Appendix A Details of Experimental Methods for the 1-bar and 500MPa experiments

1. One-bar experimental setup

One-bar (1-bar) experiments were conducted in a vertical Deltech furnace with the oxygen fugacity controlled by a mixture of CO-CO_2 gases. Temperature was monitored by an S-type thermocouple, placed at the hot spot of the furnace, which has an uncertainty of ±3 degrees at temperatures of 1200-1250°C. The thermocouple was calibrated at the melting temperature of gold, and found to be within ±1˚C of the accepted value (1064˚C; 1 bar). The combined uncertainty in temperature is ±4°C.

Oxygen fugacity (fO_2) of the CO-CO_2 gas mixture was monitored with an yttria-stabilized zirconia oxygen sensor (SIRO2; Ceramic Oxide Fabricators, Eaglehawk, Australia) that was placed in the hot spot of the furnace adjacent to the location of the thermocouple and samples. The oxygen sensor measures the electrochemical potential (EMV) between the atmosphere outside (air) and inside the furnace (CO-CO_2 gas mixture); the EMV measurement allows the fO_2 inside the furnace to be calculated with the Nernst Equation. The oxygen sensor was calibrated against the Ni-NiO buffer by measuring the EMV when an adjacent Ni wire inside the furnace became oxidized (detected by a change in its electrical conductivity). This calibration of the oxygen sensor was performed at 1200, 1250 and 1270˚C; it was found to be accurate within 0.1 log unit of the accepted value based on the empirical equations from O'Neill and Pownceby (1993) and Frost (1990). All 1-bar experiments in this study were conducted at fO_2-temperature conditions along the Ni-NiO buffer (NNO).

The glass starting material was crushed to a powder and mixed with a poly-vinyl alcohol (PVA) solution to make a paste, which was placed on two $Au_{60}Pd_{40}$ wire loops (for duplication purposes) that were hung from a Pt wire cage. The Pt cage was suspended into the furnace so that the wire-loop samples were located in the hot spot of the furnace, adjacent to the thermocouple and oxygen sensor. Samples were quenched when a 110 V was run across a thin (0.127 mm) Pt wire that held the Pt cage between two thicker (0.502 mm Pt) wires. This caused the thin wire to melt and the Pt cage to drop into a cup of cold, distilled water at the base of the furnace. The experimental run products consisted of glass beads attached to the $Au_{60}Pd_{40}$ wire loops. The glass beads were readily removed and embedded in epoxy grain mounts for compositional analyses. Multiple glass chips from the two beads per experiment were mounted for analysis.

All $Au_{60}Pd_{40}$ wire used in the experiments were first pre-saturated to minimize loss of Fe and Ni to the wire loop. Pre-saturation runs were conducted under identical conditions (temperature, fO_2, duration) as the final experimental runs. The glass attached to the pre-saturation run products was mechanically removed, and the wires were re-used in the final experiments.

2. Piston-cylinder (PC) experimental setup

2.1 Determination of hotspot through double thermocouple measurements

The location of the hotspot in the PC assembly was determined through five experiments where temperature was measured by two thermocouples (TCs) at different distances from the bottom of the base plug, with one at the top of the 4-bore alumina tube, and the other at an additional opening that was filed down at a measured distance below the tip of the 4-bore alumina tube. Since the graphite furnace is 30 mm long, one TC was always located in the center, which is 15 mm from the bottom of the base plug. The other TC was located at 11.5, 12.5, 13.5, 17.5, and 19 mm from the bottom of the base plug in five different experiments (Fig. A1). All distances were measured prior to loading and compression of the assembly. For each experiment, the sample assembly was pressure-soaked at 500 MPa for an hour before heating up. The pressure was maintained at 500 MPa while the temperature was ramped up from room temperature to 1300 ˚C and came back down to 1050 ˚C before the termination of the experiment by shutting off the power. The reading of each thermocouple (TC) was recorded when the TC 15 mm was at 1050, 1125, 1200 and 1250 °C, both during heating up and cooling down. After the first set of measurements, the power was shut down at 1050 ˚C, and the two TC readers were switched between the two TCs. This step eliminated any systematic error between the two TC readers, with one TC connected to a EuroTherm Controller and the other TC connected to an external OMEGA TC reader. The final reported temperature from each location is the average of four measurements (during heating and cooling and using two different TC readers).

