REVISION 01

A New High-Pressure Experimental Apparatus to Study Magmatic Processes at Precisely Controlled Redox Conditions

ALICE ALEX[1] AND ZOLTÁN ZAJACZ[2]

[1] Department of Earth Sciences, University of Toronto, Canada, alice.alex@mail.utoronto.ca

[2] Department of Earth Sciences, University of Geneva, Switzerland, zoltan.zajacz@unige.ch

ABSTRACT

Oxygen fugacity (fO_2) is typically controlled in high P-T experiments by using solid state redox buffer assemblages. However, these are restricted to impose discrete fO_2 values often with significant gaps between neighbouring assemblages. Semi-permeable hydrogen membranes (Shaw 1963) are often used in internally heated pressure vessels for more flexible fO_2 control in hydrous experiments; however, their implementation in more widely available externally-heated pressure vessels have not yet gained space. We propose a prototype Molybdenum-Hafnium Carbide (MHC) pressure vessel apparatus that simultaneously allows rapid quenching and flexible, precise, and accurate redox control via a custom-designed hydrogen membrane. Test runs with two membranes at a time, one imposing and another one monitoring fH_2, demonstrated that 95% of the imposed hydrogen pressure was attained inside the pressure vessel within 2 hours at 800 – 1000ºC, after which a steady state equilibrium was established. Furthermore, experiments comparing redox-dependent Cu solubility in silicate melts at fO_2 imposed by the fayalite-magnetite-quartz, Re-ReO_2 and MnO-Mn_2O_3 buffers and identical target fO_2 imposed by the hydrogen membrane confirmed consistency between the two methods within 0.25 log units fO_2 deviation at T=900ºC and P=2000 bar. This powerful yet cost-effective and low-maintenance apparatus may open up new pathways for studying redox reactions in hydrous magmas and magmatic fluids. As a proof of concept, we conducted near-liquidus phase equilibrium experiments with H_2O-saturated calc-alkaline basalt and shoshonite melt compositions at 5 different fO_2 values equally distributed between half log unit below the Ni-NiO buffer (NNO-0.5) and NNO+2.7. Most experiments crystallized olivine, clinopyroxene and Ti-magnetite. The Mg# of the olivine increased with fO_2, and the Fe^{3+}/Fe_{total} ratios in the silicate melt were determined based on Fe(II)-Mg exchange between olivine and melt. The Fe^{3+}/Fe_{total} ratios in the shoshonite melt were systematically higher by about 0.06 ± 0.01 than those in the calc alkaline basalt melt at identical fO_2. The values determined for the basaltic melt were consistent within 1σ error (<0.033 deviation) from those predicted by the equation of Kress and Carmichael (1991). The Fe-Ti exchange coefficient between magnetite and silicate melt increases from 1.73±0.19 (1σ)at NNO-0.5 to 7.12±0.36 at NNO+2.7 for shoshonite and has a similar range for the calc-alkaline basalt.

INTRODUCTION

Because of the abundance of heterovalent elements such as Fe and S in magmatic and hydrothermal systems, accurate control of fO_2 , in high pressure (*P*) – temperature (*T*) experiments, is essential for studying phase equilibria, element partitioning and the solubilities of ore minerals and ore metals in silicate melts and hydrothermal fluids. Several techniques have been developed to control fO_2 in high *P-T* experiments. Most take advantage of the high permeability of metals to hydrogen at magmatic temperatures and impose fH_2 in the experimental capsule by controlling fH_2 in its external environment. In hydrous experimental charges, fO_2 is defined in turn through the water decomposition reaction. Following are the methods used currently to control the oxygen fugacity in high *P*-*T* experiments.

1. Redox buffers: Developed by Eugster (1957), solid oxygen buffers control the fO_2 in an experimental charge. This technique allows imposing well-constrained fO_2 either directly or by regulating fH_2 when using the double capsule technique (Eugster 1959; Chou 1986) with water added to the buffer assemblage. The direct use of redox buffers is however limited by unwanted chemical reactions between the buffer assemblage and the experimental phase assemblage and/or the experimental assembly itself. An important general limitation of the technique is that it can only be used to impose discrete fO_2 values using the available buffer assemblages, often with 1-2 log unit gaps between the fO_2 of neighboring buffers. Most importantly, there is a nearly two log unit gap between the neighboring Ni-NiO and the Re-ReO_2 buffers, and a major part of the characteristic fO_2 range of convergent plate magmatism on Earth falls within this gap. An additional drawback of the redox buffer technique is the limited lifetime of the buffer assemblages, which limits the maximum time that can be provided for the attainment of equilibrium in the experimental phase assemblage.
2. Ni-alloy pressure vessels: Externally heated pressure vessels (EHPV) made of nickel rich alloy (e.g. Rene-41) can be used with H_2O pressure medium. In this case, H_2O-saturated experiments are buffered at an fO_2 close to that of the Ni-NiO buffer due to reaction between the vessel alloy and water producing NiO and H_2. The inner walls of the vessel need to be cleaned regularly to expose a fresh layer of the metal. Using the same

principle, Matthews et al. (2003) employed filler rods of different compositions to impose a variety of hydrogen fugacities.

3. Gas mixtures: A more flexible control of fO_2 can be achieved in gas-pressurized experimental apparatus by admixing CH_4 or H_2 with the Ar pressure medium to impose desired fH_2 in the pressure medium and thus also fO_2 in hydrous experimental charges (Gaetani and Grove 1997; Moore and Carmichael 1998; Cottrell et al. 1999; Zajacz et al. 2010, 2011, 2012; Pichavant et al. 2014). The initial ratio of gas mixtures loaded to achieve a certain fH_2 at experimental T is not a straightforward calculation and requires additional verification using redox sensors. The major drawback of this method is that hydrogen diffuses through the walls of the EHPV resulting in progressive oxidation during the experiment rendering the method non-ideal for experiments requiring accurately controlled redox conditions (Shea and Hammer 2013; Alex and Zajacz 2020). A new method was proposed by Alex and Zajacz (2020) to estimate the amount of H_2 - required to impose target fO_2 values and it was shown that in optimized Molybdenum-Hafnium Carbide pressure vessel assemblies, the imposed fO_2 can be maintained relatively constant (e.g. 0.36 log unit/day fO_2 increase at T=1000ºC and a water activity of 1). However, some types of experiments require even better control of redox conditions.
4. Shaw membrane: A more sophisticated method would be to use Shaw membranes to impose and control a desired fO_2 in the pressure vessel. The technique of using a metal as a semi-permeable membrane to hydrogen at high T has been widely used in internally heated pressure vessels (IHPV) but only one design was proposed for EHPV (Schmidt et al. 1995). However, this design is difficult to put in practice and, more importantly, it

prevents rapid quenching when used with conventional EHPV, with one opening. Therefore, until now, the control of fO_2 in EHPV experiments has commonly been achieved by using redox buffers and/or admixing CH_4 or H_2 to the Ar pressure medium.

The application of Mo-based alloys such as Titanium-Zirconium-Molybdenum (TZM) and more recently Molybdenum-Hafnium Carbide (MHC) with high tensile strengths and slow aging characteristics up to 1100 and 1250ºC, respectively, facilitate the expansion of the use of EHPV to study a broad range of magmatic processes at upper crustal pressures. As EHPVs are cheaper and easier to construct, maintain and operate than IHPV, the use of MHC and TZM pressure vessels is rapidly gaining space in experimental petrology.

In this paper, we propose a novel externally-heated MHC pressure vessel apparatus that can be used with a Shaw-membrane while preserving rapid-quench capability. A new type of Shaw-membrane specifically designed for use with this apparatus is also presented along with direct performance tests and successful proof of concept experiments comparing the fO_2 dependence of Fe^{3+}/Fe_{tot} ratios in hydrous calc-alkaline basalt and shoshonitic melts and Fe-Ti exchange coefficients between magnetite spinel and silicate melt.

