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The loss of Fe and Na from a basaltic melt during experiments using the wire-loop method

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SUMMARY. Losses of Fe and Na from a typical basaltic liquid during experiments using the wire-loop method have been determined for both Pt and $Ag_{40}Pd_{60}$ alloy wire by electron-microprobe analyses of the quenched glasses. The amount of Fe lost is dependent on the duration of the experiment and is particularly sensitive to the ratio of sample to metal in direct contact with it. Fe losses can be minimized by using the thinnest wire possible in conjunction with the largest amount of sample that will adhere to the wire and, if Ag-Pd wire is used, can be kept below the 1 % level even in long experiments. Much more serious in terms of changes in the bulk composition are losses of Na, which appear to be in direct linear proportion to the length of the experiment and in inverse proportion to the mass of the sample. Even when samples in excess of 200 mg are used the Na losses are unlikely to be less than 5 % except in experiments of less than a few days' duration or on samples with very low initial Na contents.

ONE of the most serious problems facing experimental petrologists working on natural silicate compositions at or near their liquidus temperatures is finding a suitable container material. Most simple materials that retain adequate physical strength at the required temperatures either react with the sample (e.g. iron, silica, alumina, and various refractories), absorb elements such as Fe from the sample (e.g. platinum), or are usable only over a very restricted, and often inappropriate, range of physical conditions (e.g. molybdenum (Biggar, 1970; O'Hara and Humphries, 1977)). Attempts to minimize changes in the bulk composition of samples during experiments have centred mainly on the use of various noble metal alloys such as Ag-Pd (Muan, 1963) and Pd-Au (Duke, 1976; Biggar, 1977). Considering the number of experimental studies utilising Ag-Pd containers surprisingly little quantitative information has been published about the loss of Fe from natural silicate melts to these alloys but the evidence (e.g. Fudali, 1965; Gibb and Henderson, 1971; Stern and Wyllie, 1975) suggests that, although Ag-Pd alloys are better than Pt, significant losses of Fe still occur. In the case of Pt-Au alloys, Biggar (1977) concluded that they are less satisfactory than either Ag-Pd or Pt. He also suggested that Pt-Fe alloys might prove to be satisfactory but subsequent work (Ford, 1978; Biggar (pers. comm.)) suggests that it may be difficult to obtain the correct alloy composition for any given experiment and changes in the Fe content of the sample during experiments may still be considerable.

A recent, more promising approach for atmospheric-pressure experiments was the introduction of the 'wire-loop' method (Presnall and Brenner, 1974; Donaldson *et al.*, 1975) in which the area of contact between the metal and the sample, and hence the loss of Fe, was substantially reduced by eliminating the container and suspending the sample from a loop of thin Pt wire, to which it adheres by surface tension.

We are at present carrying out a programme of experiments to study supercooling, nucleation, and crystal growth in basic lavas and minor intrusions. In an earlier related study (Gibb, 1974) $Ag_{40}Pd_{60}$ alloy containers were used but as the amounts of Fe taken up by the containers during the experiments could affect the results we have since adopted the wire-loop method. Also (Donaldson *et al.*, 1975), heterogeneous nucleation can occur on the walls of the container and this should be substantially reduced by the much smaller metal/melt interface in the wire-loop method. Parallel sets of experiments using the two methods revealed that for the same sample the field of plagioclase non-nucleation (Gibb, 1974) is significantly larger in the Pt wire-loop experiments than in those carried out in Ag-Pd containers. This could be due to the reduction of heterogeneous nucleation or a reduced Fe loss in the wire-loop experiments or both, but it could also be a consequence of increased viscosity of the melt resulting from loss of alkalis from the sample (O'Hara and Humphries, 1977). This uncertainty, together with the fact that routine tests of the wire after the experiments indicated a definite magnetic susceptibility suggesting that the uptake of Fe was not negligible, led us to investigate further the

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changes in the bulk composition of the samples during experiments using wire-loops. As a result of our findings we have adopted a modification of the wire-loop method using alloy wire and the purposes of this contribution are first to report the extents of the changes in bulk compositions, especially Fe loss, for a typical basaltic composition when experiments are carried out using Pt and Ag-Pd alloy wires, and secondly to suggest ways in which they might be minimized.

