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Control of loss of iron to platinum capsules and effects on samarium partitioning between garnet and melt

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Abstract

The influences of temperature, oxygen fugacity, bulk composition, and run duration on loss of iron from silicate liquids to platinum capsules has been investigated. The prior formation of a Fe–Pt alloy skin on the interior of Pt capsules has been achieved using a saturating charge of wüstite, run at 1100° C and an f_{O_2} of $10^{-12.5}$. The rate of diffusion of Fe into Pt is strongly correlated with increasing temperature and decreasing f_{O_2} of the Fe pretreatment.

Garnet in near-liquidus run products made in Fe-treated capsules shows Fe-zonation, with significantly Fe-enriched cores, even in runs in which there is no net loss of Fe. This probably reflects an earlier net flux of Fe from the Fe-treated Pt capsule into the sample that is later reversed by continued Fe diffusion into the interior of the capsule wall. An autoradiographic study was made of Sm partition coefficients (K_D) for garnet/liquid between andesite run in Fe-treated Pt capsules and Ag (non-Fe absorbing) capsules. Comparison of results indicates that where the zoned solid is a small proportion of the run product, valid equilibrium K_D values can be obtained from the ratio of trace element concentration between the rim of the solid phase and the liquid.

Introduction

The loss of iron from experimental charges to noble-metal capsules has long been a serious problem for phase-equilibrium studies (*e.g.*, Yoder and Tilley, 1962; Muan, 1963). Reduction of iron oxides at high temperature is favored as oxygen fugacity is decreased, resulting in a consequent increase of metallic-iron (Fe^0) activity in the charge. This Fe^0 readily diffuses into and forms alloys with the capsule metal. In general, this loss of Fe is a function of temperature, oxygen fugacity (f_{O_2}), capsule size, type of noble metal, bulk composition of the system, and run duration. The latter is important because the continual loss of Fe precludes attainment of equilibrium, as bulk composition becomes a function of run duration (Merrill and Wyllie, 1973; Nehru and Wyllie, 1975; Stern and Wyllie, 1975).

The ideal capsule material must possess the following properties: it must be inert relative to all the principal chemical components of the charge, neither forming solutions nor leading to a change in valence state of any components. In addition, it must withstand high temperatures, be sufficiently malleable to withstand deformation at high pressure, be capable of being welded and, for some uses, be permeable (or, alternatively, impermeable) to hydrogen.

The criteria for chemical inertness and non-brittle behavior rule out graphite and Mo containers for most applications. Ag is not refractory enough for melting experiments in basaltic and peridotitic compositions. Alloys of Ag and Pd (Muan, 1963) have been shown to be effective in minimizing loss of Fe at low pressures, but they alloy with Fe at higher (>10 kbar) pressures (Nehru and Wyllie, 1975; Stern and Wyllie, 1975). Pt and Au alloys (Osborn and Arculus, 1975) are no better than pure platinum with regard to iron solid solution at high pressure (Biggar, 1977; Johannes and Bode, 1978). Iron or steel capsules either prevent net Fe uptake from samples or result in an increase of Fe within samples; however, these capsules maintain f_{O_2} at levels far below that applicable to many terrestrial igneous conditions.

An increasing effort has been devoted to producing Pt capsules (or foils) that have been pretreated (alloyed) with Fe (Huebner, 1973; Helz, 1978; Ford,

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1978; Johannes and Bode, 1978). This treatment acts to minimize the differential chemical potential of Fe (μ_{Fe}) between the wall and the encapsulated powder that drives the diffusion or iron into the capsule.

The effects of T–f_{O_2} on Fe-pretreatment of Pt capsules, using wüstite and hematite saturating charges, where determined. Basalt and andesite were run in Fe-treated Pt capsules to evaluate bulk composition effects, and the change in Fe content of the run products as a function of duration of Fe-treatment was investigated. An autoradiographic study was made of Sm partition coefficients (K_D) for garnet/liquid in andesite, run in Fe-treated Pt capsules and Ag capsules. Because Ag capsules do not absorb Fe, synthesis and reversal runs could be made to bracket an equilibrium K_D value. The K_D results from the Fe-treated runs were contrasted with equilibrium K_D's to determine the feasibility of pre-treatment of Pt with Fe for studies of trace element behavior in mafic and ultramafic compositions.

