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A modification of the wire-loop technique to reduce alkali loss during 1-atmosphere experiments

THIS report extends the work of Corrigan and Gibb (1979) who determined losses of Fe and Na from a typical basaltic liquid during 1-atmosphere experiments using the wire-loop method (utilizing both Pt and $Ag_{40}Pd_{60}$ wires) by electron-microprobe analyses of the quenched glasses. They found that Na losses were much more serious than Fe losses, the former being in direct linear proportion to the length of the experiment and in inverse proportion to the mass of the sample, such that the Na loss was 25 % after 120 hours for samples of 60 mg. Even using samples with weights in excess of 200 mg would mean that Na losses would be unlikely to be less than 5 % except in experiments shorter than a few days or on samples with very low initial Na contents.

Donaldson *et al.* (1975) reported a loss of almost 39 % of the original Na content of a basalt using the wire-loop method after a run time of 24 hours at 1250 °C, but only a loss of 2.8 % after a run time of 6 hours at the same temperature (but a lower f_{O_2}). Also the results of Donaldson *et al.* (1975) and Bow *et al.* (1976) suggest that f_{O_2} also influences alkali loss. Donaldson (1979) has since shown that an inverse relationship exists between f_{O_2} and alkali loss and he has shown that the loss of Na varies with the rate of gas flow through the furnace such that increasing the flow rate increased Na losses but did not alter FeO losses (in the experiment reported here the flow rate of the gas mixture was 189 cc/min). Donaldson (1979) found that losses of Na + K were larger than Fe losses from an alkali olivine basalt held above its liquidus temperature using $Pt_{80}Rh_{20}$ wire-loops with the percentage loss of Na being 1-9 times greater than Fe loss.

It is evident that the major drawback of the wire-loop method is loss of alkalis rather than iron losses. This paper reports a new method of experimentation such that alkali losses are considerably reduced.

Experimental method. The present investigation of alkali losses has been confined to a single basaltic composition GC 338 (Table I) at a temperature of 1250 °C which is in excess of the sample's liquidus temperature, a run time of 40.6 hours, a P_{total} of 1 atmosphere and an f_{O_2} of 10^{-8} atmospheres. Pellets (diameters of 5 mm) were made from weighed amounts of the rock powder and then a weighed length of 0.2 mm diameter $Ag_{40}Pd_{60}$ wire was gently twisted around each pellet. The pellets were then partly fused to form beads by suspending them in a muffle furnace in air at a temperature (~1320 °C) substantially above their solidus temperature (< 1160 °C) for 2 minutes. The beads and their wire-loops were then reweighed after removal from the muffle furnace to allow determination of the mass of the samples prior to the experiment. Each bead weighed 7 mg.

The experiment was conducted 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. After the experiment the samples (complete with suspending wires and ceramic insulators, see Donaldson *et al.*, 1975, fig. 2) were quenched into cold water. The whole beads were then mounted in epoxy and polished for electron-microprobe analysis. A sufficiently large number of spots were analysed to permit evaluation of any inhomogeneity and calculation of the bulk composition of the glass.

If it is assumed that any loss of alkalis is to the furnace atmosphere by volatilization then enclosure of a bead in a crimped capsule might considerably reduce the alkali loss. Thus in an attempt to reduce alkali losses an experiment was carried out in which two beads were suspended in the furnace at the same time but one of the beads was enclosed in a crimped $Ag_{40}Pd_{60}$ capsule to prevent it being exposed to the full effects of the gas stream. Great care had to be taken to ensure that the bead in the capsule did not adhere to the capsule walls to avoid increasing the iron loss (Corrigan and Gibb, 1979). Pt capsules would be better containers as hydrogen would be able to diffuse through the capsule wall, but if the bead touched the capsule wall iron losses would be higher.

