A fusion method for preparing glass samples of peridotitic and picritic rock compositions for bulk analysis

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Abstract

A design for a micro furnace and a fusion technique are described by which silicate materials (in particular picritic and peridotitic rock compositions) may be fused and quenched to a homogeneous glass without significant loss of components, for the purposes of bulk analysis. The furnace consists of a Pt wire electrical resistance heater mounted in a furnace assembly which is fitted to a microscope stage. Microscopic examination of the sample during the fusion process allows the sample to be quenched as soon as all crystalline material has been fused and thus minimizes the loss of iron and alkalis due either to over-heating or prolonged fusion time. Analysis of glass beads of a model peridotite composition (analysed independently by X-ray fluorescence analysis) shows that for typical fusion times (5–10 seconds) the bulk composition is preserved at distances of > 25 μm from the margins of the glass beads. Analysis of natural rock powders of known composition shows that the method can be used to analyse whole rock compositions. The furnace is simple to construct and cheap to run and provides a simple and rapid method of producing glass samples for bulk analysis.

KEYWORDS: glass, silicate minerals, micro furnace, fusion technique, picrite, peridotite.

Introduction

IN experimental studies it is essential that 'starting' mixes are checked for both accuracy of composition and homogeneity on the scale of an experimental charge (generally 2–10 mg). This is particularly true of mixes of synthetic origin (e.g. sintered oxide or 'gel' mixes (Hamilton and Henderson, 1968)) but may also be desirable when the experimental starting material is composed of mixtures of crystals and/or glass of natural origin. The technique most frequently used for the determination of the bulk composition of sample powders is electron microprobe analysis of glasses prepared on a precious metal strip heater (e.g. Nicholls, 1974). The effectiveness of this technique is limited by a number of factors. Firstly, although the temperature and time of fusion must be sufficient to eliminate any crystalline material and allow thorough mixing, prolonged heating of the sample can lead to selective loss of some components from the melt. The high temperatures necessary to melt many silicate materials can result in both loss of Fe by dissolution in the precious metal strip and preferential loss of alkalis from the top surface of the melt by loss of volatiles to the atmosphere. However, provided the fusion time is short, it is generally assumed that these effects may deplete only the margins of the melt, leaving the interior unmodified.

Secondly, if the melts generated are highly fluid (e.g. alkali picrites or peridotites) the melt forms a shallow film rather than thick 'bead', the resulting high ratio of surface area to volume may result in loss of iron and alkalis across the entire thickness of the melt layer. Thirdly, highly depolymerized melts generally quench to mats of crystals with interstitial glass and so are grossly inhomogeneous on the scale of an electron microprobe analysis volume. Average compositions may be obtained by rastering the electron beam over a sufficiently wide area of the sample, however, quench mats are often too coarse to allow high precision analyses to be obtained.

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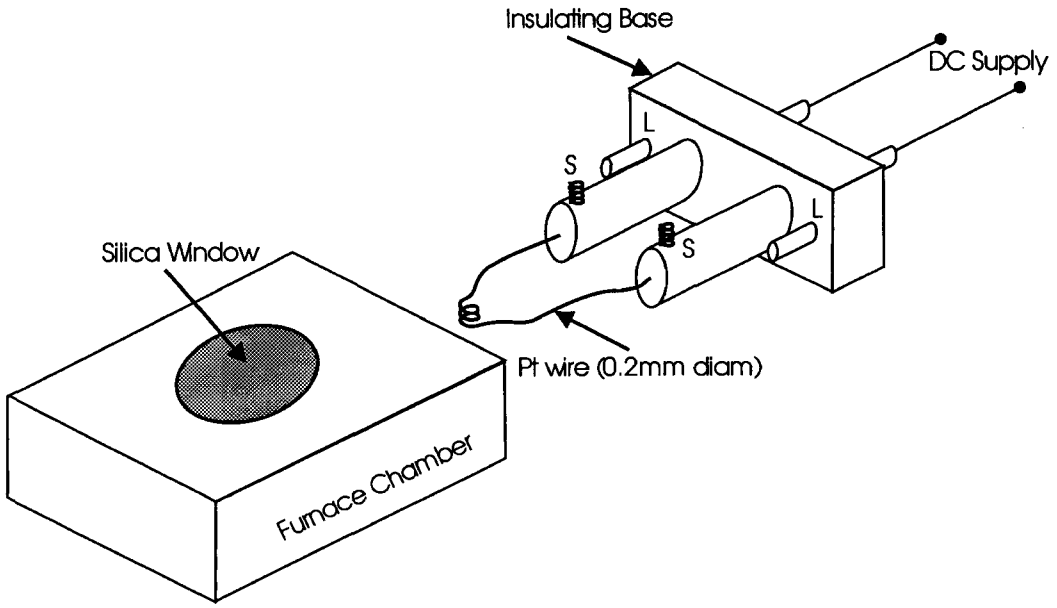

FIG. 1. Schematic diagram of the micro furnace. S — securing screws. L — locating pins.

