

The differences between the two studies can be explained perfectly, however, by the assumption that some of immiscibility found by Visser and Koster van Groos took place during quenching, as the melt passed down through a field of metastable subliquidus immiscibility. The existence of such a field under the liquidus surface for silica in the system as I depicted it is self-evident from the geometry of the two immiscibility fields in a T-X section from the FeO-SiO₂ sideline through points C and D on Fig. 1. Furthermore, experimental evidence has been found for the existence of this metastable field, as well as for a metastable extension out under the very flat fayalite liquidus⁷. This evidence consisted of the presence of minute (~1 μm) globules having a high index, presumably high-FeO melt, in those glasses formed on relatively slow quenching, whereas the same charge quenched more rapidly yielded an optically uniform glass. Unfortunately, neither paper provides details on the quenching procedures. In my work, I quenched by dropping the iron foil envelope (~1×5×5 mm) containing the charge on to mercury while still in pure nitrogen. If the results suggested that phase changes had taken place on quench (for example, the minute globules, or dendritic crystals), faster quench was obtained by attaching platinum weights to the charge in the furnace to cause it to sink in the mercury on dropping⁸. All such minute globules were eliminated by this procedure.

The metastable sub-liquidus immiscibility indicated on Fig. 1 was originally drawn solely on the basis of the thermodynamic necessity of metastable extensions of the experimentally determined stable equilibria. It has been verified experimentally by Irvine¹⁰, who determined the stable and metastable phase relations for composition Q (Fig. 1) at 1,350 °C. The stable assemblage consisted of tridymite crystals and a liquid. Irvine was able to realise metastable immiscibility in this composition, with exsolved globules as much as 7 μm diameter, by superheating to 1,550 °C for 1–2 h, then supercooling for 10–15 min before quenching. The metastable solvus was 'roughly bracketed at 1,350 °C', which agrees well with the extension sketched in Fig. 1. Additional corroboration of the phase relations as sketched in Fig. 1 comes from some runs by Watson¹¹, establishing the 1,180 °C isotherm on the upper surface on the stable immiscibility field. He found this isotherm to intersect the stable two-liquid field at point P on the section (Fig. 1).

Metastable sub-liquidus immiscibility is commonly observed in the field of ceramics, and an extensive literature

exists⁹. Visser and Koster van Groos have used a very sensitive test for such immiscibility (electron scanning microscopy on etched surfaces), and they may even have detected such metastable immiscibility in samples that would seem optically homogeneous. Such metastability would explain many of the features they describe that are otherwise extremely puzzling. (Thus the field of immiscibility as drawn by Visser and Koster van Groos indicates a precipitous drop of 517 °C in the liquidus for silica in the system FeO-SiO₂ by the addition of only 1.35% FeO, and the metastable subliquidus extension of the immiscibility field would have to be even steeper). In view of the above evidence, I cannot accept their diagram as representing stable equilibria. I would suggest that the 'submicroscopic' immiscibility reported by them probably is metastable immiscibility from too slow quenching, and that only their coarser globules (as much as to 3 mm) represent stable immiscibility at furnace temperature.

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VISSER and Koster van Groos¹ have delineated a two-liquid phase field in the system K₂O-FeO-Al₂O₃-SiO₂ which is considerably larger than that reported by Roedder². Furthermore, the extent of the revised two-liquid region on the fayalite-silica join contradicts the phase equilibrium data for the system FeO-Fe₂O₃-SiO₂ (ref. 3). In our opinion the new data probably overestimate the extent of the stable liquid immiscibility field of this system for the following reasons.

(1) The submicroscopic glass-in-glass textures found in charges quenched from between 1,250 and 1,400 °C (ref. 1) are probably not equilibrium associations formed at the run temperature. They probably formed as the melt was quenched through a metastable immiscibility field below the liquidus surface. This explanation would account for the anomalous situation of certain conjugate liquid pairs forming

globules no larger than a few tenths of a micron, whereas macroscopic globules up to 3 mm in diameter form in charges differing only slightly in bulk composition¹. The textures figured¹ are identical in scale and morphology to those produced by quenching silicate melts through sub-liquidus immiscibility domes or by heat-treating supercooled silicate liquids^{4,5}.

(2) Previous studies⁶ show that minor amounts of molybdenum (up to 0.5 weight %) are dissolved by melts held in molybdenum capsules, where the oxygen fugacity is buffered at Fe-FeO by gas mixtures. The technique used by Visser and Koster van Groos¹ depends on the equilibration of melt and molybdenum sample container to buffer the oxygen fugacity of the charge, and is likely to be very favourable to the solution of Mo. Experiments in this laboratory show that the addition of 1 wt % molybdenum to the composition 40 fayalite, 26 leucite, 34 silica raises the upper limit of the two-liquid field by >30 °C. This exceeds the difference in temperature between the fayalite-tridymite cotectic and the leucite rich limit of the miscibility gap¹. Solution of molybdenum from the sample container⁶ would extend the stable two-liquid regions, as observed^{1–3}.

Using ⁸⁰Pt ²⁰Rh wire loop sample containers to minimise iron loss from the charge⁷ and controlled oxygen fugacity at the Fe-FeO buffer, we have confirmed the existence of a low temperature stable immiscibility field isolated from the fayalite-silica join, reported by Roedder². Glass beads formed using the wire loop technique have been analysed and show about a 10% loss of K₂O during an 18-h run; the effect of this loss on the geometry of the immiscible field is minor and where we have analysed the run products can be allowed for on the diagram. In conclusion, the statement that "at least for dry magmas an FeO-rich basalt must yield an immiscible granitic liquid during the later stage of crystallisation"¹ would seem to be premature.

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