Synthetic olivine capsules for use in experiments ⚐

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ABSTRACT

We have developed a method for the manufacture of polycrystalline olivine capsules, suitable as containers for olivine-saturated melts in near-liquidus experiments. The aim was to avoid some of the problems found in 1-atm gas-mixing experiments, notably iron loss from silicate melts to Pt wire loops and reaction between noble metal loops and sulfide liquids. Use of olivine capsules of fixed Mg/Fe enables the Mg# of the coexisting melt to be controlled and doping of the capsule with minor elements of interest enables partition coefficients to be determined at measureable concentrations. Capsules with olivine compositions ranging from $Fo_{.70}$ to $Fo_{.90}$ have been manufactured and found to remain impermeable to basaltic melts for extended periods. In the case of magnesian compositions ($\sim Fo_{90}$), we found that several cycles of heating and cooling from (1250 to 1550 °C) were needed to enhance grain growth and reduce permeability to an acceptable level. In contrast, our iron-rich composition (Fo_{70}) functioned well after a single cycle of heating from 800 to 1350 °C.

Keywords: Olivine capsules, high-temperature experiment, olivine, trace element partitioning, iron loss, igneous petrology

INTRODUCTION

A commonly encountered problem in experimental petrology is the tendency for experimental charges to react with their containers or supporting wire loops. The classic example is Fe-loss from silicates into platinum capsules or Pt-wire loops (e.g., Donaldson 1979). This problem may be largely overcome by pre-conditioning the Pt with an Fe-bearing silicate melt at appropriate oxygen fugacity (e.g., Grove 1981) or by using metals such as, depending on temperature, Au, Ag, or Re that dissolve iron less readily than Pt. Another potential hazard is the dissolution of the container or suspension wire by the charge itself, a problem we have encountered using sulfide melts with Re suspension wires. These interactions between charge and container have led some experimenters to successfully use machined single crystals of natural olivine as their capsules (Brey et al. 2008; Berry et al. 2005). In this case, however, one is limited by the availability of natural crystals and almost all experiments have been performed with San Carlos olivine of Fo_{90} composition. Use of natural single crystals also restricts the possibilities for investigation of the partitioning of minor and trace elements between olivine and other phases because natural abundances are very low for many elements of geochemical interest. To expand the possible applications of olivine as a capsule material we therefore set out to manufacture polycrystalline olivine capsules from synthetic starting materials of Fo_{90} and Fo_{70} composition. As an example of the potential applications of such capsules we doped some olivine starting materials with moderate levels of NiO and MnO and investigated the equilibration of capsule with a melt of approximately basaltic (although fairly iron-rich) composition at

1-atm pressure. As we will show, the "art" of manufacture turns out to be the development of a heat-treatment procedure that renders the polycrystalline capsule impermeable to the melt, overcoming the largest obstacle to melt retention: absorption by the capsule into the spaces between the grains.
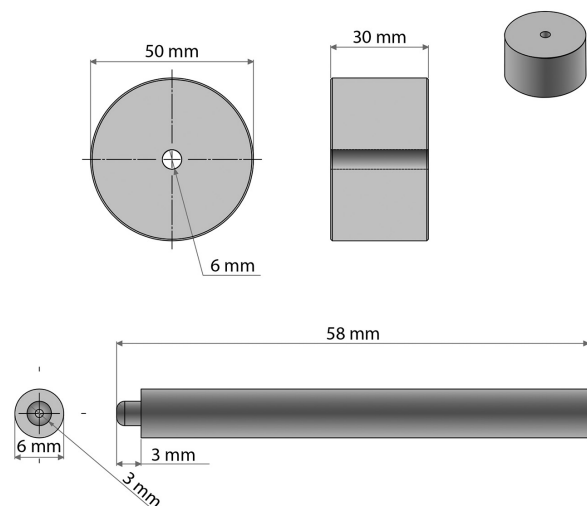
THE MANUFACTURE METHOD

The capsule manufacture is essentially a two-stage process. In our case the desired olivine composition was first prepared from a mixture of analytical grade MgO, SiO_2, and Fe_2O_3. Small amounts (1–2 wt%) of NiO and MnO were added together with the stoichiometric amount of SiO_2 to make olivine, as required. Because of the non-stoichiometry of "FeO" and the difficulty of obtaining complete reaction between Fe metal and Fe_2O_3, the initial heat treatment involves substantial reduction in addition to olivine synthesis.