The experiments: rationale and method. As in the case of Pt and noble metal alloy containers, any loss of Fe from the sample to the wire during an experiment will depend on the temperature and duration of the experiment, the oxygen fugacity (f_{O_2}), the relative masses of sample and metal (and their inter-facial area), and the activity of Fe in the sample. In addition, there is a possibility that alkalis may be lost during an experiment and O'Hara and Humphries (1977) have suggested that this is more serious when the wire-loop method is employed than when containers are used. Since, for many natural basalts, the ranges of liquidus temperatures, magmatic f_{O_2}, and total iron contents are relatively restricted, we have confined the present investigation to the effects of duration and metal: sample ratio on a single basaltic composition G.9 (Table I) at a temperature of $1251° \pm 5$ °C (the liquidus temperature of this basalt is 1242 °C), a P_{total} of 1 atmosphere and an f_{O_2} of 10^{-8}. Few basalts other than those enriched in olivine phenocrysts have 1 atmosphere liquidus temperature higher than 1251 °C, and an oxygen fugacity of 10^{-8} at this temperature is towards the lower end of the range appropriate to natural basaltic magmas (e.g. Fudali, 1965; Carmichael *et al.*, 1974). These experimental conditions were deliberately chosen in order that the Fe losses reported herein should be as high as any likely to arise during 1 atmosphere liquidus experiments on natural basaltic compositions, but higher temperatures or lower f_{O_2} could substantially increase Fe losses. [A contemporary study by C. H. Donaldson (1979) evaluates the effects of varying these parameters on Fe loss using $Pt_{80}Rh_{20}$ wire loops and it seems probable that they will be at least as great in the case of Pt loops.]

TABLE I. *Composition of G.9*

SiO_2	45.74	MnO	0.19	P_2O_5	0.14
Al_2O_3	17.96	MgO	8.47	H_2O^+	1.32
TiO_2	1.43	CaO	10.31	S	0.05
Fe_2O_3	2.96	Na_2O	2.47	CO_2	0.20
FeO	8.60	K_2O	0.15		
				Total	99.99

Weighed amounts of rock powder were pressed into pellets 5 mm in diameter. Attempts to 'tack' the pellets on to the wire by heating the wire (cf. Donaldson *et al.*, 1975) had a high failure rate and frequently led to subsequent handling problems due to the fragile nature of the pellets. Instead, a weighed length of 0.2-mm diameter wire was gently twisted round the pellet and the entire pellet was partly fused to form a bead by suspending it in a muffle furnace substantially above its solidus temperature for a short interval. During this preliminary fusion, which generally took between 1 and 6 minutes, the muffle-furnace atmosphere was controlled by mixtures of CO, CO_2, and N_2 to prevent excessive oxidation of the Fe. After removal from the muffle furnace and prior to the experiment the bead and its wire loop were weighed in order to determine the mass of the sample at the start of the experiment. The experiments were carried out in an ordinary 30-mm bore, Pt-wound, vertical, quench furnace in which the f_{O_2} was controlled by a CO_2-H_2 mixture. At the end of the experiment the sample (complete with suspending wire and ceramic insulator (see Donaldson *et al.*, 1975, fig. 2)) was quenched into cold water. Generally this led to shattering of the bead[1] but in some cases it remained intact and in such cases the bead and wire were reweighed and the wire protruding from the bead cut off and weighed, thus permitting calculation of the ratio of sample to metal inside, i.e. in direct contact with, the bead. Although it must be admitted that this calculation based on post-experiment weights produces slightly incorrect results (it ignores any alkali loss, it is difficult to cut the wire off right at the surface of the bead, Fe might diffuse out along the wire, etc.) it does have the advantage that the 'lost' Fe is still weighed and it does provide the best readily obtainable value for the sample:metal ratio. After the experiments, fragments of the glass and wire or, whenever possible, the whole bead with wire inside, were mounted in epoxy and polished for electron-microprobe analysis. Where the bead remained intact after quenching, both the wire and glass were analysed with a traverse of points being made from the wire/sample interface to the outside of the bead. In the cases where the bead shattered, several fragments were mounted and a sufficiently large number of spots analysed to permit evaluation of any inhomogeneity and calculation of the bulk composition of the glass.

