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Fe pre-enrichment: a new method to counteract iron loss in experiments on basaltic melts

Revision 2

YANN-AURELIEN BRUGIER, MARINA ALLETTI, AND MICHEL PICHAVANT

Institut des Sciences de la Terre d'Orléans (ISTO), UMR 7327, Université d'Orléans, 45071 Orléans, France and ISTO, UMR 7327, CNRS, 45071 Orléans, France and ISTO, UMR 7327, BRGM, BP 36009 Orléans, France

ABSTRACT

Capsule pre-saturation has been traditionally employed to circumvent Fe loss from the charge to the container in petrological experiments. However, the method is time-consuming and fraught with theoretical and practical difficulties. An alternative method, based on the use of starting materials pre-enriched in Fe, is presented. Test experiments on two natural basalts, both non Fe-enriched and Fe-enriched with the addition of Fe oxides, have been carried out at 1 atm and 50 MPa (H_2O-saturated), 1200 and 1250°C, between NNO and NNO-1 and in Pt and $Au_{80}Pd_{20}$ capsules. Glasses and capsules were analyzed by electron microprobe. Fe-concentrations in the capsule near the glass interface strongly depend on the capsule material, being 5-10 times less for $Au_{80}Pd_{20}$ than for Pt. For non Fe-enriched compositions, Fe loss reaches -15% ($Au_{80}Pd_{20}$) and -60% (Pt). Increasing the level of Fe-enrichment reduces Fe loss, the amount of Fe alloyed with the capsule being compensated by the amount of Fe added to the starting composition. FeO_t concentrations in high pressure glasses bracket the nominal FeO_t of the two starting basalts, demonstrating that Fe alloying has been successfully counteracted. Combination of AuPd containers with Fe pre-enriched starting materials offers

excellent perspectives to solve the Fe loss issue in high pressure experiments on basaltic compositions.

Keywords: experiments, capsules, iron loss, pre-enrichment, basalts

INTRODUCTION

Fe loss from the charge to the container is one of the most difficult problems in experimental petrology. Classically, in a high pressure experiment, the charge is contained in a chemically inert noble metal such as Pt, Au, or Ag (e.g., Chou 1986). For temperatures < 1050°C, Au capsules are commonly used. However, the relatively low melting point of Au makes it inappropriate for experiments on basaltic systems. The use of Pt enables working at temperatures > 1050°C but Pt is known to interact strongly with the charge, leading to the formation of a PtFe alloy, which removes most of the Fe from the starting material (Stern and Wyllie 1975). Various methods have been proposed to mitigate Fe loss, the most commonly used being capsule Fe *pre-saturation* (see Grove 1982). This method involves the preparation at 1 atm of an alloy (PtFe in early studies) in equilibrium with the Fe-bearing charge at high temperature and pressure, and the use of that alloy as a container, instead of pure Pt (e.g., Ford 1978; Grove 1982). More recently, AuPd alloys have attracted much interest as a substitute to Pt because of their lower susceptibility to alloying with Fe (Kawamoto and Hirose 1994). However, large amounts of Fe can dissolve in AuPd alloys depending on fO_2 (Hall et al. 2004; Di Carlo et al. 2006; Barr and Grove 2010; Balta et al. 2011). Therefore, the Fe pre-saturation approach has been extended to AuPd capsules (Gaetani and Grove 1998; Barr and Grove 2010; Balta et al. 2011 and references therein).

There are however several theoretical and practical difficulties with the Fe pre-saturation method. Balta et al. (2011) emphasized that defining the conditions needed to saturate either Pt or AuPd with the proper amount of Fe for a high pressure experiment is difficult. Even

after the correct 1 atm pre-saturation conditions are determined for one high pressure experiment, these conditions will differ from those needed for the next experiment in ways that are difficult to predict. In particular, one parameter that must be known precisely for the planning of the pre-saturation conditions is the fO_2 of the high pressure experiment. For example, for a hydrogen buffered (i.e., constant fH_2) gas vessel experiment with charges of different fH_2O ran together (e.g., Di Carlo et al. 2006), fO_2 must vary between charges. Theoretically, for each charge, a specific alloy would need to be prepared if the pre-saturation method is to be used. Another major shortcoming of the pre-saturation method concerns the long durations necessary to prepare chemically homogeneous Fe-noble metal alloys even at high temperatures (Gaillard et al. 2003; see below). Dissolution of the Fe doping material following capsule pre-saturation can be also sluggish, the whole method being very time-consuming.

Difficulties with capsule Fe pre-saturation leave room for alternative approaches to reduce Fe loss in petrological experiments. In this paper, we present a new empirical method to mitigate Fe loss in high pressure experiments on basaltic systems. The method is based on a new approach, i.e., the use of starting materials *pre-enriched* in Fe.