EXPERIMENTAL METHODS

The principal concept of the new MHC pressure vessel apparatus

The hydrogen permeability of the MHC alloy is significantly lower than that of Ni-based superalloys (Alex and Zajacz, 2020) and thus a Shaw membrane may effectively be used to control fH_2 in the pressure medium. However, the membrane needs to be at the same temperature as the experimental capsule, and consequently needs to be placed right next to the capsule in the thermally homogeneous hot zone of the pressure vessel. A traditional EHPV is drilled from one side with the capsule sitting in the far end of the vessel from the water-cooled pressure seal, and therefore the membrane must sit right behind the capsule. This setup prevents rapid-quenching of the experiment because the capsule would be blocked from moving into the cold part of the vessel assembly should this be attempted by dropping or by moving with an magnet - filler rod assembly (e.g. Matthews et al. 2003).

To counteract the above problem, we designed a new type of MHC pressure vessel apparatus which uses a pressure vessel that is drilled completely through and has water-cooled pressure seals on both ends (Fig. 1). The vessel assembly is placed in a purpose-designed split-hinge furnace equipped with rod-type SiC heating elements powered through a phase angle-fired SCR power controller. The vessel is 45 cm long and the hot zone is in the middle section of the vessel. Therefore, the Shaw-membrane can be introduced from one end of the vessel, whereas the experimental capsule is introduced from the other end. As the membrane blocks the way towards only one of the water-cooled ends of the vessel, the capsule can be freely dropped toward the other water-cooled end for quenching by rotating the vessel from the default sub-horizontal to vertical position.

Technical implementation of the new MHC pressure vessel apparatus

The MHC alloy quickly oxidizes in air at high *T* and therefore needs to be isolated from the atmosphere. In classical designs, this is accomplished by enclosing the vessel in an oxidation-resistant Inconel 600 alloy sheath which is welded closed on one end and attached through a threaded connection to the water-cooled closure nut of the vessel at the other end. The tight volume between the Inconel sheath and the vessel is either continuously flushed with argon or is kept air-tight by sealing the threaded connection. Here, we use the same solution, except that the Inconel sheath cannot be connected by a thread to both water-cooled closure nuts because of the differential thermal expansion of the MHC and the Inconel 600 alloys. Therefore, one of the closure nuts has an inner O-ring pressing tight against the outer surface of the sheath. This design facilitates up to a few millimeters of relative movement between the sheath and the closure nut while maintaining a gas-tight seal. Argon flushing is not required. Efficient water cooling of the closure nut near the O-ring groove facilitates the use of inexpensive Viton O-rings, which need to be replaced only once in every 3-5 experiments.

The MHC pressure vessel has high-pressure closure nuts on both sides made of 304 stainless steel, which are continuously water-cooled. The pressure seal is achieved via an easily replaceable 9.53 mm (3/8”) diameter 304 or 316 stainless steel high-pressure nipple with a 59^o cone facing the 60^o – 7.62 mm (0.30”) diameter female cone on the end of the vessel. To ensure its parallel alignment with the long axis of the vessel, the high-pressure nipple is led through a 36 mm long hole in the back end of the closure nut that has only a slightly larger diameter than the nipple itself (10 vs 9.52 mm). Both closure nuts have a welded water-cooling collar providing 36 mm wide contact surface between the closure nut and the cooling water.

The pressure vessel is placed inside a custom-built split furnace that is equipped with 5 pairs of rod-type SiC heating elements and has a 27.95 cm (11”) long heated zone. The furnace along with the pressure vessel is placed on a 180^o rotating axis (Fig. 2). The furnace is equipped with a phase-angle fired SCR power controller and can reach up to about 5200 W of power output. The hotspot of the vessel spans symmetrically across the middle section and yields a gradient of $<12^oC$ across a length of 6 cm in a water-cooled vessel.

Control and/or monitoring of hydrogen fugacity

Classical Shaw-membrane assemblies are composed of a membrane made of a metal with high hydrogen permeability, typically AgPd alloys or Pt, and a supporting tubing assembly that facilitates the delivery of hydrogen to the membrane (Shaw 1963; Hewitt 1977; Gunter et al. 1979; Scaillet et al. 1992). The membrane itself is supported from the inside by an incompressible but gas-permeable porous media, and it must be connected to the supporting tube assembly by a gas tight seal that can handle up to thousands of bars of overpressure from the outside. This connection is technically challenging to accomplish and it imposes limitations in membrane lifetime and the maximum temperature of applicability (Schmidt et al. 1995). For example, the connection is most typically attained by gold brazing, and thus the melting point of Au (1064ºC) defines the maximum temperature of use. Furthermore, the diffusion of Au into the AgPd alloy with ageing will reduce the membrane's hydrogen permeability.

To counteract the above problems, we developed a new type of the Shaw membrane, which uses a single tube that runs the entire length of the membrane assembly and attains high hydrogen permeability in the membrane section by the thinning the tube rather than brazing a Pt or AgPd alloy tube onto it. For this purpose, we used Ni-Cu alloy (Ni-400 / Monel-400) tubing which has high hydrogen permeability and at the same time good machinability, weldability and ductility as well as high corrosion resistance (Ball 1960). Its melting range is 1300-1350 ºC, and therefore the membrane can be used up to the temperature limits imposed by the MHC alloy. Most importantly, due to its loose lattice, Monel falls under the high permeation group for hydrogen gas with permeability constant 10 times higher than that of Pt at 1000ºC (Gorman and Nardella 1962). An additional advantage is that Monel alloy tubing is widely available at a relatively low price. The design and dimensions of the membrane are shown in Figure 3.

The primary structural element used for the construction of the membrane assembly is a 208 mm long Monel tube with 4.57 and 6.35 mm inner and outer diameter, respectively. The hot end of the tube is welded shut by using a Monel plug as filler. The membrane portion is generated by thinning down the Monel tube to about 150-200 µm wall thickness over 22 – 25 mm length near the hot end of the membrane assembly because the rate of hydrogen permeation through materials shows inverse linear relationship to thickness (Gorman and Nardella 1962). This membrane section is physically supported from inside by densely packed spherical zirconia powder with sphere diameter of 30 µm to prevent collapse under external pressure while facilitating rapid hydrogen flow. The advantage of using spherical powder is that it easily takes a close-packed arrangement at ambient conditions, and therefore, it cannot be compressed significantly more under confining pressure preventing any significant deformation of the membrane at experimental conditions. The remaining part of the membrane is fitted inside with 304 stainless-steel tubing (2.08 mm I.D X 4.55 mm O.D.) with a hollow alumina thermocouple tubing placed in the center to facilitate hydrogen flow while preventing the collapse of the steel and Monel tubes under confining pressure at elevated temperatures. The hollow part of the alumina rod is also packed with spherical zirconia powder. The hydrogen permeability of stainless steel is about 3 times lower than that of the Monel alloy (Gorman and Nardella 1962) and the combined wall thickness of the stainless steel and Monel tubes on the non-membrane section is about 10-13 times larger than the wall thickness of the Monel at the membrane section. Therefore, hydrogen permeation through this part of the membrane assembly can be considered negligible even if the temperature difference is not considered. This is important, because this section of the membrane assembly is at lower *T* than the experimental capsule. Note that the external pressure presses the ductile Monel tube very tightly onto the stainless-steel tube preventing any backflow of hydrogen in between the two tubes. The transition between the membrane and non-membrane sections of the Monel tube is made gradual with approximately 40-50 degrees angle. In addition, this step on the Monel tube is supported from underneath by a porous MgO ceramic rod. This ceramic rod is also critically important for preventing any backflow of the spherical zirconia powder into the alumina tubing and then the steel pressure capillary, which would induce unwanted deformation of the membrane portion of the Monel tube and would increase the chance of membrane failure during experimental runs.

