

## Pt-Fe alloys in experimental petrology applied to high-pressure research on Fe-bearing systems

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### ABSTRACT

A double capsule technique is described of Pt-Fe alloy inserts in Pt capsules aimed at eliminating Fe loss in high-pressure experiments. Alloy compositions in equilibrium with a silicate melt are calculated following Grove's (1981) approach, which has been extended to include the effect of pressure. The experimental lifetime of the double capsule is limited because of Fe diffusion from the alloy insert to the Pt outer capsule; it is mainly dependent on thickness of the insert and the temperature of the experiment. Pressure causes a small decrease in diffusivity. The lifetime expectancy of the double capsule assembly is given for various temperatures, and it is compatible with the commonly chosen duration of the experiments. The Pt-Fe alloy controls the  $(a_{\text{FeO}})^3/(a_{\text{Fe}_2\text{O}_3})$  and  $f_{\text{O}_2}$  of the sample through the exchange of  $\text{Fe}^0$ . For anhydrous samples, an absolute change in the percentage of  $\text{Fe}^{3+}$  of  $\text{Fe}_{\text{tot}}$  ( $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ) is associated with a relative change of half that percentage of Fe content of the sample. Hydrrous, Fe-bearing samples require the application of an external equilibrium  $f_{\text{H}_2}$  in addition to the use of Pt-Fe alloys. With lower than equilibrium  $f_{\text{H}_2}$ , the sample gains Fe from the alloy and loses  $\text{H}_2\text{O}$ ; with higher than equilibrium  $f_{\text{H}_2}$ , the sample loses Fe and gains  $\text{H}_2\text{O}$ . Preliminary results from three sets of experiments are presented to illustrate the effectiveness of this technique. Fe losses can occur if samples are not properly contained by the alloy.

### INTRODUCTION

Progress in phase equilibrium studies of natural compositions at elevated temperatures and pressures has been seriously hindered by problems with Fe loss from the sample to the capsule. Virtually no reliable high-pressure data exist for natural systems at  $f_{\text{O}_2}$  in the range of  $\text{FeO}/\text{Fe}_3\text{O}_4$ -Ni/NiO (WM-NNO). Many solutions to prevent Fe loss have been proposed for studies at 1 atm based on the use of Pt-Fe alloys (e.g., Ford, 1978; Biggar, 1981; Grove, 1981). From these studies, it is clear that Fe loss can be successfully prevented through the use of Pt-Fe-alloy capsule in equilibrium with sample. In this paper we extend the approach of Grove (1981) to high pressures and describe a technique that allows studies in anhydrous and hydrous Fe-bearing systems.

### EXPERIMENTAL RATIONALE

#### Choice of capsule material

A variety of materials has been used to encapsulate experimental samples in high-pressure experiments. Au and Ag are restricted by their low melting points. Metals of the Pt group dissolve significant amounts of Fe. Mo, Fe, and W interfere chemically and require a low oxidation state in the experimental charge (Biggar, 1970;

O'Hara, 1976; Visser and Koster van Groos, 1979). Graphite-lined Pt capsules (e.g., Leshner and Walker, 1988; Koyaguchi, 1989) also require reducing conditions. Solid mantle phases have been used as container material in the study of solid-melt assemblages (e.g., Stolper, 1980; Takahashi and Kushiro, 1983; Fujii and Scarfe, 1985), but the saturation of the melt with the container material severely limits the compositional range of study. The obvious approach to overcome Fe loss is to use Fe alloys such as Pt-Fe for capsule material. However, in current techniques the composition of the Pt-Fe alloy has not been based on capsule-sample equilibrium and, therefore, appears inadequate (Ford, 1978; Chen and Lindsley, 1983; Baker and Eggler, 1987).

A general analysis of capsule-sample interaction indicates the potential to use the capsule composition to control the activities of components in the sample. At thermodynamic equilibrium in the capsule-sample system, no net transfer of any component occurs between the capsule and the sample, and the chemical potential of each component is constant throughout the system. In experiments, this leaves the option to use a container material in which the solubility of a component is either so low that a negligible amount needs to be transferred to reach equilibrium concentrations in the capsule material or so high that the capsule forms an infinite reservoir for that component, in which case the chemical potential of the component can be controlled with the capsule composition.

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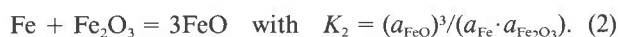
When using Pt capsules in Fe-bearing samples in the  $f_{O_2}$  range NNO-WM, the sample is dominated by  $Fe^{2+}$  and  $Fe^{3+}$  species. However, the concurrent very low  $Fe^0$  activity in the sample still requires high equilibrium concentrations of Fe in the capsule material because of the small activity coefficient for  $Fe^0$  in Pt (e.g., Grove, 1981). This behavior is not unique for Fe in Pt but is observed for alloys of many first-series transition elements with Pt-group metals (Hultgren et al., 1973).

### Capsule-sample interaction

The capsule-sample equilibrium for Fe involves  $Fe^0$ , FeO,  $Fe_2O_3$ , and  $O_2$ . When controlling  $a_{Fe}$  in the Pt-Fe capsule and  $f_{O_2}$  in the system at a given  $P$  and  $T$ , the activities of FeO and  $Fe_2O_3$  are fixed by the reactions

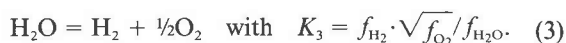


and



Because a sealed capsule is closed to O exchange, adjustments of these activities can only be made internally through transfer of Fe between sample and foil. The composition of the alloy and the sample impose a  $f_{O_2}$  on the system (Eq. 1), whereas the  $a_{Fe}$  of the alloy imposes a specific  $(a_{FeO})^3/(a_{Fe_2O_3})$  on the sample (Eq. 2). To reach equilibrium, the Fe exchange between the alloy and sample is generally minor. For example, a melt with 20%  $Fe^{3+}/Fe_{tot}$  ( $Fe^{3+}$  of  $Fe_{tot}$ ) at NNO and 10%  $Fe^{3+}/Fe_{tot}$  at WM and containing 10 wt% FeO ( $Fe_{tot}$  as FeO) will undergo approximately a 0.5 wt% FeO change ( $Fe_{tot}$  as FeO) adapting from one  $f_{O_2}$  to the other.

Under hydrous conditions  $f_{O_2}$  is also affected by



It is well known that capsules are permeable with respect to  $H_2$  (e.g., Shaw, 1963; Hewitt, 1977). This implies that in studies on Fe-bearing hydrous systems both an externally applied  $f_{H_2}$  and a fixed  $a_{Fe}$  in the capsule are necessary. With knowledge of the equilibrium constant of Equation 3 as a function of  $P$  and  $T$ , the required  $f_{H_2}$  can be readily calculated using appropriate fugacity-composition models (e.g., Holloway, 1987).