Experimental technique

Following the procedures adopted by Helz (1978), 3-mm-O.D. Pt tube was cut into 17-mm lengths. One end was sealed by a plug of alumina paste. Sintered wüstite (or hematite) powder was loaded into the capsule to a height sufficient to cover that part in contact with the sample during the run. All traces of the saturating powder were removed above this level to avoid Fe alloying with Pt in this region. This prevented embrittlement and difficulties in folding and welding of capsules.

Capsules loaded with wüstite were placed upright into a gas-mixing furnace, pre-set for the wüstite stability field ($f_{O_2} = 10^{-15.0}$ at 900° C and $f_{O_2} = 10^{-12.5}$ at 1100° C). Such reducing conditions increase the chemical potential of Fe^0 over normal atmospheric conditions, promoting an increase in the rate of diffusion of Fe^0 into the capsule. Higher pretreatment temperatures are practically limited by the oxidation of the heating element of the gas-mixing furnace. For comparison, capsules with hematite were heated at 1100° C in atmospheric furnaces. Usually a slight crimping of the capsule and treatment in an ultrasonic water bath were sufficient for complete removal of both the saturating charge and the alumina plug after treatment.

After removal of the wüstite (or hematite), the end of the capsule sealed by the ceramic was welded. Distilled, deionized water and powdered samples of a 1921 Kilauea olivine tholeiite or a Mt. Hood andesite (Allen and Boettcher, 1978; Apted and Boettcher, 1981) were loaded into the capsule to a level immediately below that of the Fe treatment. The open end was then crimped flush with the sample and welded. Capsules were placed overnight in a 110° C oven and reweighed to detect possible loss of volatile components. Relative losses greater than 1% were attributed to incomplete welds and were discarded. Experimental runs were carried out in piston-cylinder apparatus at f_{O_2} buffered at NNO, as outlined by Apted and Boettcher (1981) and Allen *et al.* (1975). All runs were 48 hours in duration. For the tholeiite, all runs were made at H_2O vapor-saturated, near-liquidus conditions of 20 kbar, 1060° C. The run product assemblage was garnet + clinopyroxene + quench clinopyroxene + glass + vapor. The andesite was run at vapor-saturated, near-liquidus conditions of 20 kbar, 980° C, with garnet + quench mica + glass + vapor as the run product assemblage.

A small part of each run was melted directly on a Mo–strip heater (Brown, 1977), embedded in a plastic mount, polished, and analyzed on an ARL electron microprobe equipped with a Tracor-Northern NS 880 energy dispersive unit. A 15 kV accelerating potential and a beam current of 20 nA on benitoite was used. Some loss of volatile elements, especially Na, is expected in any such fusion (Brown, 1977) but identical fusion procedures for all samples should minimize this factor.

Samples of Mt. Hood andesite were doped with approximately 10 ppm of beta-active ^{151}Sm and run at high-pressure conditions in Ag and Fe-treated Pt capsules. An autoradiographic study (Mysen and Seitz, 1975; Apted and Boettcher, 1981) was made of Sm partitioning between garnet and melt close to the H_2O-vapor-saturated liquidus. A scanning electron microscope equipped with a Tracor-Northern NS 880 energy dispersive unit was used to make integrative counts of Ag $L\alpha$ radiation over a 20 × 20 μm area on nuclear emulsions exposed to these run products, determining quantitative concentrations for Sm in garnet and quench glass. From these data, garnet/liquid partition coefficients, K_D's, can be formulated as a function of capsule treatment.