Fig. A2 shows the thermogradient of the assembly when it is composed of MgO only without an AuPd capsule. The hotspot is about 13.5 mm from the bottom of the base plug based on results from the five experiments. This result is in good agreement with the hotspot position of 12.7 mm by Tenner (2005) and Tenner et al. (2007), who measured the thermal gradient of the same piston cylinder apparatus at the University of Michigan Experimental Petrology Laboratory. The Tenner et al. (2007) experiments were conducted in a ½ inch piston assembly at 2.0 to 3.0 GPa, whereas the measurements in this study were conducted in a ¾ inch piston assembly at 0.5 GPa.

Based on the determination of the hotspot, the AuPd capsule in all PC experiments of this study was carefully placed with its center at 13.5 mm from the bottom of the base plug (Fig. A3).

2.2 Determination of the thermal gradient through bracketing of NaCl melting at 500 MPa

The center of each 5 mm-long capsule is about 13.5 mm from the bottom of the base plug, whereas the tip of the thermocouple is 9.5-10 mm from the bottom of the base plug (Fig. A3). According to the thermal gradient measurements through double thermocouple technique

(Fig. A2), the temperature difference between the ~9.5-10 and 13.5 mm locations could range from 16 to 33˚C. However, as pointed out by Moore et al. (2008), there is a damping effect on the thermal gradient with the presence of a noble metal capsule (Fig. A3), compared to the thermal gradient measured in a MgO-Al_2O_3 only assembly (Fig. A1).

In order to apply a more accurate temperature correction between the recorded temperature at the tip of thermocouple and the center of the AuPd capsule, NaCl melting experiments were conducted in the same assembly configuration as performed for all the olivine-melt equilibration experiments in this study (Fig. A3). NaCl powder was heated at 450˚C overnight to remove any absorbed H_2O, loaded into a 5 mm AuPd capsule (same size and length as the experiments in this study), with a small platinum bead placed on top of the NaCl powder prior to welding the capsule shut. If melting of NaCl occurred, the bead would fall through the low-viscosity NaCl liquid and end up at the bottom of the capsule. If no melting occurred, the platinum bead would remain at the top of the capsule. The bottom vs the top of the capsule was well marked prior to each experiment. The melting curve of NaCl has been well documented by Clark (1959) to be 910 (±3) ˚C at 500 MPa. Moore et al. (2008) demonstrated that there is no pressure correction needed for this PC assembly (NaCl-pyrex) at 500 MPa.

Three sets of NaCl experiments were conducted with TC temperatures (9.5-10 mm below base plug) of 890˚C, 896˚C and 900˚C. Each NaCl experiment was held at run conditions (500 MPa and run temperature) for 45 minutes. The Pt bead dropped in the run with recorded temperature at 900˚C and stayed on top with recorded temperatures at 896˚C and 890˚C (Fig. A4). Therefore, the temperature correction between the TC reading and the center of the capsule is >10 and <14 ˚C. Therefore, a correction of +12 (± 1) ˚C was applied to the recorded TC temperature of all PC experiments in this study.

A temperature gradient of 12°C for a ¾ inch PC assembly with a metal capsule is in good agreement with the those reported in the literature. For example, Watson et al. (2002)

report a thermal gradient of 15°C in a ¾ inch PC assembly (with a graphite capsule smaller than 4mm), whereas slightly larger thermal gradients of 18-20 °C and 17°C, respectively, were reported in ½ inch PC assemblies by Medard et al. (2008) and Hui et al. (2008).