### Pressure dependence of the alloy-sample equilibrium

Using the  $f_{O_2}$  associated with the  $Fe_2O_3/FeO$  of a melt (Sack et al., 1980) and including the effect of pressure, we can calculate equilibrium alloy compositions from Equation 1 (cf. Grove, 1981). The  $f_{O_2}$  at 1 bar for constant  $Fe_2O_3/FeO$  and temperature ( $T$ ) may be obtained using

$$\ln f_{O_2} (P = 1) = [\ln(X_{Fe_2O_3}/X_{FeO}) - b/T - c - d_i X_i]/a \quad (4)$$

where  $a$ ,  $b$ ,  $c$ , and  $d_i$  are constants, and  $d_i X_i$  represents the compositional dependence of the  $f_{O_2}$  with the  $Fe_2O_3/FeO$  ratio of the bulk composition (Sack et al., 1980). The effect of pressure ( $P$ ) on  $f_{O_2}$  can be approximated following Mo et al. (1982) with

$$\ln f_{O_2} (\text{at } P) = \ln f_{O_2} (P = 1) + (2\bar{v}_{Fe_2O_3} - 4\bar{v}_{FeO})(P - 1)/RT \quad (5)$$

for the pressure range, where  $\delta v/\delta P = 0$ . The pressure dependence of the equilibrium of Equation 1 may be evaluated from the partial molar volumes of Fe in the alloy and FeO in the melt,  $\bar{v}_{Fe}(\text{alloy})$  and  $\bar{v}_{FeO}(\text{melt})$ . Assuming that the volume of reaction is independent of  $P$  and  $T$  in the experimental range, the following expression was obtained:

$$\ln K_1 = -[\Delta G^0(T) + \Delta\bar{v}_T(P - 1)]/RT \quad (6)$$

Values for  $\Delta G^0(T)/(RT)$  are from Grove (1981), and  $\Delta\bar{v}_T = 4.34 \text{ cm}^3$  was derived for  $T = 1250 \text{ }^\circ\text{C}$  as follows: For the partial molar volume of  $Fe^0$  in Pt a value  $\bar{v}_{Fe}(\text{alloy}) = 7.484 \text{ cm}^3$  was obtained from the molar volume of  $\gamma\text{Fe}$  (fcc structure) at  $1250 \text{ }^\circ\text{C}$  (Skinner, 1966), and another value of  $7.53 \text{ cm}^3$  at  $20 \text{ }^\circ\text{C}$  and  $8.47 \text{ cm}^3$  at  $1250 \text{ }^\circ\text{C}$  was obtained by extrapolating the cell parameters for Pt-Fe compounds with fcc structure (Cabri and Feather, 1975) to an Fe end-member. An intermediate value  $\bar{v}_{Fe}(\text{alloy}) = 8.0 \text{ cm}^3$  was adopted, and a value  $\bar{v}_{FeO}(\text{melt}) = 12.34 \text{ cm}^3$  ( $1250 \text{ }^\circ\text{C}$ ) (Nelson and Carmichael, 1979) was used. The volume term in Equation 6 is not important. At  $1250 \text{ }^\circ\text{C}$  and 10 kbar, this term contributes less than 3% to the value of  $\ln K$ . The calculation of the alloy's  $a_{Fe}$  is thus dependent on our ability to determine  $f_{O_2}$  of the melt properly.

With a value for  $a_{FeO}$  and using the calculated  $f_{O_2}$  for a bulk composition of known  $Fe_2O_3/FeO$ , the  $a_{Fe}(\text{alloy})$  can be calculated from Equation 6. We used  $a_{FeO} = X_{FeO}$  since Grove (1981) showed that for a diverse range of natural magmas this did not cause a much poorer fit in his regression to derive the constants of Equation 6. Using the activity-composition relation of Heald (1967), the equilibrium alloy composition can be obtained. In this procedure a pressure effect on  $\gamma_{Fe}$  in the alloy has not been taken into account (Gudmundsson and Holloway, 1989). The pertinent numerical values to perform these calculations are summarized in Appendix 1.

## EXPERIMENTAL METHOD

### Capsule preparation

A double capsule design was developed in which an outer capsule of Pt (wall thickness, 0.1 mm) is lined with a Pt-Fe alloy foil that is 0.025–0.1 mm thick. The thicker foils were used in experiments of longer duration. The foil insert is shorter than the capsule so that only the outer Pt capsule is welded after both the capsule and the foil are crimped shut. The foils are prepared by uniformly electroplating a thin Pt cylinder. The weight gain from plating determines the Pt-Fe ratio of the foil. After plating, the foils are annealed to produce a homogeneous foil. Details of the plating and annealing procedure are described in a manual (van der Laan and van der Laan, unpublished data), which is available upon request. The design is similar to that of Chen and Lindsley (1983), but

TABLE 1. Starting compositions for experiments

Sample	TGI*	Margi**	Bonin**	CV-46**	TT152†
SiO <sub>2</sub>	59.66	54.93	58.82	59.34	50.63
TiO <sub>2</sub>	0.44	0.51	0.14	0.51	1.88
Al <sub>2</sub> O <sub>3</sub>	13.57	13.15	11.06	10.62	13.91
Fe <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.00	0.00	2.27
FeO	6.33	8.20	8.43	9.27	10.20
MgO	9.66	11.52	11.71	12.57	6.56
CaO	6.25	10.21	7.79	5.74	11.42
Na <sub>2</sub> O	2.66	1.17	1.61	1.37	2.64
K <sub>2</sub> O	1.30	0.26	0.42	0.49	0.17
P <sub>2</sub> O <sub>5</sub>	0.13	0.04	0.02	0.10	0.21
Total	100.00	99.99	100.00	100.01	99.88

\* Prepared as gel.

\*\* Details about compositions are described in van der Laan et al. (1989).

† TT152-21, basalt glass from Juan de Fuca ridge segment 6. Major elements analyzed on the University of Washington ARL-EMS electron probe (J.R. Delaney, unpublished data).

we used a different method of plating and annealing, which resulted in more homogeneous foils.

### Starting materials and experimental technique

Three sets of experiments were performed with the starting materials listed in Table 1. The first data set was obtained using three boninite and one sanukitoid composition (Table 2). The experiments were performed in an internally heated pressure vessel (IHPV) (Holloway, 1971), equipped with a double-wound W furnace, that allowed heating rates to 450 °C/min. The pressure medium was Ar. Temperature was controlled to within 3 °C, but a gradient of 25–30 °C was usually observed with respect to a second thermocouple at 8 mm vertical distance. The reported temperatures (Table 2) are averages of the two readings; they are believed precise to within 5

°C because of the constant capsule-thermocouple geometry for all experiments and the reproducibility of the experiments. Pressure, measured using high-precision Heise gauges and a Harwood manganin cell, is accurate to within 1%. The samples were quenched within seconds by turning the vessel vertical, allowing the capsules to drop into the cooler part of the furnace.

The second data set (Table 3) consists of two experiments, JED-2 and JED-3, on a natural basalt glass (Table 1) under H<sub>2</sub>O-saturated conditions. They were done in an IHPV of different design (Holloway, unpublished data). Conditions were 1160 ± 30 °C at 310 bars and 1170 ± 30 °C at 520 bars with an external P<sub>H<sub>2</sub>O</sub> of 5 and 10 bars, respectively. Duration was 2 h. Details of these experiments will be published elsewhere (Dixon, in preparation).

