American Mineralogist, Volume 58, pages 16-20, 1973

Absorption of Iron by Platinum Capsules in High Pressure Rock Melting Experiments

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Abstract

Samples of hornblende eclogite (olivine basanite composition), containing 0.38 wt percent H_2O bound in amphibole, were sealed in Pt capsules, held above the liquidus at 1250°C, 10 kbar, in ½-inch piston-cylinder apparatus for various time periods, and then sectioned for microprobe analyses. The resultant liquids lost about half of their initial 14 wt percent FeO (total Fe as FeO) to the Pt capsule during an experiment of only thirty minutes duration, and lost 97 percent during a run lasting four hours. This rate is significantly greater than rates of iron loss reported previously, and can affect significantly the interpretation of experimental results in high temperature studies of basaltic and periodotitic compositions.

Introduction

Comparison and interpretation of results from various laboratories in experimental studies of the phase relationships of natural rocks at high pressures are complicated by disagreements in the literature as to magnitude and significance of the effects of iron exchange between samples and various capsule materials. Capsule materials employed include iron, molybdenum, graphite, gold, platinum and various silver-palladium alloys. Of these, only gold is inert with respect to iron in the samples, but gold and the Ag-Pd alloys melt at temperatures below those at which many reactions of petrological interest take place, including the dry melting interval of basaltic rocks. Iron, molybdenum, and graphite capsules are not suitable for experiments including water because they cannot be sealed. Therefore, although platinum absorbs iron, it continues to be used as a capsule material in high temperature studies involving water because no satisfactory substitute is known.

Yoder and Tilley (1962) reviewed in detail the process of absorption of iron by platinum capsules. They noted that dry basalt charges lost small amounts of iron, but concluded that platinum was the most satisfactory metal available for high temperature hydrothermal studies. D. H. Green and Ringwood (1967a,b) concluded from experimental tests that the loss of iron from dry basalt samples to platinum capsules is "not so large as to destroy the basaltic chemistry or even the general character of the normative mineralogy" (1967b, p. 115). Ito and Kennedy (1968), comparing relative effects of iron, graphite and platinum capsules on samples of dry picrite, considered "that a significant amount of iron was taken into the platinum capsule" (p. 182). Ito and Kennedy (1970, 1971) employed iron capsules in subsolidus studies of dry basalts, and found that outer regions of their charges became contaminated with iron from capsule walls. Holloway and Burnham (1972) reported losses of small amounts of iron to $Pd_{60}Ag_{40}$ capsules from charges consisting of basalt, H_2O, and CO_2, which is consistent with the data of Muan (1963). Nishikawa, Kono and Aramaki (1970), studying dry lherzolite compositions, indicated that "molybdenum is suitable as capsule material because of the relatively low diffusivity of foreign materials" (p. 138), although Hansen and Anderko (1958) reported extensive alloying of iron with molybdenum.

We report here a quantitative study of the effects of platinum capsules on the iron content of molten hornblende eclogite at high pressures.

Experimental Methods

Our starting material, a hornblende eclogite from Kakanui, New Zealand, kindly provided by Dr. Brian Mason, has the chemical composition of an olivine basanite. Mason (1968, Table 3, column 1) reports the following analysis in weight percent: SiO_2, 41.20; TiO_2, 3.20; Al_2O_3, 16.35; Fe_2O_3, 2.87; FeO, 11.40; MnO, 0.20; MgO, 10.93; CaO, 9.61; Na_2O, 2.33; K_2O, 0.86; P_2O_5, 0.14; V_2O_3, 0.04; H_2O^+, 0.38; H_2O^-, 0.20; CO_2, 0.00; Total, 99.71. All Fe recalculated as FeO gives 13.98 percent, and the 0.38 percent H_2O is bound in the hornblende. Starting material was ground to pass 200 mesh and then dried at 110°C for 24 hours. Five aliquots, ranging in mass from 5.2 to 5.3 mg, were weighed into platinum tubes sealed at one end. After drying at 110°C for 50 hours, the other end was sealed with a carbon arc.