2.3 Temperature uncertainty in PC experiments

Several factors contribute to the uncertainty in temperature in the PC experiments. First, the S-type thermocouple has an uncertainty of ±3 °C at temperatures of ~1100-1200 °C, and an additional ±1 °C is added when calibrated against the melting temperature of gold. The NaCl melting curve of Clarke (1959) has a ± 3 °C uncertainty, and the temperature correction of 12 °C, obtained in this study, has an uncertainty of ± 1 °C. Therefore, the combined temperature uncertainty is ± 8 °C for all the PC experiments reported in this study.

2.4 Piston-cylinder experimental procedure

Each experimental sample (in a 5mm AuPd capsule) was located with its center 13.5mm below the bottom of the base plug, which was determined to be the hotspot of the 30mm long assembly based on several calibrations (Fig. A2). The assembly of NaCl + pyrex + graphite + MgO + AuPd capsule was pressurized at experimental pressure (500 MPa) and room temperature overnight to reduce the risk for thermocouple failure. The pressure was adjusted 90-95% of the run pressure (~450-475 MPa) right before the heating, and kept within this range during the heating process. The pressure was increased to 500 MPa once the experimental temperature was reached, and maintained between 490-510 MPa during the entire experimental duration.

2.5 References

Clark, S.P.Jr. (1959) Effect of Pressure on the melting point of eight alkali halides. The Journal of Chemical Physics, 31, 6.

Frost, B.R. (1990) Introduction to oxygen fugacity and its petrologic importance. Reviews in Mineralogy and Geochemistry, 25, 1–9.

Hui, H., Zhang, Y., Xu, Z, and Behrens, H. (2008) Pressure dependence of the speciation of dissolved waterin rhyolite melts. Geochemica et Cosmochimica Acta, 72, 3229-3240.

Medard, E., McCammon, C.A., Barr, J.A., and Grove, T.L. (2008) American Mineralogist, 93, 1838-1844.

Moore, G., Roggensack, K., and Klonowski, S. (2008) A low-pressure-high-temperature technique for the piston-cylinder. American Mineralogist, 93, 48-52.

O'Neill, H.St.C., and Pownceby, M.I. (1993) Thermodynamic data from redox reactions at high temperatures. I. An experimental and theoretical assessment of the electrochemical method using stabilized zirconia electrolytes, with revised values for the Fe-FeO, Co-CoO, Ni-NiO and Cu-Cu2O oxygen buffers, and new data for the W-WO2. Contributions to Mineralogy and Petrology, 114, 296–314.

Tenner, T.J. (2005) The albite fusion curve re-examined: new experiments and the density and compressibility of NaAlSi3O8 liquid with pressure. University of Michigan M.S. thesis.

Tenner, T.J., Lange, R.A., and Downs, R.T. (2007) The albite fusion curve re-examined: New experiments and the high-pressure density and compressibility of high albite and NaAlSi3O8 liquid. American Mineralogist, 92, 1573–1585.

Watson, E.B., Wark, D.A., Price, J.D. and Van Orman, J.A. (2002) Mapping the thermal structure of solid-media pressure assemblies. Contributions to Mineralogy and Petrology, 142, 640-652.

Figure A1. *The configuration of double thermocouple measurements for hot spot and thermal gradient in a ¾ inch piston cylinder assembly*