The third data set (Table 3) consists of a few experiments on the same basalt glass as in set 2, conducted in a ½-in. piston cylinder apparatus using talc assemblies. The experiments were at 1300 ± 10 °C and 10 ± 0.5 kbar nominal pressure (hot piston in) for 6 h.

After the experiments, the capsules were weighed, sectioned, polished, examined microscopically, and analyzed. The first set was analyzed with a JEOL 35CF SEM with Tracor Northern EDS using ZAF data correction for the Pt-Fe alloys (with pure metal standards) and using the Bence and Albee correction (1968) for the silicates (with the common mineral standard set). For the distance measurements of the diffusion profiles, the magnification scale bar was calibrated on a diffraction grating replica. The other experiments were analyzed on a JEOL 733 Superprobe with CIT-ZAF correction. Fe<sup>3+</sup>/Fe<sup>2+</sup> was determined for all the glassy products of the second and third set of experiments using wet chemistry (Sack et al., 1980). H<sub>2</sub>O contents were determined by FTIR spectros-

TABLE 2. Experimental conditions and results on boninites (data set 1)

Sample	Experiment	Duration (min)	Phases*	P total (kbar)	T (°C)	Wt%** H <sub>2</sub> O	FeO-total gain†	Olivine†		% Fe <sup>3+</sup> (based on K <sub>0</sub> )	% Fe <sup>3+</sup> (calculated)‡	Wt% Fe in Pt§	
								Forsterite	K <sub>0</sub> '			Start	End
Margi	31.4	28	L + ol + opx	1.0	1215	3.0	1.5	88.3–88.8	0.267–0.28	6.5–11.0	14.2	6.1	
	25.2	30	L + ol + opx	1.0	1220	1.6	0.8	87.2	0.335		11.5	7.6	
	26.3	30	L + ol + opx	1.0	1240	1.6	1.0	87.7	0.294	2.0	12.7	6.6	
	42.1	26	L(Q) + ol + opx	4.0	1200	4.0	1.3	88.8	0.273	9.1	15–18	5.7	4.8
Bonin	30.4	30	L + ol + opx	1.0	1278	1.0	–0.4	90	0.290	3.4	16–19	5.2	4.4
	46.1	27	L + ol + opx	1.8	1210	4.2	0.3	90.2–91.1	0.234–0.261	13.1–21.9	26.0	3.2	
	46.2	27	L + ol + opx	1.8	1210	4.7	0.4	90.7	0.243	18.9	26.1	3.2	
	47.2	27	L(Q) + ol	3.0	1180	6.1	0.5	90.3–91.2	0.226–0.252	16.0–24.6	22.8	3.8	
TGI	47.3	27	L(Q) + V + ol	3.0	1180	6.6	0.0	90.4–91	0.246–0.264	12.0–18.1	21.3	3.9	
	31.2	28	L + ol	1.0	1215	3.4	1.5	91.6	0.202	32.5	14–17	5.9	5.0
	47.4	27	L + ol	3.0	1180	5.0	0.5	88.0–90.6	0.263–0.345	12.4	20.9	4.1	4.2
	45.1	27	L + ol + opx	3.0	1240	2.2	0.0	89.6–90.9	0.274–0.317	8.8	18.4	4.4	4.4
CV-46	49.3	27	L(Q) + ol	7.5	1107	10.9	0.5	90.2–90.9	0.253–0.275	8.3–15.5	21.2	3.9	3.7
	46.4	27	L + ol + px	1.8	1210	4.9	0.4	89.7–90.0	0.257–0.265	11.6–14.5	25.5	3.2	
	40.2	27	L(Q) + V + ol	2.0	1181	6.0	2.2	87.2–89.1	0.238–0.286	4.7–20.6	16–21	5.3	3.9
	40.3	27	L + V + ol + cen	2.0	1181	7.1	1.5	87.1–89.4	0.246–0.307	18.0	15–16	5.6	5.2

\* L = liquid; Q = quench crystals; V = vapor; ol = olivine; opx = enstatite; cen = clinoenstatite; px = ortho- and clinoenstatite.

\*\* Estimated error: less than ±0.5 wt%.

† Error margins discussed in text.

‡ Range is calculated with start and end alloy compositions.

§ Error: ±0.2 wt%.

TABLE 3. Experimental conditions and results on basalt glass (data sets 2 and 3)

Sample	Experiment	Duration (h)	P total (kbar)	T (°C)	Wt% H <sub>2</sub> O*		FeO total change	Measured**			Calculated			Wt% Fe in Pt‡	
					Start	End		% Fe <sup>3+</sup>	FeO	Fe <sub>2</sub> O <sub>3</sub>	% Fe <sup>3+</sup> †	FeO	Fe <sub>2</sub> O <sub>3</sub>	Start	End
TT152	JED-2	2	0.31	1160	0.36	1	-0.5	17.9	9.6	2.33	19-21	9.34	2.66	6.5	6.5
	JED-3	2	0.52	1170	0.36	1.4	-0.4	21.5	9.26	2.82	20-22	9.33	2.77	6.1	6.1
	JdF-1	6	10	1300	0.36	n.d.	-4.4	5.7	7.35	0.5	6.1	7.67	0.55	11.7	10.4
	JdF-3	6	10	1300	0.36	n.d.	-4.8	14.6	6.32	1.2	6.1	7.3	0.53	9.7	10
	JdF-5	6	10	1300	0.36	1.7	-6.2	10.5	5.37	0.7	6.7	5.97	0.48	6.6	9.1
	JdF-6	6	10	1300	0.36	2.1	-1.8	1.7	10.22	0.2	5.5	10.01	0.65	14.5	11.8
	JdF-7	6	10	1300	0.36	2.1	-2.5	12.3	8.5	1.33	12.9	8.66	1.43	4.7	6

\* Error: less than 10%.

\*\* Relative error is 5% in % Fe<sup>3+</sup> in JED experiments (cf. Christie et al., 1986); other errors discussed in text.

† Range in values is obtained with minimum and maximum temperature of the experiment (see text).

‡ Error: less than 0.2 wt%.

copy using the molar absorption coefficients of Dixon et al. (1988).

## RESULTS AND DISCUSSION

### Lifetime of the capsule assembly

A concentration step exists between the Pt-Fe foil and the Pt capsule, causing Fe to diffuse across the foil-capsule interface during the course of an experiment (Fig. 1). Eventually Fe at the foil-sample interface will be affected, which limits the foil's effective life span.

The temperature dependency of Fe diffusion in Pt at 1 atm and at 1100–1400 °C was determined by Berger and Schwartz (1978). Data concerning the pressure dependency were not available and have been determined from the first set of experiments—those on boninite compositions (van der Laan et al., 1989). In these experiments, temperatures were usually reached within 15 min and in less than 3 min after reaching 900 °C. Experiments were carried out between 1100 and 1300 °C at 1 kbar to 7.5 kbar and accurately timed durations were between 25 and 30 min. The Fe concentration profile was measured with SEM-EDS on a cross section perpendicular to the interface.