Each sample was held at 1250° ± 10°C, 10 ± 0.5 kbar (known from previous experiments to be about 40°C above the vapor-absent liquidus) for the desired time in half-inch diameter single-stage piston-cylinder apparatus. Temperature was measured with Pt–Pt 10 percent Rh thermocouples, with no corrections for effect of pressure on thermocouple *emf*. The "piston-out" procedure (Boyd *et al.*, 1967) was followed, and no friction corrections were applied. During a run, the flattened capsule was oriented with length (from 2.8 to 3.1 mm) and width (from 1.4 to 2 mm, see Figure 1) perpendicular to the long axis of the graphite furnace, and thus perpendicular to the greatest temperature gradient. Thickness of flattened capsules averaged 0.5 mm, measured parallel to the long axis of the graphite furnace. Within the graphite furnace, the pressure medium consisted of talc and pyrex glass.

Each capsule—see Boettcher and Wyllie (1968, Plate 1A) for illustration of a capsule after a run—then was mounted in epoxy and ground down until a horizontal section, perpendicular to the long axis of the furnace, was exposed approximately halfway through the capsule. Analyses, made with a 5 micron spot, were recorded at 100 micron intervals along two traverses across the width of each sample, using an ARL-EMX-SM microprobe with basalt glass (S-12g; Murata and Richter, 1966) as a standard. After these analyses had been performed, each capsule was reoriented and ground to expose a plane perpendicular to the analyzed traverses. Analyses in this second plane confirmed that patterns of iron distribution observed in the horizontal traverses (Fig. 1) were not affected by vertical or longitudinal positioning within capsules. Raw data were reduced with a modified version of the EMPADR correction program (Rucklidge, 1967).

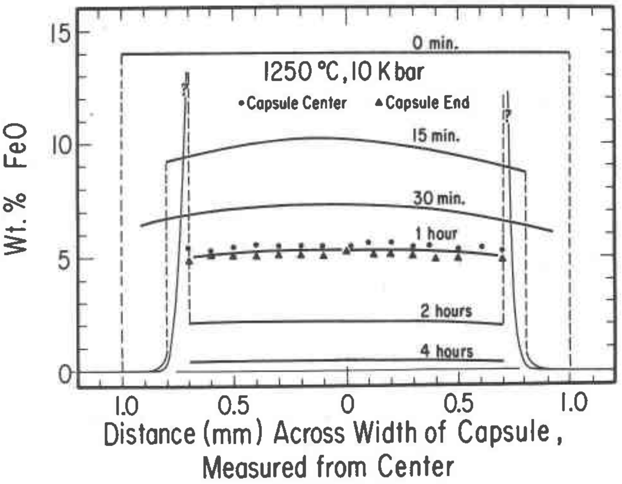

FIG. 1. Distribution of iron (total Fe as FeO) within samples of hornblende eclogite (0.38 wt percent H_2O bound in amphibole) which were sealed in Pt capsules and held above the vapor-absent liquidus for various lengths of time. Heavy solid curves, each labelled with run duration, are averages of microprobe analyses of glass taken along two traverses across the width of each capsule and hence perpendicular to the experimental temperature gradient. Analyses are plotted for the 1 hour run; results for other experiments displayed similar precision. The curve labelled "0 min" is an hypothetical construction of the distribution assumed to exist if a sample were to melt immediately upon being subjected to experimental conditions. Vertical dashed lines represent the interface between glass and platinum of the capsule wall. Light solid curves, which represent measured distribution of iron within Pt, are shown for the 15 min and 2 hour experiments.

Results

Upon completion of experimental runs, samples consisted of clear, light brown glass, without quench crystals or opaque phases.

Analyses for iron content (reported as wt percent FeO) are plotted in Figure 1 as a function of position within capsules and run duration. The curve labelled "0 min" shows the hypothetical starting condition, assuming instantaneous melting of the crystalline charge when the temperature exceeds the liquidus. The horizontal line depicts uniformly distributed iron in the liquid, and the vertical dashed lines represent the drop to zero percent iron in the surrounding platinum.

Each curve for a run of specific duration is the average of two traverses across the short dimension of the polished run slug, one at the center and the other at an end of the capsule, except that the four hour curve is the average of traverses across each end of the capsule. For each run, analyses on the end-traverse reported slightly less iron than those on the traverse across the center. This difference is attributed to the greater surface area of platinum to which the charge is exposed near the ends of a capsule. An example of the difference between traverses for short duration runs is illustrated by the measured values plotted for the one hour run; for other runs the two traverses usually plot closer to the average curve given, and for the longer runs they are barely distinguishable from it. Figure 1 shows that the iron content in each traverse is greater at the center than at the edges of the glass, and that this differential decreases with increased run duration.