EXPERIMENTAL AND ANALYTICAL METHODS

The new method was developed within the framework of two experimental projects on natural basaltic melts which required Fe loss to be minimized. In the first project, S solubilities are measured at high temperatures (1200°C) and pressures (200 MPa) under moderately reducing conditions (i.e., at $fO_2 \leq$ the Ni-NiO buffer, NNO), using Pt capsules in order to prevent the formation of complex Pd-, S-bearing compounds (Pichavant et al, 2006). The second project is a phase equilibrium study at 50-400 MPa, 1100-1200°C and a $fO_2 \sim$ NNO-0.5 on transitional basalts from La Réunion Island (Indian Ocean), with $Au_{80}Pd_{20}$

capsules used as containers (Brugier et al., in preparation). Both projects require Fe loss to be minimized. Initially, the Fe capsule pre-saturation method was attempted but difficulties of the type summarized above were encountered. Consequently, a new methodology based on specific experiments performed at 1 atm and 50 MPa was tested, in parallel with Pt and $Au_{80}Pd_{20}$ capsules.

A basaltic pumice from Stromboli (PST-9, Pichavant et al. 2011) and a basaltic scoria erupted in 2009 from the Piton de la Fournaise (REU-04) were used as starting materials. PST-9 has been previously experimentally investigated by Di Carlo et al. (2006) and Pichavant et al. (2009). The two samples were separately crushed, ground, and then fused at 1 atm, 1400°C for 4 hours in a large Pt crucible open to air to produce crystal- and volatile-free homogeneous glasses. Chips of each starting glass were mounted in epoxy and their composition checked by electron microprobe (Table 1), the rest ground and stored in an oven at 120°C. An aliquot of each glass was used to prepare Fe-enriched (or Fe pre-enriched) starting materials by physically mixing with Fe oxide, either magnetite or hematite powders (chemical reagent grade purity). Iron enrichments are reported as wt% Fe added to the glass-oxide mixture (Tables 2 & 3).

1 atm experiments

The PST-9 and REU-04 starting compositions (either glass or glass-Fe oxide powders) were loaded respectively in Pt and $Au_{80}Pd_{20}$ tubes (diameter: 2.5 mm, length: 20-25 mm, wall thickness: 0.2 mm), previously welded at one end. Capsules were side by side and vertically held in an alumina tube which was suspended through a Pt wire in the furnace. A 1 atm vertical gas mixing furnace was used, both at 1200°C (NNO and NNO-0.5) and 1250°C (NNO-0.5). The fO_2 was controlled by CO-CO_2 gas mixtures monitored by certified electronic flowmeters (Deines et al. 1974). Temperature was read by an S-type thermocouple

and is accurate to within 2°C. The sample holder and thermocouple were both located in the hot spot of the furnace. The thermal gradient is less than 5°C along the length of the capsules.

For the PST-9 experiments, two runs of ~ 100 h were conducted at 1200 and 1250°C with three capsules corresponding to three Fe-enrichments (0, 5, and 13 wt.% Fe added). The two 72 and 194 h REU-04 experiments (1200°C), which started from a non Fe-enriched composition, were in fact classical pre-saturation experiments (Table 2). Charges were quenched by electrically fusing the Pt wire, resulting in the drop of the sample holder in the cold bottom part of the furnace. Capsules were mounted in epoxy and polished parallel to their axial plane (Fig. 1), so that they could be analyzed at different positions (top, i.e., the closest to the gas atmosphere, middle, bottom, i.e., the closest to the welded end) along their length.

High pressure experiments

Pt (for PST-9) and $Au_{80}Pd_{20}$ (REU-04) capsules were used in the high pressure experiments similarly to those at 1 atm, apart from being welded shut. About 5 mg distilled-deionized water and ~ 50 mg of either glass or glass-Fe oxide mixture were loaded so as to yield H_2O-saturated conditions. Both non Fe-enriched and Fe-enriched compositions were investigated (Table 3). Two similar experiments were performed at 50 MPa, 1200°C in a rapid-quench internally heated pressure vessel operating vertically and pressurized with an Ar-H_2 gas mixture (Di Carlo et al. 2006). Total pressure was recorded by a transducer calibrated against a Heise Bourdon tube gauge (uncertainty ± 2.0 MPa). The double-winding molybdenum furnace allowed a near-isothermal hot-spot zone of 2-3 cm length, with a gradient of < 3°C/cm. Temperature was monitored by two S-type thermocouples with an uncertainty of ± 5°C. H_2 and Ar, loaded sequentially at room temperature, were used to pressurize the vessel and to control the fO_2, the two experiments being performed with the

same initial H_2 pressure (3 bar). Experimental fH_2 (i.e., the fH_2 at 50 MPa, 1200°C) was measured by CoO-CoPd sensors (Taylor et al. 1992) in separate capsules. A fO_2 of NNO-0.8 was determined for all high pressure capsules (calculations performed with K_{water} from Robie et al. 1979, $f_{H2O}°$ from Burnham et al. 1969, the NNO equation from Pownceby and O'Neill 1994 and the CoPd sensor calibration of Taylor et al. 1992). Run durations were in both cases ~ 40 h, longer than most experiments with hydrous basaltic melts but approaching the duration of the 1 atm series. The experiments were terminated by drop-quenching the sample holder (Di Carlo et al. 2006). Capsules were then weighed and checked for possible leaks. Only capsules that did not show any change in weight were retained and mounted in the same way as the 1 atm capsules.

