has shown that potassium mobility under the microprobe beam is a serious problem even with crystalline compounds, and the mobility in glass is even greater than in crystals. In our analyses, an appreciable drop-off in K count rate was observed. *Second,* there are very large differences in "matrix" composition for the 2 members of a pair (e.g., 10 vs. 50 wt.% FeO). This combination of light elements along with extremely variable amounts of a heavy element seriously taxes the available correction routines.

The microprobe analyses in Table 1 were made using an ARL-EMX-SM[2] microprobe automated by the method of Finger and Hadidiacos (1972). A variety of standards were tried but most analyses were made using orthoclase and a basalt glass as standards. Operating conditions were 15 kV at 0.05 μA beam current, and a 10-μm beam (Huebner et al. 1976). Counting was limited to 20 seconds or 20,000 counts, but an appreciable drop-off in K count rate was still observed. Four 20-s counts were taken and averaged (discordant sets were discarded). Correction procedures used were the Krisel control probe system V5A-A6P1 with alpha corrections (for dead time and beam current fluctuation), and the Bence-Albee system with 1968 empirical α-matrix factors. The totals were excellent (average = 99.75), but in all 6 samples, the probe results averaged uniformly lower in FeO (-1.33%) and K_2O (-0.54%), and higher in SiO_2 ($+1.32\%$) and Al_2O_3 ($+0.38\%$) than the compositions determined by synthesis. As iron contents cannot be controlled accurately in synthesis procedures, the amounts of each oxide are not too significant, but the K/Al *ratio* was uniformly low, averaging 0.85. Many more reasonable data but *still* not good agreement resulted when the glasses were used as standards against each other.

Analyses of 4 immiscible melt pairs, using a 5-μm beam and whichever of the 6 glasses in Table 1 was closest as a standard resulted in reproducible differences in K/Al between pair members (1.01 for the low-iron and 0.76 for the high-iron), but some data were inexplicable, and I have no assurance that the results are correct. I do not *know* how much these analytical problems have affected the analyses of the other workers, but Naslund, Watson, and Koster van Groos all agree (personal communications, 1979–1980) that there are serious analytical problems. In the absence of valid and closely similar glass standards, the only real control on the accuracy of these analyses has always been a good summation, but as shown above, that is a necessary but not sufficient criterion, and I must assume that similar systematic errors may well be present in other such analyses in this system and, for example, in analyses of immiscible lunar glasses (Roedder and Weiblen 1970, and later papers in that series).

There have been 15 reports of analyses of immiscible-liquid pairs from natural rocks, and from experimental runs on similar multicomponent compositions (Fig. 2). All but 2 of these data sets show a much lower ratio for the more iron-rich members of the pairs, and *all* values for (Na + K)/Al are <1.0. These differences in ratio between conjugate
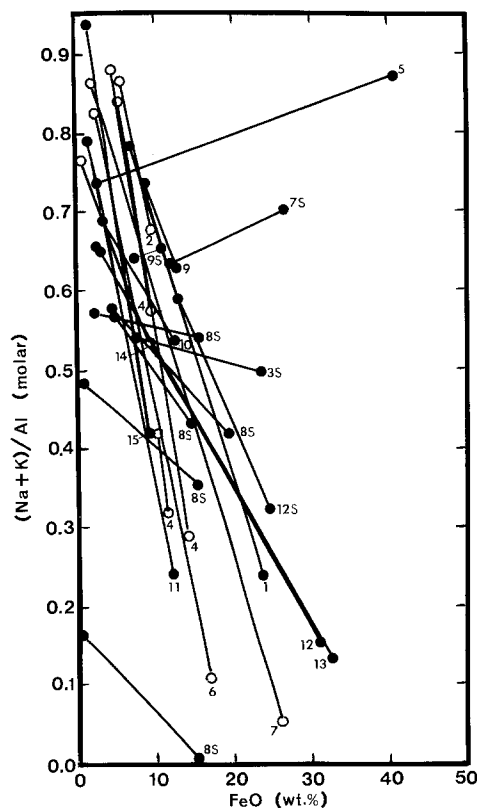
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2 Any use of trade names in this report is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey

Fig. 2. All available analyses of pairs of natural ocelli and their matrices, or of late-stage globules in mesostasis glass, and of some experimental runs on natural or synthetic mixtures (designated "s") having similar compositions, from the literature. Dots = electron microprobe analyses; circles = analyses by other methods (wet chemical, X-ray fluorescence, etc.). "FeO" = (FeO + 0.9 Fe_2O_3). Sources are as follows: 1) Anderson and Gottfried (1971), Hat Creek high-alumina tholeiites; 2) Currie (1975), Ice River; 3) Dixon and Rutherford (1979), averages for 7 pairs of mid-oceanic rift compositions; 4) Ferguson and Currie (1972), Barberton Mountain Land; 5) Fujii et al. (1980) Fuji Volcano. (The very unusual composition of the high-iron globules here, very high in TiO_2 (12.9 and 6.30 wt.%), and low in Al_2O_3 (0.80 and 0.82), has been verified, I. Kushiro, personal communication, 1980); 6) Gelinas et al. (1976), averages of 5 pairs of Archean variolites; 7) McBirney and Nakamura (1974), Skaergaard (high-iron = av. of UZa, UZb, and UZc); 8) Massion and Koster van Groos (1973), one pair shows considerably *more* K and Na in the products than in the starting composition; 9) Philpotts (1971), "just north of the Island of Montreal"; 10) Philpotts (1976), Monteregian province, averages for 9 high-silica and 10 high-iron analyses; 11) Quick et al. (1977), Lunar rock 12013; 12) Roedder and Weiblen (1970), averages for 35 high-silica and 7 high-iron glasses from Apollo 11; 13) Roedder and Weiblen (1971), averages for 15 high-silica and 5 high-iron glasses from Apollo 12; 14) Vogel and Wilband (1978), Winnsboro dike, South Carolina; and 15) Yoder (1973), Breiddalur, Iceland

pairs are probably not just analytical in origin, because 5 of the data sets shown on Fig. 2 involve analytical methods other than electron microprobe.

Biggar's Interpretation of 1982 Data from "Freestone and from Freestone and Powell"

I am at a disadvantage here, because details of these studies are not available to me. (The Freestone reference is a per-

sonal communication to Biggar, and the Freestone and Powell (1983) reference is listed by Biggar (1983) simply as "PhD Thesis, Univ. of Leeds".) From Biggar's Fig. 16, however, it appears that only 9 compositions were studied, and Biggar states that 5% to 13% of the original K_2O was lost from these melts, making comparisons with data from the 1:1 plane difficult at best.

Biggar's Interpretation of Data from Visser and Koster van Groos (1979 a, b, c)

The inadequacies of the documentation in these 3 reports, as indicated by Biggar, and the extreme K_2O losses, make intercomparison of these data with those of other workers too nebulous and speculative to merit further discussion.

Biggar's "Intercomparison of the Re-Interpreted Data"

Biggar's thesis is that "... some of the problems are resolved here by careful consideration of the geometrical construction of the phase diagrams." Here Biggar makes two points. The first concerns the exact sequence of phase changes in the vicinity of the small temperature range where two liquids, fayalite, and silica coexist. This, he indicates, seems "... to occur over too small a temperature range to be easily distinguishable." I agree, and must add that the distinction is rather academic and yields almost negligible changes in the final result; hence, it is of no real consequence to most possible uses of the data. My own tentative interpretation of my data is implicit in the directions of the tielines between conjugate liquids relative to the composition point of fayalite (Roedder 1978, Fig. 3), but this must certainly be up for re-interpretation when more precise data become available.

His second point concerns the deviation from 1:1 of K/Al in coexisting melts from compositions starting in the 1:1 plane. This point is difficult to clarify, because the supporting data require a knowledge of the true bulk composition of each given quench run and of the composition of each of its coexisting melts. The analyses by Visser and Koster Van Groos (1976, 1979a), Biggar (1978), Freestone (1978), Watson and Naslund (1977), and Watson (1976) yield ratios differing from each other and from the 1:1 ratio of the starting materials. However, most of this published work, supposedly on equilibria *in* the 1:1 plane, is based on melts that are known to be out of the plane because of alkali loss, and hence not directly applicable.

The major problem here is whether or not the immiscible melts shown by the immiscibility field boundary ABDB'A'C in the system leucite-fayalite-silica (Fig. 1) lie *in* that plane. *Every* point along that field boundary, from A' through C, A, and B to the point of tangency of a line from fayalite with the curved segment BD *must lie in that plane*. This is obvious from simple geometric considerations, because each of these points represents a melt that started in the plane, and on cooling to that point consisted of fayalite and/or silica plus a single melt. Similarly, each of the points on the balance of the field boundary, through D and B' to A', must also represent liquids actually *in* the plane, because on losing the last tiny droplet of conjugate liquid, the phase assemblage consists solely of the remaining single liquid plus fayalite. There is no restriction on the composition of the first (or last) tiny droplet of conjugate liquid that is in equilibrium with each of these

liquids along the field boundary – they *could* be out in the quaternary system on one (or the other) side of this 1:1 plane – and I have not indicated any tielines across the field for such compositions. However, there are additional constraints. Both liquids *must* lie essentially in the plane in the vicinity of points C and D, and, except for the $\sim 6°$ C "range," also at points A-A', and probably at B-B'.