The powdered starting material was ground under ethanol until fine and homogeneous. The mixture was then pressed into pellets of 12.7 mm diameter and 5 mm thickness (approx.) using PVA binder and reduced and recrystallized into olivine in a one-atmosphere gas-mixing furnace for >2 h at 1300 °C and an oxygen fugacity of 1 log unit below the FMQ buffer. After breaking the pellet open to confirm that the product was uniformly green and reduced the sample was pulverized using a percussion mortar and re-ground under acetone.

The second stage employs a die made of hardened tool steel (Fig. 1). Ours are of high-chromium ($\sim$12%) D2 steel, which can be hardened in air and undergoes little distortion. They were machined leaving the bore slightly undersize, hardened to R_c 56 and the bores honed to the desired dimensions. The pistons (Fig. 1) were fabricated from standard drill "blanks" with a nipple machined and then polished at one end to produce the sample space in the interior of the olivine capsule. We found that a rounded and highly polished end to the nipple (as shown) helps release the capsule from the piston. For 1-atm experiments we routinely use capsules of 6 mm O.D., 3 mm I.D., and 6 mm height, but we have also successfully produced capsules of 3 mm O.D. and 1 mm I.D. that would be suitable for high-pressure experiments. To make 6 mm O.D. capsules, we used about 0.37 g of reacted starting materials. These were placed in a mortar and moistened with an aqueous solution of PVA (50 g/L), which was worked into the mixture (initially stiff), until a "flaky" consistency was obtained. This material was then transferred to the die and compressed to a pressure not exceeding 1 GPa. Liberal application of PTFE spray to the die bore and piston was found to be necessary for a smooth removal of the capsules after pressing. Finally, the pressed capsules were suspended in the gas-mixing furnace and subjected, initially, to a single anneal at 1550 °C, in a 67%CO_2:33%CO gas

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FIGURE 1. Technical drawing showing the specifications of our 6 mm hardened-steel die and piston (J. Long, University of Oxford).
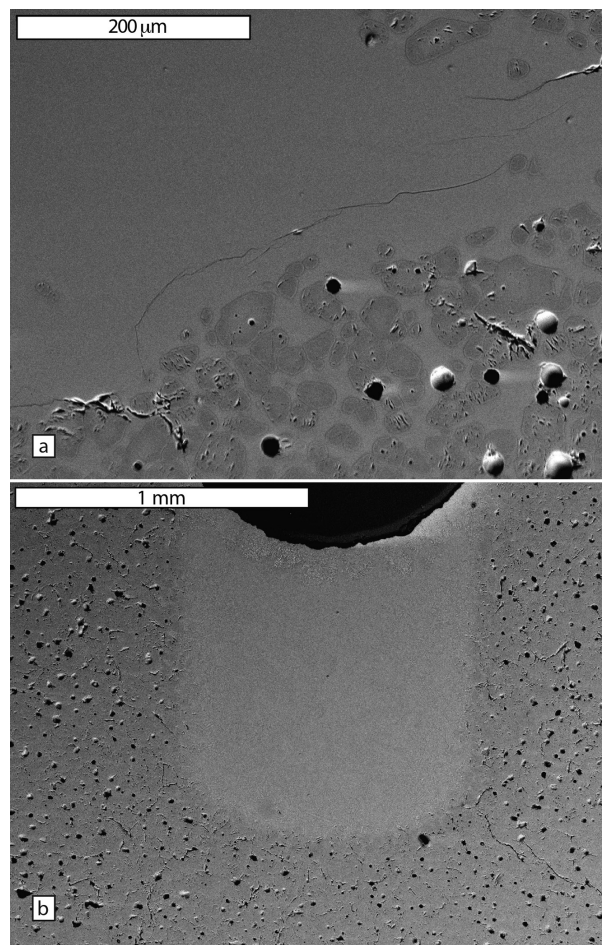
mixture. We found, however, that for Fo_{90} composition the capsule is too porous and that basaltic melt soaked away through the capsule walls as discussed below.