Electron microprobe analyses

The experimental products were analyzed with a CAMECA SX FIVE electron microprobe at ISTO, Orléans. Analyses mainly were performed along traverses several hundred μm long positioned across and perpendicular to the glass-capsule interface (Fig. 1). Analytical conditions were set, for experimental glasses, at 15 kV (acceleration voltage), 6 nA (sample current), 10 s (counting time on peak) and 5 s (counting time on background). Capsules were analyzed for Fe under the same conditions except for capsules HP4, HP5, HP7 and HP8 which were analyzed at 15 kV, 30 nA, 30 s and 5 s. CoPd sensor alloys were analyzed separately under higher acceleration voltage (20 kV) and a 20 nA sample current. Relative analytical errors are 1% (SiO_2, MgO, CaO), 1-2% (Al_2O_3), 2-4% (FeO, Na_2O) and 5-10% (TiO_2, K_2O) for glasses. For capsules, the detection limit for Fe is around 4500 ppm, corresponding to 1.5 at% Fe, except for HP4, HP5, HP7 and HP8 (detection limit around 270 ppm, corresponding to 0.08 at% Fe). For sensors, the error on the alloy composition is $\pm$ 1-2 at%.

RESULTS

1-atm experiments

Fe concentrations in capsules at the glass interface, obtained from the analytical traverses, depend markedly on the capsule material (Table 2). At 1200°C and NNO-0.5, they range between 4 and 10 at% Fe for Pt (reaching 24 at% Fe at 1250°C), but barely exceed the limit of detection for $Au_{80}Pd_{20}$ at 1200°C, NNO (0.5-1.5 at% Fe). The Fe distribution within $Au_{80}Pd_{20}$ capsules could not be precisely evaluated due to low Fe capsule concentrations and the rather elevated Fe detection limit. Charges in Pt capsules define a positive correlation between the Fe interface concentration and the level of Fe-enrichment (Table 2). Capsule Fe concentrations progressively decrease toward their external rim (Fig. 1), emphasizing the lack of bulk chemical equilibrium in our experiments. An equilibrium Fe distribution between capsule and melt is only attained near the capsule-glass interface. This stresses the long durations needed to homogenize Fe concentrations in Pt capsules of "normal" thickness (0.2 mm).

The REU-04 glasses have $\Delta FeO_t < 5\%$ [$\Delta FeO_t = 100*(FeO_t$ glass $- FeO_t$ starting glass$)/(FeO_t$ starting glass), see Table 4] indicating that no significant Fe loss occurred, consistent with the low Fe interface concentrations observed in $Au_{80}Pd_{20}$ capsules. In comparison, the PST-9 glasses exhibited a complex behavior in Pt capsules. Although glasses along a given traverse are chemically homogeneous, a systematic vertical stratification of glass compositions inside capsules is present. As a result, the glass data have been distinguished as a function of the position of the analytical traverse in the capsule (either top, middle or bottom, Table 4). For a given capsule and from bottom to top, glass FeO_t, MgO and CaO decrease, and SiO_2, Al_2O_3, Na_2O and K_2O increase. The same type of trends were observed both in non Fe-enriched and Fe-enriched charges. This compositional stratification

makes difficult to evaluate the pre-enrichment method. For example, for a given capsule, large differences in Fe loss (ΔFeO_t) occur between bottom and top glasses (e.g., -2% and -31% respectively for bottom and top in experiment 2, 5 wt% added Fe, Table 4). We attribute the observed zonations mainly to the persistence of a redox gradient inside capsules, the bottom part of the melt layer keeping oxidizing conditions (since the starting glasses were synthesized in air), only the top part of the melt layer being equilibrated with the fO_2 of the gas mixture.

High pressure experiments

Fe-concentrations in the capsules near the glass interface range between 24 and 38 at% Fe for Pt and 3 and 4 at% Fe for $Au_{80}Pd_{20}$ capsules (Fig. 2), higher than in the corresponding 1 atm charges and in general positively correlated with the Fe-enrichment (Table 3). Both Pt and $Au_{80}Pd_{20}$ capsules display heterogeneous Fe distributions, with Fe concentrations progressively decreasing from the glass interface toward the capsule external rim. For capsules analyzed under specific analytical conditions, the data show that Fe concentrations > 1.5 at% extend to distances longer in $Au_{80}Pd_{20}$ than in Pt (Fig. 2). Contrasting with the 1 atm glasses, the high pressure glasses are chemically homogeneous at the scale of the entire charge. For the non-enriched starting compositions, ΔFeO_t values are elevated. They differ with the capsule material, reaching -60% (Pt) and -15% ($Au_{80}Pd_{20}$, Table 5). Upon increasing the level of Fe-enrichment, ΔFeO_t progressively evolves from negative (Fe loss) to positive (Fe gain). For PST-9 in Pt capsules, ΔFeO_t from -60%, -1%, +10%, +106% to +138% are obtained and, for REU-04 in $Au_{80}Pd_{20}$ capsules, of -15%, -6% and +12% (Table 5). Results of representative glass traverses obtained on the two starting compositions with different Fe-enrichments are illustrated on Fig. 3. For both compositions and types of capsule materials, the nominal FeO_t of the starting basalt is bracketed by the glass FeO_t concentrations,

demonstrating that Fe loss toward the capsule has been effectively counteracted. The 5 wt% Fe added PST-9 composition (HP2, Table 5) illustrates the case of an optimum level of Fe pre-enrichment, defined as the amount of Fe added that yields < 5% Fe loss/gain.