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[1] Quenching into liquids other than water, or even very shallow water, may significantly reduce the incidence of shattering—(Dr G. M. Biggar, pers. comm.). Also, beads suspended from Ag-Pd wire appear to be less prone to shattering than those suspended from Pt wire.

Loss of iron

Experiments using Pt wire. Presnall and Brenner (1974) determined that for a basalt liquid held at 1265 °C and an f_{O_2} of $10^{-7.5}$ for 16 hours the loss of Fe from the sample was negligible. After 3 days 2% of the original Fe was lost and 6% after 7 days. Donaldson *et al.* (1975) reported a loss of 2.5% of the Fe in a basaltic composition after 6 hours at 1250 °C and an f_{O_2} of 10^{-8} and almost twice as large a loss in half the time when the f_{O_2} was 10^{-13}.

To evaluate the effect of run duration on bulk composition we have conducted a series of experiments on basalt G.9 in which pellets of almost identical weight (60 ± 5 mg) were run under the conditions specified above for up to 5 days. This assumes that the mass of wire in contact with the sample was the same in each case, but this may not be absolutely true as the shape of the beads and the exact position of the wire within them varied slightly. After 24 hours up to 5% of the initial Fe content was lost rising to over 10% after 48 hours and even higher values in longer runs. These losses are comparable with those reported by Donaldson *et al.* (1975) for a different basalt under similar experimental conditions.

The effect of sample: metal ratio (this refers to metal actually inside the bead) on Fe loss is more difficult to evaluate accurately, especially as we only succeeded in recovering one of the quenched beads unshattered in the Pt wire-loop experiments. However, a good estimate can be obtained by comparing the results of almost identical experiments on pellets of markedly different initial weights. For example, after 73 hours at 1256 °C a pellet that initially weighed 55.9 mg had lost almost 14% of its Fe whereas after 72 hours at 1250 °C a 101.6 mg pellet had lost less than 5% of its Fe. Doubling the volume of a spherical bead results in an increase in its diameter by just under 26% and, if the wire passed through the centre of the bead, an increase in sample: metal ratio of just under 59%. As the beads are in reality teardrop-shaped and the wire generally passes through the narrow upper part of the bead, the increase in sample: metal ratio resulting from the 82% increase in volume in the example cited above is likely to be at least 50%. Evidently this increase results in a considerable reduction in Fe loss and the sensitivity of the amount of Fe lost to the sample: metal ratio might well account for the much lower loss levels recorded by Presnall and Brenner (1974), who used 0.05-mm diameter wire, than those reported here and by Donaldson *et al.* (1975) for 0.2-mm wire.

Iron losses from basaltic liquids in Pt wire-loop experiments, while undoubtedly less than those for experiments in Pt and Pt/Fe containers, are thus far from insignificant and could seriously affect the results of the experiments.

Experiments using Ag-Pd wire. It is generally assumed that Fe losses from basaltic compositions in experiments in the range 1100–1200 °C are small (< 1%) when $Ag_{60}Pd_{40}$ *containers* are used and there is some evidence to support this view (e.g. Fudali, 1965; Gibb and Henderson, 1971). Unfortunately this alloy is of very limited use at temperatures above 1200 °C and, for conditions such as those required for the experiments reported here, it is necessary to resort to a more Pd-rich alloy such as $Ag_{40}Pd_{60}$. To the best of our knowledge only a small amount of information has been published on the levels of Fe loss from basaltic compositions in experiments run in containers of this latter alloy (Bow *et al.*, 1976). Following a previous study in which $Ag_{40}Pd_{60}$ containers were used (Gibb, 1974) and the early part of the programme of experiments referred to in the introduction, attempts were made to evaluate the levels of Fe loss to such containers and it was found that, although they are subject to considerable variations due to uncontrollable factors such as the amount of creep of the liquid up the container wall, the losses are less than for Pt containers, similar to those for Pt wire loops in short experiments, and greater than for Pt wire loops in long experiments. We attribute this latter effect to the selective volatilization of Ag from the alloy resulting in an increased capacity of the container to absorb Fe with time.

