MINERALOGICAL MAGAZINE, MARCH 1979, VOL. 43, PP. 115-19

Changes in sample composition during experiments using the 'wire-loop' technique

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ATTEMPTS to minimize changes in the bulk composition of samples during experiments at high temperatures have led in recent years to the development of the wire-loop technique. The two papers by Donaldson and by Corrigan and Gibb to which this is a preface detail the extents of these changes and evaluate the factors controlling them with respect to basaltic melts.

These two studies of the use of wire-loop sample containers for experiments on basaltic melts were conceived and executed independently and it was only after the manuscripts reached Professor W. S. MacKenzie that we became aware of each other's work. Fortuitously, the two studies do not overlap to any great extent and are, in fact, complementary with Corrigan and Gibb having worked at a fixed temperature and examined the effects of wire type, sample mass, and time on Fe and Na losses from the sample, whereas Donaldson has studied the effects of superheat, oxygen fugacity, and time. In addition Donaldson's study utilizes a type of wire ($Pt_{80}Rh_{20}$) not covered by the work of Corrigan and Gibb who were concerned primarily with Ag-Pd alloy wire. Where the two projects involved experiments carried out under similar conditions the results from the two laboratories are in remarkably good agreement; a fact that may reflect both the precision and simplicity of the wire-loop technique. Together the studies emphasize the value of the technique in minimizing Fe loss but, at the same time, stress the possible risks of serious losses of alkalis. In addition they provide comprehensive data on the chemical changes to be expected during experiments on the melting and crystallization of basaltic compositions under a wide range of conditions.

Composition changes in a basalt melt contained in a wire loop of $Pt_{80}Rh_{20}$: effects of temperature, time, and oxygen fugacity

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SUMMARY. Losses of FeO, Na_2O, and K_2O from an alkali olivine basalt melted above the liquidus temperature in $Pt_{80}Rh_{20}$ wire loops are reported as a function of temperature, time, and P_{O_2}. Increasing temperature and decreasing P_{O_2} increase the losses. Compared to open capsules the wire-loop container reduces FeO loss to a minimum but may exacerbate Na_2O loss. Nonetheless for most types of experiment involving melt these losses are acceptable.

NOBLE-METAL wire loops are used as sample containers for basalt melting and crystallization studies in one-atmosphere gas-mixing furnaces (e.g. Weill and McKay, 1975; Lofgren *et al.*, 1974), in order to reduce Fe loss from the sample and also to increase contact between the sample and the gas atmosphere. Losses of FeO in melting runs of 1-24 hours duration were reported by Donaldson *et al.* (1975) to be 2.5-5% of the initial amounts. They noted, however, that Na_2O loss was greater, particularly at low oxygen fugacity. Rates of FeO, Na_2O, and K_2O losses from several basalts run in open Mo, Pt, and AgPd alloy capsules have been reported by Bow *et al.* (1976), but no such data exist for the wire-loop sample container. Neither have the quantitative effects of P_{O_2} and superheat on these rates been determined.

TABLE I. *Composition of SK 918* (Skye Main Lava Series alkali olivine basalt. Thompson* et al., *1972, Table 1)*

	1	2	Maximum deviation
SiO_2	46.66	48.68	0.63
TiO_2	2.22	1.87	0.05
Al_2O_3	14.64	16.73	0.49
FeO†	12.70	11.49	0.19
MnO	0.20	0.23	0.01
MgO	10.65	8.41	0.12
CaO	8.84	9.10	0.14
Na_2O	3.27	3.20	0.12
K_2O	0.54	0.44	0.04
P_2O_5	0.27	n.d.	
	100.00‡	100.12	

1. XRF analysis by Thompson *et al.* (1972).
2. Composition obtained by energy-dispersive electron probe analysis of six charges melted at 10–60 °C above the liquidus temperature for 2–10 minutes. (Average of 52 analyses.)

* Liquidus temperature 1232 ± 2 °C at $-\log f_{O_2} = 7.6$.

† All iron as FeO.

‡ Recast to 100.00.