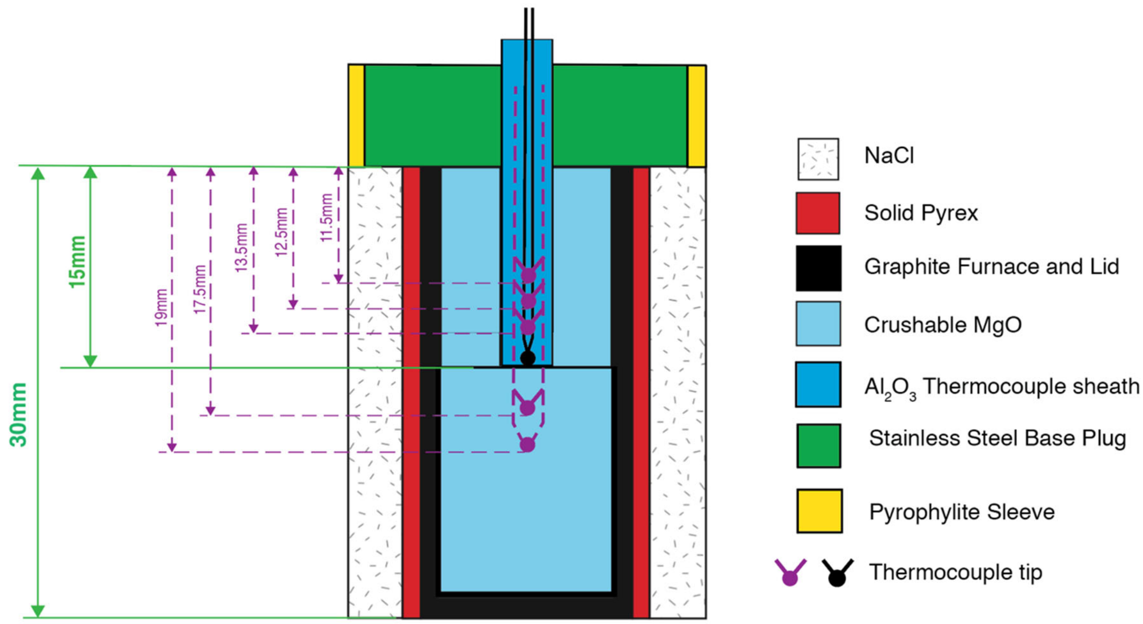

Figure A2 *Thermal gradient at different temperature across the 30mm PC assembly in the ¾ inch piston setup*