Hydrogen gas is introduced into the membrane via stainless steel high-pressure capillary tubing (0.5 X 1.60 mm, 300 MPa rated) which is Ag-brazed into the inner steel tube of the assembly. At the same time, the cold end of the Monel and the stainless-steel tubes are brazed together as well. The brazed end of the membrane assembly sits approximately 10 mm from the termination of the vessel and therefore never reaches temperatures above ~280ºC. Another key aspect is that the contact surface between the membrane assembly and the inner wall of the pressure vessel must be minimized to avoid the diffusion of Ni and Cu into the MHC alloy, which could lead to its weakening and/or early recrystallization. This is achieved by leaving two narrow and sharp collars with about 6.25 mm OD on the membrane assembly surface (the rest of the Monel tube is thinned down to 5.9 – 6.0 mm OD) one close to the hot end and another one close to the cold end. These collars protrude from the membrane surface by only 0.1 – 0.2 mm and make a relatively tight fit to the inner diameter of the vessel. This way, the physical contact between the membrane and the vessel is restricted to the sharp edge of the collars, minimizing the diffusive exchange of metals between the two.

The schematic diagram of the pressure lines and valves used to supply H_2 to the membrane is provided in Figure 4. The system contains a 1.1 liter-volume 304 stainless steel H_2 reservoir in which the pressure can be set to the value of the desired fH_2 in the experiment. The relatively large volume of the reservoir ensures nearly constant pressure despite the slow loss of hydrogen from the system by permeation through the MHC vessel walls during the experiments. In addition, there is a dual stage vacuum pump connected to the line which facilitates the vacuuming of the Shaw membrane, and if needed, also the H_2 reservoir and the rest of the pressure line. The pressure of H_2 gas is monitored using a factory-calibrated digital pressure transducer with a range of 0-34.47 bar and ±0.25% full-scale error attached to valve 4. The pressure transducer is always connected to the membrane, but this section of the system can be fully isolated from the H_2 reservoir and the vacuum pump so that the operation mode of the membrane can easily be switched from “supply” to “monitoring” by closing the isolation valves. To improve the response time in the monitoring mode, all free wetted spaces within the connecting blocks are 90% filled with stainless steel rods to reduce the internal volume of the isolated section of the pressure line. The readout from the pressure transducer is continuously recorded by a computer.

Experimental strategy

To test how efficient the membrane is at imposing fH_2, so called “two-membrane test experiments” were conducted in which two membranes were inserted in the vessel at the same time, one from each end. One of the membranes was imposing fH_2 whereas the other one was monitoring it (Fig. 5). No argon was loaded into the vessel for these experiments. Tests were conducted at a variety of imposed PH_2. To test the working of the experimental setup at elevated pressure, a set of CoPd alloy redox sensors experiments were carried out at T=900ºC and P=2000 bar for experimental durations of 6, 24 and 48 hours at fO_2 of NNO + 0.5, and an additional run at NNO + 2.5 for 12 hours. As these experiments indicated that the activity model for the CoPd alloy is inaccurate at low Co concentrations. We also compared the membrane-imposed fH_2 values to those imposed by well-established redox buffer assemblages. These test experiments constrained the timelines required for the attainment of equilibrium between the membrane and the pressure medium and proved the consistency of the target and apparent fH_2. We conducted proof of concept experiments to demonstrate the power of the new apparatus in studying natural systems under controlled redox conditions. This involved the comparison of the effect of fO_2 on the Fe^{3+}/Fe^{2+} ratios in calc-alkaline basalt and shoshonite melts, and the determination of Fe-Ti exchange coefficients between magnetite spinel and the same basalt and shoshonite melts as a function of fO_2. The methods, analytical procedure, and results for these sets of experiments are described in detail below.

Two-membrane tests

As hydrogen membranes had to be inserted from both side of the vessel in these experiments, no argon was introduced into the vessel other than a minor amount used to flush air out of the vessel during the insertion of the second membrane. The membrane used to supply hydrogen to the internal volume of the pressure vessel was connected to the H_2 reservoir. The other "sensor" membrane was connected to a hydrogen pressure transducer with a range of 0 – 34.47 bars and a full-scale accuracy of 0.25%. The interior of both membranes was flushed with ~10 bar H_2 and vacuumed to <0.01 bar in 3 consecutive cycles to remove all air residues. At high temperatures, the H_2 diffused into the inner volume of the pressure vessel from the supply membrane and consequently diffused into the sensor membrane. The hydrogen pressure in both the supply and sensor membrane was automatically recorded as a function of time.

Redox sensor experiments

We used a CoPd alloy sliding redox-sensors as proposed by Taylor et al. (1992). A detailed description of the employed redox sensor capsule design can be found in Alex and Zajacz (2020). A 6 mm long, 6.0 X 3.0mm (OD X ID) hollow MgO ceramic rod was used as a spacer between the end of the Shaw membrane and the sensor capsule inside the pressure vessel to prevent direct contact and potential alloying between them at high temperatures (Fig. 1). The capsule was dropped to the water-cooled end of the vessel before the start of the experiment. After pressurizing with ~700 bars of argon, the vessels were heated to the desired run temperature (900ºC) in 50 minutes and held there for various durations, typically 6, 24 and 48 hours. The final pressure of Argon achieved at high *T* was 2000±20 bars. During the heating step, the membrane was isolated from the hydrogen reservoir. Before the introduction of H_2, the membrane was vacuumed to <0.01 bar to remove any air. At the experimental *T,* the Shaw membrane was opened to the H_2 reservoir by a needle valve (valve 4, Fig. 4) and left to equilibrate with the argon pressure medium in the vessel. As a precaution, to remove any traces of impurities in the gas supply or degassing products of membrane material, we vacuumed the membrane to 0.01 bar after ~3 hours of equilibration in a quick succession and then opened it again to the hydrogen reservoir. Subsequently, the capsule was dropped from the water-cooled end to the hotspot by rotating the vessel-furnace assembly to a vertical position and left to equilibrate for the reported run duration (Table 1). After the termination of the experiment, the capsules were drop-quenched, extracted and weighed to check for weight loss due to potential leakage of water. Capsules showing weight loss larger than expected, resulting from hydrogen diffusion out of the capsule,) were discarded. Intact capsules were pierced in one corner, heated to 130ºC for 30 min to evaporate any remaining water, and reweighed again to determine that excess water was present after completion of experiment. Afterwards, they were cut open, and the run product CoPd-CoO pellet was extracted, vacuum impregnated and mounted in epoxy and polished for electron microprobe analysis. Redox sensor experiments with NiPd alloy were also performed at 900ºC, but they were discarded for this study as the alloy did not equilibrate within the timeframe explored (12 and 48 hours) as shown by comparatively much greater compositional heterogeneity relative to the CoPd alloys.

Test experiments using redox buffers

These experiments included a double capsule using redox buffers and an unbuffered capsule simultaneously. The fH_2 in the Shaw membrane was set to attain identical fO_2 in the unbuffered capsule to that imposed by the redox buffer in the buffered capsule. As capsule material, $Au_{97}Ag_2Cu_1$ alloy was used which imposed a Cu activity of 0.0097 and the apparent solubility of Cu in a phonolite melt was used as a redox sensor. Water was added in excess of its solubility in the phonolite melt to ensure $aH_2O=1$ in the capsule. Copper has been shown to dissolve in silicate melts in 1+ oxidation state within the fO_2 range studied here (Holzheid and Lodders 2001; Ripley et al. 2002; Zajacz et al. 2012) and therefore, the apparent Cu solubility in the silicate melt is fO_2 dependent.

The experiments were conducted at 900ºC and 2000 bar of pressure. The sketch of the experimental setup is shown in Figure 6. The three buffers that we used were fayalite-magnetite-quartz (FMQ), Re-ReO_2 and MnO-Mn_3O_4 imposing an fO_2 of -0.7, 1.9 and 3.5 log units relative to the Ni-NiO buffer, respectively. The buffer capsule, with outer capsule made of the same alloy as the inner capsule had an O.D. of 5mm. At run *T*, after 3 hours of equilibration given to diffuse the H_2 from the reservoir into the vessel through the membrane, both the buffered and unbuffered capsules were dropped from the water-cooled end to the hotspot by rotating the furnace-vessel assembly. After 48 hours with the vessel in 10º tilted from horizontal position, the capsules were drop quenched by rotating the entire setup by 80º. After confirming the physical integrity of the capsule by checking for any weight loss, the quenched capsules were opened, and the phonolite glass was mounted and polished for analysis.