Obviously, Fe losses of the level recorded for Pt wire loops and $Ag_{40}Pd_{60}$ containers are unsatisfactory in experiments of several days' duration designed to study supercooling effects and nucleation and crystal growth at near-liquidus temperatures. On the basis that the Pt wire loops proved a significant improvement on Pt containers, we have modified the method to use $Ag_{40}Pd_{60}$ wire in the hope that a similar improvement over the alloy containers could be effected thus reducing Fe losses in our experiments to a more tolerable level. [Similarly Pt-Fe alloy wire loops might give lower changes in Fe content than containers of the same metal and initial evaluations (Biggar, pers. comm. and in press; Benhamou, in press) indicate this to be the case.]

The results of a set of experiments to determine the effects of time and sample: metal ratio on the loss of Fe from basalt G.9 to the $Ag_{40}Pd_{60}$ wire are given in fig. 1. The experiments represented by solid symbols in fig. 1 illustrate the relationship between Fe loss and run duration. In these the sample: metal weight ratio is known to be within the range 3.7–4.25 from post-experiment weighings of unshattered beads (circles) or, in the case of shattered

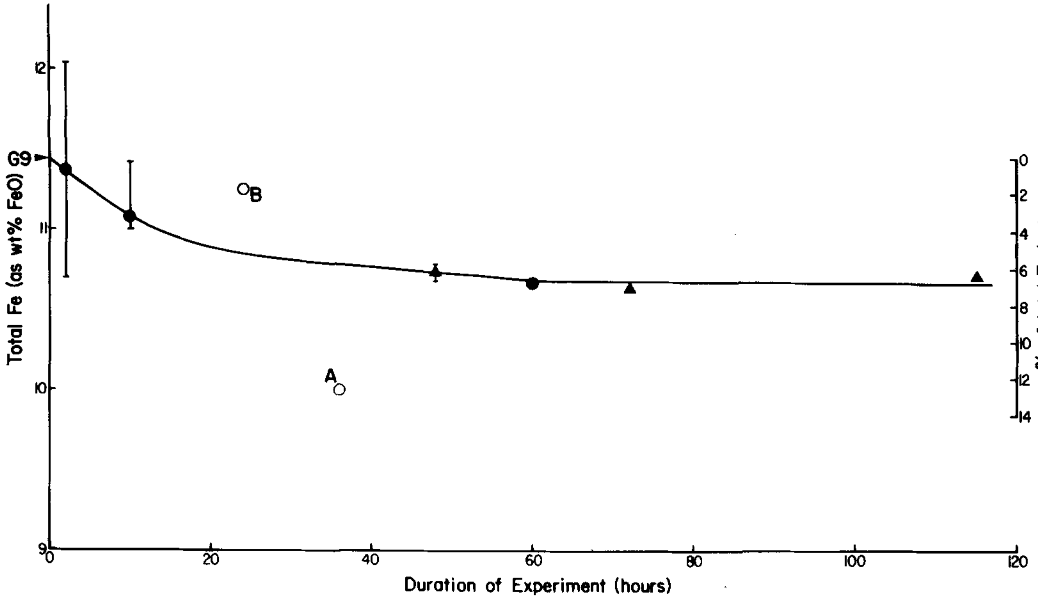

FIG. 1. Average Fe contents of quenched glasses from experiments on basalt G.9 using 0.2-mm-diameter $Ag_{40}Pd_{60}$ wire loops. Vertical bars indicate the range of Fe contents determined by electron-probe spot analyses. The symbols are explained in the text.

beads, is inferred to be within this range from pre-experiment weight and length and position of the wire within the sample (triangles). The beads used in these experiments were of similar size and initial weight (i.e. approximately 60 mg) to those used in the corresponding experiments for Pt wire but have slightly higher sample:metal weight ratios due to the lower density of the alloy. Spot analyses by electron-microprobe revealed that the glasses produced are not homogeneous in runs of up to 60 hours. This inhomogeneity, which is particularly pronounced in the very short experiments, is not due to the establishment of an iron concentration gradient towards the sample/wire interface and is presumed to be a relic of the original mineral distribution in the rock powder. It can be seen from the average Fe contents of the glasses in fig. 1 that the loss after 24 hours is not very different from that reported above for Pt wire but, in contrast to the Pt wire, it does not appear to increase substantially above the 6 % level, which it reaches after approximately 40 hours. This would seem to indicate that the alloy wire is significantly better than either Pt wire or $Ag_{40}Pd_{60}$ containers for experiments longer than 24 hours, and under the optimum conditions (see below) could be very much so.