Results

Figure 1 shows the progressive loss of Fe with run duration from a 1921 Kilauea olivine tholeiite run in an untreated Pt capsule. Over 50% of the original Fe is lost from the sample in the first hour;

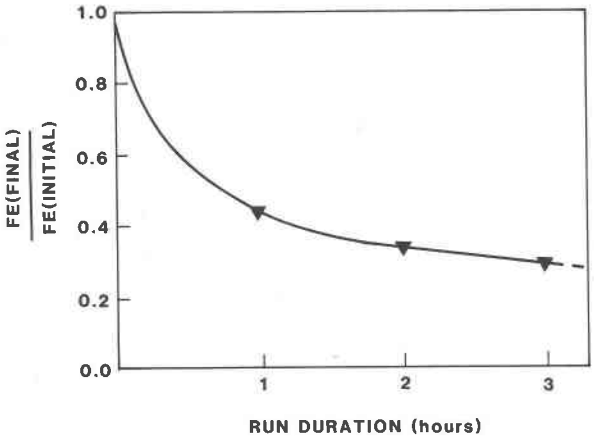

Fig. 1. Plot of loss of Fe from 1921 Kilauea olivine tholeiite to Pt capsule as a function of run duration.

the rate of loss decreases with run duration. For comparison, Stern and Wyllie (1975) found a loss of Fe of almost 70% in the first hour from a natural andesitic liquid in a Pt capsule at 1100° C, 15 wt.% H_2O.

Table 1 compares the effectiveness of wüstite pretreatments with hematite, each run at 1100° C for 3 hours. These Fe-treated Pt capsules were run with the tholeiite at identical conditions, and the run products analyzed for loss of Fe. For equal pretreatment durations and temperatures, the wüstite pretreatment was more effective at minimizing loss of Fe. It was also discovered that the removal of wüstite after pretreatment was, in general, easier than removal of hematite. The extra picking and mechanical working to remove hematite might have damaged the Fe-alloy skin of the Pt capsule, explaining the greater variability in the net loss of Fe in these runs.

Durations of Fe-treatment at several different T–f_{O_2} conditions are plotted in Figure 2 against relative loss of Fe in the run products. Clearly, a decrease in oxygen fugacity or an increase in temperature of Fe-treatment causes a faster rate of Fe uptake (increasing μ_{Fe}) in the Pt capsule. It can also be seen from Figure 2 that so much Fe can be sequestered in the Pt capsule that Fe is added to the charge.

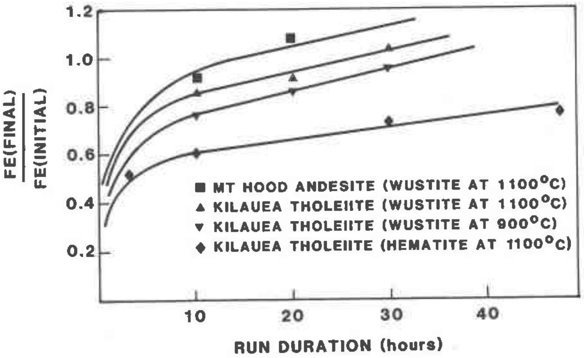

Fig. 2. Loss of Fe in near-liquidus experiments to Pt capsule as a function of duration of pretreatment. Durations for all near-liquidus runs were 48 hours.

Table 1. Comparison of Fe-treatment techniques using 1921 Kilauea olivine tholeiite run at 20 kbar, 1080° C, Ni/NiO buffer for 8 hours.