METHOD DEVELOPMENT

Our intention with the two-stage manufacturing process was to minimize pore space by separating the recrystallization of the starting powder to form olivine (together with its disruptive volume change) from the process of annealing the olivine grains into a capsule. Nevertheless, basaltic melts showed a strong tendency to infiltrate the pore spaces in our prototype capsules, due to their high wetting angles with olivine (Fig. 2a). Interconnected networks of pore spaces therefore made these capsules permeable, and incapable of retaining large pools of melt for extended periods. To reduce interconnectivity we experimented with cycles of heating and cooling. For the Fo_{90} composition capsules we found that the saw-tooth cycling shown in Figure 3 generated capsules of low permeability after 12 h of heat-treatment. We speculate that the cooling cycles "unlock" the grain boundaries, enhancing grain-growth during the succeeding heating cycle and isolating the pore space. Figure 2b is a BSE-image of a Fo_{90} capsule treated in this way. As can be seen, there is no evidence of infiltration by the melt into the capsule wall, especially since the large vesicles left behind by the PVA binder remain empty.

Interestingly, the Fo_{70} composition capsules did not require a complex heat-treatment to become impermeable. We found that a single cycle of heating from 800 to 1250 °C in 1 h followed by a 3 h temperature ramp from 1250 to 1350 °C and a 30 min anneal at the latter temperature in a gas mixture of 67% CO_2 and 33% CO was sufficient to reduce permeability to acceptable levels.

Cracks that formed during removal of the pressed capsules from the die represented an important source of unwanted porosity. To suppress their formation we experimented with various non-contaminating binding agents, which were mixed into the recrystallized mixture before it was pressed, with the aim of holding the capsule together during removal from the
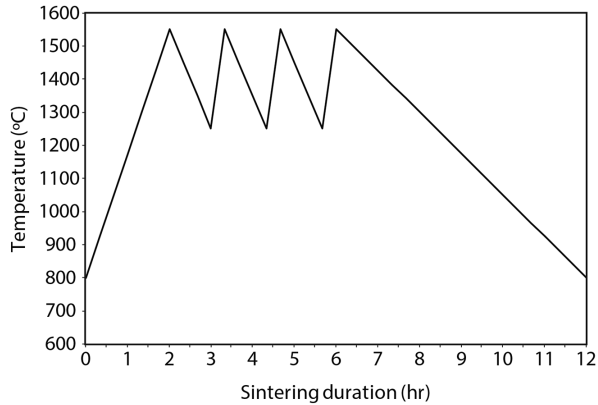

FIGURE 2. (**a**) Backscattered electron (BSE) image of the melt-capsule boundary for an unsuccessful (permeable) capsule—the separation of olivine grains by the melt makes the capsule permeable, and it quickly absorbs the melt into the capsule walls. (**b**) BSE image of the melt pool in a successful (impermeable) capsule. A sharp discontinuity exists between the melt and the capsule wall. The impermeability of the capsule is demonstrated by the absence of melt in the large vesicles formed by the PVA binder. The example shown here is an average terrestrial MORB (Gale et al. 2013) in a Fo.90 capsule after a run time of 12 h.

die. Water, ethanol, ammonia solution, tetraethyl orthosilicate, and polyvinyl alcohol solution (PVA 50 g/L) were tried, and PVA was found to be the only suitable binder. Use of PVA does leave pores (gas bubbles) within the sintered capsules, but these are not problematic because they do not generally form an interconnected network (Fig. 2b).
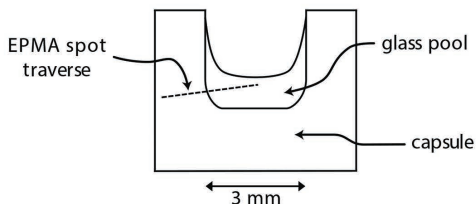
CAPSULE EVALUATION