The importance of sample:metal ratio in controlling the loss of Fe can be evaluated by comparing the results of the above experiments with those in which the ratio is markedly different. Two examples of the latter are shown in fig. 1 by the open circles A (sample:metal = 2.85) and B (9.87) and the differences in Fe loss speak for themselves. If the not unreasonable assumption is made that the Fe-loss *v.* time curves have a similar shape for the different sample:metal ratios, losses should be less than 2 % in experiments where the ratio is around 10 and, by extrapolation, could be kept below the 1 % level if ratios greater than about 15 were achieved. We have not attempted to verify this prediction for the same reasons that our experiments were confined to relatively low sample:metal ratios, namely, that the inaccuracies inherent in microprobe analyses would become serious at loss levels below 1 % and the increase in bead size necessary to obtain higher ratios would greatly reduce the chances of recovering an unshattered bead.

Electron-microprobe analyses of the Ag–Pd wire indicate that the amounts of Fe in the wire outside the bead are generally small, but that there is some diffusion of Fe from the sample along the wire and this increases with time. By contrast, the wire in direct contact with the sample absorbs substantial quantities of Fe as the following data illustrate. After a 2-hour experiment the alloy at the sample/wire interface contains 5.3 % (weight) of Fe while the centre of the wire shows only 0.8 % Fe.

After 10 hours the interface Fe content is the same but the Fe content of the centre of the wire has risen to 3 %. In longer experiments the radial concentration gradients disappear and typical Fe contents are 8 % after 60 hours and 9.5 % after 72 hours.

Loss of alkalis

When liquidus-temperature experiments are made on basaltic compositions in sealed containers the loss of alkalis from the sample can safely be assumed to be zero, but this may not be so when crimped, but not welded, containers are used as is common practice in 1-atmosphere experiments. Little information has been published on such losses but they seem likely to be small. This view is supported by the results of Bow *et al.* (1976), although they do report losses of up to 50 % under fairly extreme experimental conditions. In the case of wire-loop experiments however, losses of alkalis could be considerable. Donaldson *et al.* (1975) reported a loss of almost 39 % of the original Na_2O content of a basalt after 24 hours at 1250 °C but only 2.8 % after 6 hours at the same temperature (but a lower f_{O_2}).

Basalt G.9 has a low K_2O content (Table I) and consequently we have only attempted to evaluate the loss of Na_2O in our experiments. Assuming that any loss of alkalis is to the furnace atmosphere by volatilization, it should depend largely on the temperature and duration of the experiment, the mass and surface area of the sample, and the original Na_2O content, but should be independent of the type of wire used. The results of Donaldson *et al.* (1975) and Bow *et al.* (1976) suggest that f_{O_2} also influences alkali loss and an inverse relationship between the two has been confirmed by Donaldson (1979), who has also shown that the loss of Na_2O varies with the rate of gas flow through the furnace (in experiments reported here the flow rate of the gas mixture was 189 cc/min). Na_2O contents of the glasses have been determined for the same sets of experiments as are described in the section on Fe loss, and these are plotted against the length of the experiment in fig. 2. The experiments represented by solid symbols had initial sample weights of 60 ± 5 mg and the results demonstrate the effect of run length on Na_2O loss. In the shortest experiments inhomogeneities similar to those recorded for Fe exist and are attributed to the same cause. It appears that the loss of Na_2O is approximately linear with time reaching 25 % after about 120 hours for samples of 60 mg. The effects of varying the size of the sample can be seen from the