Proof of concept experiments

We experimentally determined Fe^{3+}/Fe_{tot} ratios as a function of fO_2 in water-saturated near-liquidus calc-alkaline basalt and shoshonite melts at identical *P*-*T* conditions (*T* = 1020ºC and *P*=2000 bar) and fO_2 ranging from NNO-0.42 to NNO+2.73 to investigate the effect of melt alkalinity on the oxidation state of iron. The same experiments also allowed us to determine Fe-Ti exchange coefficients as a function of fO_2 between magnetite spinel and silicate melt. To constrain Fe^{3+}/Fe_{tot} ratios in the silicate melt, we used the Toplis (2005) model equation to estimate the Fe – Mg exchange coefficients between olivine and melt ($K_{d,Fe-Mg}^{olivine/melt}$). As Fe is incorporated in the structure of olivine only as Fe^{2+}, the composition of olivine in combination with the measured Mg concentration in the silicate melt can be used to estimate the Fe^{2+} concentration in the melt. Deducting the latter from the measured total Fe concentration in the melt yields the Fe^{3+} concentration in the melt.

The starting calc-alkaline basalt powder was prepared by fusing a basalt lava powder from the Planchon volcano of the Southern Volcanic Zone of the Andes at 1400ºC for 90 minutes in air. The shoshonite glass was prepared from high purity oxide and carbonate reagents following the procedure described by Sullivan et al. (2018). The homogeneity of the glasses was confirmed by using EMPA. The glasses were loaded into Au capsules after grinding them in agate mortar. The starting glass compositions are provided in Table 2. Each capsule was loaded with 20 mg of the glass powder and 4.5 µl distilled water ensuring water saturation at run conditions. The fO_2 conditions investigated are provided in Table 3. The experimental protocol of pressurizing, heating, fO_2 control and quenching were the same as described in section 2.3.

ANALYTICAL TECHNIQUES

The composition of the run products from the redox sensor experiments and the glasses of the proof of concept experiments were determined by using a JEOL JXA-8230 electron microprobe equipped by 5 WDS detectors at the Department of Earth Sciences, University of Toronto. The composition of the CoPd alloy blebs and the interstitial CoO was determined using 15 kV accelerating voltage, 20 nA sample current and 1 µm beam diameter. The alloy and oxide phases were additionally analysed for Al, Ti, and Ag to make sure that the pellet was not contaminated during the experiment. The glasses were measured using 15 kV accelerating voltage, 7 nA beam current and 20 µm beam diameters. Elemental standards were used for Al, Ti, Co and Pd with peak counting time of 20 s and background counting time of 10 s. Synthetic alloy of $Au_{80}Ag_{20}$ was used as a standard for Ag analysis with peak counting time of 60 s and background counting time of 30s. An interference correction was used to eliminate the contribution of the Pd Lα peak to the Ag Lα peak. For the analysis of the glasses from the proof of concept experiments, we used the Smithsonian VG2 glass as a standard for Si, Al, Fe, Ca and Mg. Alkali feldspar standards were used for Na and K. Synthetic Fo85 was used as the standard for Fe and Mg analysis in olivine, whereas ilmenite (NMNH96189) was used to quantify Fe and Ti concentrations in spinels.

The major and trace elements in the quenched glass for the buffer experiments were analysed by using an NWR 193 UC laser ablation system coupled with an Agilent 7900 inductively coupled plasma quadruple mass spectrometer (LA – ICP – MS) at the Magmatic and Ore Forming Processes Research Laboratory, University of Toronto. In all the analytical sessions, the

ICP-MS was tuned to mass-21/^{42}Ca and ThO/Th <0.3% and U/Th~1. Helium carrier gas was used at 1.00 l/min flow rate, which was mixed with about 0.85 l/min Ar after the ablation cell, before entering the ICP torch. A dwell time of 10 ms was used for P, K, Ca, V, Cr, Mn, Fe and Cu, whereas Na, Mg, Al, Si and Ti were measured with 5 ms dwell time. The USGS basaltic glass standard GSD 1-g was used as external standard and was analyzed twice at the beginning and end of each analysis block corresponding to about 1 hour of analysis time. A beam diameter of 30 to 40 µm was used for most analyses. The LA-ICP-MS data was quantified by using the software, SILLS (Guillong et al., 2008).

RESULTS

Results of the two membrane tests

As shown on Figure 7a, it takes about 1 hour to attain equilibrium between the hydrogen membrane and the Ar pressure medium at 1000 ºC if no hydrogen is added to the pressure medium initially. The time required for equilibration is approximately doubled for 100 ºC drop in in temperature. The results show that 95-96% of the imposed hydrogen pressure is reached as equilibrium fH_2 in the inner volume of the pressure vessel at 900 and 1000 ºC. Additional tests have shown that fH_2 at about 96% of the imposed value can be maintained in the pressure medium on the long term (Fig. 7b) and that the ratio between hydrogen pressure inside the membrane and the fH_2 in the Ar pressure medium remain at a value of about 0.96 independent of the value of the imposed hydrogen pressure (Fig. 7 a, b, c). In addition, we tested the effect of aging on the efficiency of the hydrogen membrane. For this purpose, we conducted a two-membrane test with using a supply membrane which was previously used for a total of ~300 hours at 1000 and 900 ºC. When using this aged membrane, equilibrium was attained when the ratio of the PH_2 inside the membrane and the fH_2 in the pressure medium was about 0.90 (Fig. 7d). This difference in fH_2 corresponds to only 0.06 log unit difference in fO_2.

Results of the Co-Pd redox sensor and the redox buffer experiments

In the CoPd alloy redox sensor experiments, the measured Co concentrations in the run product was used to determine the fO_2 in the vessel based on the equation of Taylor (1992). The results of the sensor experiments are shown in Figure 8. At T=900ºC and an imposed fO_2 of 0.5 log units above the Ni-NiO buffer (NNO+0.5), 0.14 log units increase is seen in the fO_2 with increasing run duration from 6 hours to 48 hours, with the 24 and 48 h runs showing identical values within 1 σ uncertainty. An average offset of 0.42 log units is observed between the target fO_2 and the imposed fO_2 at these conditions. The experiment at higher fO_2 (NNO + 2.5) shows larger difference between the predicted and measured fO_2 (0.76 log units).

The “redox buffer experiments” showed that the difference in the apparent Cu solubility between the buffer technique and the Shaw membrane method are minimal: 2% relative difference at NNO – 0.7 (FMQ), 11% at NNO + 1.9 (Re-ReO_2) and 9% at NNO + 3.5 (MnO – Mn_3O_4) as shown in Figure 9. The largest observed differences at nominal fO_2 of NNO+1.9 and NNO + 3.5 correspond to 0.3 log unit difference in fO_2 based on the slope of the fitted fO_2 vs. apparent Cu solubility function (Fig. 9).

Results of the proof of concept experiments

Based on the run products, both the calc-alkaline basalt and shoshonite experiments yielded a stable phase assemblage of silicate melt - olivine - clinopyroxene - magnetite. We were not able to find olivine crystals in the calc-alkaline basalt of the experiment conducted at NNO + 2.73, possibly due to the accidental lack of surface exposure at low crystal fractions. Hence, we do not report the compositions for that particular experiment here. For all other experimental runs, the run product glass and olivine compositions are provided in Table 4, the calculated Fe^{3+}/Fe_{total} in the melts are given in Table 5, and the magnetite compositions are given in Table 6. All calculations are discussed further below.

The Mg# of the olivine and silicate melt increases with fO_2 in both the basalt and shoshonite experiments. In case of the olivine crystallized from the calc-alkaline basalt, the Mg# increases from 0.817 ± 0.004 at NNO - 0.42 to 0.883 ± 0.003 at NNO + 1.9. For the olivine crystalized from the shoshonite melt, the Mg# increases from 0.792 ± 0.004 at NNO - 0.42 to 0.899 ± 0.002 at NNO + 2.73. In the calc-alkaline basalt melt, the Mg# increases from 0.532 ± 0.007 at NNO – 0.42 to 0.585 ± 0.005 at NNO + 1.9. In shoshonite melt, the Mg# increases from 0.469 ± 0.011 at NNO – 0.42 to 0.548 ± 0.010 at NNO + 2.73.