DISCUSSION

Our tests establish the potential of the pre-enrichment method to circumvent the Fe loss problem in experiments with basaltic melts. Working with starting materials enriched in Fe enables the influence of Fe alloying with the capsule material to be counteracted. The method has been successfully tested on both Pt and $Au_{80}Pd_{20}$ capsules, at a pressure of 50 MPa, relatively high temperatures (1200°C) and moderately reducing fO_2 (from NNO to NNO-1). Under more reducing conditions, more Fe would alloy with capsule materials but the method should still be applicable in principle. It is important to stress that the proposed pre-enrichment method is empirical and should be adjusted for each particular set of starting compositions and experimental conditions. In particular, the experimental duration should be considered as a variable since equilibrium between melt and capsule is not attained in experiments of a few days on basaltic melts and, therefore, Fe loss is expected to increase with experimental duration, all other parameters being equal.

In our experiments, the additional Fe was introduced as Fe oxide. This has the advantage of simplicity and flexibility, since Fe enrichments can be sensitively adjusted. Results show that changing the type of Fe oxide (magnetite vs. hematite) does not influence the final glass compositions. Fe oxides rapidly dissolve in basaltic melts under our experimental conditions. The vertical stratification of glass compositions in the 1 atm Pt charges is not the result of Fe oxide sedimentation. In contrast with the 1 atm charges, the high pressure glass layers are chemically homogeneous indicating that Fe diffuses rapidly in the melt. However, our tests were conducted at high temperatures, above the liquidus and for hydrous melts. Other

procedures might be needed if the pre-enrichment method is to be used at lower temperatures (or under H2O-poor conditions), because (1) Fe oxide dissolution might take more time and (2) Fe might diffuse less rapidly in the melt. It is important to recognize that the success of the approach is based on a marked diffusivity contrast between Fe in capsule (slow) and Fe (bulk) in the melt (fast). Use of Fe-enriched glasses instead of glass-Fe oxide mixtures would eliminate the oxide dissolution step. However, we caution that the method needs further testing under conditions leading to slow bulk melt Fe diffusivities.

In addition to the pre-enrichment methodology, several aspects of this study are worth being emphasized. *First*, our results confirm the quite good performance of $Au_{80}Pd_{20}$ capsule materials with respect to alloying with Fe. At 1200°C, Fe concentrations (at the glass-capsule interface) are 0.5-1.5 at% Fe in the 1 atm NNO experiments, increasing to 2-4 at% Fe in the high pressure NNO-0.8 experiments. These Fe concentrations are consistent with the measurements of Balta et al. (2011), noticing that their $Au_{74}Pd_{26}$ alloys were equilibrated with pure Fe oxide and with their calculations for equilibration with a Kilauea basalt. We stress that, for experiments on basaltic melts at around NNO, Fe interface concentrations for AuPd alloys are 5-10 times less than for Pt. Yet, these concentrations are sufficient to affect the FeO_t concentration of the encapsulated melt. In addition to differences in interface concentrations between capsule materials, Fe diffuses to longer distances in $Au_{80}Pd_{20}$ than in Pt capsules. In our high pressure experiments at NNO-0.8, Fe losses with $Au_{80}Pd_{20}$ capsules are -15% (Table 5). Comparable Fe losses (-13% on average) were reported by Di Carlo et al. (2006) despite fO_2 (between NNO-0.1 and NNO+2.3) being on average higher than in this study. Although these Fe losses are significant, the use of $Au_{80}Pd_{20}$ instead of Pt (Fe loss of -60%, HP1, Table 5) clearly represents a major improvement. We conclude that the combination of AuPd containers and Fe pre-enriched starting materials offers excellent perspectives to solve the Fe loss issue in high pressure experiments on basaltic compositions,

when sulfur is not involved. Indeed, Au-Pd alloys tend to react with S to form complex Pd- and S-bearing compounds (Pichavant et al, 2006), weakening the capsule walls and falsifying the composition of the resulting glasses. *Second*, the melt zonation problem encountered provides an additional illustration of the difficulty to apply 1 atm methodologies to high pressure experiments. In our 1 atm experiments, chemical stratification of the melt prevented precise evaluation of Fe gains/losses and so our tests remain inconclusive. Furthermore, chemical gradients in the melt affected all major oxides in addition to FeO_t, thus introducing a bias on melt composition that is not limited to Fe. More work is needed if the pre-enrichment method is to be applied to 1 atm experiments. *Third*, compared to the traditional capsule pre-saturation, the pre-enrichment method presents important advantages. Capsule preparation at 1 atm prior to the high pressure experiment (synthesis of alloy, removal of Fe doping material, cleaning) is totally avoided, which saves time. Fe incorporation to the capsule takes place *in situ* during the high pressure experiment and, so, no estimation of the alloy composition under high pressure conditions (e.g., Barr and Grove 2010) is needed. Overall, the proposed method is fast, easy to implement, and robust even if the optimum level of Fe pre-enrichment is left to be empirically determined.