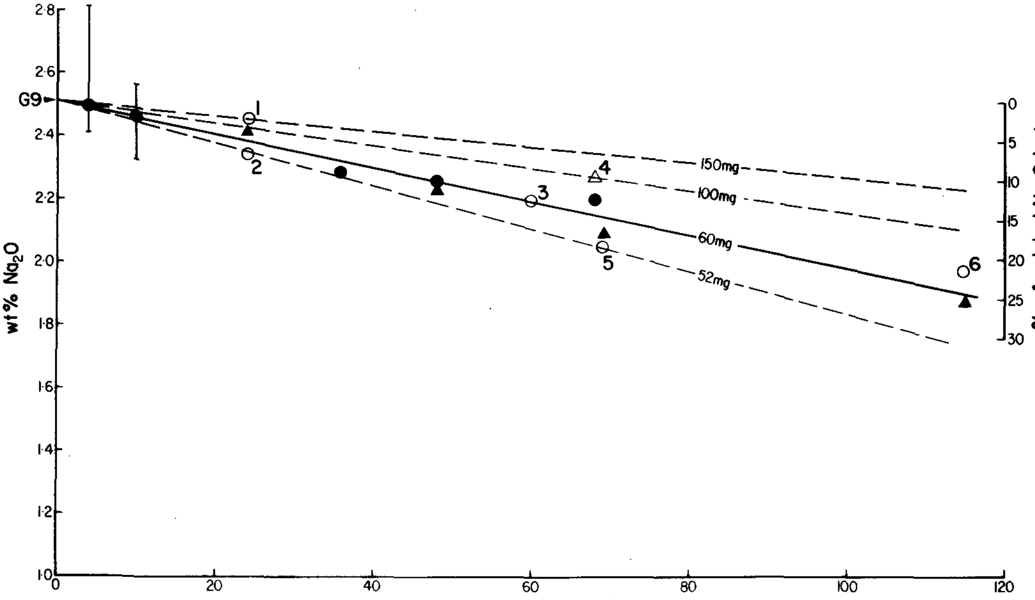

FIG. 2. Average Na_2O contents of quenched G.9 glasses from experiments using loops of Pt (▲) and $Ag_{40}Pd_{60}$ (●) wire. Solid symbols represent samples with an initial weight between 55 and 65 mg. Numbered open symbols represent lighter or heavier samples (see Table II). Vertical bars give the range of individual spot analyses.

TABLE II. *Sample weights of numbered experiments in fig. 2*

Number	Weight	Number	Weight
1	159 mg	4	102 mg
2	52 mg	5	52 mg
3	67 mg	6	71 mg

numbered open symbols in fig. 2, which have the initial weights given in Table II; samples larger than 60 mg show correspondingly smaller losses while the two 52 mg samples show slightly higher loss levels. If Na_2O losses are similarly linear for the different sample sizes, lines of approximate sodium loss can be drawn for various initial weights as in fig. 2 (dashed lines) and the disposition of these lines suggests that the best that can be hoped for in wire-loop experiments on basaltic melts are losses below the 5% level and this would require sample sizes in excess of 200 mg.

Conclusions

The wire-loop technique was developed to minimize Fe loss from the sample and appears to be relatively successful in doing so. The results of our experiments suggest that when $Ag_{40}Pd_{60}$ wire is used the relative loss of Fe from a basaltic melt can be kept below the 1% level however long the experiment, provided that the weight ratio of sample to metal in direct contact with it is greater than 15 and the f_{O_2} is not less than 10^{-8}. This is best achieved by using the thinnest grade of wire possible in conjunction with the largest amount of sample that will adhere to it by surface tension without complex internal looping.

Much more serious than the Fe loss is the relative loss of Na_2O, which can easily reach 5% in week-long runs under unfavourable conditions. Significant amounts of other alkalis may also be lost but the evidence (e.g. Donaldson *et al.*, 1975) suggests that K_2O losses are much less severe than Na_2O, although this may only be a result of the lower K_2O contents of the rocks in question (see Donaldson, 1979). However, under the optimum conditions of using samples in excess of 200 mg it appears that this loss could be kept below the 5% level except in long experiments.

Obviously considerable scope exists for more detailed evaluation of the compositional changes that occur during experiments on natural silicate melts, but we hope the data presented herein will prove useful to experimentalists in assessing whether or not to use the wire-loop method rather than the more traditional noble metal envelopes and tubes.

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