Concentration gradients never developed over more than 20 μm on each side of the interface, much less than the foil or capsule thickness. A value for the Fe-diffusion coefficient was derived from the profile by regressing the data to fit the solution of Fick's second law for diffusion between two semi-infinite media (Shewmon, 1963). The diffusion coefficient was assumed to be independent of composition in the Fe range studied, 3.2–7.6 wt%. The concentration profile across the interface is described by

$$C(d,t) = \frac{1}{2}C_0[1 - \operatorname{erf}(z)] \quad (7)$$

where  $C_0$  = initial concentration of Fe in foil,  $d$  = distance from the interface,  $z = d/\sqrt{4Dt}$ ,  $D$  = the diffusion coefficient, and  $t$  = time. The value of  $z$  is determined by rearranging Equation 7 and then taking the inverse error function of the concentration term  $1 - 2C(d,t)/C_0$ . Values for  $D$  were obtained by plotting  $d$  against  $z$ . Diffusion coefficients thus obtained were pressure and temperature

specific. Multiple profiles were measured on a single sample, and average diffusion coefficients for each sample are reported in Table 4.

A multiple linear regression of  $\ln(D)$  vs.  $1/T$  and  $(P - 1)/T$  yielded the pressure and temperature dependence of the diffusion coefficient (Shewmon, 1963) of

$$D = D_0 e^{-(Q/RT) - \Delta V(P-1)/RT} \quad (8)$$

A weighting factor was applied to the averaged  $D$ -values based on the observed temperature gradient during the experiment. This factor was calculated as  $100/\Delta T$ .

Our values for  $D_0$ ,  $Q$ , and  $\Delta V$  together with the values of Berger and Schwartz (1978) are presented in Table 5, and our values with the extrapolated 1 bar and 10 kbar diffusivities are shown in Figure 2. The slightly higher  $D$  values found in our study compared with those of Berger and Schwartz are attributed to diffusion of Fe during the heating stage before the temperature of the experiment was attained. The activation volume of diffusion ( $\Delta V = 3.26 \pm 0.98$  cm<sup>3</sup>/mol) contributes a small decrease in  $D$  with pressure. It needs mentioning, however, that the  $P$  and  $T$  conditions of the experiments roughly correlate; experiments at higher  $P$  are generally conducted at lower

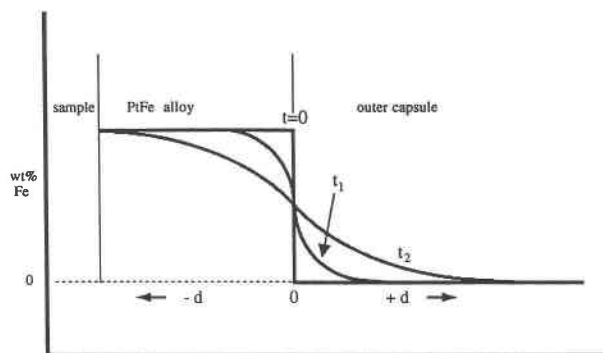


Fig. 1. Progressive homogenization through Fe diffusion across the interface between the foil and outer capsule as described by Equation 7. Eventually the Fe content at the foil-sample interface will be affected.

TABLE 4. Results of the Fe diffusion measurements

Experiment	<i>P</i> (kbar)	<i>T</i>	$\Delta T$	<i>D</i>		<i>R</i> <sup>2</sup>	$1\sigma R^2$	No.	<i>N</i>	$1\sigma N$
		(°C)		(10 <sup>-10</sup> cm <sup>2</sup> /s)						
27	1	1273	10	1.659	0.232	0.973	0.037	4	7.5	0.3
29	1	1265	45	2.888	0.370	0.987	0.005	4	12.25	3.6
30	1	1274	17	3.192	0.906	0.994	0.001	2	9.5	1.0
31	1	1210	15	0.976	0.113	0.993	0.005	3	8.33	0.6
33	3	1262	14	3.237	0.441	0.990	0.007	3	11.33	2.1
34	7	1270	16	1.801	0.128	0.991	0.005	4	9.5	1.3
35	7	1241	8	1.377	0.179	0.994	0.003	5	7.2	1.8
37	7	1207	17	0.832	0.130	0.989	0.010	3	7.67	2.3
40	2	1181	12	0.721	0.138	0.990	0.007	3	9.33	3.8
41	4	1225	13	0.992		0.996		1	14	
42	4	1200	12	0.779	0.068	0.996	0.003	6	5.67	2.6
45	3	1240	16	1.378	0.093	0.994	0.002	4	10.75	1.3
47	3	1180	13	0.509	0.036	0.991	0.004	3	7.67	1.2
49	7.5	1107	15	0.182	0.017	0.990	0.014	6	5.83	1.3

Note: *P* = pressure; *T* = temperature and range ( $\Delta T$ ); *D* = per experiment averaged diffusivity in cm<sup>2</sup>/s and the standard error in its mean value ( $1\sigma D$ ); *R*<sup>2</sup> = mean *R*<sup>2</sup> of goodness of fit and its standard deviation ( $1\sigma R^2$ ); No. = number of profiles contributing to the average; *N* = average amount of points per profile and the standard deviation in the average number of points contributing ( $1\sigma N$ ).

*T*. As an artifact of this correlation, *Q* and  $\Delta V$  obtained by regression become correlated which introduces additional uncertainties in their values.

Based on our 1-bar diffusion coefficients (highest mobility), a conservative estimate for the lifetime of these foils was calculated as a function of thickness and the rate of diffusion at the temperature of the experiment:

$$t_d = d^2/(4Dz^2) \quad (9)$$

where *d* represents the thickness of the foil and *z* is the argument of the error function erf(*z*). Values of *z* were obtained by calculating the erf(*z*) corresponding to changing values of *C/C*<sub>0</sub>. In Equation 7 a value of erf(*z*) = 1 corresponds to no change in foil composition. It is also noted that doubling the foil thickness results in a fourfold increase in the lifetime of the foil. Figure 3 shows the lifetime of a foil 0.1 mm thick (*t*<sub>0.1mm</sub>) as a function of temperature. This figure can be used to estimate the potential lifetime (*t*<sub>d</sub>) of any foil of thickness *d* (in millimeters) since

$$t_d = (d/0.1)^2 \cdot t_{0.1mm} \quad (10)$$

This expression is strictly valid only for an alloy adjacent to the sample that still has its original composition, that is, for a semi-infinite couple geometry.