The TiO_2 content of the magnetite spinel decreases with increasing fO_2 while the TiO_2 content of the melt remains relatively constant (<16% decrease). In the calc-alkaline basalt, the TiO_2 content of the magnetite decreases from 5.12 ± 0.26 wt% at NNO – 0.42 to 1.89 ± 0.03 wt% at NNO + 2.73. In case of the magnetite crystallized from the shoshonite melt, the TiO_2 concentrations decrease from 5.68 ± 0.49 wt% to 2.21 ± 0.03 wt% across the same range of fO_2.

DISCUSSION

The two membrane tests demonstrated the effective operation of the hydrogen membrane at magmatic temperatures. The difference in the supply and sensor measurements is due to the loss of H_2 from the pressure medium through the pressure vessel walls at high *T*. As fH_2 increases in the pressure vessel after opening the Shaw-membrane to the H_2 reservoir, the fH_2 gradient driving the mass transfer of hydrogen from the interior of the membrane to the pressure medium decreases. At the same time, the fH_2 gradient between the pressure medium and the exterior environment of the pressure vessel (atmosphere) increases and so does the rate of diffusive hydrogen loss from the pressure vessel. At a certain fH_2 in the pressure medium, the total flux of hydrogen from the membrane to the pressure medium and from the pressure medium to the atmosphere becomes equal and an equilibrium is established. Our experiments showed that this equilibrium fH_2 is about 95.5% of the imposed fH_2 at 1000ºC with a new membrane and decreases to about 90% of the imposed fH_2 as the membrane ages. This difference corresponds to only 0.04 log units in fO_2, and even the 10% difference in fH_2 observed for the aged membrane corresponds to only 0.09 log unit difference between the target and actually imposed fO_2 inside a capsule at a water activity of 1. Therefore, the aging of the membrane appears to cause a very minor offset in fO_2. As the temperature dependence of the hydrogen permeability of the MHC and Monel alloys is similar (Steward 1983; Alex and Zajacz 2020), this value is predicted to not show significant variations with temperature as demonstrated by comparing the results of our two-membrane tests at 900 and 1000°C (Fig. 7a, b). Furthermore, as mentioned earlier, the target PH_2 /equilibrium PH_2 ratio is independent of the actual value of the target PH_2 and therefore the offset in fO_2 is also independent of the actual value of the target fO_2.

Our time series experiments at T=900ºC with the CoPd alloy redox sensors confirmed the constancy of fO_2 in the $Ag_{70}Pd_{30}$ experimental capsules at a water activity of 1 and thus the constancy of fH_2 in the pressure medium at elevated pressure. Keeping in mind that the redox buffer experiments have confirmed the accurate operation of the hydrogen membrane, the observed offset between the imposed and measured fO_2 values (0.42 log units at NNO+0.5 and 0.76 log units at NNO+2.5) must relate to inaccuracy in the activity model used for the CoPd alloy in the equations of Taylor (1992). The offset observed at a log fO_2 of NNO+0.5 and

NNO+2.5 would require 16 and 40 relative % error on the activity coefficient of Co in the CoPd alloy, respectively. Therefore, it is apparent that there is a systematic error in the activity models used for the CoPd alloy, which, in a relative sense, increases with decreasing Co concentration. Hence, we do not recommend the use of this redox sensor at fO_2 significantly above that of the Ni – NiO buffer.

Considering the buffer experiments, the good agreement attained between the buffered and unbuffered capsules for apparent Cu solubility is a strong evidence for the accurate operation of the Shaw membrane over the fO_2 range spanning between the FMQ and MnO-Mn_3O_4 buffers ($\log fO_2$ of NNO-0.7 to NNO+3.5). It is worthy to emphasize that the hydrogen membrane yields accurate fO_2 values even at highly oxidizing conditions with the offset in apparent Cu solubility observed at the MnO-Mn_3O_4 buffer corresponding to 0.3 log unit difference in fO_2 (Fig. 9). The imposed fH_2 at this condition was 0.182 bar.

Inferring the Fe^{3+}/Fe^{2+} ratios in the melt from the composition of silicate melt – olivine pairs require the accurate estimation of the value of $K_{d,Fe-Mg}^{olivine/melt}$. The partitioning of Mg between olivine and melt was shown to be influenced by H_2O (Putirka et al. 2007; Pu et al. 2017, 2021), whereas the dissolved H_2O content has been shown to have no significant effect on the ferric/ferrous ratio in silicate melts (Moore et al. 1995; Gaillard et al. 2001). Nevertheless, it is likely that all melt compositional variables affect Fe^{2+} and Mg^{2+} similarly as melt composition has only a minor effect on $K_{d,Fe-Mg}^{olivine/melt}$ (O'Neill and Eggins 2002). Any little variation of $K_{d,Fe-Mg}^{olivine/melt}$ seen as a function of P, T, and melt composition (including H_2O concentration) has been described by a model equation by Toplis (2005). We used this equation to estimate the value of $K_{d,Fe-Mg}^{olivine/melt}$ for our experiments. Within the fO_2 range imposed in our experiments, the

$K_{d,Fe-Mg}^{olivine/melt}$ value ranged from 0.27 to 0.29 and from 0.30 to 0.31 for the shoshonite and the calc-alkaline basalt, respectively. In turn, these values allowed us to estimate the Fe^{2+} concentration in the silicate melt based on the measured olivine compositions and the measured Mg concentrations in the melt. The concentration of Fe^{3+} in the melt was obtained by calculating the difference between the measured total Fe in the melt and the estimated Fe^{2+} concentration. The corresponding Fe^{3+}/Fe_{total} ratios are shown in Figure 10 and given in Table 5. It is apparent that shoshonite has higher Fe^{3+}/Fe^{2+} ratio in the same fO_2 range than in the calc-alkaline melt. With increasing ferric/ferrous ratio, Fe^{3+} shows increasing preference for tetrahedral sites in the silicate melt structure relative to octahedral site (Baiocchi et al. 1982; Mysen 1987; Burkhard 2000; Farges et al. 2004). The Si^{4+} to Fe^{3+} substitution is facilitated by charge balancing by alkali cations, in particular K^+ (Fudali 1965; Thornber et al. 1980; Sack et al. 1981; Kilinc et al. 1983; Tangeman et al. 2001), which explains the higher Fe^{3+}/Fe_{tot} ratios in the shoshonite melt relative to the calc-alkaline basalt at identical fO_2.

The results were compared to Fe^{3+}/Fe_{total} ratios predicted by using the model equation of Kress and Carmichael (1991). The experimentally determined Fe^{3+}/Fe_{tot} ratios in the calc-alkaline basalt melt appear to be systematically slightly (by 2-5 absolute%) higher than the values predicted by the Kress and Carmichael (1991) model but all overlap with the model curve within 1σ error (Fig. 10a). However, the Kress and Carmichael (1991) method appears to more significantly under predict the Fe^{3+}/Fe_{tot} ratios in the more alkaline shoshonite melt, consistently with previous observations (Tangeman et al. 2001; Borisov et al. 2017) (Fig. 10b).

