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# Platinum-iron alloy sample containers for melting experiments on iron-bearing rocks, minerals, and related systems

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SUMMARY. A method of producing platinum-iron alloy sample containers has been developed that allows experiments to be carried out on iron- and volatile-bearing systems with minimal net exchange of iron between the sample and its container. Preliminary experiments carried out using these containers in the temperature range from 1100 °C to 1250 °C and at pressures up to 10 kb over periods of up to 75 hours produced an average iron loss of 10% to 16% (as FeO) compared with more than 50% FeO loss obtained using pure platinum containers. A more judicious choice of alloy composition would reduce this loss still further.

MELTING experiments on igneous rocks and analogous synthetic systems can provide considerable information on the crystal-liquid equilibria involved in magmatic processes. Unfortunately systems containing iron in both of its oxidation states and also containing small but significant amounts of volatile components, such as $CO_2$ and $H_2O$, have been particularly difficult to investigate at high temperatures, largely due to the lack of a suitable container material. The loss of iron to noble metal sample containers is a well-known but poorly quantified phenomenon.

Attempts to minimize iron loss to platinum have involved an unsuccessful method of saturating the container with iron from a silicate melt, adding sufficient excess iron to the sample to compensate for the subsequent iron loss (Nicholls, 1974) and reducing the experiment duration to a minimum. The latter methods risk failure to achieve equilibrium, especially with respect to the distribution of the minor and trace elements between crystals and liquids.

It is possible to carry out melting experiments without iron loss in container materials such as graphite (Thompson, 1974), molybdenum (Biggar, 1970), and iron metal (O'Hara and Humphries, 1977). These containers are suitable for volatile-free systems and the low oxygen fugacities appropriate for the moon, meteorites, and the terrestrial mantle. A recent comparison has demonstrated substantial losses of Fe to $Ag_{40}$-$Pd_{60}$, Pt, and $Pt_{95}$-$Au_5$ (more than 50% FeO loss) with most iron loss to the latter (Biggar, 1977).

This paper reports a method of producing platinum-iron alloy sample containers in which it is possible to carry out experiments with a minimum of iron exchange between the sample and its container in systems containing mixed volatiles and both ferrous and ferric oxide and at temperatures above those for which the more silver-rich silver-palladium alloys could be used.

*Platinum-iron alloy containers.* The ideal container material is chemically inert by being saturable at very low concentrations with all of the chemical species present in the system under investigation. Platinum is saturable with respect to almost all components except iron (and nickel). The activity of iron in a silicate melt is specified by the bulk composition, temperature, and pressure. If a platinum-iron alloy can be made with exactly the same activity of iron as that in the silicate system then there will be no net exchange of iron with the capsule. If the mechanical properties of such an alloy, or range of alloys, is acceptable then they would constitute near-ideal container materials. The range of alloys that would be required to cover the oxygen fugacity range of the magnetite stability field is 0-15 wt% Fe (Taylor and Muan, 1962).

Since platinum-iron alloy tubes are not commercially available and it would in any case be impractical to stock the wide range of alloy compositions that might be required, the following method of producing containers approaching the required composition has been developed: starting materials are laboratory reagent grades of hydrated crystalline sodium meta-silicate, which is melted to produce glass and then ground, and magnetite. A physical mixture of these materials is made with compositions in the range from 10% to 25 wt% of magnetite. Cut lengths of 0·1 mm wall thickness platinum tube, either 2 mm or 3 mm in diameter and 1 cm or 2 cm long with both ends open, are immersed vertically in a crucible containing about 20 grams of the mixture, which is then held at 1200 °C for 24 hours or more in an atmospheric pressure furnace in which the oxygen fugacity is controlled by mixing $H_2$ and $CO_2$. At the end of this period the crucible is removed and the tubes recovered by dissolving the glass in hot agitated water. This may take several days.

Typical distributions of iron in the platinum tube wall after 24 and 72 hours are illustrated in fig. 1.