IMPLICATIONS

We have presented a new methodology to counteract Fe loss from experimental charges to capsule materials in high temperature/high pressure experimental studies. The method is based on the use of starting materials pre-enriched in Fe. During the experiment, Fe alloys with the capsule material but the amount of Fe lost to the capsule is compensated by the amount of Fe added to the starting composition. Fe pre-enrichment has been demonstrated to work at high pressure (50 MPa), high temperature (1200°C), moderately reducing fO_2 (NNO-0.8) and for both Pt and $Au_{80}Pd_{20}$ capsule materials. The method is empirical, i.e., an optimum

level of Fe enrichment must be determined for each particular set of starting compositions and experimental conditions, the latter including the run duration. Although tested on hydrous basaltic melts, the method offers potential for other types of experimental conditions and compositions, and is highly adaptable. Compared to the traditional pre-saturation, Fe pre-enrichment eliminates the need to prepare appropriate container capsules at 1 atm prior to high pressure experiments; estimating the alloy composition in the high pressure experiment becomes unnecessary. For high pressure experiments on basaltic compositions under moderately reducing fO_2 such as volatiles solubility and phase equilibria, the combination of AuPd containers and Fe pre-enriched starting materials provides excellent perspectives to solve the Fe loss problem.

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FIGURE CAPTIONS

Fig. 1. Distribution of Fe (Fe Kα intensity map, 15 kV acceleration voltage) in 1 atm charge 5 (experimental conditions in Table 2) illustrating the chemically homogeneous glass layer and the progressive decrease in Fe concentration in the Pt capsule from the glass interface toward its external rim.

Fig. 2. Representative electron microprobe traverses through different capsules from the same high pressure experiment. Fe concentrations in capsules (at%) are plotted against distance (μm). Experimental conditions in Table 3. (a) Pt capsule, charge HP5. Error bars are smaller than symbols. (b) $Au_{80}Pd_{20}$ capsule, charge HP4. Melt compositions and Fe enrichments in Table 5. Note the heterogeneity in the Fe distribution inside capsules, especially in (a), the difference in Fe interface concentrations between Pt and $Au_{80}Pd_{20}$ and the longer Fe diffusion distances in $Au_{80}Pd_{20}$ than in Pt.

Fig. 3. Results of electron microprobe traverses showing glass FeO_t concentrations (wt%, normalized to 100%) plotted against distance (μm) for the high pressure charges. Experimental conditions in Table 3. Glass averages in Table 5. Data points are distinguished with Fe pre-enrichments expressed as wt% Fe added to the glass. (a) PST-9 charges ran in Pt capsules. (b) REU-04 charges ran in $Au_{80}Pd_{20}$ capsules. The horizontal lines mark the FeO_t of

the starting PST-9 and REU-04 glasses (Table 1). In (a), the starting PST-9 glass composition is bracketed by charges HP2 and HP5 (both with 5% Fe added) and, in (b), the REU-04 by charges HP8 (2 wt% Fe) and HP4 (10 wt% Fe).

Table 1. Composition of starting glasses.

Oxide	PST-9	REU-04
SiO_2	50.6	50.5
TiO_2	0.88	2.56
Al_2O_3	16.2	13.8
FeO_t	7.95	10.6
MnO	0.13	0.14
MgO	7.16	7.63
CaO	12.1	11.3
Na_2O	2.38	2.64
K_2O	1.88	0.69
P_2O_5	0.61	0.17
Cr_2O_3	0.03	0.05
NiO	0.05	0.03
Total	99.7	99.1

Data are averages calculated on multiple (10-50) glass analyses. Concentrations are normalized to 100%; total is unnormalized.

Table 2. Experimental conditions for 1 atmosphere experiments.

Charge#		1	2	3	4	5	6	7	8
T	(°C)	1200	1200	1200	1250	1250	1250	1200	1200
Log fO_2		- 8.2	- 8.2	- 8.2	- 8.2	- 8.2	- 8.2	- 7.7	- 7.7
ΔNNO[1]		- 0.5	- 0.5	- 0.5	- 0.5	- 0.5	- 0.5	0	0
Capsule material		Pt	Pt	Pt	Pt	Pt	Pt	$Au_{80}Pd_{20}$	$Au_{80}Pd_{20}$
Wt% Fe added[2]		0	5	13	0	5	13	0	0
Duration	(h)	110	110	110	100	100	100	72	194
Fe in capsule	(% at.)[3]	4	5-8	7-10	4-7	8-11	20-24	0.5	1.5
Glass		PST-9	PST-9	PST-9	PST-9	PST-9	PST-9	REU-04	REU-04

[1]Log fO_2 charge – Log fO_2 NNO at the same P and T. NNO equation from Pownceby and O'Neill (1994).
[2]Amount of Fe (metallic iron) added to the glass in wt%.
[3]Fe concentration in capsule at the glass interface.

Table 3. Experimental conditions for high pressure experiments.

Experiment	1200°C, 485 bar, 42 h				1200°C, 475 bar, 40h			
Charge#	HP1	HP2	HP3	HP4	HP5	HP6	HP7	HP8
Log fO_2	-8.5	-8.5	-8.5	-8.5	-8.5	-8.5	-8.5	-8.5
ΔNNO[1]	-0.8	-0.8	-0.8	-0.8	-0.8	-0.8	-0.8	-0.8
Capsule material	Pt	Pt	Pt	$Au_{80}Pd_{20}$	Pt	Pt	$Au_{80}Pd_{20}$	$Au_{80}Pd_{20}$
Wt% Fe added[2]	0	5	13	10	5	13	0	2
Fe in capsule (% at.)[3]	24-25	26-27	30-33	3.2-3.4	26	38	4	2.9
Glass	PST-9	PST-9	PST-9	REU-04	PST-9	PST-9	REU-04	REU-04

[1]Log fO_2 charge – Log fO_2 NNO at the same P and T. NNO equation from Pownceby and O'Neill (1994).
[2]Amount of Fe (metallic iron) added to the glass in wt%.
[3]Fe concentration in capsule at the glass interface.