Wüstite $fo_2=10^{-12.5}$ 1100°C 3 hr pretreatment		Hematite fo_2=air 1100°C 3 hr pretreatment	
Run #	$^{Fe}{}_{Final}/^{Fe}{}_{Initial}$	Run #	$^{Fe}{}_{Final}/^{Fe}{}_{Initial}$
MA-1	0.815	MA-4	0.527
MA-2	0.831	MA-5	0.578
MA-3	0.830	MA-7	0.451
MA-6	0.823		
Ave	0.825±0.006	Ave	0.519±0.052

Table 2 compares the Sm partition data from a Mt. Hood andesite run at 20 kbar, 980° C in both Ag and Fe-treated Pt capsules. The garnet/liquid partition coefficient, K_D, for Sm in the Ag capsules has been bracketed by run reversals (Apted and Boettcher, 1981) and represents equilibrium K_D's at these conditions. The garnets from runs made in Fe-treated Pt capsules show zonation of major elements and Sm concentrations. The garnet cores are Fe-rich relative to the rims, reflecting an early enrichment of Fe in the coexisting liquid.

The Sm concentration also decreases from the garnet core to the rim, although the large portion of the exposed image required for instrumental autoradiography and the small diameter of garnet grains (10 to 60 μm) severely limit resolution of this effect. Because Sm does not form appreciable solid solu-

Table 2. Fe and Sm contents in garnets from Fe-treated Pt-capsule and Ag-capsule runs. Starting material was Mt Hood andesite, run at 20 kbar/90° C vapor-saturated conditions for 8 hours. Bracketed number for $K_D{}^{Sm}$ refers to value of run reversal in Ag-capsule.

	Fe-Pt Capsule (6 analyses)	Ag Capsule (10 analyses)
Garnet Composition (core)	$Alm_{41.1}Py_{31.0}Gr_{27.0}Sp_{0.9}$	$Alm_{38.8}Py_{33.8}Gr_{26.4}Sp_{1.0}$
Garnet Composition (rim)	$Alm_{37.5}Py_{35.2}Gr_{26.0}Sp_{1.2}$	as above
K_D^{Sm} (core)	2.33±0.15	1.92(1.90)±0.12
K_D^{Sm} (rim)	1.97±0.14	as above

tion with Fe or Pt, this variation in K_D probably arises from changes in the bulk chemistry of the garnet and, to a much lesser extent, the coexisting liquid.

Analysis of Sm concentration in the glass does not reveal zonation within the analytical uncertainty of the method. Again, the sampling area for autoradiography limits the spatial resolution of any zonation. The lack of variation in Sm concentration suggests that Fe is homogeneous on the same scale, because the diffusion rate of Sm^{+3} in a silicate melt is expected to be less than that for Fe^{+2} (Hofmann and Magaritz, 1977; Magaritz and Hofmann, 1978). Excellent agreement exists between rim values for K_D^{Sm} in Fe-saturated Pt runs and reversed K_D^{Sm}'s in Ag runs.

Discussion

Excess pretreatment with Fe in Pt capsules is reflected by the formation of Fe-rich cores of garnets and the gain of Fe in some long-duration treatments (Fig. 2). This indicates that a zero net loss of Fe in these experiments is a transitory occurrence. There is an initial gain by the liquid from the Fe-treated Pt capsule, followed by loss of Fe into the capsule walls.

Figure 3 outlines a possible explanation for this process. At t_0, the Pt capsule shows the diffusional profile of Fe introduced by pretreatment. The chemical potential (μ_{Fe}) in the capsule near the interior wall must be higher than the initial uniform μ_{Fe} in the adjacent sample. As time progresses, the profile of μ_{Fe} in the Pt capsule changes in response to two factors. Fe continues to diffuse down the μ_{Fe} gradient into the relatively Fe-poor region of the capsule walls. Simultaneously, Fe will diffuse into the sample, thus raising the μ_{Fe} of the sample (reflected by the iron-rich cores of garnets and the net increase in Fe achieved in some runs). At some time t_1, the μ_{Fe} at the interior surface of the capsule equals that of the sample. Mass-balance arguments demand that the total amount of Fe in the capsule (diagonally ruled area) must be less at t_1 than at t_0. However, the distance of Fe diffusional penetration into the capsule is greater at t_1 than at t_0.