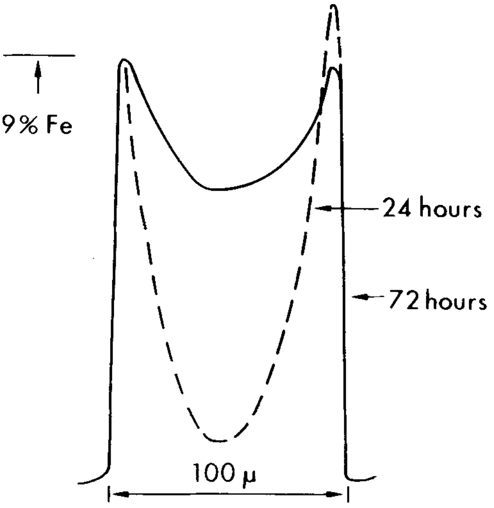


FIG. 1. Distribution of iron in platinum tube wall as a function of time.

The iron content of the platinum quickly reaches a maximum value at the tube surface. There is virtually no iron in the centre of a 0·1 mm thick wall after 24 hours, about 66% of the maximum amount after 72 hours, and about 70% of the maximum amount after 200 hours. In subsequent discussion the iron content referred to is the maximum iron content at the internal surface of the tube wall. The 24-hour iron distribution, although bound to lead to iron exchange with the charge in subsequent experiments, produces a capsule with sufficient ductility to withstand the deformation involved in high-pressure experiments, except perhaps those in solid media apparatus. Capsules with the 72-hour iron distribution tend to disintegrate when crimped, especially at iron contents in excess of 15%. The capsules are arc welded with an iron electrode in an argon stream.

The iron content of the tubes is dependent on oxygen fugacity and the composition of the starting mixture. At 1200 °C the starting mixtures used contain only liquid, although magnetite crystallizes readily on cooling. Fig. 2 shows the iron contents of alloys produced as a function of oxygen fugacity and melt composition at 1200 °C. The scatter in the data probably represents failure to fully equilibrate the large mass of melt with the gas phase and consequent variation of the alloy composition at the tube wall of ± 1% Fe. In addition, at low iron contents and low oxygen fugacities, the melt may become significantly depleted in iron. No iron is absorbed from a melt in equilibrium with pure $CO_2$.

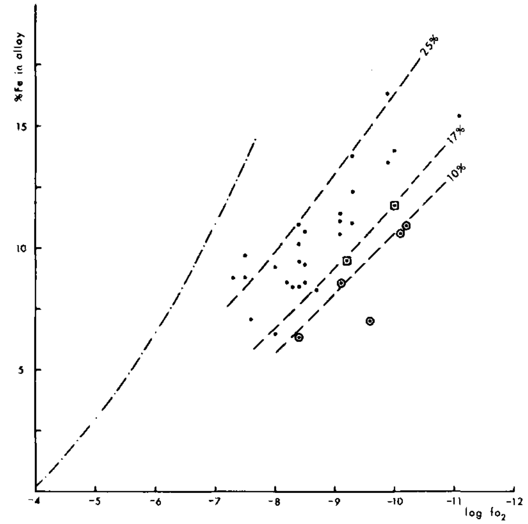


FIG. 2. Iron content of platinum-iron alloys as a function of oxygen fugacity and composition of the $Na_2SiO_3$–$Fe_3O_4$ melt at 1200 °C. Symbols: ● preparation in 25% magnetite mixture; ⊡ preparation in 17% magnetite mixture; ⊙ preparation in 10% magnetite mixture. Dash lines show the maximum iron contents to be expected. The dash-dot line represents alloy compositions in equilibrium with magnetite at 1300 °C (Taylor and Muan, 1962).

Other methods of producing the alloys were tried and proved unsatisfactory. Iron or magnetite sank in molten sodium chloride or sodium carbonate and produced an uneven iron distribution. Ferrous chloride in sealed tubes heated at pressure liberated sufficient chlorine to rupture the capsules on depressurisation.