### Changes in sample composition

Our experiments were not designed to test this double capsule technique, and they are complicated by hydrous conditions. The experiments demonstrate the intricacies of multiple redox equilibria and the importance of H<sub>2</sub>

buffering for hydrous samples. Three cases emerge: (1) Fe content of a sample increasing without H<sub>2</sub> buffering, (2) Fe content remaining constant under equilibrium external *f*<sub>H<sub>2</sub></sub>, and (3) Fe content decreasing with higher than equilibrium external *f*<sub>H<sub>2</sub></sub>. The presence of H<sub>2</sub>O in the capsule and the transport of H<sub>2</sub> through the capsule wall indirectly create an additional O<sub>2</sub> source or sink; e.g., reduction of FeO or Fe<sub>2</sub>O<sub>3</sub> is accommodated by formation of H<sub>2</sub>O, whereas values of *f*<sub>O<sub>2</sub></sub> remain in agreement with the alloy-sample equilibrium. Mass balance for O<sub>2</sub> should be maintained as long as O<sub>2</sub> is not transferred across the capsule wall. In order to calculate the O<sub>2</sub> mass balance, H<sub>2</sub>O contents have to be accurately known before and after an experiment. Compositional parameters of all experiments are listed together with the experimental conditions in Tables 2 and 3.

### Boninite experiments

In the first set of experiments on boninite-H<sub>2</sub>O, no external H<sub>2</sub> pressure was applied, and short durations of 25–30 min were chosen to reduce H<sub>2</sub> loss. Temperatures were at near-liquidus conditions. Loss of H<sub>2</sub> (and thus H<sub>2</sub>O) continuously increased *f*<sub>O<sub>2</sub></sub> during the experiment. The glasses of the products are heterogeneous with respect to Fe, and values represent averages, with Fe<sub>tot</sub> as FeO varying by as much as ±0.7 wt% FeO. Most samples gained Fe, but the exchange of Fe was minor: in nine out of 16 experiments less or equal 0.5 wt% FeO, in six between 0.8 and 1.5 wt%, and in one 2.2 wt%.

In the experiments a decrease in alloy Fe content is accompanied by an increase in Fe<sub>tot</sub> (as FeO) of the melt.

TABLE 5. *D*<sub>0</sub> and the parameters *Q* and  $\Delta V$  for the *P* and *T* dependence of Fe diffusion in Pt

<i>D</i> <sub>0</sub> (cm <sup>2</sup> /s)	<i>Q</i> (kJ/mol)	$\Delta V$ (cm <sup>3</sup> /mol)	
0.50 (+0.49/−0.25)	275 (±8.4)	3.26 (±1.0)	this study
2.5 (+1.6/−0.9) 10 <sup>-2</sup>	243.4 (±6.3)		Berger and Schwartz (1978)

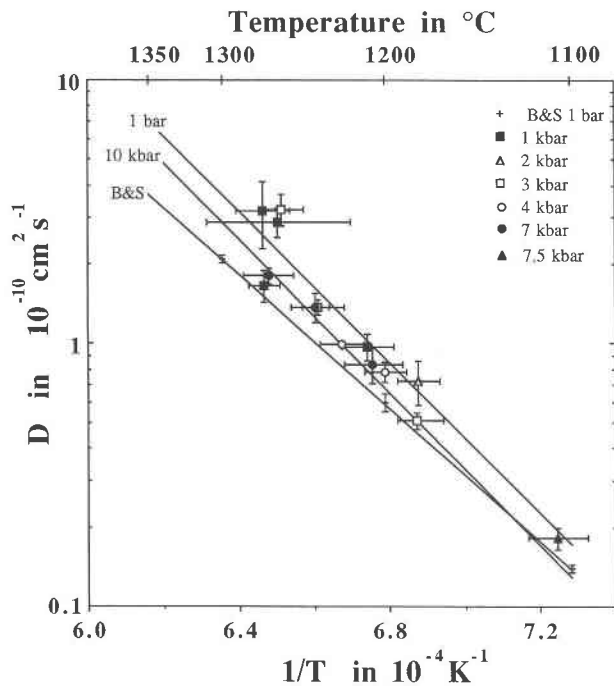


Fig. 2. Diffusion coefficients for Fe in Pt from this study compared with those of Berger and Schwartz (1978). For each experiment, an average  $D$  with  $1\sigma$ -error margins and  $\Delta T$  range is plotted. Lines represent best fits to our data, extrapolated to 1 bar and 10 kbar, and to the 1-bar data (marked B&S) of Berger and Schwartz (1978).

Alloys with high Fe content (>5 wt%) result in a larger Fe gain by the sample and have larger Fe losses from the foil except in experiment Bonin 30.4 (Table 2).

The  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  of the products of crystals + melt was determined by comparison of

$$K_d' = (\text{Fe}^{2+}/\text{Mg})_{\text{ol}}/(\text{Fe}_{\text{tot}}/\text{Mg})_{\text{melt}} \quad (11)$$

to the Roeder and Emslie (1970) value  $K_d = 0.3$  for

$$K_d = (\text{Fe}^{2+}/\text{Mg})_{\text{ol}}/(\text{Fe}^{2+}/\text{Mg})_{\text{melt}} \quad (12)$$

the ratio  $K_d'/K_d$  gives the  $\text{Fe}^{2+}/\text{Fe}_{\text{tot}}$  in the melt. Some  $K_d'$  values are larger than  $K_d = 0.3$  and cannot be applied to estimate the  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  of the melt (experiments 25.2, 47.4, 45.1). Such high  $K_d'$  values could often be related to opaque inclusions in olivines.

The effective initial oxidation state of the starting material was  $\text{Fe}^{2+}/\text{Fe}_{\text{tot}} = 100\%$ . Oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  generally resulted in  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  below 20%. Experiments with low  $\text{H}_2\text{O}$  contents, i.e., experiments 30.4, 26.3, and 45.1, developed the lowest  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  because of minor  $\text{H}_2$  loss as a result of a small  $\text{H}_2$  gradient between the inside and outside of the capsule. All except one experiment (31.2) stayed below the calculated alloy equilibrium value of  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ . Loss of Fe from the sample in order to attain  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  values in equilibrium with the alloy was expected but not observed. The most likely reason for the lower than equilibrium values of  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  of the melts

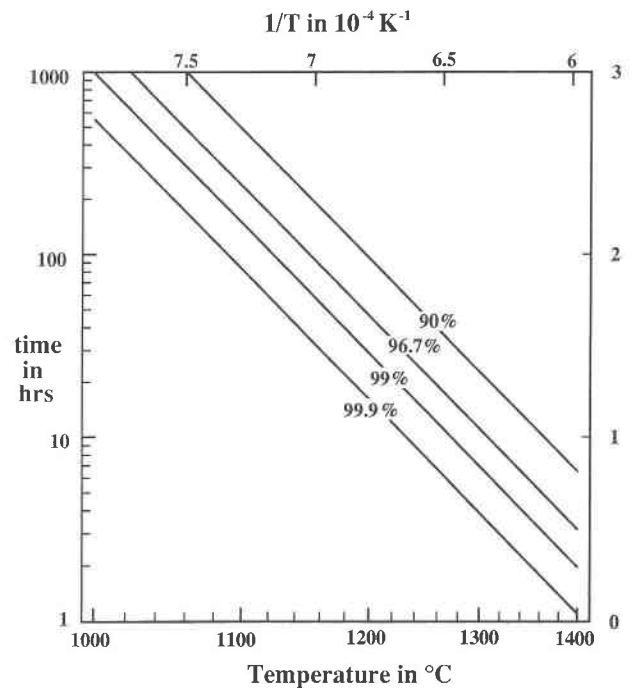


Fig. 3. Lifetime of a double capsule with a 0.1 mm Pt-Fe foil insert as function of temperature calculated using our 1-bar diffusion coefficient. Isoleths are for the remaining percentage of Fe in the foil at the interface with the sample.