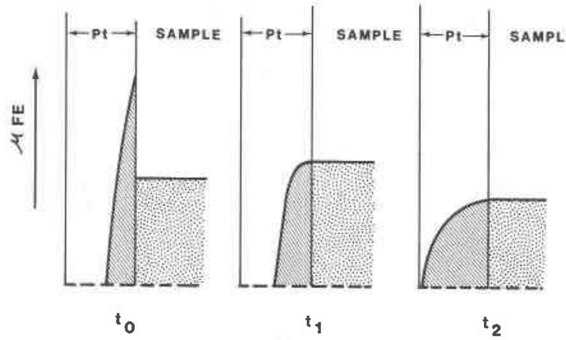

Fig. 3. Schematic interpretation of the change in the chemical potential of Fe (μ_{Fe}) as a function of run duration.

Beyond this stage, the value of μ_{Fe} for the sample is coupled to the value of μ_{Fe} of the Pt at the capsule's interior surface. With greater run duration, continued Fe diffusion into the Pt capsule, away from the sample, results in a gradual lowering of the μ_{Fe} in the sample. At some time between t_1 and t_2, this value of sample μ_{Fe} will match that of the original sample μ_{Fe} at t_0. Further run duration beyond that point will result in loss of Fe from the sample relative to the original μ_{Fe}, and a net increase in the overall Fe content of the Pt capsule (*i.e.*, the diagonally lined area of t_2 is greater than that of t_0).

This construction makes several assumptions. One is that the concentration of Fe, both in the garnet and the whole sample, can be used as a measure of μ_{Fe}. Activity coefficients, relating Fe concentration and μ_{Fe} in a non-ideal multicomponent system, are unknown. This model also requires that Fe diffusion in a hydrous silicate liquid be much faster than diffusion of Fe in Pt. The diffusion coefficient of Fe in Pt is between 10^{-10} and 6×10^{-11} cm^2/sec (Dekhtyar *et al.*, 1974; Helz, 1978) at 1100° C. Thin-source autoradiography studies of dry basaltic liquids (Hoffman and Margaritz, 1977) suggest that diffusion coefficients of about 10^{-8} cm^2/sec would be expected for divalent ions, such as Fe, in basalt at 1100° C. The effect of much higher water contents (Shaw, 1974; Watson, 1979) in these experiments may increase this rate, perhaps by as much as four orders of magnitude. This supports the assumption that Fe gradients in the silicate melt, generated by exchange with the Pt container, are quickly homogenized by the rapid diffusion of Fe in the silicate melt relative to the slower, rate-limiting step of Fe diffusion in Pt.

The autoradiographic data for K_D^{Sm} from the rims of garnets in runs made with Fe-saturated Pt capsules overlap with that for reversed K_D^{Sm} values obtained in Ag capsules. This is not unexpected, for the rim region of the garnets was deposited from a liquid composition similar to that of the quench liquid. The overall quench liquid composition between these runs is probably similar, given the small volume percentage (5 to 10%) represented by the garnets to the overall equivalence in final composition (*i.e.*, no loss of Fe over the duration of the run), and the limited zonation of garnets from the Fe-saturated Pt runs.

Conclusion

The pretreatment of Pt capsules, creating an interior skin of Fe–Pt alloy, can be adjusted to prevent the net loss of Fe from a sample during an experimental run, even at near-liquidus conditions. However, this technique leads to continuous changes of μ_{Fe} in the sample, causing major- and trace-element zonations of crystalline phases. To alleviate this problem would require the creation of a Fe–Pt alloy capsule in which the μ_{Fe} was constant and equal to the μ_{Fe} of the sample. This is not yet a practical solution (Ford, 1978). There is also the problem that such a Fe–Pt alloy would be far less refractory than pure Pt as a capsule material. From analyses of trace-element partitioning behavior, this study has shown that the pretreatment of the Pt capsule's interior can be used to obtain K_D data closely approaching equilibrium values obtained in non-Fe-absorbing capsules, such as Ag. This technique may permit the study of trace-element behavior in natural basaltic and peridotitic composition that require containers more refractory than Ag.

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