The technique described here uses a combination of favourable geometry and the addition of a polymerizing agent (flux) to reduce fusion time and temperature, surface area to volume ratio and inhibit the growth of quench crystals to facilitate the production of glasses from peridotitic and picritic compositions. The technique was devised with the small sample sizes typical of experimental charges in mind. However, provided sufficiently homogeneous samples may be obtained the technique can be equally well applied to natural samples.

The micro-furnace and fusion procedure

The design devised is a modification of that devised by Welch (1954) by which the melt is maintained on a Pt wire resistance heater of 'elbow' form. The modification consists of replacing the 'elbow-type' heater geometry by a three turn coil (1.5 mm diameter) of Pt wire (0.2 mm thickness) which is held in place and connected to the electrical supply by two, heavy-gauge brass pillars (Fig. 1). The fusion chamber is fitted to the stage of a standard petrologic microscope such that the 'hot-spot' of the heater can be viewed through a silica glass window. This arrangement allows the melt to be quenched immediately all crystalline material has been eliminated and so minimizes the loss of iron and alkalis (see discussion below).

The sample material is powdered to a grain size of approximately 20 μm and mixed with a small amount of polyvinyl acetate (PVA) solution to enhance adhesion of the powder to the coil. A DC current is passed through the Pt wire generating a 'hot-spot' within which the sample is fused. The current is gradually raised until complete fusion is observed and then immediately quenched by cutting off the power. The time taken for this procedure and, therefore, the susceptibility of the sample to iron and alkali-loss is a function of composition but generally takes less than 10 s for basaltic compositions. After fusion the glass bead and Pt wire are easily separated by pulling the ends of the wire causing the coil to straighten and the bead to separate from the wire intact. This can then be mounted and polished using conventional methods for microanalysis.

Fusion of highly magnesian samples

Although, in theory, the furnace can maintain a temperature capable of melting most rock compositions, in practice not all compositions will fuse and quench to a homogeneous glass. Compositions rich in silica and alumina either melt to a highly viscous melt and/or retain metastable refractory aluminosilicates which can result in significant heterogeneities. More mafic compositions (e.g. picrites and

peridotites) fuse more readily to produce highly fluid melts generally free of metastable crystals. These compositions, however, frequently fail to quench to a glass and unmix to form mats of quench crystallites and interstitial glass. As in the case of the more silica-rich compositions, the presence of crystals and glass indicate heterogeneities on a scale which cannot be easily accommodated by analysis using electron beam rastering techniques.

One solution to this problem is to add a component which will both reduce the fusion temperature and polymerize the melt so that, on quenching, a homogeneous glass will be produced. In the case of picritic melts, the addition of silica or alumina would have the desired effect, however, the addition of these components is undesirable as they are intrinsic to the peridotite compositions. Phosphorus, however, behaves in a manner similar to silica and alumina (Mysen *et al.*, 1981; Ryerson, 1985), but is present in most picrites and peridotites in only trace amounts. Phosphorus may be conveniently added to silicate compositions in the form of ammonium-orthophosphate monohydrate ($(NH_4)_2HPO_4$). This decomposes to form P_2O_5 at $\sim$ 250°C (Weast, 1974) by the loss of volatile components and avoids the problem of the addition of another cation to the system. The glass produced is then analysed for all the major components including P_2O_5 to account for any possible modification of matrix effects during the analysis calculations. The bulk composition of the silicate composition may be derived simply by numerical subtraction of all of the P_2O_5 component.