Method. In this study 120 ± 5 mg samples of an alkali olivine basalt (Table I) were melted for times ranging between 0.05 and 168 hours, at values of P_{O_2} ranging between those of the hematite-magnetite and iron-wüstite buffers, and at temperatures from 10–60 °C above the liquidus temperature (fig. 1). The samples of pelletized rock powder (< 10 μm) were mounted on loops (2.5 mm in diameter) of $Pt_{80}Rh_{20}$ wire (0.2 mm thick) and fused to tear-drop shaped beads in a one-atmosphere quenching furnace in which the P_{O_2} was controlled by mixing of CO_2 and H_2 gases and was monitored electrochemically [see Donaldson *et al.* (1975) and Williams and Mullins (1976) for details]. In a sequence of runs of increasing temperature a constant gas-mixing ratio was used rather than a constant value of P_{O_2} (fig. 1). Samples were quenched in water. Polished thin sections of the glasses (quenched melts) were analysed with the energy-dispersive electron microprobe, using 100-second counting times; at least eight spots (2–3 μm diameter) were analysed on each sample. (The low-sample current used (4nA) prevents migration of Na in the glasses.) Within the errors of the analytical method the glasses are homogeneous, except for enhanced Fe depletion within 5 μm of the wire: it is emphasized that no concentration gradients have been found from the centre to margin of samples.

Results. Losses of Na and K by volatilization and of Fe to the wire occur during experiments (Table II; SiO_2 was not found to have volatilized). In very short runs (nos. 7, 10, 14, 25, 26, and 27) the glass composition differs significantly in SiO_2, Al_2O_3, FeO, and MgO from the published XRF analysis (Table I). Assuming that no significant chemical changes occur during the shortest melting runs of 5–10 minutes, there exists a deviation between the two methods of analysis. (Analysis of the Fe content of the wire loops of the short duration runs indicates that the Fe content of analysis 2, Table I, should be increased by < 0.1 wt%). Hence, in computing the percentage losses of FeO, Na_2O, and K_2O during melting (Table II, figs. 2, 3, and 4a, b), analysis 2 in Table I was taken as the true composition of the starting material.

In general there is a smaller percentage loss of FeO compared to both Na_2O and K_2O (Table II), with percentage Na_2O loss being from 1–9 times greater than the FeO loss. Plots of FeO and Na_2O losses as a function of time, temperature, and P_{O_2} are shown in figs. 2 and 3. The exponential forms of the curves and their relative positions in the two

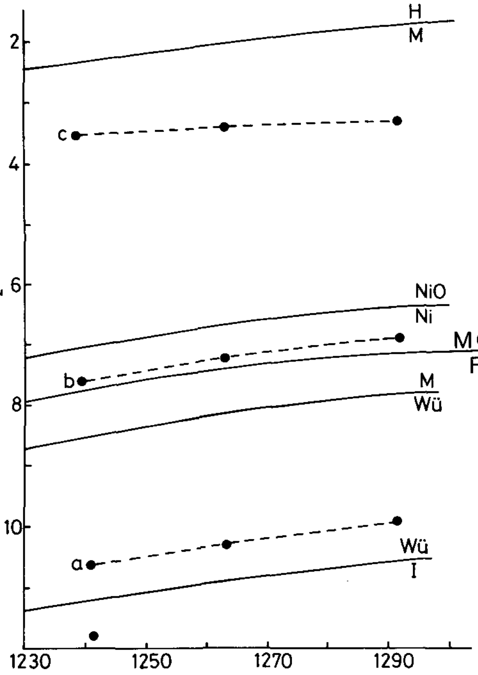


FIG. 1. Temperature – P_{O_2} conditions of melting experiments (filled circles). Buffer curves constructed from data of Eugster and Wones (1962).