Table 4. Composition of representative 1 atm experimental glasses.

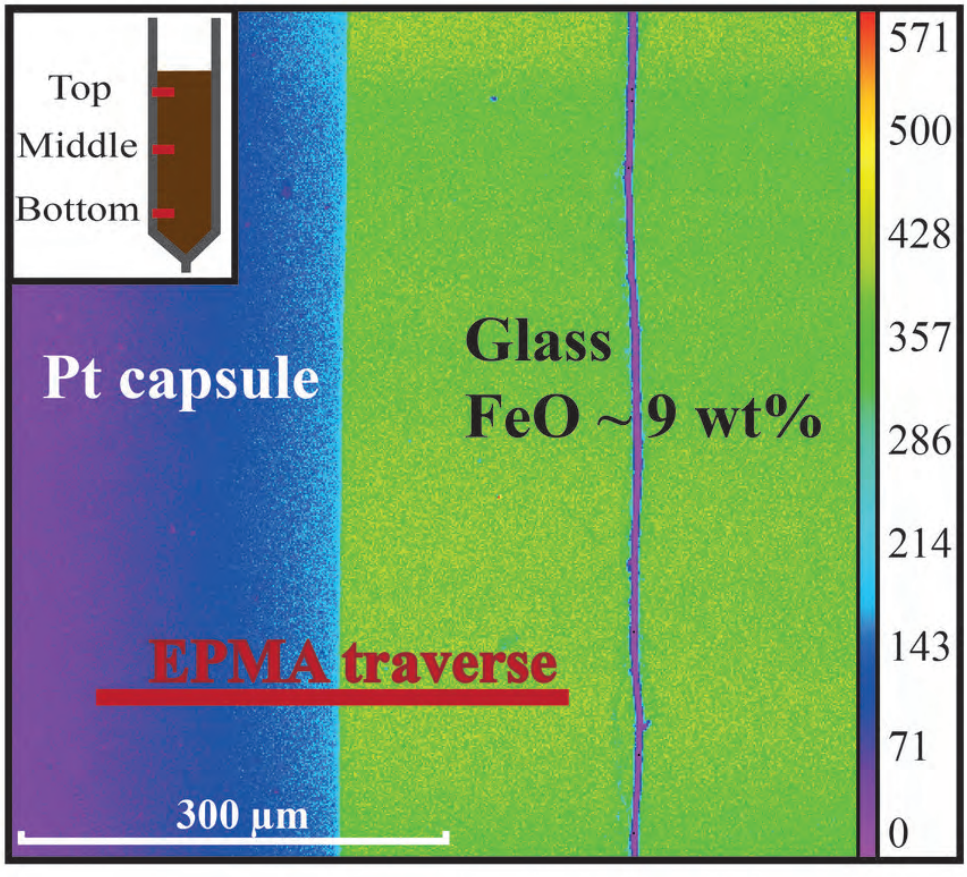
Oxide	1	2	2	3	3	4	5	5	6	6	7	8
SiO_2	50.2	49.9	53.8	49.3	54.3	51.1	49.3	51.7	46.2	52.4	48.8	49.7
TiO_2	1.00	1.03	1.06	0.90	0.93	0.85	0.89	0.82	0.79	0.80	2.53	2.52
Al_2O_3	16.6	16.3	17.0	16.4	17.0	17.3	16.7	17.1	15.7	16.9	13.6	13.7
FeO_t	7.54	7.79	5.48	9.86	6.30	7.24	9.95	7.89	15.2	9.95	10.8	10.6
MnO	0.20	0.16	0.13	0.17	0.12	nd	nd	nd	nd	nd	0.17	0.18
MgO	7.25	7.72	6.44	6.65	5.45	6.40	6.31	5.82	6.31	4.7	8.22	7.91
CaO	11.5	11.4	9.62	10.9	8.75	12.2	11.9	11.7	11.69	9.53	12.4	12.2
Na_2O	2.77	2.60	2.88	2.73	3.12	2.57	2.56	2.55	2.14	2.80	2.53	2.26
K_2O	2.30	2.40	2.77	2.34	3.23	1.94	1.89	1.97	1.52	2.47	0.65	0.55
P_2O_5	0.67	0.65	0.71	0.71	0.70	0.49	0.50	0.51	0.48	0.48	0.31	0.29
Cr_2O_3	0.04	0.04	0.05	0.05	0.04	nd	nd	nd	nd	nd	0.03	0.03
NiO	0.02	0.01	0.02	0.01	0.01	nd	nd	nd	nd	nd	0.01	0.06
Total	97.7	97.0	97.6	97.6	97.0	97.7	96.9	100	97.6	97.7	95.7	97.8
Wt% Fe added[1]	0	5	5	13	13	0	5	5	13	13	0	0
ΔFeO_t (% relative)	-5	-2	-31	+24	-21	-9	+25	-1	+91	+25	+2	0
Position	bottom	bottom	top	bottom	top	bottom	bottom	top	bottom	top	middle	middle
Glass	PST-9	PST-9	PST-9	PST-9	PST-9	PST-9	PST-9	PST-9	PST-9	PST-09	REU-04	REU-04

Charge# as in Table 2.
Data are averages calculated on multiple (10-50) glass analyses. Concentrations are normalized to 100%; total is unnormalized.
ΔFeO_t = 100* (FeO_t glass – FeO_t starting glass) / (FeO_t starting glass).
[1]Amount of Fe (metallic iron) added to the glass in wt%.