is that the rims of olivine are actually higher in Fo than the analyzed spots. Olivine rim compositions are difficult to determine because of overlap contamination with the surrounding glass in the analyses. A change in forsterite content from  $\text{Fo}_{89}$  to  $\text{Fo}_{91}$  will mean a relative decrease of 20% in the  $\text{Fe}^{2+}$  fraction of the melt (e.g.,  $\text{Fe}^{2+}/\text{Fe}_{\text{tot}} = 90\%$  with  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}} = 10\%$  will become  $\text{Fe}^{2+}/\text{Fe}_{\text{tot}} = 72\%$  and  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}} = 28\%$ ). It appears that  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  values of Table 2 lie largely within the range of error. The observations therefore agree with the expected buffering of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  by the alloy. The  $\text{Fe}^0$  of the alloy enters the melt to maintain the alloy-melt equilibrium for the Fe species.

#### Experiments at controlled $f_{\text{H}_2}$ on basalt glass

The two experiments with an externally imposed  $f_{\text{H}_2}$ , JED-2 and JED-3 (Table 3), were done at  $\text{H}_2\text{O}$ -saturated conditions. The  $\text{H}_2\text{O}$  content of the glass products was analyzed using FTIR spectroscopy, and the observed variation in  $\text{H}_2\text{O}$  content of  $\pm 0.2$  wt% is attributed to quench effects.

The melts have a slightly lower Fe content than an earlier analysis of the starting composition (Delaney, unpublished data). This could reflect compositional variation in the starting material, because a difference of 1 wt% was also observed in CaO content, or capsule-sample Fe exchange. In JED-2, if Fe exchange with the alloy had occurred, vigorous convection must have homogenized the melt. In JED-3, heterogeneities in  $\text{Fe}_{\text{tot}}$  (as FeO) of

$\pm 0.3$  wt% are larger than the analytical error and probably point to some alloy-sample exchange. However, the unchanged alloy compositions and only slightly, if at all, changed melt compositions appear to indicate equilibrium for the Fe reaction.

The  $f_{O_2}$  was controlled with an external  $f_{H_2}$  at QFM. Based on the expression of Sack et al. (1980),  $Fe^{3+}/Fe_{tot}$  percentages of 13.2–13.3 were expected at QFM; however, measured values were 17.9 and 21.5. Our calculations based on alloy composition,  $Fe_{tot}$  of the melt, and the alloy controlling  $(a_{FeO})^3/(a_{Fe_2O_3})$  (Eq. 2) of the melt give  $Fe^{3+}/Fe_{tot}$  of 19–21% and 20–22%, which is in better agreement with the respective measured values. The  $f_{O_2}$  must therefore have been close to  $(QFM + 1.3) \pm 0.5$  log  $f_{O_2}$  units (or NNO + 0.4) for  $p_{H_2O} = 310$  and 520 bar and for  $p_{H_2} = 5$  and 10 bar. Alternatively, capsule, sample,  $Fe^{3+}/Fe_{tot}$ , and  $f_{O_2}$  were in equilibrium at QFM during the experiments, and  $Fe^{3+}/Fe_{tot}$  changed upon quench and fortuitously matched our calculation.

#### Piston-cylinder experiments on basalt glass

In all these experiments, which were carried out at 10 kbar, Fe is lost from the sample. The Fe concentration of the alloy at the foil-sample interface converges at about 10 wt%. Alloys with lower than 10 wt% initial  $Fe^0$  showed a maximum Fe content at the sample-alloy interface. Alloys with higher than 10 wt% Fe had a maximum in their Fe profiles but had lower value than their initial alloy composition. In these experiments Fe contents in the alloy dropped both toward the sample as well as the outer capsule, indicating an Fe flux in both directions. The observed Fe loss from the sample is therefore attributed to loss via direct sample-outer capsule pathways and not to exceeded lifetime of the double capsule. Note that this does not contradict our theory since the alloy only controls  $(a_{FeO})^3/(a_{Fe_2O_3})$  (Eq. 2) and not the absolute amounts.

Measured values of  $Fe^{3+}/Fe_{tot}$  range from 1.7 to 14.6%. In cases where the alloy had a maximum in its profile, indicating Fe supply to the sample,  $Fe^{3+}/Fe_{tot}$  is exceedingly low (5.7% and 1.7%). In the experiments where the alloy gained Fe,  $Fe^{3+}/Fe_{tot}$  is 10.5%, 12.3%, and 14.6%. In Figure 4, we plotted calculated percentage  $Fe^{3+}/Fe_{tot}$  isopleths as a function of  $f_{O_2}$  and pressure for Juan de Fuca basalt at 1300 °C as well as the isopleths for equilibrium alloy compositions. Using the range of alloy composition from start to end of the experiments, three of the five experimental  $Fe^{3+}/Fe_{tot}$  ratios lie within the alloy-sample equilibrium range. Experiments that deviate from this range are JdF-3, with measured  $Fe^{3+}/Fe_{tot}$  of 14.6% and calculated equilibrium value of 6.1–6.4%, and JdF-6, with 1.7% measured and 4.1–5.5% calculated.

In addition to Fe loss,  $H_2O$  gain of 1.5–1.8 wt% occurred in the experiments. The piston-cylinder assembly imposes a  $f_{H_2}$  on the sample because of talc-graphite reactions, but the value is unknown because of thermal gradients over the graphite heater. The  $H_2$  diffuses through the capsule and reduces Fe oxides of the sample to form

