A method for studying iron silicate liquids under reducing conditions with negligible iron loss*

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Abstract—In studies of iron silicate liquids under reducing conditions at 1 atm pressure, iron losses from the melt can be minimized by suspending the liquid as a drop from a short segment of fine Pt wire. For a basaltic composition at 1275°C and oxygen fugacities appropriate to terrestrial magmas, iron losses from the melt are less than 0·5 wt. % of the amount present for run times less than about 20 hr.

INTRODUCTION

THE STUDY of phase relationships in iron silicate systems at 1 atm pressure and under conditions more reducing than air has long been hampered by the problem of loss of iron to the crucibles (for example, see MUAN and OSBORN, 1956; ROEDER and OSBORN, 1966; PRESNALL, 1966). Platinum is the normal crucible material for liquidus studies, but under reducing conditions large amounts of iron can be removed from the sample and taken into solid solution in the crucible (TAYLOR and MUAN, 1962).

Under certain conditions of temperature, oxygen fugacity, and run duration, the severity of this problem can be decreased by using alloys of Pd and Ag (MUAN, 1962, 1963). These alloys take up much less iron in solid solution than platinum at comparable oxygen fugacities and temperatures. However, they are not suitable for use at high temperatures when the oxygen fugacity is low, the exact limits of temperature and oxygen fugacity being dependent on the proportions of Ag and Pd in the alloy (MUAN, 1963).

Another limitation, caused by preferential volatilization of Ag from these alloys at high temperatures, may cause a Pd–Ag alloy that is suitable for runs of short duration to become unsuitable for long runs. Since the solid solubility of Fe in Pd–Ag alloys increases as the Ag content decreases, gradual elimination of Ag from the crucible by volatilization causes the crucible to extract increasing amounts of iron from the sample.

Under reducing conditions at and slightly below the oxygen fugacity of the iron–wüstite equilibrium, BIGGAR (1970) found that the use of molybdenum crucibles results in only moderate loss of iron from the sample. However, this metal cannot be used in the range of oxygen fugacity of interest to terrestrial rocks.

The problem of iron loss has been minimized in some subsolidus studies by eliminating the crucible. Instead, a pellet is formed and suspended in the furnace by a small platinum wire, the mass of the wire being sufficiently small that it removes very little iron from the sample even at extremely low oxygen fugacities (for example, see TAYLOR and MUAN, 1962). RIBOUD and MUAN (1962) applied this

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* Contribution No. 207, Institute for Geological Sciences, University of Texas at Dallas.

technique also to liquidus studies and found that a small drop of silicate liquid will remain suspended in a loop of wire. They did not discuss the amount of iron lost to the Pt wire loop.

We have modified the method of RIBOUD and MUAN (1962) so as to reduce even further the mass of Pt wire in contact with the sample, and have determined the amounts of iron lost from a basaltic composition at oxygen fugacities representative of terrestrial basaltic and andesitic magmas. We have found that a drop of basaltic liquid will remain suspended from a short segment of wire. It is not necessary to extend the wire completely around the drop. Also, we have used wire with only half the diameter of that used by Riboud and Muan. They did not state their sample size but if it were assumed to be the same as ours, the mass of Pt in contact with our samples is less than one tenth that of Riboud and Muan.

DESCRIPTION OF THE METHOD

In our studies of a basaltic composition (synthetic Skaergaard chilled margin) we first completely melt the oxide mixture in air, quench it to a glass, and crush it to pass an 80 mesh screen. Sintered pellets are then formed by heating the crushed glass for about 20 min at 1100°C (slightly below its solidus temperature) in a Pt crucible about 5 mm long and 3 mm in diameter. This heating is done in air so as to avoid loss of iron to the crucible. For the crucible, we used a section of Pt tubing folded over at the bottom and stretched on a spindle into the form of a truncated cone so that the top has a larger diameter than the bottom. During sintering, the sample contracts away from the walls slightly, and the shape of the crucible allows the pellet to be tapped out easily. A support is then made that consists of a loop of Pt wire 0·002 in. in diameter formed into a teardrop shape. Another Pt wire of the same diameter is tied with an overhand knot around the bottom of the teardrop-shaped loop. The ends are cut off short and bent into a vee shape with the apex upward (Fig. 1, left). A small groove is made halfway around the center of the pellet with a diamond scribe, and the pellet is slipped into the teardrop-shaped support with the groove facing down (Fig. 1, center). The pellet is then placed in a vertical quench furnace (SHEPHERD et al., 1909) in air at a temperature (1225°C for our basalt) between its solidus and liquidus. When the pellet melts it falls out of the loop and is left as a drop suspended by the short segment of wire at the bottom of the loop (Fig. 1, right). The sample is then lifted out of the furnace and stored for later use.

DISCUSSION

The teardrop shape of the support wire is important. If this wire is wrapped tightly around the pellet, the melt frequently forms as a drop held within the support wire, as in the method of RIBOUD and MUAN (1962). The teardrop shape causes the pellet to be in contact only with the lower part of the support wire. This prevents wetting of the upper part during melting and allows the drop to fall.