Ferric-ferrous ratio of hydrous silicate melts depends strongly on melt composition (Thornber et al. 1980; Sack et al. 1981; Kilinc et al. 1983; Dickenson and Hess 1986; Borisov et al. 2015). Magnetite accommodates Ti in its structure and the equilibrium concentration of Ti in magnetite depends on the composition of the silicate melt and fO_2 as shown by Arató and Audétat (2017). It was proposed that the ratio between the silicate melt/magnetite partition coefficients of Fe and Ti, i.e. the Fe/Ti exchange coefficient between the magnetite and the silicate melt, can be used to constrain magmatic fO_2. The Fe/Ti exchange coefficient ($K_{d,Fe-Ti}^{magnetite/melt}$) between the magnetite and melt was calculated using the following equation 1,

$$K_{d,Fe-Ti}^{magnetite/melt} = \frac{X_{magnetite}^{Fe}/X_{melt}^{Ti}}{X_{magnetite}^{Ti}/X_{melt}^{Fe}} \quad \textbf{(1)}$$

A strong positive correlation can be observed between the imposed fO_2 and $K_{d,Fe-Ti}^{magnetite/melt}$ and the values for basalt and shoshonite melt are consistent within 1 σ error (Fig. 11). The observed trend is primarily induced by the decreasing Ti concentration in the magnetite as the TiO_2 concentration in the melt shows only a slight drop with increasing fO_2 (<15.6 relative %). The drop in the Ti concentration in the magnetite is due to the increase in the ratio between the activities of Fe_2O_3 and FeO constituents in the silicate melt, which supress the ulvöspinel substitution in the structure of magnetite occurring via exchanging 2 Fe^{3+} by (Fe^{2+} + Ti^{4+}).The observation that the alkalinity of the melt does not affect $K_{d,Fe-Ti}^{magnetite/melt}$ suggest that the higher Fe^{3+}/Fe_{total} ratio in the shoshonite melt relative to that in the basalt melt is primarily due to a decrease in the activity coefficient of Fe_2O_3 in the melt in response to the increased alkali-oxide concentration (i.e. the Fe_2O_3/FeO activity ratio remains the same and is tied only to fO_2). The relationship between $K_{d,Fe-Ti}^{magnetite/melt}$ and log fO_2 can be described by the following second order polynomial function, given below in equation 2.

$$\log fO_2(\Delta NNO) = 0.9925(\pm 0.27)K_{d,Fe-Ti}^{magnetite/melt} + 0.3202(\pm 0.14)(K_{d,Fe-Ti}^{magnetite/melt})^\wedge 2 + 2.1 \pm 0.17 \quad \textbf{(2)}$$

IMPLICATIONS

We introduced a new type of rapid-quench Molybdenum-Hafnium Carbide pressure vessel apparatus facilitating accurate and flexible redox control by using a new type of Shaw membrane designed for this apparatus. It has been experimentally demonstrated that in hydrous experimental charges, a stable fO_2 value anywhere between those of the FMQ and $MnO-Mn_2O_3$ buffer (log fO_2 between NNO-0.7 and NNO+3.4) can be imposed with an accuracy better than 0.3 log units by using this apparatus (theoretically, the accuracy and precision is better than 0.1 log units). The new Shaw membrane is cost effective and easier to construct than previous varieties. Furthermore, it has a long operational lifetime and may potentially be used up to T as high as 1300ºC. The new MHC pressure vessel apparatus may serve as an attractive alternative to internally-heated pressure vessels for experimentation targeting hydrous upper crustal magmatic systems, in particular if accurate, precise, and flexible control of redox conditions and/or flexible quenching – heating cycles are required. Controlling the oxidation state of iron and sulfur in magmas is a prerequisite for meaningful phase equilibrium experiments targeting the understanding of equilibrium between crystalline phases and silicate, carbonate or sulfide melts, as well as those aiming to understand magma degassing and the generation of ore-forming fluids at depth. Therefore, the new apparatus introduced in this article may significantly contribute to the disciplines of igneous petrology and economic geology in the future.

Proof of concept experiments have shown that the Fe^{3+}/Fe_{tot} ratios in hydrous calc-alkaline basalt melts are significantly lower than in hydrous shoshonite melts at identical fO_2. Furthermore, the Fe^{3+}/Fe_{tot} ratios in hydrous basaltic melts are successfully predicted by the model equation of Kress and Carmichael (1991) in the log fO_2 range of NNO-0.5 to NNO+2.5, whereas the same model underpredicts the abundance of Fe^{3+} in a shoshonite melt by about 12 relative%. In addition, it has been shown that the exchange coefficient of Fe and Ti between magnetite and hydrous mafic silicate melts increases from 1.73 ± 0.19 to 7.12 ± 0.36 with log fO_2 increasing from NNO-0.5 to NNO+2.5, independent of the alkalinity of the melt. The empirical equation provided to describe the relationship between $K_{d,Fe-Ti}^{magnetite/melt}$ and fO_2 can be used to estimate fO_2 for near-liquidus hydrous mafic magmas in natural systems.

Acknowledgements

Alice Alex acknowledges the help of Dr. Boris Foursenko (Lab Technician, Department of Earth Sciences, University of Toronto) who provided immense technical support during the entire project. Mr. George Kretschmann, (Engineering specialist, Department of Earth Sciences, University of Toronto) is credited in setting up the communications for the pressure transducers. Dr. Yanan Liu (Microprobe Technician, Department of Earth Sciences, University of Toronto) is acknowledged for all her help with the EMPA analysis and Dr. Alexandra Tsay is thanked for her help with the LA-ICP-MS analyses. Carter Grondahl contributed the calc-alkaline basalt sample. Zoltán Zajacz acknowledges the financial support of the National Sciences and Engineering Research Council of Canada in the form of a Discovery Grant. Most facilities used for this research were constructed with the financial support of a Canada Foundation for Innovation – Leaders Opportunity Fund grant and an Ontario Research Fund – Small Infrastructure grant to Zoltán Zajacz.

REFERENCES

Alex, A., and Zajacz, Z. (2020) A new method to quantitatively control oxygen fugacity in externally heated pressure vessel experiments. European Journal of Mineralogy, 32, 219–234.

Arató, R., and Audétat, A. (2017) FeTiMM – A new oxybarometer for mafic to felsic magmas. Geochemical Perspectives Letters, 19–23.

Baiocchi, E., Bettinelli, M., Montenero, A., and Di Sipio, L. (1982) Spectroscopic Behavior of Iron(III) in Silicate Glass. Journal of the American Ceramic Society, 65, C-39-C-40.

Ball, F.A. (1960) The welding of monel and k-monel. In Symposium on non-ferrous metal industry in India pp. 211–222. Symposium on non-ferrous metal industry in India.

Borisov, A., Behrens, H., and Holtz, F. (2015) Effects of melt composition on Fe3+/Fe2+ in silicate melts: a step to model ferric/ferrous ratio in multicomponent systems. Contributions to Mineralogy and Petrology, 169, 1–12.

——— (2017) Effects of strong network modifiers on Fe3+/Fe2+ in silicate melts: an experimental study. Contributions to Mineralogy and Petrology, 172, 1–14.

Burkhard, D.J.M. (2000) Iron-bearing silicate glasses at ambient conditions. Journal of Non-Crystalline Solids, 275, 175–188.

Chou, I.M. (1986) Permeability of precious metals to hydrogen at 2kb total pressure and elevated temperatures. American Journal of Science, 286, 638–658.

Cottrell, E., Gardner, J.E., and Rutherford, M.J. (1999) Petrologic and experimental evidence for the movement and heating of the pre-eruptive Minoan rhyodacite (Santorini, Greece), 135, 315–331.

Dickenson, M.P., and Hess, P.C. (1986) The structural role and homogeneous redox equilibria of iron in peraluminous, metaluminous and peralkaline silicate melts. Contributions to Mineralogy and Petrology, 92, 207–217.

Eugster, H.P. (1959) Reduction and oxidation in metamorphism, 397–426 p. Abelson, P. H., ed., Researches in geochemistry. Elsevier.

Farges, F., Lefrère, Y., Rossano, S., Berthereau, A., Calas, G., and Brown, G.E. (2004) The effect of redox state on the local structural environment of iron in silicate glasses: A combined XAFS spectroscopy, molecular dynamics, and bond valence study. Journal of Non-Crystalline Solids, 344, 176–188.

Fudali, R.F. (1965) Oxygen fugacities of basaltic and andesitic magmas. Geochimica et Cosmochimica Acta, 29, 1063–1075.

Gaetani, G.A., and Grove, T.L. (1997) Partitioning of moderately siderophile elements among olivine, silicate melt, and sulfide melt: Constraints on core formation in the Earth and Mars. Geochimica et Cosmochimica Acta, 61, 1829–1846.

Gaillard, F., Scaillet, B., Pichavant, M., and Beny, J.-M. (2001) The effect of water and fO_2 on the ferric-ferrous ratio of silicic melts, 255–273 p. Chemical Geology Vol. 174.