As iron migrates from the basaltic liquid, it is alloyed with the platinum of the capsule walls. Distributions of iron within platinum capsule walls are shown for the initial conditions (0-minute hypothetical curve), and after experiments lasting 15

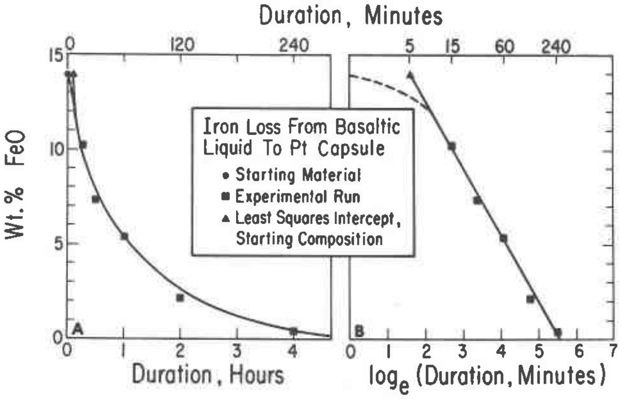

FIG. 2. (a) Change in iron content (total Fe as FeO) of glass at center of capsule as a function of run duration in hours. Solid curve is fitted to five experimental points (squares) and to the least squares intercept (triangle) taken from 2b. Dashed curve joins experimental points to initial composition ("0 min" curve of Fig. 1).

(b) Change in iron content of glass at center of capsule as a function of natural logarithm of run duration (t). Best fit to the five experimental points, derived by least squares technique, is a straight line: wt percent FeO $= 19.81 - 3.58 \ln t$. Extrapolation of this line intercepts the initial iron content (13.98%) at $\ln t = 1.63$ ($t = 5.1$ min). Dashed line indicates route by which initial iron content can be approached at $t = 0$. See text for discussion.

minutes and 2 hours. Similar analyses of platinum in the other capsules, omitted from Figure 1 for clarity, show the iron content of platinum to increase directly with run duration.

The change in iron content of glass at the center of each traverse in Figure 1 is displayed as a function of run duration in Figure 2a, and as a function of natural logarithm of run duration in Figure 2b. A straight line, fitted to experimental data in Figure 2b by the technique of least squares, extrapolates to the initial iron content of the starting material at a run duration of about 5 minutes (marked by triangles in Figures 2b and 2a). A similar plot and extrapolation of iron contents of glass at the ends of traverses in Figure 1, and thus near the platinum, intercepts the initial content at about 2.5 minutes. A non-zero intercept of this sort probably reflects a delay between exposure to run conditions and complete melting of the crystalline sample. Loss of iron from a partially melted sample presumably is slower than from liquid, and this is represented schematically by the dashed lines in Figures 2a and 2b. The delay-interval decreases with proximity to the platinum, suggesting that it also involves the time required for the difference in chemical potential of iron in liquid from that in platinum to become important in liquid remote from the platinum.

Discussion

The results plotted in Figure 2a show that a basaltic liquid containing initially 14 percent FeO and a small amount of dissolved H_2O (0.38 percent), when held at 10 kbar and 1250°C (just above its liquidus temperature) in a platinum capsule, loses about 50 percent of its initial iron in a run of only 30 minutes duration. After 2 hours, about 85 percent of initial FeO has been lost. There is indirect evidence (Fig. 2b) that the rate of iron loss is slower during an early non-equilibrium interval while unmelted crystals remain suspended in the liquid.

There are many factors that influence the rate of iron loss to platinum capsules. Temperature probably is the most significant, while the effect of pressure probably is small. Diffusion through subsolidus crystalline charges may be slower than through liquids, and rates may vary within the melting range according to relative proportions of liquid and crystals. Subsolidus diffusion rates may differ between glass and crystalline starting materials. Diffusion rates may be increased by the presence of water, and may be sensitive to the amount of water available.

Rates of attainment of equilibrium within experimental systems are affected by these same variables. True equilibrium between experimental charge and platinum capsule requires that the iron initially in the charge be transferred almost completely to the platinum (Fig. 2), but this is not the equilibrium state which interests most investigators. Experimental designs must balance the need to keep runs as short as possible in order to minimize iron loss, against the need for runs to be of duration sufficient to attain a reasonable approach to equilibrium among phases in the silicate sample. Several experiments designed specifically to evaluate problems inherent in such a compromise have been reported, but from published data we can discern no consistent patterns of iron loss with respect to run duration, temperature, amount of liquid present, initial starting material, or initial iron content. Most iron losses reported previously were considerably lower than those illustrated in Figure 2 for comparable run durations.