*Melting experiments on ZP422*, an alkali basalt from the Midland Valley of Scotland, illustrate the advantages of platinum-iron alloys over pure platinum. The results of these experiments will be described in detail elsewhere. The composition of ZP422 is as follows: $SiO_2$ 46·50, $TiO_2$ 2·20, $Al_2O_3$ 14·87, $Fe_2O_3$ 4·04, FeO 8·64, MnO 0·19, MgO 7·16,

TABLE I. *Results of experiments on ZP422 in platinum and sealed and unsealed platinum-iron alloy capsules*

| | | | | A | | | B | | | | C | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Sealed Pt tube | % FeO loss | | Sealed Pt/Fe tube | | % FeO loss | | Open Pt/Fe tube | | % FeO loss | |
| No. | *T*(C) | *P*(kb) | *t*(H) | Assemblage | *a* | *b* | Tube % Fe | Assemblage | *a* | *b* | Tube % Fe | Assemblage | *a* | *b* |
| 16 | 1200 | 1 | 2 | Gl | 22 | 14 | | | | | 13 | Gl | 11 | 0 |
| 17 | 1200 | 1 | 55 | Gl | 55 | 50 | 13 | Gl | 11 | 5 | 13 | Gl* | 68 | 66 |
| 23 | 1180 | 1 | 25 | Gl | 44 | 42 | 9 | Gl+Ol | 6 | 3 | 9 | Gl+Ol+Plag | 23 | 14 |
| 19 | 1150 | 1 | 48 | Gl | 38 | 36 | 13 | Gl+Ol+Plag | 14 | −3 | 13 | Gl+Ol+Plag | 15 | 25 |
| 20 | 1125 | 1 | 48 | Gl+Ol+Ore | 33 | 25 | 13 | Gl+Ol+Ppx+Plag | 11 | −4 | 13 | Gl+Ol+Cpx+Plag | 21 | 25 |
| 18 | 1100 | 1 | 26 | Gl+Ol+Cpx+Ore | 25 | 15 | 13 | Gl+Ol+Cpx+Plag +Ore | 16 | 7 | 13 | Gl+Ol+Cpx+Plag +Ore | 9 | −1 |
| 21 | 1200 | 5 | 66 | Gl | 66 | 54 | 16 | Gl | 22 | 17 | 16 | Gl | 14 | 10 |
| 22 | 1150 | 5 | 24 | Gl+Cpx | 40 | 28 | 10 | Gl+Ol+Cpx | 5 | 12 | 10 | Gl+Ol+Cpx+Plag | 5 | 5 |
| 33 | 1160 | 5·5 | 49 | Gl+Cpx | 54 | 51 | 9 | Gl+Ol+Cpx | 22 | 21 | 9 | Gl+Ol+Cpx+Plag | 33 | 10 |
| 30 | 1170 | 6·5 | 18·5 | Gl | 37 | 30 | 11 | Gl+Cpx | 17 | 20 | 11 | Gl+Ol+Cpx+Plag | 40 | 29 |
| 31 | 1150 | 6·5 | 18·5 | Gl+Cpx+Ore | 38 | 28 | 11 | Gl+Cpx+Ore | 22 | 14 | 11 | Gl+Ol+Cpx+Plag | 30 | 6 |
| 32 | 1130 | 6·5 | 27 | Gl+Cpx+Ore | 36 | 32 | 11 | Gl+Cpx+Plag+ Ore | 36 | 16 | 11 | Gl+Ol+Cpx+Plag +Ore | 45 | 22 |
| 28 | 1180 | 7·5 | 18·5 | Gl | 38 | 33 | 9 | Gl+Cpx | 0 | 1 | 9 | Gl+Ol+Cpx+Plag | 8 | 2 |
| 29 | 1160 | 8 | 28 | Gl+Cpx | 38 | 33 | 9 | Gl+Cpx | −2 | −5 | 9 | Gl+Ol+Cpx+Plag | 8 | 6 |
| 24 | 1250 | 10 | 6 | Gl | 29 | 27 | 9 | Gl | 19 | 17 | 9 | Gl | 15 | 17 |
| 27 | 1225 | 10 | 139 | Gl | 68 | 67 | 11 | Gl+Cpx | 36 | 33 | 11 | Gl+Cpx+Plag | 72 | 70 |
| 25 | 1200 | 10 | 19·5 | Gl | 42 | 39 | 11 | Gl+Cpx | 18 | 15 | 11 | Gl+Cpx+Plag | 30 | 16 |
| 26 | 1150 | 10 | 73 | Gl+Cpx | 68 | 63 | 9 | Gl+Cpx+Plag+ Ore | 19 | 2 | 9 | Gl+Ol+Cpx+Plag +Ore | 19 | 13 |