Time-series experiments

We performed a time-series of experiments (2, 4, 8, and 24 h) at 1200 °C and an f_{O_2} of FMQ-1 log units to test whether or not our capsules could retain silicate melts for extended periods and to investigate the approach to equilibrium partitioning. Four Fo_{70} capsules containing 1% Mn_2SiO_4 and 2% Ni_2SiO_4 were packed with powdered oxides constituting an iron-rich basaltic composi-
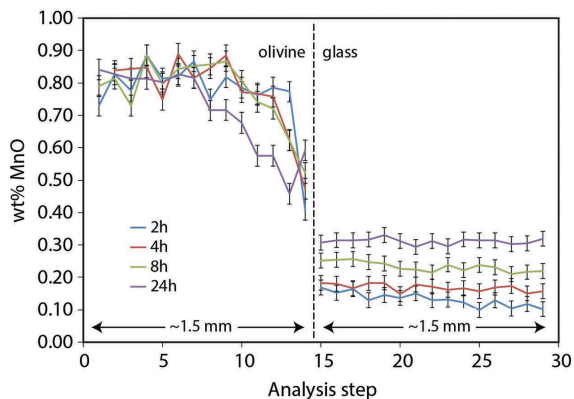
FIGURE 3. The temperature profile for an impermeable Fo.90 capsule. A single CO/CO$_2$ gas mixing ratio of 33/67 can be used for the whole sintering process, since it keeps the oxygen fugacity close to QFM-1 log units, and gives rise to capsules of pure olivine.
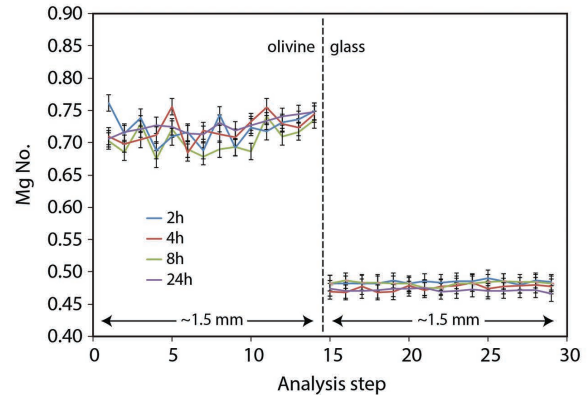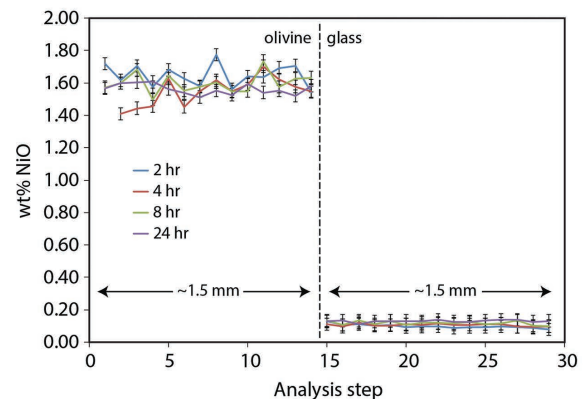

FIGURE 4. Three Fo.70 capsules hosting martian (iron-rich) basaltic melts, as they appear shortly after their removal from the furnace. Reflections from the concave melt pools are clearly visible. The capsules shown here are supported by an alumina crucible, with a platinum grill holding them above the crucible base (so that they do not fuse themselves to it), but it is also, of course, possible to suspend the capsules in individual platinum cages.

a

b

c

d

FIGURE 5. (**a**) Section through a capsule showing an EPMA spot traverse. (**b**, **c**, and **d**) The MgO/(MgO+FeO), MnO, and NiO analysis profiles for traverses through capsules from experiments of 2, 4, 8, and 24 h duration (see traverse map above). Olivine analysis spots were positioned in the centers of grains so that approach to crystal-liquid equilibration could be evaluated.

tion. The composition chosen (limited to the CFMAS system) was a putative martian basalt (Bertka and Holloway 1994), with its Mg# modified such that it would be in equilibrium with Fo.70 olivine. Each experiment was quenched rapidly by dropping into

water. Quenched capsules are shown in Figure 4.