D. H. Green and Ringwood analyzed run products from dry basalt glass starting materials between

9 and 27 kbar in near liquidus runs from 1370°C to 1510°C (1967b) and in subsolidus runs at 1100°C (1967a). Run durations varied from 20 minutes to one hour in near-liquidus runs and from 1 to 4 hours in subsolidus runs. Most iron losses recorded ranged from 1.5 percent to 3.5 percent FeO (total Fe as FeO), or about 13 percent to 28 percent of the initial FeO contents, with no obvious distinction between near-liquidus and subsolidus runs. The presumably higher rate of iron loss from the liquids at greater temperatures apparently was offset by shorter run durations. Their results indicate that the presence of crystals in basaltic liquid does not affect the rate of migration of iron from sample into platinum; this suggests that rates of iron loss shown in Figure 2 may be equally applicable to crystal-liquid assemblages containing dissolved water.

Bultitude and Green (1971) and Ito and Kennedy (1968), studying dry basaltic systems, reported that near-liquidus olivines in platinum capsules are 2-4 mole percent richer in forsterite than are olivines in similar near-liquidus runs in graphite capsules. Run durations at the high temperatures (1450°C to 1550°C) involved in these tests ranged from 5 to 15 minutes.

Iron losses from water-bearing systems were examined by T. H. Green and Ringwood (1968) in experiments with "wet" basaltic and andesitic liquids in crimped but unsealed platinum capsules. The water content of their charges during runs was uncertain. They reported an average loss of 2.3 percent FeO (total Fe as FeO) during runs lasting from 4 to 8 hours at 10 kbar between 920°C and 1040°C. This loss constitutes about 20 percent of the initial FeO content of their samples and lies within the range found for dry basalts at temperatures of 1100°C and above (D. H. Green and Ringwood, 1967a and b).

In a subsolidus study at pressures between 20 and 31 kbar, using dry crystalline ultrabasic compositions, D. H. Green and Ringwood (1970) presented results indicating that rates of iron loss increase markedly between 1200°C and 1300°C. They reported iron losses to platinum capsules of "less than 25% of the amount present." Examination of their tabulated data and recalculation of total Fe as FeO for comparison with the results presented and reviewed above shows FeO losses ranging from 30 percent to 37.2 percent of the total in runs at 1300°C, 1400°C and 1500°C with durations of 2 hours, 1 hour, and 20 minutes, respectively. In contrast, a 2-hour run at 1200°C lost only 12.6 percent of the total FeO, and a 4-hour run at 1100°C lost 13.7 percent. The state of disequilibrium in a 20-minute run at 1500°C and 36 kbar is shown by the loss of 31.4 percent of total FeO from the edge of the sample, and only 21.4 percent from the center.

The high rates of iron loss shown in Figure 2 must have significant effects on determinations of patterns of element distributions among crystals and liquid, even in runs of short duration. Increase of Mg/Fe in basaltic compositions has the effect of increasing liquidus temperatures, provided that no field boundary is crossed; however, if the bulk composition is shifted across a field boundary, the primary mineral can change, for example, from olivine to pyroxene.

These results indicate that capsule materials which are more inert than platinum, such as Ag-Pd alloys, should be used to the limits of their temperature ranges, especially for studies of element distributions among crystalline and liquid phases. Unfortunately, theories of basalt petrogenesis require testing with experiments in basaltic and peridotitic systems with volatile components which are beyond the capabilities of Ag-Pd alloys; thus Pt remains the only known capsule material suitable for use at these higher temperatures. Furthermore, our preliminary results using $Pd_{70}Ag_{30}$ capsules indicate that for the conditions specified in Figure 2, iron losses are as great as those to platinum. More detailed study of the effects of iron absorption by capsules obviously is required for evaluation of experimental results. This is true not only for liquidus studies, but also for subsolidus investigations which require long duration runs, such as those described by O'Hara, Richardson, and Wilson (1971).

Acknowledgments

We thank Dr. Brian Mason for supplying a sample of the hornblende eclogite, and Dr. R. C. Newton for his critical review of this manuscript. Dr. A. T. Anderson kindly provided an analyzed sample of the S-12g basalt glass. We are grateful to the National Science Foundation for grant GA-32266X, to the Advanced Research Projects Agency for apparatus supplied under grant DAHC-15-67-C-0220, and to the Fannie and John Hertz Foundation for the fellowship held by R. B. Merrill.

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Manuscript received May 25, 1972; accepted for publication, September 7, 1972.