TABLE II. *Conditions of melting and FeO, Na_2O, and K_2O contents of glasses*

Run	T °C	$-\log f_{O_2}$	time (hr)	FeO wt %	% loss	Na_2O wt %	% loss	K_2O wt %	% loss
1	1236	7.6	168	11.14	3.1	2.62	18.1	0.39	11.4
2	1236	7.6	94.5	11.22	2.4	2.88	10.0	0.41	6.8
3	1239	7.6	48.0	11.39	0.95	2.98	6.9	0.45	—
4	1238	7.6	21.25	11.35	1.3	3.11	2.8	0.44	—
5	1263	7.3	22.5	11.36	1.2	3.09	3.4	0.42	4.5
6	1261	7.3	70.5	11.07	3.7	2.88	10.0	0.38	13.6
7	1261	7.3	0.13	11.02	4.1	3.23	—	0.44	—
8	1293	6.9	47.5	11.00	4.3	2.78	13.1	0.40	9.1
9	1293	6.9	23.5	11.23	2.3	3.02	5.6	0.43	2.3
10	1292	6.9	0.17	11.50	0	3.19	0.3	0.43	2.3
11	1292	3.3	45.5	11.39	0.95	3.05	4.7	0.41	6.8
12	1292	10.0	47.75	9.35	18.7	1.36	57.5	0.36	18.2
13	1261	10.4	47.0	9.94	13.6	1.73	45.9	0.38	13.6
14	1262	10.4	0.17	11.44	0.05	3.21	—	0.43	2.3
15	1262	10.4	21.75	10.63	7.6	2.28	28.8	0.41	6.8
16	1265	3.3	46.5	10.76	6.4	3.00	6.3	0.42	4.5
17	1263	3.3	25.0	11.28	1.9	3.13	2.2	0.44	—
18	1245	3.3	43.75	10.47	8.9	3.09	3.4	0.42	4.5
19	1241	10.6	141	8.93	22.3	1.12	65.0	0.39	11.4
20	1242	10.6	46.5	10.54	8.3	2.05	35.9	0.40	9.1
21	1240	10.6	24.0	11.00	4.3	2.70	15.6	0.44	—
22	1242	11.9	24.1	9.97	13.3	2.01	37.1	0.40	9.1
23	1239	11.9	70.5	8.58	25.4	0.79	75.3	0.40	9.1
24	1242	9.0	71.0	10.83	5.8	2.53	20.9	0.41	6.8
25	1242	7.6	0.18	11.52	—	3.19	0.3	0.44	—
26	1261	7.3	0.05	11.46	0.3	3.18	0.6	0.44	—
27	1292	6.9	0.05	11.46	0.3	3.22	—	0.45	—
28	1262	10.4	48.2	9.89	13.9	1.70	46.9	0.38	13.6
29	1242	10.6	24.1	10.98	4.4	2.72	15.0	0.42	4.5
30	1240	7.6	47.2	11.42	0.6	3.02	5.6	0.44	—

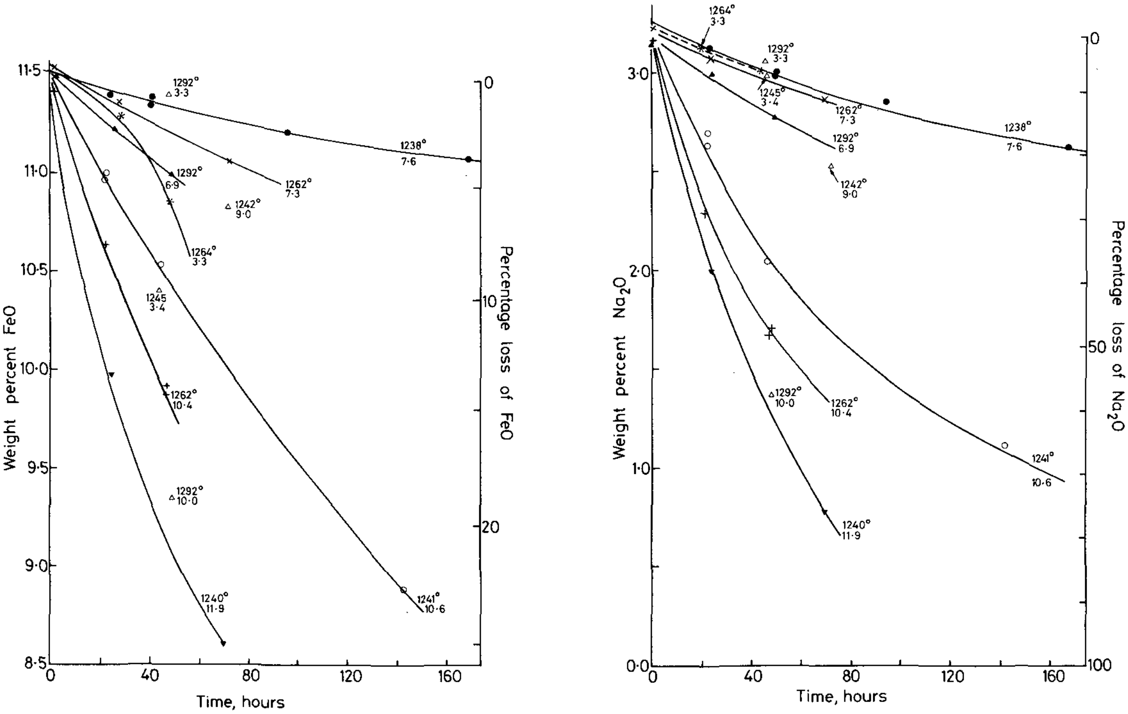
For reproducibility compare nos. 13 and 28, 21 and 29, and 3 and 30.