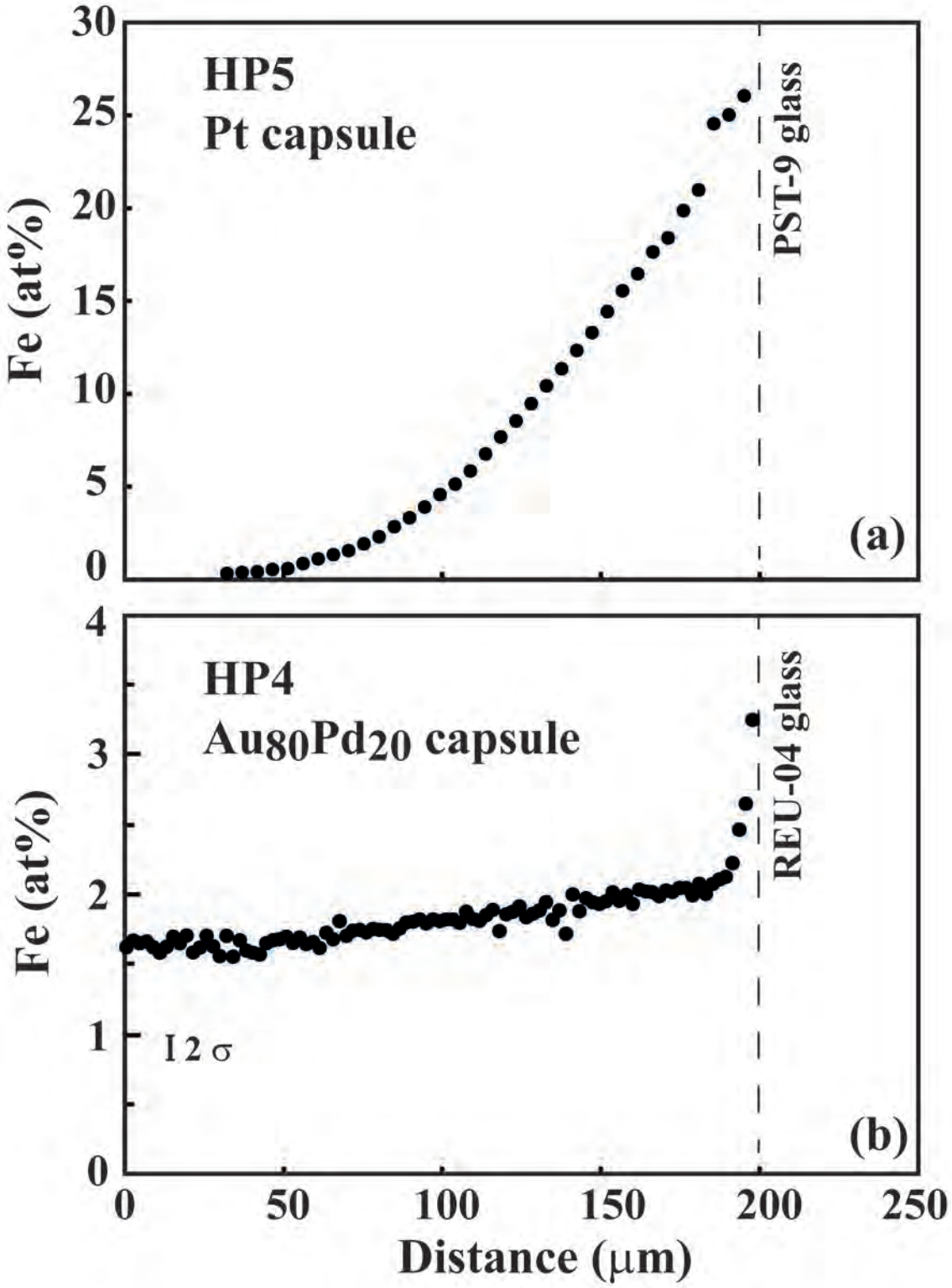
Table 5. Composition of representative high pressure experimental glasses.

