Silica-glass containers for high-temperature experiments

Daniel J. Malvin

Lunar and Planetary Laboratory, The University of Arizona, Tucson, Arizona 85721, U.S.A.

Abstract

High-purity silica-glass tubes have been used as containers for synthetic silicate melt and mineral-melt experiments. Experiments were conducted in air at 1300–1400 °C using compositions in the system CaO-MgO-Al_2O_3-SiO_2. During an experiment, part of the interior of the silica container dissolves into the starting mixture at high temperature resulting in a melt composition that is saturated with silica. An open container can maintain its integrity for at least 95 h; evacuated containers for at least 46 h. Diopside and protoenstatite along with a SiO_2 phase have each been crystallized in different experiments. Silica-glass containers are useful when conventional container materials are unsuitable.

Introduction

Experimental petrology has often been complicated by the inescapable requirement that the sample be contained by some means within the furnace (the "container problem"). Pt as wire loops, open crucibles, or sealed capsules, has been employed extensively as a container material because of its refractory nature and because it is essentially inert with regard to silicate chemistry, save for the solubility of Fe and other siderophile elements in Pt. W wire loops have been employed in this laboratory for experiments at very low oxygen fugacities. Alumina crucibles have been used successfully as containers for metallic systems (e.g., Jones and Drake, 1983), but in silicate systems, several exploratory experiments have shown that a portion of the interior of the alumina crucible dissolves into the melt and usually stabilizes a spinel phase at the interface between the crucible and the melt. Natural olivine crystals have been used as containers in high-pressure experiments (Brey and Nickel, 1986) and in a few exploratory experiments at 1 atm in this laboratory. A 1981 summary of the various types of container materials that have been employed in experimental silicate petrology (Basaltic Volcanism Study Project, 1981) does not include high-purity silica glass.

We have developed a technique using high-purity silica-glass tubing as a container for silicate mineral/melt partitioning studies and for studies of the solubility of metals into silicate melts. The use of silica tubing was motivated by the need to provide a container that would be inert to siderophile elements, especially noble metals, and still provide a means of investigating both the solubility of noble metals in silicate melts and their partitioning between minerals and melts in synthetic basaltic systems (Malvin et al., 1986). In addition, the use of high-purity reagents for the experiment compositions results in a sample that is uncontaminated by spurious trace elements. The control of sample purity is of importance to future work in which trace-element techniques will be used for the analysis of experimental partitioning. In particular, the utility of the Si(Li) detectors on the Los Alamos National Laboratory (LANL) proton microprobe and the Brookhaven National Laboratory (BNL) synchrotron X-ray fluorescence microprobe is enhanced when spectral interferences can be avoided.

Experimental methods

Starting materials

The purity of the silica-glass tubing is of the highest importance to the success of the experiment. Impurities in the silica tubing will cause the container to melt at temperatures too low to be of interest to most igneous petrologists. We have employed commercially available, high-purity silica-glass ("quartz") tubing with a 10-mm outside diameter and a 1-mm wall thickness (General Electric, 214 glass). Other sizes of tubing should be equally suitable as containers. The tubing was cut into lengths of roughly 5 cm, and one end was sealed using a torch.

We have used high-purity oxides of the elements (Johnson Matthey Chemicals, Puratronic grade) for the preparation of our starting compositions in the system CaO-MgO-Al_2O_3-SiO_2. The oxides were weighed together and fused in a Pt crucible for several hours at 1400 °C, ground for 30 min under acetone, fused a second time, and ground again. Starting composition 1 (Table 1) was deficient in SiO_2 in order to investigate the addition of SiO_2 to the sample by reaction of the starting mixture with the container during the experiment. Starting mixture 1 sintered but did not fuse at 1400 °C because of this silica deficiency. Starting mixtures 2 and 3 were prepared to have compositions that would be nearly in equilibrium with the SiO_2 phase at the temperature of the experiment and have compositions in the phase fields for protoenstatite + SiO_2 and diopside + SiO_2, respectively, at a temperature of approximately 1325 °C. The starting compositions were chosen by using oxygen-unit projections onto ternary liquidus diagrams in the anorthite-forsterite-wollastonite-silica tetrahedron (Longhi, 1987).