Gorman, J.K., and Nardella, W.R. (1962) Hydrogen permeation through metals. Vacuum, 12, 19–24.

Gunter, W.D., Myers, J., and Wood, J.R. (1979) The Shaw Bomb, an Ideal Hydrogen Sensor. Contributions to Mineralogy and Petrology, 70, 23–27.

Hewitt, D.A. (1977) Hydrogen fugacities in Shaw bomb experiments. Contributions to Mineralogy and Petrology, 65, 165–169.

Holzheid, A., and Lodders, K. (2001) Solubility of copper in silicate as funcdtion of oxygen and sulfur fugacities teperatures, and silicate composition. Geochimica et Cosmochimica Acta, 65, 1933–1951.

Kilinc, A., Carmichael, I.S.E., Rivers, M.L., and Sack, R.O. (1983) The ferric-ferrous ratio of natural silicate liquids equilibrated in air. Contributions to Mineralogy and Petrology, 83, 136–140.

Kress, V.C., and Carmichael, I.S.E. (1991) The compressibility of silicate liquids containing Fe2O3 and the effect of composition, temperature, oxygen fugacity and pressure on their redox states. Contributions to Mineralogy and Petrology, 108, 82–92.

Matthews, W., Linnen, R.L., and Guo, Q. (2003) A filler-rod technique for controlling redox conditions in cold-seal pressure vessels. American Mineralogist, 88, 701–707.

Moore, G., and Carmichael, I.S.E. (1998) The hydrous phase equilibira (to 3 kbar) of an andesite and basaltic andesite from western Mexico: Constraints on water content and conditions of phenocryst growth. Contributions to Mineralogy and Petrology, 130, 304–319.

Moore, G., Righter, K., and Carmichael, I.S.E. (1995) The effect of dissolved water on the oxidation state of iron in natural silicate liquids. Contributions to Mineralogy and Petrology, 120, 170–179.

Mysen, B.O. (1987) Redox equilibria and coordination of Fe2+ and Fe3+ in silicate glasses from 57Fe mossbauer spectroscopy. Journal of Non-Crystalline Solids, 95–96, 247–254.

O’Neill, H.S.C., and Eggins, S.M. (2002) The effect of melt composition on trace element partitioning: An experimental investigation of the activity coefficients of FeO, NiO, CoO, MoO2 and MoO3 in silicate melts. Chemical Geology, 186, 151–181.

Pichavant, M., Scaillet, B., Pommier, A., Iacono-Marziano, G., and Cioni, R. (2014) Nature and

Evolution of Primitive Vesuvius Magmas: an Experimental Study. Journal of Petrology, 55, 2281–2310.

Pu, X., Lange, R.A., and Moore, G. (2017) A comparison of olivine-melt thermometers based on DMg and DNi: The effects of melt composition, temperature, and pressure with applications to MORBs and hydrous arc basalts. American Mineralogist, 102, 750–765.

Pu, X., Moore, G.M., Lange, R.A., Touran, J.P., and Gagnon, J.E. (2021) Experimental evaluation of a new H2O-independent thermometer based on olivine-melt Ni partitioning at crustal pressure. American Mineralogist, 106, 235–250.

Putirka, K.D., Perfit, M., Ryerson, F.J., and Jackson, M.G. (2007) Ambient and excess mantle temperatures, olivine thermometry, and active vs. passive upwelling. Chemical Geology, 241, 177–206.

Ripley, E.M., Brophy, J.G., and Li, C. (2002) Copper solubility in a basaltic melt and sulfide liquid/silicate melt partition coefficients of Cu and Fe. Geochimica et Cosmochimica Acta, 66, 2791–2800.

Sack, R.O., Carmichael, I.S.E., Rivers, M., and Ghiorso, M.S. (1981) Ferric-ferrous equilibria in natural silicate liquids at 1 bar. Contributions to Mineralogy and Petrology, 75, 369–376.

Scaillet, B., Pichavant, M., Roux, J., Humbert, G., and Lefevre, A. (1992) Improvements of the Shaw membrane technique for measurement and control of fH2 at high temperatures and pressures. American Mineralogist, 77, 647–655.

Schmidt, B.C., Scaillet, B., and Holtz, F. (1995) Accurate control of fH2in cold-seal pressure vessels with the Shaw membrane technique. European Journal of Mineralogy, 7, 893–903.

Shaw, H.R. (1963) Hydrogen-Water Vapor Mixtures: Control of Hydrothermal Atmospheres by Hydrogen Osmosis. Science (New York, N.Y.), 139, 1220–2.

Shea, T., and Hammer, J.E. (2013) Oxidation in CSPV experiments involving H_2O-bearing mafic magmas: Quantification and mitigation. American Mineralogist, 98, 1285–1296.

Steward, S.A. (1983) Review of Hydrogen Isotope Permeability Through Materials. Lawrence Livermore National Laboratory, UCRL-53441, 1–28.

Sullivan, N.A., Zajacz, Z., and Brenan, J.M. (2018) The solubility of Pd and Au in hydrous intermediate silicate melts: The effect of oxygen fugacity and the addition of Cl and S. Geochimica et Cosmochimica Acta, 231, 15–29.

Tangeman, J.A., Lange, R., and Forman, L. (2001) Ferric-ferrous equilibria in K2O-FeO-Fe2O3-SiO2 melts. Geochimica et Cosmochimica Acta, 65, 1809–1819.

Taylor, J.R., Wall, V.J., and Pownceby, M.I. (1992) The calibration and application of accurate redox sensors. American Mineralogist, 77, 284–295.

Thornber, C.R., Roeder, P.L., and Foster, J.R. (1980) The effect of composition on the ferric-ferrous ratio in basaltic liquids at atmospheric pressure. Geochimica et Cosmochimica Acta, 44, 525–532.

Toplis, M.J. (2005) The thermodynamics of iron and magnesium partitioning between olivine and liquid: criteria for assessing and predicting equilibrium in natural and experimental systems. Contrib. Mineral Petrol, 149, 22–39.

Zajacz, Z., Seo, J.H., Candela, P.A., Piccoli, P.M., Heinrich, C.A., and Guillong, M. (2010) Alkali metals control the release of gold from volatile-rich magmas. Earth and Planetary

Science Letters, 297, 50–56.

Zajacz, Z., Seo, J.H., Candela, P.A., Piccoli, P.M., and Tossell, J.A. (2011) The solubility of copper in high-temperature magmatic vapors: A quest for the significance of various chloride and sulfide complexes. Geochimica et Cosmochimica Acta, 75, 2811–2827.

Zajacz, Z., Candela, P.A., Piccoli, P.M., Wälle, M., and Sanchez-Valle, C. (2012) Gold and copper in volatile saturated mafic to intermediate magmas: Solubilities, partitioning, and implications for ore deposit formation. Geochimica et Cosmochimica Acta, 91, 140–159.

FIGURES

FIGURE 1. An overview drawing of the new MHC vessel assembly. The vessel is open and water-cooled at both ends. It is placed in a rotatable split hinge furnace with rod-type SiC heaters distributed over a 28 cm long heated zone. The Shaw membrane and the experimental capsule sit at identical temperature at either side of the hot zone in the central section of the vessel. Quenching of the capsule is facilitated by rotating the furnace-vessel assembly into vertical position so that the capsule drops into the water-cooled end of the vessel on the non-membrane side.

FIGURE 2. An image of the experimental setup with the furnace-vessel assembly on a rotating axis. The long cylindrical metal container mounted on the frame to the left of the furnace is the H_2 reservoir connected to the Shaw membrane.

FIGURE 3. Schematic diagram of the system supplying hydrogen to the Shaw membrane. In “supply mode” valve no. 4 is open, and the Shaw membrane is connected to hydrogen reservoir. With the closure of valve no. 4, the membrane switches to monitoring role. The rupture disk (7) protects the pressure transducer (6) in case of the backflow of argon caused by membrane failure. Due to safety considerations, valve no. 2 and the main valve on the hydrogen cylinder are only open while adjusting pressure in the H_2 reservoir.