Glasses of peridotite composition: an assessment of alkali and Fe-loss during fusion

To test the efficiency of the technique and to assess the magnitude of alkali and Fe loss during fusion of magnesian samples, glass beads were prepared of a model peridotite (pyrolite — 40% olivine, Green (1973), Table 1). The pyrolite was prepared by the gel method (Hamilton and Henderson, 1968) and was analysed by X-ray fluorescence spectrometry (XRF) by the method described in Fitton and Dunlop (1985) to provide an independent analysis (Table 1). Sufficient $(NH_4)_2HPO_4$ was added to the pyrolite to give approximately 10 wt.% P_2O_5. Seven aliquots ($\sim$ 3 mg) of the mixture were fused and quenched to glass (fusion in air; time <5 s). The resulting beads were mounted and polished such that the exposed surface was axial to the heater coil.

Electron probe analysis. The glasses were analysed on a Cameca Camebax electron microprobe operating at an accelerating voltage of 20 kV, a beam current of 10 nA and a rastered area of 10 μm. Three analyses were made on different areas of the centre of each bead at least 40 μm from margins of the bead. The means and standard deviations of the components (Table 1) show that the method gives very low uncertainties and that the analysed composition is indistinguishable from that obtained by XRF analysis. To establish the extent and range over which diffusive loss has depleted the melts in iron and alkalis, two traverses were made using a 5 μm^2 rastered beam. Both traverses were chosen to track perpendicular to the margins of the glass, the first relative to the melt/Pt contact, the second relative to the melt/air interface. The analyses were spaced 10 μm apart and extended 70 μm into the glass away from the air and Pt interfaces. Fig. 2*a,b* shows the resulting variations obtained for Na_2O and FeO up to 70 μm from the margins of the glass. The iron contents determined in both traverses are within error and are indistiguishable from the XRF analysis. It may be assumed, therefore, that the procedure does not lead to significant iron-loss at total iron concentrations less than 10 wt.%. The Na_2O analyses are also all within error except for the values determined for the area scans centred 10 μm from the glass margins.

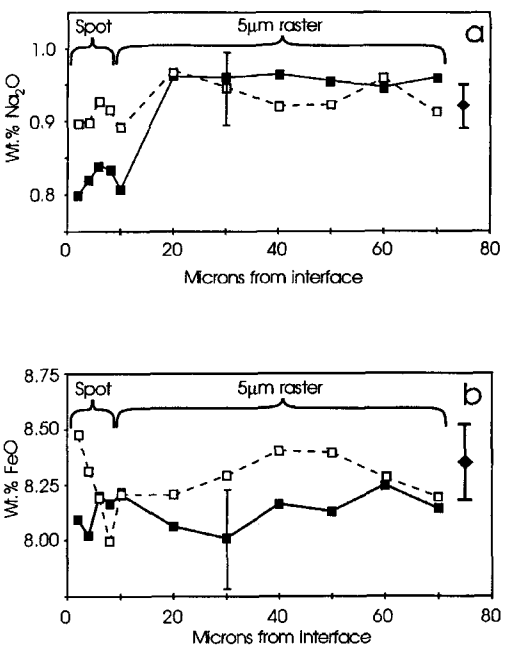

FIG. 2*a,b*. Na_2O and FeO concentrations determined for traverses perpendicular to margins of glasses produced by the fusion method. Solid squares: traverse adjacent to Pt heater wire; empty squares: traverse adjacent to air/glass contact. Error bar at 30 μm: 2σ error for 21 analyses obtained at random positions greater than 50 μm from margins of the glass fragment. Filled diamond; XRF analysis (error bar: 2σ).

TABLE 1. Compositions of pyrolite and standard materials used to test the fusion technique