Results. It has been found that alkali losses from the sample during an experiment using the wire-loop technique can be drastically reduced by enclosing the bead in a capsule. The bead in the capsule lost only 3.7 % of its original Na whereas the bead not enclosed in a capsule lost 39.4 % of

TABLE I. *Composition of GC 338*

SiO_2	47.77	MnO	0.17	P_2O_5	0.98
Al_2O_3	17.40	MgO	3.36	H_2O^+	0.98
TiO_2	2.96	CaO	8.17	S	0.09
Fe_2O_3	3.35	Na_2O	5.50		
FeO	6.34	K_2O	2.27	Total	99.34

its original Na. K losses were also markedly different as the bead enclosed in a capsule lost 7.8 % of its original K whereas the bead not enclosed in a capsule lost 23.8 % of its original K. It is unknown why the bead enclosed in the capsule loses a higher percentage of K than Na.

Due to the small sample weight (7 mg) and small sample:metal ratio (~ 0.4) used, Fe losses were very high (22.2–22.8 % of the original Fe was lost). The bead size used in future experiments must be much larger such that the percentage of total Fe lost is considerably less. Corrigan and Gibb (1979) using beads with weights of approximately 60 mg showed that the percentage of total Fe lost during a 40-hour run would be about 6 % and could be even further reduced to less than 2% if larger sample:metal ratios of around 10 were used. Also increasing the bead size in a capsule would mean that the percentage loss of initial alkalis would be even further reduced as Corrigan and Gibb (1979) showed that the percentage of original Na lost from a basaltic melt decreased as the mass of the sample increased. There are, however, practical limitations to the bead size if it has to go in a capsule, which might prevent attainment of acceptably small Fe losses unless very large capsules (and furnaces) were used. It has been assumed that enclosing a sample bead in a capsule will still permit f_{O_2} equilibration, however, it is possible that the sample may not achieve the correct Fe^{2+}/Fe^{3+} ratio. As the two samples showed no difference in their colour it seems likely that enclosure of a bead in a capsule (which is only crimped) does not affect the Fe^{2+}/Fe^{3+} ratio. The samples were too small for the post experimental determination of this ratio by wet chemical methods.

Conclusions. The experimental results indicate that alkali losses from silicate melts during experiments using the wire-loop technique can be reduced by running the sample bead in a crimped container. It is, therefore, recommended that when using the wire-loop technique on alkali-bearing samples the beads are run inside Pt or $Ag_{40}Pd_{60}$ capsules using sample:metal ratios of at least 10 to keep Fe losses to acceptable levels (Corrigan and Gibb, 1979).

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Synthesis of $Li_2ZrSi_6O_{15}$, a zektzerite-related phase

CONSIDERABLE recent interest has been shown in a group of double-chain silicate phases which includes the new mineral zektzerite, $LiNaZrSi_6O_{15}$ (Dunn *et al.*, 1977; Ghose and Wan, 1978), and a family of isotypic phases (Marr and Glasser, 1979*a* and *b*). These phases are closely related structurally to $Na_2Mg_2Si_6O_{15}$ (Cradwick and Taylor, 1972), tuhualite, $(Na,K)_2Fe_2^{2+}Fe_2^{3+}Si_{12}O_{30}.H_2O$ (Merlino, 1969), and emeleusite, $Na_2LiFeSi_6O_{15}$ (Upton *et al.*, 1978). All contain a corrugated, double-chain silicate anion, $Si_6O_{15}^{6-}$ and with a variety of possible cation combinations to balance the charge on the anion, viz.

$Li^+ + Na^+ + Zr^{4+}$	zektzerite
$2Na^+ + 2Mg^{2+}$	$Na_2Mg_2Si_6O_{15}$
$(Na,K)^+ + Fe^{2+} + Fe^{3+}$	tuhualite
$2Na^+ + Li^+ + Fe^{3+}$	emeleusite

All have similar-sized, *C*-centred orthorhombic unit cells.

Here we report the synthesis of $Li_2ZrSi_6O_{15}$. It is monoclinic, $\beta = 89.5°$, but has a pseudo-