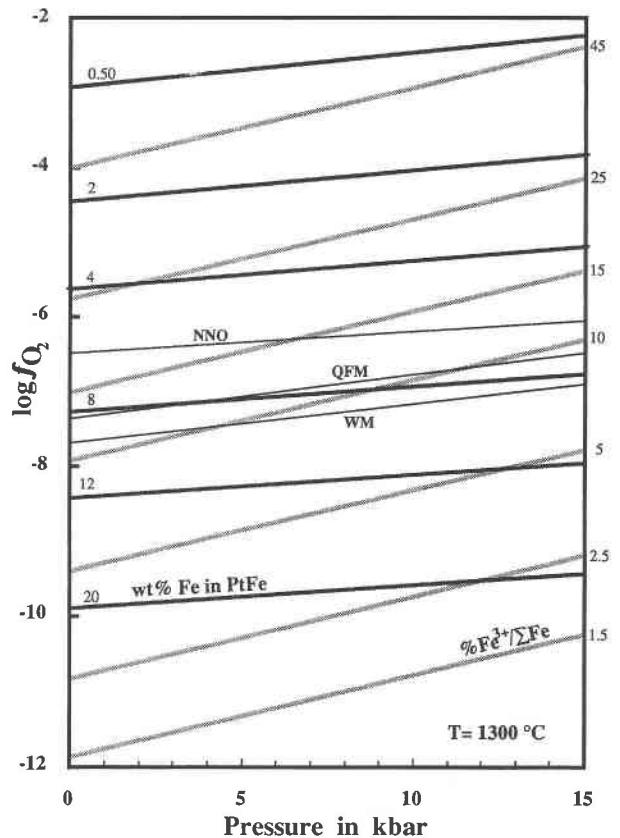


Fig. 4. Calculated equilibria for Pt-Fe alloys and Juan de Fuca basalt TT152-21 as a function of pressure and  $f_{O_2}$  at 1300 °C. Isopleths for  $Fe^{3+}/Fe_{tot}$  percentages are marked on the right and for wt% Fe in Pt on the left. The figure is valid only for the exact bulk composition of Table 1, and isopleth positions will change with Fe exchange. Oxygen fugacity buffers NNO, QFM, and WM are according to Huebner (1971).

$H_2O$ . In a system only open to  $H_2$  exchange, loss of 1.0 wt%  $FeO$  corresponds to a 0.25 wt%  $H_2O$  gain by mass balance. However,  $H_2O$  gain after the experiment (Table 3) is not in agreement with the Fe losses and  $FeO$  and  $Fe_2O_3$  contents in JdF-6 and JdF-7. An excess of at least 1 wt%  $H_2O$  is unaccounted for, and an additional source of O needs to be invoked.

In the experiments, the Fe loss of the sample is highly variable (Table 3). Wet chemical analyses to determine  $Fe^{3+}/Fe^{2+}$  contents are not necessarily more accurate than the olivine- $K_d$  method applied in set 1 when dealing with heterogeneous Fe distribution. The observation that Fe was lost from all samples does indicate a possible heterogeneity in Fe content. Because the  $Fe^{2+}$  content was determined on bulk sample and  $Fe_{tot}$  was determined from spot analyses, errors in  $Fe^{3+}$  content may result as  $Fe^{3+}$  is determined by difference.

Some deviation is to be expected in our experiments for reasons other than lack of agreement between pre-

dicted and observed  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ . The discrepancy can be partly attributed to inaccuracies in calculating the alloy composition. Because our alloy calculations are based on Grove's (1981) measurements at 1 atm, it is necessary to assess the error margins of that study. Grove's data (see Grove, 1981, Fig. 5) show a spread about the calculated vs. observed  $a_{\text{Fe}}$  one-to-one relation, with calculated alloy compositions being generally within 10% of the measured values. The  $\text{Fe}^{3+}/\text{Fe}^{2+}$  contents in Grove's study were calculated rather than measured for the temperature and  $f_{\text{O}_2}$  conditions of the experiments using the relationship of Sack et al. (1980). Difficulties in predicting alloy compositions must therefore be attributed to the effect of bulk composition on the activities of Fe species and the approximate predictive quality of the empirical calibration by Sack et al., because identical alloy compositions could be readily produced starting with both high-Fe and Fe-free Pt in Grove's experiments. Christie et al. (1986) reported an uncertainty of  $\pm 0.5 \log_{10}$  units in  $f_{\text{O}_2}$  value in the experimental calibration of Sack et al. Figure 4 can be used to evaluate the effect of these uncertainties on alloy and melt composition.

#### O mass balance

In our experiments at 10 kbar, the sample is open to  $\text{H}_2$  and  $\text{Fe}^0$  exchange. The  $\text{O}_2$  released by Fe oxide reduction reacts with  $\text{H}_2$  resulting in increased  $\text{H}_2\text{O}$  contents. Based on  $\text{O}_2$  mass balance, it appears that approximately 1 wt% excess  $\text{H}_2\text{O}$  is present in experiments JdF-6 and JdF-7. This  $\text{H}_2\text{O}$  gain requires an additional source for the  $\text{H}_2\text{O}$  in the capsule. No obvious source could be identified. The alloys used in the experiments showed no signs of surface oxidation after annealing. Glass cylinders of the starting material rather than powder were used to minimize the effect of adhered  $\text{H}_2\text{O}$ , and air contained in the capsule was insufficient to explain the large excess  $\text{H}_2\text{O}$  gain. It is possible that recrystallization of the Pt and Pt-Fe alloys created permeability for  $\text{O}_2$  or  $\text{H}_2\text{O}$  along grain boundaries and that contamination occurred during the experiments. An alternative source for O could be the reduction reaction of silica to form Si-Pt alloy as was observed by Chen and Presnall (1975). This would imply very reducing conditions for the piston-cylinder experiments. We have not analyzed alloys for Si. There is some evidence of problems with  $\text{O}_2$  mass balance in experiments by other workers, but an unexplained loss rather than a gain of  $\text{O}_2$  seems to be the case. In Chen and Lindsley's (1983) experiments using Pt-Fe alloy capsules, progressive Fe losses from the samples were reported with time. Thoroughly dried BN assemblies were used, and no source of  $\text{H}_2$  could be invoked. They concluded that FeO reacts to form Fe metal and  $\text{Fe}_2\text{O}_3$ . Although they did observe blebs of metallic Fe, they did not substantiate the presence of large amounts of  $\text{Fe}_2\text{O}_3$  nor the absence of  $\text{H}_2\text{O}$  in their products. Mysen and Virgo (1978) argued that released O from  $\text{Fe}^{3+}$  reduction in their experiments on melts in the system acmite-jadeite dissolved into the

melt. In both experiments, loss of  $\text{O}_2$  from the capsule would also explain the observations.

#### The effect of pressure on $\text{Fe}^{3+}$ - $\text{Fe}^{2+}$ speciation

The effect of pressure on the  $2\text{FeO} + \frac{1}{2}\text{O}_2 = \text{Fe}_2\text{O}_3$  equilibrium is expressed by the volume of reaction term. A change in activity coefficients with pressure cannot be evaluated with the existing data. The large positive value at 1 atm for  $\bar{v}_{\text{Fe}_2\text{O}_3} - 2\bar{v}_{\text{FeO}}$  implies a preference for  $\text{Fe}^{2+}$  at elevated pressures, but a change from fourfold to sixfold coordination of  $\text{Fe}^{3+}$  could drastically reduce the partial molar volume of  $\text{Fe}_2\text{O}_3$ . No such coordination change was found by Luth and Brearley (1989) in basalt glass quenched from 20 kbar pressure. Kress and Carmichael (1989) reported that  $\bar{v}_{\text{Fe}_2\text{O}_3} - 2\bar{v}_{\text{FeO}}$  remains positive and is approximately independent of pressure to greater than 40 kbar based on the isothermal compressibilities for FeO and  $\text{Fe}_2\text{O}_3$  derived from acoustic velocity measurements. Based on these studies, very low  $\text{Fe}^{3+}/\text{Fe}^{2+}$  would be expected in  $f_{\text{O}_2}$ -buffered melts at high pressure. Indeed, such results were reported by Luth and Brearley (1989), and the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratios agreed with predictions based on the volume of reaction. However Gudmundsson et al. (1988) presented contradictory experimental results and concluded that the pressure effect on  $\text{Fe}^{3+}/\text{Fe}^{2+}$  is either non-existent or causes a slight increase in this ratio.