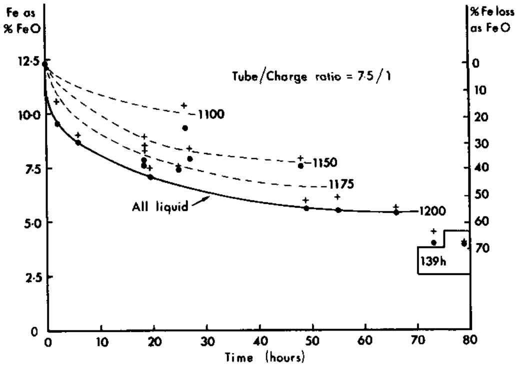
*a*: value derived from microprobe analysis.
*b*: value derived from the FeO/MgO ratio of the microprobe analysis.
* Glass from outside a leaked capsule.
Gl = Glass, Ol = Olivine, Cpx = Clinopyroxene, Plag = Plagioclase.

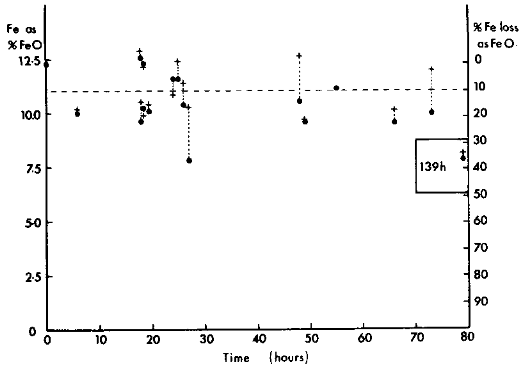
CaO 10·15, $Na_2O$ 2·77, $K_2O$ 0·93, $H_2O+$ 1·08, $H_2O-$ 0·24, $P_2O_5$ 0·37, total 99·14 (analyst: S. Rizzelo).

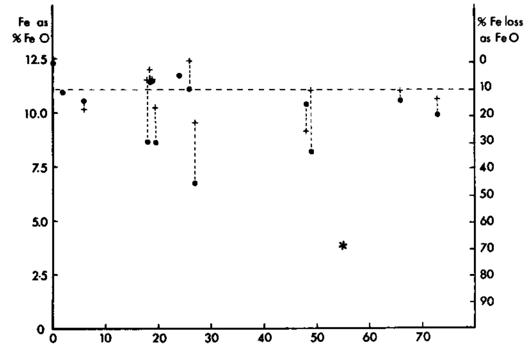
Finely ground rock powder, dried at 110 °C, was loaded and sealed into platinum tubes, and both sealed and unsealed platinum-iron alloy tubes containing about 10% iron. The open-tube experiments lose combined volatiles, including oxygen, during the experiment. Experiments were carried out in internally heated gas media pressure vessels (Ford, 1976) and solid media pressure vessels (O'Hara *et al.*, 1971). The oxygen fugacities of the experiments are unknown in exact numerical terms. However, if there is no iron exchange between charge and capsule the oxygen fugacity of the charge may be considered as being defined by the platinum-iron alloy composition used. If there is substantial iron loss from the charge then the oxygen fugacity is lower than that appropriate for the platinum-iron alloy used. Conversely, substantial iron gain by the charge indicates that the oxygen fugacity is higher than that appropriate for the alloy composition used.