Also, we have found greater success when the temperature is kept somewhat below the liquidus so the pellet does not melt too rapidly. If it melts rapidly, it is more likely to stay as a drop held within the teardrop-shaped loop.

For our basalt (which contained 10·70 wt. % total Fe as Fe_2O_3) the amount of iron lost to the platinum wire was very small. At a temperature of 1275°C and a gas mixing ratio (CO_2/H_2) of 24, the Fe–Pt alloy formed in equilibrium with the silicate melt contained 5·1 wt. % Fe, as determined by electron microprobe analysis using the ZIEBOLD and OGILVIE (1964) correction procedure. This concentration was achieved in less than 10 hr and was found to be uniform across the diameter of the wire. It is therefore considered to be an equilibrium value. From a knowledge
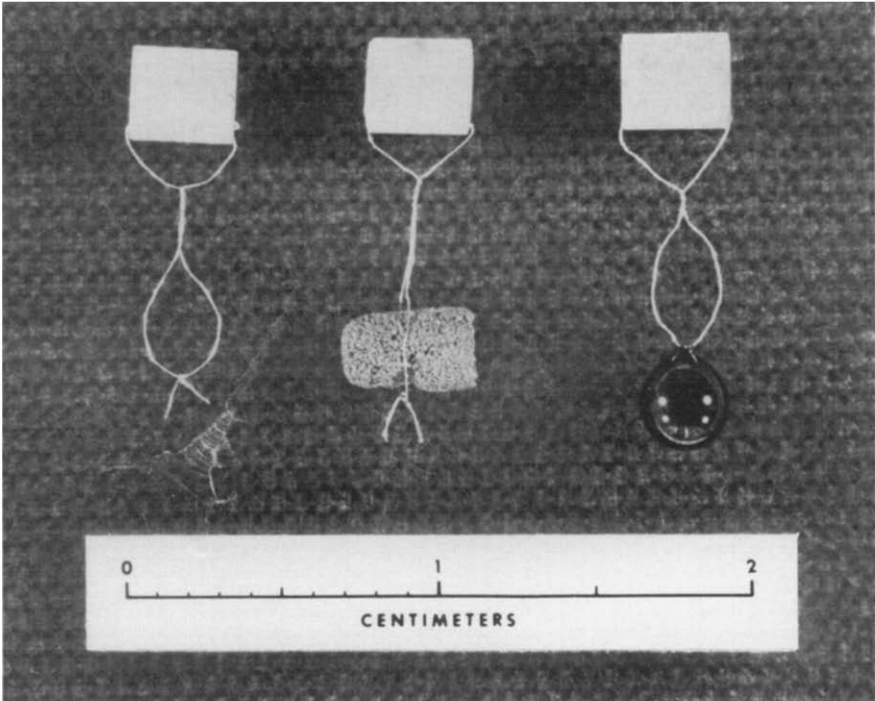
Fig. 1. Three stages of sample preparation. See text for explanation.

of the weight of the sample (0·033 g) and of the wire in contact with the melt (0·00015 g), the wt. % total Fe as Fe_2O_3 in the sample was calculated to be reduced from 10·70 to 10·67 or only 0·3 per cent of the amount present. At the same temperature and a CO_2/H_2 gas mixing ratio of 132, the Fe–Pt alloy contained 2·5 wt. % Fe and the wt. % Fe_2O_3 in the sample was reduced an even smaller amount from 10·70 to 10·68 or 0·2 per cent of the amount present. These calculated iron losses are less than the uncertainty of an electron microprobe analysis ($\pm$ 0·5 per cent of the amount present).

As a check on the iron loss, we have analyzed with an electron microprobe a basalt glass that was held at 1265°C, CO_2/H_2 = 24, for various times up to 7 days. For a 16-hr run, we found, as expected, that the iron loss could not be detected. However, for longer runs of 3 and 7 days, the iron loss was 2 and 6 per cent of the amount present, respectively. These iron losses were uniform throughout the charge and were not confined to a narrow region around the wire. Microprobe analyses of the upper part of the wire not in contact with the melt revealed that these iron losses are caused by iron diffusing along the length of the wire. However, for run times less than about 20 hr, iron losses would still be less than the uncertainty of an electron microprobe analysis, and this amount of time is twice that necessary for equilibration of the Fe_2O_3/FeO ratio of the melt with the furnace atmosphere.

For each range of oxygen fugacity and temperature and for each system studied, the amount of iron loss will, of course, vary. The data given here for the Skaergaard chilled margin basalt composition are intended to serve only as an illustration of the magnitude of iron loss to be expected. Because the CO_2/H_2 mixing ratios of 24 and 132 used here bracket the range of oxygen fugacities found for terrestrial basalts and andesites (FUDALI, 1965; SATO and WRIGHT, 1966), the method would appear to be useful in most studies applicable to terrestrial rocks.

At lower oxygen fugacities, greater iron losses would occur, but the method could still give excellent results with some additional effort. Preliminary experiments could be carried out to determine the exact amount of iron lost under the conditions to be studied. A second composition could then be made that duplicates the first except for a small excess of iron oxide equalling that to be lost during the experiment. Alternatively, Pt–Fe alloy wire could be used, similar to HUEBNER's (1973) procedure of using Pt–Fe alloy foil.

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