

VISSER AND KOSTER VAN GROOS REPLY—The data which suggested to us that the liquid immiscibility field was significantly larger¹ than previously determined² were based on two independent phenomena. Runs at high temperatures (1,550 and 1,735 °C), made in molybdenum capsules in an induction furnace, showed extensive development of two immiscible liquids for compositions containing up to 7 wt % $\text{Al}_2\text{O}_3 + \text{K}_2\text{O}$. Spheres up to 1 mm in diameter were formed. The P_{O_2} was bracketed between the Mo– MoO_2 buffer and the Fe–FeO buffer (Fig. 1), and is estimated at 10^{-8} . Because the low-temperature two-liquid field at about 1,250 °C was found with compositions containing 8 wt % $\text{Al}_2\text{O}_3 + \text{K}_2\text{O}$, we thought the two immiscibility fields to be continuous. Therefore we investigated the intermediate temperature range between 1,250 and 1,500 °C. In the runs at these temperatures we found only submicroscopic separation between two liquid phases. We interpreted these as a stable phenomena because quench was relatively fast (5–10 s). Development of submicroscopic separation textures was identical to those at lower temperatures where we found a continuous range from large spheres (2 mm) to submicroscopic textures (Fig. 2a (1)). This suggested some kinetic problem for the phase separation at these temperatures. On the basis of the above we suggested a revision of the liquidus in the system K_2O – FeO – Al_2O_3 – SiO_2 .

Our recent findings, however, indicate that the major criticism of Freestone and Hamilton³ and Roedder⁴ is substantially correct. Thus, a large part of the immiscibility field as depicted in

our paper¹ is metastable, the stable part is in good agreement with Roedder's data². Before elaborating on this, we shall make some remarks on our experimental procedure. Most of our earlier runs were made by wrapping 250-mg samples in molybdenum foil, and sealing under vacuum in quartz tubing. We selected this technique because the wire loop method will most likely result in serious K_2O losses. Bow *et al.*⁷ report 20% loss (open capsules); O'Hara *et al.*⁵ 15% loss (open capsules); Freestone and Hamilton³ 10% (wire loop); while Naslund (wire loop)⁶ considers the loss insignificant. It is very important to keep the $\text{K}_2\text{O} : \text{Al}_2\text{O}_3$ ratio close to 1, or at least at a constant value, because change in this ratio effects the phase relations and the extent of the immiscibility field.

Several high temperature runs were made in an induction furnace, using molybdenum capsules sealed in platinum capsules. In our current research

we use sealed molybdenum capsules in an argon atmosphere. The gas flow through the furnace is set at the Mo– MoO_2 buffer. While these capsules develop hairline cracks during the run, K_2O losses are minimal. Furthermore, quenching times are reduced to about 0.25 s from the previous 5–10 s. As shown in Fig. 1, the prevailing molybdenum buffer, is Mo– MoO_2 , the partial pressure of MoO_3 still very low.

In the experiments, the FeO loss to the sample holder was found to be insignificant; furthermore, the MoO_2 content of the silicate glasses is less than 0.1 wt % (detection limit) in all runs except those made in the induction furnace. Here the MoO_2 content of the glasses was about 0.6 wt %.

With our current method we repeated the high-temperature (1,735°, 1,550 °C) runs. We were unable to reproduce our previous results showing immiscibility textures. Comparison with the previous analytical data show that the $\text{K}_2\text{O} : \text{Al}_2\text{O}_3$ ratio of the earlier runs was very low (0.1) as compared with the new data (0.6–1.1). The MoO_2 content of these glasses is below the detection limit. It seems therefore that the low $\text{K}_2\text{O} : \text{Al}_2\text{O}_3$ ratio, possibly combined with the high MoO_2 content, resulted in the formation of immiscible textures. Results of the larger scale separation were in excellent agreement with our earlier runs. The submicroscopic separation features, however, were not reproduced in most runs owing to a better quenching method.

The submicroscopic phase separation was investigated with an energy dispersion in combination with a scanning electron microscope. Tie-lines of the co-existing liquids are much longer than those determined from the microscopic scale phase separation in the same sample. The lengths of these tie-lines roughly delineate the immiscibility field, as it was shown earlier¹, supporting the revised interpretation that this extend of this field represents the metastable extension of the two immiscibility fields found previously².

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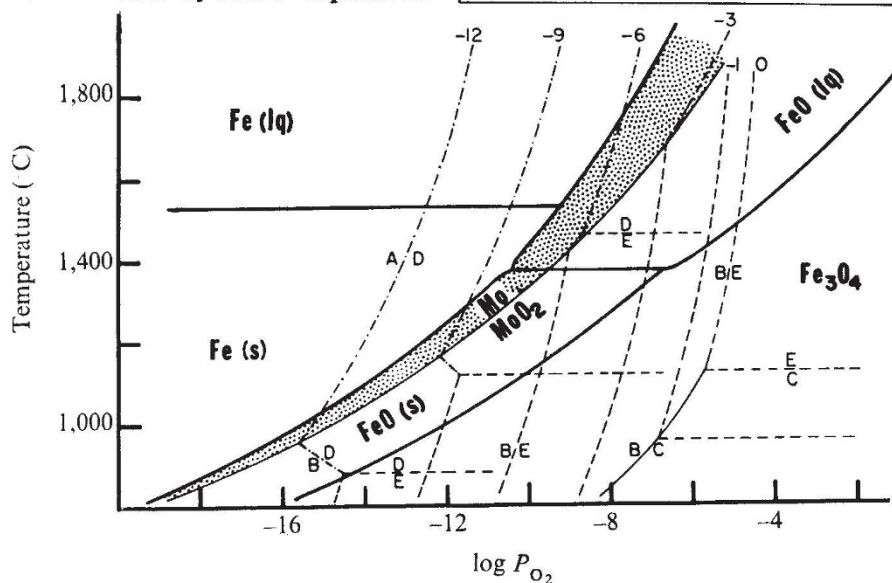


Fig. 1 Systems Fe–O and Mo–O. The heavy line depicts the stability relations of the Fe–O system. The lightly drawn lines depict reactions in the system Mo–O which are independent of the MoO_3 and $(\text{MoO}_3)_2$ vapour pressures, while the dashed lines depend on the $(\text{MoO}_3)_2$ pressure and the dot-dashed lines on the MoO_3 pressure. Runs were made in shaded areas. A, Mo (metal); B, MoO_3 ; C, MoO_3 (liquid); D, MoO_3 (vapour); E, $(\text{MoO}_3)_2$ (vapour). Data from ref. 7.