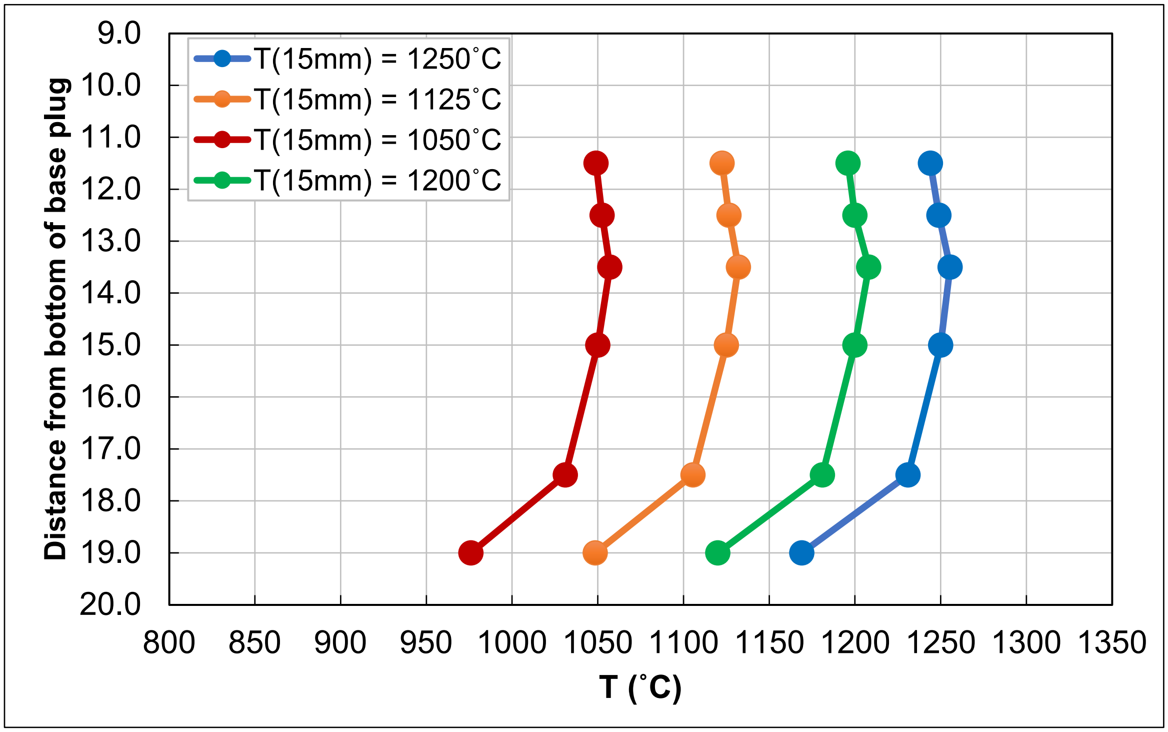

Figure A3 *The configuration of the PC assembly for all PC experiments in this study with the sample capsule located 13.5mm under the bottom of the base plug*

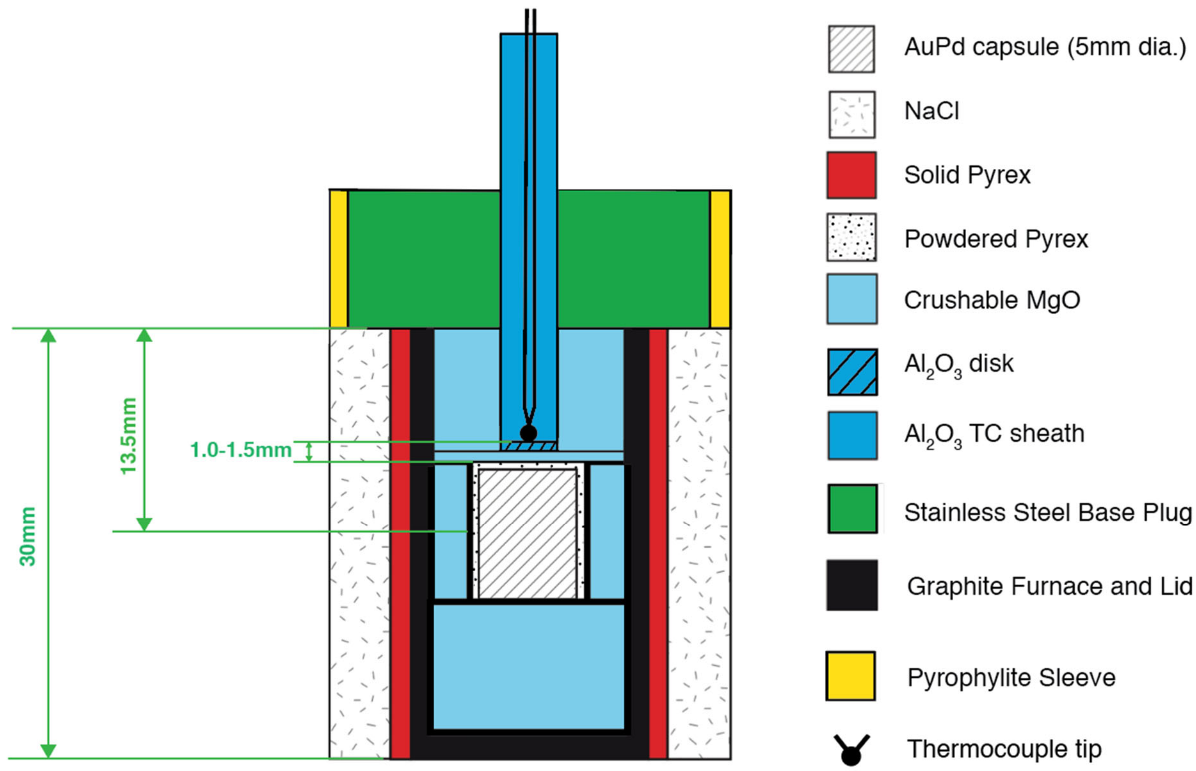

Figure A4 *Images of NaCl melting experiment to calibrate the temperature difference between the tip of the thermocouple (recorded temperature) and the capsule at 500 MPa. The melting temperature of NaCl at 500 MPa is 910 ± 3 °C (Clarke, 1959). The results indicate a correction that is >10 and <14 (12 ± 1) °C.*