
Previous high-pressure, high-temperature experiments on compositions corresponding to Apollo 14 very 'low titanium (VLT) glass attempted to elucidate the genesis of this glass by determining a multiple-saturation point on the liquidus [1,2]. However, difficulties were encountered in maintaining the desired amount of FeO in the samples, even when the samples were contained in FeO capsules. [2] showed a plot (reproduced here as Fig. la) of weight percent FeO in the liquids vs. duration of the experiment; their samples lost approximately 1 weight percent FeO per hour. Noting an increase with time in the size and quantity of FeO blebs at the bottom of their capsules, they ascribed the loss to reduction of FeO. Their preferred explanation (a) for the reduction was the establishment of the equilibrium:

\[ 3\text{FeO} \text{(liquid)} = \text{Fe}_2\text{O}_3 \text{(liquid)} + \text{FeO} \text{(bleb)} \]

along with time-dependent coalescence of initially fine FeO blebs which then settled to the bottom of the capsule. [2] predicted that 10-15 percent of the iron in the liquids at high pressure would be ferric. However, standard electron microprobe analyses do not distinguish oxidation states of iron, and all iron in the sample is conventionally reported as FeO. Following [2], we will use "FeO" to indicate total iron expressed in this way. [2] also considered two other explanations for the reduction: (b) time-dependent contamination of the capsule by an external reducing agent such as hydrogen or carbon; and (c) reduction of the sample by residual carbon left from the ethanol used in grinding the starting material [3]. [2] suggested doing further experiments to distinguish among these possible explanations.

We have replicated some of the experiments of [1,2], using starting materials that were identical to theirs, with the following exceptions: Set A was homogenized by grinding not in ethanol but in ultra-pure grade trichlorotrifluoroethane (DuPont "Freon" from SPI Supplies), a cleaning agent with a maximum residue said to be 1 ppm. Set B was ground in ethanol, but 20 percent (atomic) of the iron in the starting material was ferric. ([1] and [2] designed their starting materials so that all the iron was initially ferrous.) If explanation (c) above (reduction by residual carbon from ethanol) were correct and the Freon evaporated as completely as advertised, the experiments of set A should have shown no loss of "FeO" with time. The results (circles in Fig. 1b) indicate a rate of "FeO" loss closely comparable to that reported by [2]. We tested explanation (a) with the experiments of set B: if the initial starting material contained ferric iron in an amount equal to or greater than that required for equilibrium (1), there should be no loss of "FeO" because no blebs of FeO would form and settle from the liquid. The results (squares in Fig. 1b) show an initial gain in "FeO" (from 18.2 to 19.3 weight percent "FeO" in one hour) followed by a drastic drop in "FeO" after 6.2 hours! The gain after one hour can be explained by the reaction of some ferric iron with the capsule to produce additional FeO [the reverse of reaction (1)]; we note parenthetically that the additional FeO was well mixed, for the quenched liquid was remarkably homogeneous. However, the decrease in "FeO" after 6.2 hours seems to require the action of an external reducing agent - the only explanation that seems compatible with all the experiments. Like [2] we do not understand how the reducing agent enters the capsule at an approximately linear rate. Elimination of this problem may well require extensive redesign of the high-pressure cells used for experiments of this type.
The "FeO" content (19.3 weight percent) of the sample with "B" starting material run for one hour is broadly compatible with the assumption that approximately 15 percent of the iron in the liquid remained ferric. Both the natural glasses and the synthetic material should be investigated by means of Mossbauer spectroscopy to determine whether the inferred content of Fe$_2$O$_3$ is real.

REFERENCES


Figure 1. Change with apparent FeO content of synthetic Apollo 14 VLT liquids with run duration. (a) Starting materials were ground in ethanol and run at the pressures (top; in kbars) and temperatures (bottom; in °C) shown for each point [2]. (b) Present experiments, all at 9.3 Kbar and 1460°C, and using starting materials A (ground in Freon) and B (20% of total iron was ferric).

(Figure reproduced courtesy of American Geophysical Union)