figures are remarkably similar, except for the curves at 1264° and $\log P_{O_2} = -3.3$ (see caption for fig. 2). It can be seen that both increasing superheat and decreasing P_{O_2} increase the rates of losses and also the amount of FeO that would be lost at time $\rightarrow \infty$. For example, a rise in temperature from 1238° to 1292° at P_{O_2} near the QFM buffer (curve b, fig. 1) increases the Na_2O loss from 9 to 17 % in a run of 60 hours; reducing the P_{O_2} from the QFM buffer to below the I Wü buffer at 1240° increases the loss from 9 to 70 % in a 60-hour run (fig. 4b). At the same run conditions FeO losses are just 4 to 6 % and 4 to 23 % respectively (figs. 2, 4a).

A few runs of 20 hours duration with charges of 50 mg revealed no differences in Fe loss, but Na losses increased by up to 3 % compared to the 120 mg charges. Likewise, increasing the flow rate of the CO_2-H_2 gas mixture from 60 cc/min to 240 cc/min raised Na_2O losses by 5 % but did not alter FeO losses.

Differences between the initial amount of K_2O in the basalt and the content after melting (Table II) are generally too small for any accuracy to be attached to the smallest of the calculated percentage losses. However, using the same technique, I. Freestone (1978) has observed 4 % loss of K_2O in 1 hour and 6 % loss in 20 hours from the melt $Fayalite_{40}$-$Leucite_{26}$-$Quartz_{34}$ (K_2O = 5.6 wt %), run at 1200° near the I Wü buffer.

Clearly the major drawback of the wire-loop technique is not FeO loss but rather losses of Na_2O and K_2O. The Na_2O loss is severe under highly reducing conditions but is only slightly dependent on sample size (see Corrigan and Gibb for further data), and gas flow rate. However, equilibrium is rapidly achieved in basalt melting and crystallization studies and few runs have to exceed 24 hours in duration (indeed melting need rarely exceed a few hours); chemical changes will therefore be small (Na_2O 3-20 %), particularly under P_{O_2} conditions



FIGS. 2 and 3: FIG. 2 (*left*). FeO content of glasses, and percentage change from initial rock content. Curves are labelled with temperature and P_{O_2}. The runs at 1245°/3.4 and 1264°/3.3 contain magnetite. FIG. 3 (*right*). Na_2O content of glasses and percentage change from initial rock content (cf. pattern of curves in fig. 2).