The capsules were sectioned, ground, and polished, before being analyzed using a JEOL JXA-8600 electron-microprobe in WDS mode. A traverse from the outer wall to the center of

the melt pool was taken for each experiment (Fig. 5). Olivine analysis spots were positioned on grain centers to evaluate the approach to equilibrium (Fig. 5).

Each capsule retained a large pool of melt, indicating that absorption into pore spaces was negligible even after 24 h. Mn and Ni, initially present exclusively in the olivine, diffused into the melt pools during the experiment. Mg and Fe also show some re-equilibration, indicating that starting materials were not exactly in Mg-Fe exchange equilibrium with one another.

Diffusion profiles and approach to equilibrium

As expected, because the Ni and Mn contents of the melt were initially zero, a diffusional approach to equilibrium is observed in experiments of increasing duration (Fig. 5). As experiment duration increased, zoning of Ni in the olivine capsule wall diminished progressively, and the compositions of individual olivine grains became more uniform as the Ni content of the product glass increased. With increasing experiment duration, apparent Ni olivine-liquid partition coefficients exhibit successively closer approximations to a value of 12.2 that we consider a close approach to equilibrium. Although the $D = (124/MgO) - 0.9$ relation of Hart and Davis (1978) predicts a value of 14.4, we expect slightly lower values, as observed in earlier Fe-bearing experiments (Kinzler et al. 1990). As the variation among olivine analyses reduces with increased runtime, the calculated Mg-Fe exchange K_D [$= (Fe/Mg)_{ol}/(Fe/Mg)_{melt}$] settles to the 0.35 ($\pm0.01$) value reported for Fe-rich basalts by Filiberto and Dasgupta (2011).

Unlike their Ni contents and Mg/Fe ratios the Mn concentrations in the olivines and melts do not approach constant values even in 24 h experiments. This is almost certainly because, with D_{Mn} close to 1.0 (Watson 1977), the number of atoms of Mn required to be transported to approach equilibrium is much greater than in the case of Ni ($D_{Ni} = 12.2$). Thus, a NiO concentration in the melt of 1300 ppm indicates an approach to equilibrium while for MnO, in this case, equilibrium values of ~8000 ppm would be appropriate. After 24 h we actually reach a concentration of only 3100 ppm MnO in the quenched glass.

Despite the failure of Mn to reach equilibrium, the capsule's impermeability after even 24 h implies that longer runtimes may be used than those explored here.

Experimentation with different melt compositions showed that only those that are olivine-saturated can, in general, be retained by the synthetic capsules. Olivine-undersaturated melts are rapidly absorbed by the capsule, presumably because they preferentially dissolve olivine from the grain surfaces, connecting and widening pore spaces, and undermining the capsule's impermeability. Addition of sacrificial fine-grained olivine to such melts saturates them in olivine rapidly during the experiment and, as expected, avoids the problem of capsule impregnation.

IMPLICATIONS AND CONCLUSIONS

We have described and tested a method for the fabrication of synthetic polycrystalline olivine capsules suitable for the performance of experiments with olivine-saturated melts at high temperature. We have shown that specific olivine compositions require specific heat treatments to render them impermeable to infiltration by basaltic melts with which they are in equilibrium. We find that several cycles of heating to 1550 °C and cooling to 800 °C are required for Fo_{90} capsules to become impermeable. In this case, experiments of 24 h duration with basalt in the capsule at temperatures of 1400 °C indicated no infiltration by the melt. A simpler single-stage heat treatment to 1350 °C was found to be adequate for capsules of Fo_{70} composition.

The principal implication of this study is that, for olivine-saturated experiments for which noble metal capsules or wire loops are inappropriate, researchers will no longer be restricted to the use of natural olivine single crystals as capsules. We have found it relatively straightforward to extend the range of available capsule compositions from Fo_{90}, similar to single crystals from San Carlos (Arizona), to Fo_{70} enabling more iron-rich melts to be studied. Furthermore, the development of synthetic polycrystalline capsules enables control of trace and minor element concentrations in the olivine, which means that crystal-liquid partitioning studies can be performed at desired and appropriate concentration levels.

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