Oxide	HP1	HP2	HP3	HP4	HP5	HP6	HP7	HP8
SiO_2	53.2	51.0	46.5	49.6	49.8	44.3	51.3	50.5
TiO_2	0.98	0.87	0.79	2.59	0.90	0.79	2.61	2.55
Al_2O_3	17.3	17.2	15.0	14.2	16.9	14.8	14.0	13.7
FeO_t	3.15	7.84	16.4	11.9	8.76	18.9	8.96	9.92
MnO	0.14	0.16	0.13	0.11	0.15	0.15	0.16	0.19
MgO	6.90	6.51	5.87	7.23	6.47	5.90	7.92	8.08
CaO	13.0	11.9	10.7	11.4	12.0	10.6	11.8	11.7
Na_2O	2.45	2.06	2.14	1.93	2.46	2.20	2.43	2.57
K_2O	2.21	2.01	1.96	0.73	2.06	1.78	0.62	0.59
P_2O_5	0.67	0.52	0.53	0.36	0.49	0.46	0.21	0.20
Cr_2O_3	0.01	0.00	0.00	0.02	0.01	0.01	0.03	0.04
NiO	0.01	0.00	0.00	0.00	0.04	0.04	0.07	0.05
Total	92.7	93.5	93.6	92.7	94.1	95.1	96.0	95.4
Wt% Fe added[1]	0	5	13	10	5	13	0	2
ΔFeO_t (% relative)	-60	-1	+106	+12	+10	+138	-15	-6
Position	middle	middle	middle	all	bottom	bottom	all	all
Glass	PST-9	PST-9	PST-9	REU-04	PST-9	PST-9	REU-04	REU-04

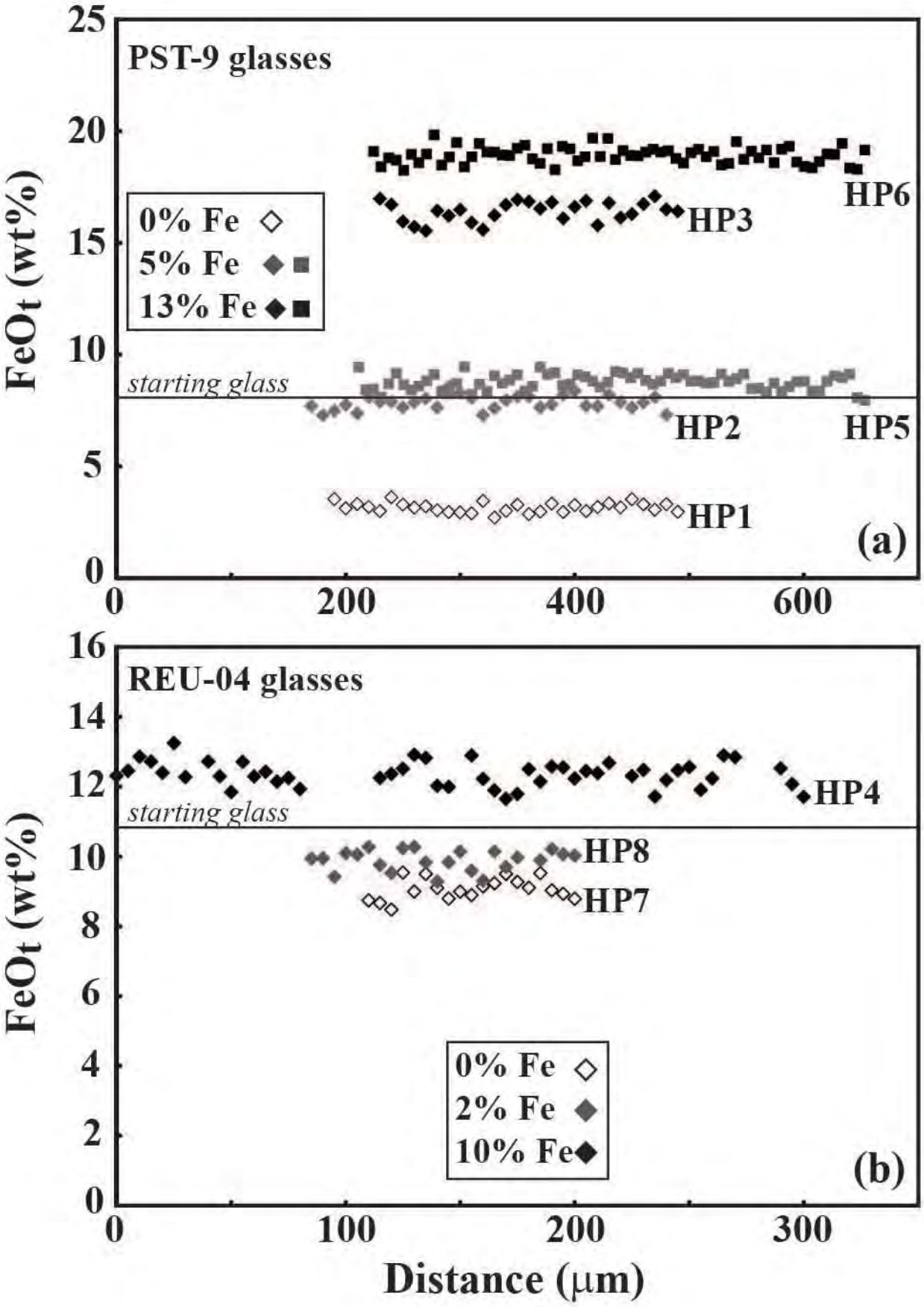
Charge# as in Table 3.
Data are averages calculated on multiple (10-50) glass analyses. Concentrations are normalized to 100%; total is unnormalized.
ΔFeO_t = 100* (FeO_t glass – FeO_t starting glass) / (FeO_t starting glass).
[1]Amount of Fe (metallic iron) added to the glass in wt%.



Brugier et al. Fig. 1



Brugier et al. Fig. 2



Brugier et al. Fig. 3