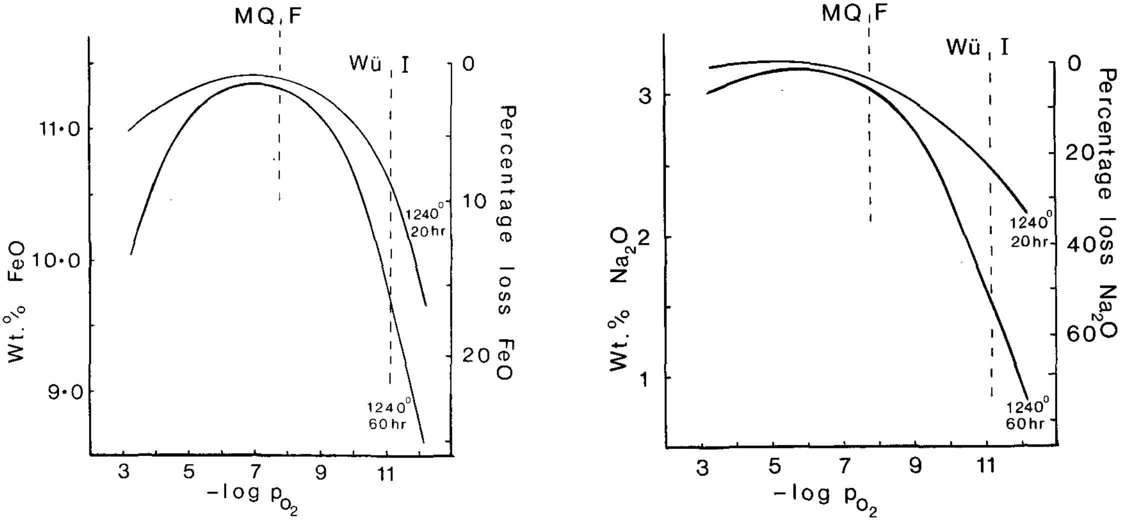


FIG. 4. (a) FeO and (b) Na_2O contents of glasses as a function of P_{O_2} at 1240° and two conditions of constant run time. (Locations of iron–wüstite and quartz-fayalite-magnetite buffers at 1240° shown as vertical lines.)

appropriate to terrestrial magmas (near the QFM buffer).

Losses of FeO using the wire-loop technique are less than with the open Mo, Pt, and AgPd capsules used by Bow *et al.* (1976). On the other hand, the Na_2O losses are generally greater, though no value can be put on this difference since the data of Bow *et al.* show that the percentage loss of Na_2O is dependent on the bulk rock composition; furthermore, the mass of sample used by them is not reported.

Causes of Fe, Na, and K losses

Fe enters the $Pt_{80}Rh_{20}$ wire as a result of the reaction:

$$\mathrm{Pt_{(metal)}} + \mathrm{FeO_{(melt)}} = \mathrm{PtFe_{(alloy)}} + \tfrac{1}{2}\mathrm{O_2}$$

for which $K_1 = a_{\mathrm{Fe(Pt)}} \cdot P_{\mathrm{O_2}}^{0.5} / a_{\mathrm{FeO(melt)}}$. This reaction continues until the activity of Fe in the melt and in the PtRh alloy is equal (Nolan, 1977). The smaller $P_{\mathrm{O_2}}$, the greater will be the loss of iron (cf. figs. 2, 4a).

The dependence of Na_2O loss on $P_{\mathrm{O_2}}$ (fig. 3) also implies a reaction involving oxygen. Volatilization studies of molten lunar basalts (Naughton *et al.*, 1971) indicate the presence of Na atoms and of Na_2 and Na_2O molecules among the volatile species degassed from the melts. Of these species, the partial pressure of Na dominates, at approximately 10^{-7} bar at 1200 °C (Naughton *et al.*, 1971). De Maria *et al.* (1971) and Sato *et al.* (1973) consider the results to be consistent with the reaction:

$$\mathrm{Na_2O_{(melt)}} = 2\mathrm{Na_{(gas)}} + \tfrac{1}{2}\mathrm{O_2}$$

for which $K_2 = P_{\mathrm{Na}}^{2} \cdot P_{\mathrm{O_2}}^{0.5} / a_{\mathrm{Na_2O(melt)}}$ (though the data of Naughton *et al.* indicate slight evaporation of Na_2O). Hence, as $P_{\mathrm{O_2}}$ increases, the P_{Na} decreases (cf. fig. 3) (P_{Na} would also decrease for melts of lower $a_{\mathrm{Na_2O}}$, e.g. lunar basalts). Since the gases in the furnace are constantly flowing, it should be possible to remove all the Na_2O from the melt, given sufficiently long run time.

K_2O is lost from the melts by the same mechanism as Na_2O (De Maria *et al.*, 1971) and the volatilization data of Gibson and Hubbard (1973) for lunar basalts show that it should be lost more rapidly than Na_2O. The generally larger losses of Na_2O compared to K_2O in the present experiments (Table II) may result from the higher activity of Na_2O in the terrestrial basalt compared to lunar ones.

Conclusion

PtRh wire loops are the best available sample containers for minimizing Fe loss in basalt melting experiments. However, samples can lose Na more rapidly than open capsules. For run times of up to one day the Na losses are acceptable. Should longer run times near the liquidus temperature be necessary (Lofgren *et al.*, 1974), Na loss may become a problem.

Acknowledgements. I thank Ian Freestone for use of his data on K loss. The work was performed in the Department of Geology, University of Manchester and was supported by a grant from the NERC to Professor W. S. MacKenzie and Dr D. L. Hamilton.

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[*Manuscript received 10 August 1978*]