	Pyrolite[1]			BIR-1[4] (n = 10)		UB-N[5] (n = 10)		PCC-1[6] (n = 10)		JP-1[7] (n = 10)	
	Green(1973)	XRF[2]	EPMA[3] (*n* = 21)	A	B[8]	A	B[8]	A	B[8]	A	B[8]
SiO_2	48.08	48.4 ± 0.2	48.3 ± 0.2	48.1	48.4 ± 1.6	45.1	45.3 ± 0.6	44.1	44.0 ± 0.4	42.4	43.6 ± 0.4
TiO_2	1.2	1.2 ± 0.01	1.19 ± 0.02	0.97	0.92 ± 0.56	0.13	0.11 ± 0.04	0.01	< 0.01	0.01	< 0.02
Al_2O_3	5.9	5.89 ± 0.12	5.73 ± 0.05	15.45	15.42 ± 2.4	3.31	3.12 ± 0.08	0.71	0.64 ± 0.04	0.62	0.66 ± 0.12
Cr_2O_3	0.7	– –	0.62 ± 0.05	0.05	0.08 ± 0.04	0.34	0.36 ± 0.08	0.38	0.41 ± 0.10	0.39	0.38 ± 0.20
FeO	8.6	8.17 ± 0.01	8.35 ± 0.17	10.20	10.16 ± 1.8	8.57	8.68 ± 0.28	7.84	8.05 ± 0.22	8.34	7.74 ± 0.50
MnO	0.1	0.09 ± 0.08	0.09 ± 0.01	0.17	0.18 ± 0.02	0.14	0.16 ± 0.10	0.13	0.14 ± 0.04	0.12	0.13 ± 0.04
MgO	28.9	29.15 ± 0.05	29.19 ± 0.23	9.92	9.53 ± 0.98	40.22	40.44 ± 0.22	45.86	45.83 ± 0.30	44.72	46.55 ± 0.80
CaO	5.1	5.17 ± 0.06	5.16 ± 0.08	13.33	13.39 ± 0.88	1.37	1.41 ± 0.14	0.55	0.56 ± 0.06	0.56	0.55 ± 0.04
Na_2O	0.96	0.87 ± 0.06	0.92 ± 0.03	1.76	1.83 ± 0.24	0.11	0.13 ± 0.08	0.03	0.02 ± 0.02	0.02	0.04 ± 0.04
K_2O	0.22	0.21 ± 0.02	0.18 ± 0.01	0.03	0.03 ± 0.02	0.02	0.02 ± 0.02	0.01	0.01 ± 0.02	0.00	< 0.01
NiO	0.2	– –	0.22 ± 0.02	0.02	0.03 ± 0.02	0.29	0.31 ± 0.06	0.32	0.33 ± 0.08	0.31	0.35 ± 0.06
Total	100.0		100.00	100.00		100.00		100.00		100.00	

1. Pyrolite –40% olivine, Green(1973).
2. XRF — X-ray fluorescence analysis of pyrolite gell.
3. Electron microprobe analysis of fused samples of gell.
4–7 Standard materials of known composition (Govindaraju, 1989) recalculated on a volatile-free basis. A — accepted working composition, B — composition established by fusion method.
8. 2σ uncertainty.
– not determined.

Spot analyses. To establish whether there are any significant depletion zones adjacent to the glass margins, spot analyses were carried out immediately adjacent to the Pt wire heater (Pt margin) and the contact with the atmosphere (air margin). The results show that apparent depletions are only resolvable for Na_2O at the interface of the glass with the Pt wire heater. However, even this may not be significant as analysis by electron probe using 'spot' mode leads to some alkali-loss in the glass. These results show, therefore, that the glass compositions are preserved throughout the glass mass. To avoid the possiblility of analysing Na_2O-depleted regions, areas less than 30 μm from the Pt-wire heater should be avoided.

Analysis of natural rock compositions. To further test the applicability of the technique, four natural rock compositions widely used as XRF standard materials were analysed. Fifty mg of each of the rock powders was mixed with 25 wt.% $(NH_4)_2HPO_4$, fused and quenched to glass using the method described above. For each composition, four beads were produced on which a total of ten analyses was carried out. The results are presented in Table 1. In only four cases do the 2σ ranges of the microprobe analysis not include the accepted standard analysis. However, as Govindaraju (1989) does not give uncertainty ranges associated with the standard analyses, it is possible that the microprobe analysis lies within error for all the components analysed.

Conclusion

The technique described has at least three positive features for the determination of bulk analyses of small samples. First, the addition of phosphorus to magnesian compositions (e.g. peridotites and picrites) acts both as a fluxing and polymerising agent and so improves the quenching behaviour of these highly fluid melts. Second, the use of a microscope to view the fusion process allows the fusion time to be just sufficient to melt all crystalline material and, therefore, minimizes diffusive loss of alkalis and Fe to the atmosphere and Pt wire heater respectively. Tests on a sample analysed independently by XRF show that the bulk composition is preserved at distances greater than 25 μm from the margins of the sample. Analysis of four natural rock samples of known composition shows that the technique can be successfully applied. Third, the furnace is simple to construct and may be fitted to a standard microscope. The fusion procedure is rapid: up to 30 samples may be fused to glass in one day.

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