Melts A and A' do not have to be in equilibrium with each other. If the equilibria are quaternary, melt A', having K/A = 1:1, *could* be in equilibrium with the two solids and a trace of a melt similar to melt A but having a ratio < 1.0; similarly, melt A could be in equilibrium with the two solids and a melt similar to A' but having a ratio > 1.0. This speculation has not been proved, and the 6° C temperature range for this assemblage *could* be solely from the ferric iron component. Note, however, that many of the analyses reported by other workers for conjugate melts from 1:1 compositions fall outside the immiscibility volume in the quaternary system as found by Roedder (1978, Fig. 5).

Any comparison of the various data sets must include the influence of fO_2 and the containers used. My runs were made in closed iron foil envelopes in nitrogen, and hence were essentially in equilibrium with metallic iron. I (1952) found that even the small amount of air trapped inside a "sealed" capsule or iron foil envelope can cause serious problems if not completely replaced with nitrogen before the run. Most of my later quench runs (1978) made use of a prerun nitrogen-flushing procedure. Similarly, the iron foil had to be carefully cleaned before being folded into envelopes, and then, to drive off any organic films, the open envelopes were bright annealed again before filling and sealing, as even a minute speck of organic matter can form an appreciable volume of partly reduced glass in a 2-mg charge.

The use of molybdenum containers (Biggar 1978) adds at least traces of molybdenum to the melt, and in an inert atmosphere, it effectively fixes the fugacity of oxygen in the melt at the $Mo-MoO_2$ buffer. In the range $1,000°-1,200°$ C, this buffer corresponds to about 1 full log unit higher fO_2 than the Fe-FeO buffer (Visser and Koster van Groos 1977). Naslund (1976) found that the field of immiscibility decreases considerably with decrease in fO_2 from 10^{-9} to 10^{-12}, but this change cannot necessarily be extrapolated.

A variety of other potential causes of discrepancy have been ignored in the above discussion, either because they were not considered to be very significant or because data were inadequate to permit an evaluation of their effects. Included here are such items as the stoichiometry and purity of the raw materials, the conditions used for dehydration and crystallization of gels prior to fusion, the homogeneity of run materials, the purity and shape (i.e., capsule, wire loop, etc.) of the container material, the various problems in phase recognition, the calibration of thermocouples and measurement of temperatures, the accuracy of control of furnace atmosphere, and attainment of equilibrium between it and melt, the length of run, and the speed of quench.

Conclusions

1. Many small and some large discrepancies exist among the phase equilibrium data from a series of published reports on the system leucite-fayalite-silica.

2. A comparison of the results obtained, and some additional work, suggest that most of these differences stem from problems in the experimental and analytical methods used.

3. Alkali loss is severe when small-volume samples in this system are exposed to furnace atmospheres, particularly in those compositions starting as gels, so that these compositions, and the phase-equilibrium data from them, are generally off of the 1:1 K/Al plane and do not apply directly to the system leucite-fayalite-silica.

4. The Geophysical Laboratory procedure used by Roedder (1978) for preparation of alkali-bearing melt compositions, though tedious, results in no detectable alkali loss.

5. Several of the published studies provide too few data to permit a complete evaluation of the differences reported.

6. Control of the state of oxidation of iron and local variations in total iron content may cause problems in interpretation.

7. Accurate analysis of these immiscible high-iron and high-silica glasses by electron microprobe is very difficult, and significant systematic errors may be present in published results.

8. The bulk of the data sets on which Biggar bases his reassessment of the of the nature, temperature, and extent of silicate liquid immiscibility in the system K_2O-FeO-Al_2O_3-SiO_2 are not directly comparable, and some of his reassessments are based on misuse of the data of Roedder (1978).

9. Biggar's assumption that compositionally gradational melts can be considered as two immiscible phases is dubious at best.

10. The geometry of the field of immiscibility in the system leucite-fayalite-silica is such that the exact nature of the phase changes within the small temperature range for coexistence of fayalite, silica, and two liquids cannot be resolved by the presently available data sets. Clarification of this problem will require many additional very tight quench runs on very carefully prepared batches.

11. *Individual* high-iron (or high-silica) melts in equilibrium with crystals on the boundaries of the field of immiscibility in the system leucite-fayalite-silica must lie *in* that plane, but the conjugate high-silica (or high-iron) melt with these assemblages may or may not lie in the plane.

12. In bulk compositions with K/Al <1, the partitioning of alkali and alumina between immiscible silicate melts apparently favors a higher K/Al ratio in the high-silica melt than in the high-iron melt, but some unknown fraction of this difference may be purely analytical error.

13. Natural (multicomponent) immiscible systems show a much larger difference in K(+Na)/Al between any two coexisting melts than does the "simple" system K_2O-FeO-Al_2O_3-SiO_2.

14. Resolution of the problem of the K/Al ratio for melt pairs in the simple system may hinge on future improvements in electron microprobe technique for such materials.

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