Experimental techniques

Approximately 100 to 200 mg of the starting mixture were loaded into the bottom of a silica tube, and the container was left open to the atmosphere. The sample tube was placed in a Pt

TABLE 1. Experiment conditions and compositions of starting materials and experimental products

Expt. no.	High T (°C)	Time (h)	Low T (°C)	Time (h)	SiO_2	Al_2O_3	MgO	CaO	Total
1 start	—	—	—	—	34.4	10.0	25.5	30.0	100.0
1B	—	—	1345	2.5	—	—	—	—	—
1C	—	—	1385	2.5	61.5	5.7	14.0	16.9	98.1
1E (Di)	1385	2	1305	2	62.5	7.11	12.6	16.8	99.0
1D	1385	2	1345	2	62.0	6.29	15.1	17.4	100.7
1F	1385	2	1345	6	62.2	6.34	14.9	17.2	100.0
1J	1385	2	1345	25	62.8	5.92	14.3	17.0	100.0
1G	1385	0.5	1345	2	59.9	6.74	15.7	18.2	100.6
1H	1385	0.5	1345	6	60.8	6.71	16.0	17.9	101.4
1L	1385	0.5	1345	32	63.8	6.15	14.6	17.1	101.6
1K	1385	0.5	1345	48	63.2	5.89	15.0	16.8	101.0
1I	1385	0.5	1345	95	63.0	5.67	14.5	16.6	99.7
2 start	—	—	—	—	51.0	18.5	17.6	12.9	100.0
2D (Pr)	—	—	1320	6	58.1	16.2	15.0	10.6	99.8
2L	—	—	1350	4	61.9	14.7	13.2	9.97	99.8
2F	—	—	1350	24	63.8	14.8	13.4	9.18	101.2
2G	—	—	1350	90	64.6	14.3	12.6	9.16	100.6
2B	—	—	1380	24	64.4	13.6	13.0	8.88	99.9
3 start	—	—	—	—	51.9	8.05	9.97	30.1	100.0
3J (Di)	1320	1	1300	46	61.6	7.22	6.82	23.8	99.5
3G	—	—	1320	44	61.8	6.4	7.56	23.3	99.1
3C	—	—	1350	24	63.3	6.54	7.57	22.5	99.8
3N*	—	—	1350	44	63.7	6.21	7.45	22.2	99.6
3E	—	—	1400	24	64.4	6.23	7.30	22.1	100.1

Note: Analyses of the glasses are in weight percent. The crystalline phases diopside (Di) and protoenstatite (Pr) are abbreviated.
* The sample was sealed under vacuum.

crucible and suspended by Pt wire from an alumina hanging rod. Experiments were conducted in a vertical, muffle-tube quench furnace in air at 1-atm ambient pressure. For one experiment (3N), the silica tube was sealed under vacuum. Temperature was monitored by a Pt-Pt$_{90}$Rh$_{10}$ (S-type) thermocouple calibrated against the melting of Au. The temperatures should be accurate to ±3 °C. Each experiment was terminated by removing the sample from the furnace and quenching it in water. No quench crystals in any of the experiments were observed by optical microscopy.

Analytical techniques

Major-element analyses were performed on polished thick sections of chips removed from the quenched charges and mounted in high-purity resin. Analyses were carried out with an ARL-SEMQ electron microprobe using a 15-kV accelerating potential and a nominal specimen current of 50 nA. The major oxides were counted for 15 s each. The analyses were calibrated relative to natural and synthetic microprobe standards and corrected using the ZAF procedure. At least six points were analyzed in the quenched melt in each sample. Diopside and protoenstatite crystals, when present, were analyzed qualitatively. The crystals were typically 30 μm in long dimension, with a few as large as 150 μm. Beam diameter was fully focused on crystals and varied from fully focused to roughly 30 μm in areas of quenched melt.

RESULTS

The variety of run conditions employed are given in Table 1 along with the major-element compositions of the starting materials and of the resulting glasses (quenched liquid). In three experiments, a crystalline phase in addition to SiO_2 is present.