In our experiments,  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  percentages calculated for the capsule-melt equilibrium agree reasonably well with the observed values at elevated pressure. The large error margin in experimental  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  values precludes definitive conclusions from the current data sets, but it seems that the pressure effect on  $\text{Fe}^{3+}$ - $\text{Fe}^{2+}$  speciation is appropriately predicted by the volume term in Equation 5 for the equilibrium constant.

#### SUMMARY

The use of alloy capsules and the control of  $a_{\text{Fe}}$  requires a conceptually different view of experimental systems. If a capsule is closed with respect to O, a change in oxidation state of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  can only be accomplished in the presence of other internal  $\text{O}_2$  sources or sinks. In the following overview, we attempt to develop systematically the redox conditions under various commonly enacted experimental conditions in Fe-bearing systems.

**Closed system involving one redox equilibrium only.** An example would be the redox equilibrium  $2\text{FeO} + \frac{1}{2}\text{O}_2 = \text{Fe}_2\text{O}_3$ . Closed-system conditions only exist with inert, nonalloying capsules and in the absence of other  $\text{O}_2$  sources or sinks in a sample such as C- $\text{CO}_2$ ,  $\text{H}_2$ - $\text{H}_2\text{O}$ , or S- $\text{SO}_2$ . In this case, although an isothermal increase in pressure will change  $f_{\text{O}_2}$  drastically,  $\text{Fe}^{3+}/\text{Fe}^{2+}$  will not change since increase in  $f_{\text{O}_2}$  involves reduction of negligible amounts of  $\text{Fe}^{3+}$ . The isothermal  $P$ - $f_{\text{O}_2}$  path can be illustrated using Figure 4 where sample compositions would stay on isopleths of  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ .

**Closed system involving two redox equilibria.** One example is  $2\text{FeO} + \frac{1}{2}\text{O}_2 = \text{Fe}_2\text{O}_3$  and  $\text{Fe}_{\text{caps}}^0 + \frac{1}{2}\text{O}_2 = \text{FeO}$ .



In this case,  $a_{Fe}$  is practically fixed by the reservoir size of the alloying capsule (assuming  $\gamma_{Fe}$  independent of pressure). With an isothermal increase in pressure,  $Fe^{3+}/Fe_{tot}$  of a sample will follow or stay close to the  $Fe^0$  isopleth as, e.g., in Figure 4. Other examples would be  $2FeO + \frac{1}{2}O_2 = Fe_2O_3$  and a metal-metal oxide buffer such as NNO or WM (Huebner, 1971) in an inert capsule or a sample contained in a graphite container. In these cases  $Fe^{3+}/Fe_{tot}$  of a sample will follow the  $f_{O_2}$  of the buffering reaction. (See Fig. 4 for examples.) With graphite in a sealed Pt capsule, the sample will follow the CCO buffer only when a free CO-gas phase is present.

**Closed or open system involving multiple (more than 2) equilibria.** Examples would include redox equilibria:  $2FeO + \frac{1}{2}O_2 = Fe_2O_3$ ,  $Fe^0 + \frac{1}{2}O_2 = FeO$ , and  $H_2 + \frac{1}{2}O_2 = H_2O$ . In this case, it is essential that  $f_{H_2}$  and  $a_{Fe}$  imply the same  $f_{O_2}$  in their respective equilibria, or large changes in the sample in  $H_2O$  and  $FeO/Fe_2O_3$  contents will result. This is illustrated by the results of our three sets of experiments. It should also be clear that the use of Fe-free alloying capsules with disequilibrium external  $f_{H_2}$  (buffered or from talc in a piston-cylinder assembly) will lead to highly suspect experimental results in Fe-bearing samples.

Carmichael and Ghiorso (1986) extensively discussed internal redox equilibria in ascending magmas, touching on many of the same problems evaluated in this paper. From our deliberations it should be clear that the outcome of experimental investigations of  $Fe^{3+}/Fe^{2+}$  equilibria is entirely dependent on the experimental approach.

#### ACKNOWLEDGMENTS

We are very much indebted to K.C. van der Laan for setting up an Fe-plating facility adapted to our special needs. T.L. Grove is thanked for reviewing an earlier version of this manuscript, and Victor Kress and Laurinda Chamberlin are thanked for their critical comments on this version. We are grateful to J.R. Delaney and Veronique Robigou-Nelson for supplying basalt glass, to Jackie Eaby Dixon for sharing experimental results, and to I.S.E. Carmichael for providing ferric-ferrous analyses. P.J. Wyllie generously made available his experimental facilities for piston-cylinder experiments. Support from the NSF grant EAR-8212738 is acknowledged.

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MANUSCRIPT RECEIVED JULY 3, 1990

MANUSCRIPT ACCEPTED JUNE 26, 1991

### APPENDIX 1. NUMERICAL EQUIVALENTS OF EXPRESSIONS IN THE TEXT

$$\ln f_{O_2} = [\ln(X_{Fe_2O_3}/X_{FeO}) - b/T - c - \sum d_i X_i]/a \quad (4)$$

where  $a = 0.21813$ ,  $b = 13184.7$ ,  $c = -4.4933$ ,  $d_{SiO_2} = -2.15036$ ,

$d_{Al_2O_3} = -8.35163$ ,  $d_{FeO} = -4.49508$ ,  $d_{MgO} = -5.43639$ ,  $d_{CaO} = 0.073113$ ,  $d_{Na_2O} = 3.54148$ ,  $d_{K_2O} = 4.18688$ .  $X_i$ 's are mole fractions of oxides,  $Fe_{tot} = FeO$ , and  $T$  is in K and  $P$  in bars (Sack et al., 1980).

$$\ln f_{O_2} \text{ (at } P \text{ bar)} = \ln f_{O_2} (P = 1) + (0.52126/T - 8.126 \cdot 10^{-5})(P - 1) \quad (5)$$

with  $T$  in K and  $P$  in bars (Mo et al., 1982).

$$\ln K = -1.187 + 20727/T - 0.0522(P - 1)/T \quad (6)$$

with  $T$  in K and  $P$  in bars where  $K = a_{FeO}^{melt}/(a_{Fe}^{Pt} \cdot \sqrt{f_{O_2}})$  (Grove, 1981; this study). Heald's (1967) activity-composition relation for Fe in Pt:

$$\ln \gamma_{Fe} = (1 - X_{Fe})^2[-3.326564 + 0.221051(4X_{Fe} - 1)].$$

$$D = 0.50 e^{-33073/T - 0.039(P-1)/T} \quad (8)$$

with  $T$  in K and  $P$  in bars.