The results of experiments are given in Table I. Iron losses to pure platinum, and to sealed and unsealed platinum-iron alloys are shown in figs. 3, 4, and 5. The iron contents of the charges were determined by electron-microprobe analysis. This method has been adopted for routine use in preference to wet chemical analysis since there is frequently insufficient material (< 10 mg) for both, microprobe analysis of the individual phases is in any case normally desirable and in those cases, involving all glass charges, where both microprobe analysis and wet-chemical analysis for FeO have been carried out the results were identical (A. Graham, pers. comm.). For wholly melted charges analyses of the glasses, which were homogenous, were obtained from a defocused beam about 10 $\mu$m in diameter. For partially melted charges analysis was of an area of about 350 $\mu$m square.

Whole-sample microprobe analysis is not entirely satisfactory for partially melted charges since the occurrence of cracks and holes tends to reduce analysis totals and non-uniform distribution of phases may produce sampling bias in the area chosen for analysis. For the purposes of estimating iron loss or gain the microprobe analysis totals have been normalized to the starting composition total minus $H_2O$ and one oxygen from $Fe_2O_3$.







FIGS. 3-5: FIG. 3 (*top left*). Iron contents of ZP422 charges after experiments in sealed platinum tubes, data from Table I. Symbols: ● FeO content determined by microprobe analysis; + FeO loss determined from FeO/MgO ratio of microprobe analysis. Curves correlate experiment temperatures with amount of iron loss. FIG. 4 (*top right*). Iron contents of ZP422 charges after experiments in sealed platinum-iron alloy tubes. Symbols are in fig. 3. FIG. 5 (*bottom*). Iron contents of ZP422 charges after experiments in open platinum-iron tubes, * glass collected from outside a leaked capsule, other symbols as in fig. 3.

The effect of sampling bias or analytical error on iron loss can be assessed from consideration of the bulk FeO/MgO ratio with the assumption that these oxides are usually associated in the ferromagnesian minerals. The + symbols in figs. 3, 4, and 5 represent iron loss estimated from the FeO/MgO ratio of the microprobe analysis (Table I, % FeO loss column *b*) and should be read in conjunction with the % FeO loss scale. The small consistent differences of about 5 % FeO loss probably represent analytical bias, either in the accepted bulk composition quoted or in the microprobe technique, while the larger differences probably represent sampling bias.

*The loss of iron to pure platinum is substantial.* It exceeds 20 % of the amount present after 2 hours and 50 % of the amount present after 50 hours. The loss of iron to sealed platinum-iron alloy tubes is very much lower, averaging 10 % or 16 % FeO loss (by FeO/MgO ratio and analysis respectively) for the series of experiments in sealed capsules over all times up to 73 hours. The use of capsules with a higher iron content would have reduced this iron loss still further. The loss of iron to open platinum-iron capsules appears to be somewhat more erratic than to sealed platinum-iron capsules. This is ascribed to various amounts of oxygen loss to the argon pressure medium, which has an oxygen fugacity below the iron-wüstite buffer assemblage; tarnished iron capsules are recovered untarnished. The analysis with 68 % FeO loss in fig. 5 is of a glass that had leaked out of the capsule and was attached to its outside where it would have lost oxygen at a faster rate.

A number of experiments were carried out in sealed platinum-iron capsules in solid media apparatus. All of these experiments lost substantial amounts of iron. This is probably due to shearing of the capsule walls, making them effectively open capsule experiments, and equilibration of the charges with the graphite furnace at a considerably lower oxygen fugacity than that intended. The results of these experiments require further verification and are not reported here. It may be possible to enclose the fairly brittle platinum-iron alloy capsules in a second more ductile membrane to ensure a hermetic seal for solid media experiments.

The platinum-iron alloy composition appropriate for an experiment on a given starting composition is dependent on the iron activity of that composition under the given experimental conditions. Initially this iron activity, and hence the required alloy composition, will be unknown. However, a few experiments in alloys of different compositions should quickly establish the one most suitable. In any case, there is an increased margin for error where the experiments are of short duration.

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