Composition 1 was experimented with at various temperatures for various durations in order to evaluate the extent of reaction of the silica-glass tube with the melt

during an experiment. Because this starting composition is very deficient in silica, it required the addition of SiO_2 from the container in order to fuse. Sample 1B did not fuse but produced a well-sintered pellet after 2.5 h at 1345 °C. Sample 1C produced a homogeneous glass after 2.5 h at 1385 °C. For this reason, 1385 °C was chosen as the homogenization temperature for the subsequent experiments on this composition.

Experiments 1D, 1F, and 1J were held for 2 h each at 1385 °C. The temperature was lowered directly to 1345 °C for durations of 2, 6, and 25 h. Experiments 1G, 1H, 1L, 1K, and 1I were held at 1385 °C for ½ h, and then at 1345 °C for durations of 2, 6, 32, 48, and 95 h, respectively. There was no significant difference between the compositions of the quenched melts held in 1385 °C for 2 h (Table 1), indicating that the initially silica-deficient starting material had approached compositional equilibrium with the silica tube within 2 h. The small variation in composition among these quenched liquids may have been due to inhomogeneity of the starting material. There was a small difference in composition between the runs of composition 1 held for 2 h at 1385 °C and those held at the same temperature for ½ h. Runs 1G and 1H did not achieve a silica-saturated composition after ½ h at 1385 °C and 6 h at 1345 °C; however, sample 1L did achieve equilibrium with the container after 32 h at 1345 °C. The rate of reaction of the container with this starting composition demonstrates the importance of the high-temperature step in establishing chemical equilibrium. It is important to note that the sample container maintained its integrity in all of the expriments even though in some cases the wall had been thinned considerably. As another test of the container, one sample of composition

3 was maintained in an evacuated container for 46 h at 1350 °C. After quenching, the tube still held a vacuum although the top of the container had softened and collapsed slightly.

Experiments using composition 2 were held at 1350 °C for durations of 4, 24, and 90 h. This starting composition is much nearer to equilibrium with SiO_2 at the temperatures of interest, and only small amounts of reaction with the container were observed. The small systematic variation in composition among these quenched glasses is entirely within the analytical uncertainty of the electron-microprobe results and may not be a real indication of compositional changes with time.

Experiments using composition 3 were performed in order to verify further agreement of the compositions of the resulting quenched glasses with published phase diagrams of Longhi (1987) in the liquid + silica ± diopside volume of phase space. One sample that was maintained in an evacuated container (3N) at 1350 °C has a composition nearly identical to that of the sample run in air (3C).

Most of the experiments produced a small number of very fine (20 μm) bladed crystals of an SiO_2 phase (tridymite?) near the interface between the melt and the silica-glass container. The presence of these crystals that grew from the melt suggests the close approach to chemical equilibrium of the melt with the container. The experiments in which temperature was lowered in order to crystallize the secondary phase (diopside or protoenstatite) also contained SiO_2 crystals.

SUMMARY

1. High-purity silica-glass tubing is capable of withstanding at least several days at 1350 °C as either an open or a sealed evacuated container for silicate melt and mineral-melt experiments.

2. Only SiO_2-saturated compositions can be investigated at equilibrium using silica-glass containers; however, a wide range of melt compositions are available for investigation in silica-saturated phase systems.

3. The crystalline phases diopside and protoenstatite have been crytallized from different melt compositions. It should be possible to similarly achieve equilibrium between melts and crystals of anorthite, orthoenstatite, and pigeonite. Olivine-saturated compositions probably cannot be studied at equilibrium using this technique, unless the olivine is extremely fayalitic.

4. Silica-glass tubes are excellent candidates for containers when the elements of interest are siderophile and would dissolve in precious metal containers. Noble-metal solubility experiments and mineral/melt partitioning experiments are feasible using this technique. The attainable purity of silica tubes is also significantly higher than for ceramics such as Al_2O_3. In combination with high-purity reagents, silica-glass containers permit the sample to remain free of spurious elements that interfere with analysis by trace-element microprobe methods.

ACKNOWLEDGMENTS

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