FIGURE 4. Schematic drawing of the new type of Shaw membrane optimized for use with externally heated pressure vessels (not to scale). The thinned section of the Monel tube near the hot end serves as the semi-permeable hydrogen membrane.

FIGURE 5. Experimental setup of the two-membrane test experiments. Cut-out from the central portion of the MHC pressure vessel.

FIGURE 6. Experimental setup for the redox buffer test experiments. Cut-out from the central portion of the MHC pressure vessel.

FIGURE 7. The variation of the hydrogen pressure in the vessel as a function of time as determined by two-membrane test experiments. **a)** At 1000ºC equilibrium PH_2 is established within about 1 hour, whereas at 900ºC approximately 2 hours are required for equilibration; **b)** A longer measurement to test the equilibrium over a typical experimental run shows a steady fH_2 at 95.5% of the target hydrogen pressure in the pressure vessel; **c)** Results of a two-membrane test with a much lower imposed H_2 pressure (PH_2 = 1.55 bar) showing that 95% of the imposed PH_2 is attained at equilibrium similarly to the other experiments; **d)** A two-membrane test conducted with an old membrane over 300 hours of experimental run at 900-1000ºC). The equilibrium PH_2 is at 90% of the target value. On **b** and **c**, note the membrane vacuuming step after a few hours of run duration to remove any potential contamination from inside the membrane. The similarity of the curvatures before and after the vacuuming steps suggests that this precautionary step was unnecessary in these experiments.

FIGURE 8. The results of the time series CoPd alloy redox experiments conducted at T=900ºC and P=2000 bar. It is apparent that the redox sensors confirm the constancy of the fO_2 as expected based on the two-membrane test experiments. However, there is an offset between the values yielded by the redox sensor and the target values imposed by the hydrogen membrane and this offset increases with increasing fO_2. We attribute this to inaccuracy in the activity model used for the CoPd alloy at low Co concentrations.

FIGURE 9. The results of the buffer experiments with the 1σ errors. The difference between the fO_2 in the buffered and unbuffered capsules is defined by the interval lengths projected onto the X axis for the data points. The difference between the redox buffer- and Shaw membrane imposed fO_2 values is only about 0.3 log units even at the highly oxidizing MnO – Mn_3O_4 buffer.

FIGURE 10. Comparison of the experimentally determined Fe^{3+}/Fe_{total} ratios in the silicate melts to those predicted by using the model equation of Kress and Carmichael (1991). In comparison to the calc-alkaline melt (a.) the Fe^{3+}/Fe_{total} ratio in shoshonite (b.) is systematically offset towards higher Fe^{3+} content. The error bars on the ratio are 1σ errors propagated from the uncertainties on the calculated exchange coefficients and the measured Fe and Mg concentrations in the olivine and the melt.

FIGURE 11. The Fe-Ti exchange coefficient between magnetite spinel and silicate melt as a function of fO_2. The 1σ error bars were calculated by propagating the analytical errors on the composition of the magnetite and the silicate melt. A polynomial fit equation is also provided.

TABLES

TABLE 1. The redox sensor experiments

Expt. no.	PH_2 imposed (bar)	Log fO_2 imposed	Run time (h)	Co content of redox sensor (mol%)	Log fO_2 based on redox sensor (bar)
R12	5.76	-11.29	6	26.62 ± *0.35*	-11.79
R13	5.76	-11.29	24	25.32 ± *0.44*	-11.69
R11	5.76	-11.29	48	24.93 ± *1.23*	-11.65
R14	0.577	-9.29	12	10.93 ± *0.50*	-10.05

TABLE 2. The composition of the starting glasses in this study.

Oxide	Calc-alkaline basalt (wt%)	Shoshonite (wt%)
SiO_2	53.19	48.93
TiO_2	0.97	0.99
Al_2O_3	17.8	14.54
FeO	8.57	9.69
MnO	0.14	0.01
MgO	6.44	9.24
CaO	8.89	10.99
Na_2O	3.46	2.86
K_2O	0.95	2.92
P_2O_5	0.21	0.49
Total	100.62	100.66

TABLE 3. Experimental conditions for the proof of concept experiment conducted at 1020ºC and 2000 bar

Experiment number	Imposed PH_2 (bar)	Imposed fO_2
F1	22.02	NNO - 0.42
F15	9.35	NNO + 0.33
F10	3.72	NNO + 1.13
F11	1.49	NNO + 1.93
F14	0.592	NNO + 2.73

Table 4. Run product glass compositions in wt% with 1 σ analytical error.

Shoshonite

	F1		**F15**		**F10**		**F11**	
	Melt	**Olivine**	**Melt**	**Olivine**	**Melt**	**Olivine**	**Melt**	**Olivine**
TiO_2	0.95±*0.06*	0.04±*0.01*	0.95±*0.06*	0.04±*0.05*	0.88±*0.07*	0.03±*0.02*	0.87±*0.04*	0.04±*0.02*
CaO	7.21±*0.2* 0	0.27±*0.02*	6.93±*0.06*	0.28±*0.04*	6.48±*0.14*	0.33±*0.15*	5.52±*0.11*	0.23±*0.03*
Na_2O	3.36±*0.16*	0.01±*0.01*	3.62±*0.07*	0.01±*0.02*	3.71±*0.14*	0.02±*0.02*	3.82±*0.12*	0.01±*0.01*
MgO	3.91±*0.11*	41.14±*0.33*	3.90±*0.07*	43.46±*0.9* 0	3.70±*0.19*	45.64±*0.31*	3.23±*0.07*	49.07±*0.22*
SiO_2	51.14±*0.21*	38.70±*0.38*	51.72±*0.2*	39.02±*0.77*	51.69±*0.12*	39.92±*0.43*	53.32±*0.62*	40.31±*0.09*
Al_2O_3	16.06±*0.25*	0.04±*0.004*	16.39±*0.06*	0.04±*0.04*	16.58±*0.1*	0.06±*0.04*	17.03±*0.13*	0.04±*0.02*
FeO	7.9±*0.26*	19.23±*0.47*	7.34±*0.11*	16.19±*0.62*	6.45±*0.12*	14.61±*0.09*	4.76±*0.17*	11.11±*0.29*
MnO	0.01±*0.01*	0.01±*0.01*	0.01±*0.01*	0.01±*0.01*	0.01±*0.01*	0.01±*0.01*	0.00±*0.00*	0.01±*0.01*
K_2O	3.68±*0.12*	0.02±*0.01*	3.89±*0.03*	0.02±*0.004*	3.98±*0.12*	0.02±*0.007*	4.24±*0.11*	0.02±*0.01*
P_2O_5	0.51±*0.05*	0.25±*0.07*	0.55±*0.05*	0.09±*0.08*	0.56±*0.04*	0.04±*0.01*	0.55±*0.06*	0.07±*0.04*
Total	100±*0.00*	99.7±*0.30*	100±*0.001*	99.2±*1.43*	94.5±*0.23*	100±*0.81*	93.3±*1.04*	100±*0.28*
Mg#	0.469±*0.011*	0.792±*0.004*	0.486±*0.006*	0.827±*0.006*	0.505±*0.014*	0.848±*0.001*	0.548±*0.010*	0.899±*0.002*

Calc-alkaline basalt

	F1		**F15**		**F10**		**F11**	
	Melt	**Olivine**	**Melt**	**Olivine**	**Melt**	**Olivine**	**Melt**	**Olivine**
TiO_2	0.93±*0.06*	0.01±*0.01*	0.93±*0.03*	0.04±*0.03*	0.94±*0.03*	0.04±*0.02*	0.87±*0.05*	0.03±*0.02*
CaO	8.94±*0.13*	0.22±*0.02*	8.83±*0.12*	0.22±*0.02*	8.98±*0.12*	0.23±*0.04*	8.26±*0.11*	0.21±*0.02*
Na_2O	3.33±*0.14*	0±*0.01*	3.42±*0.08*	0.01±*0.01*	3.28±*0.13*	0.01±*0.02*	3.32±*0.06*	0.01±*0.02*
MgO	4.93±*0.08*	43.0±*0.44*	4.93±*0.07*	43.49±*0.79*	4.92±*0.09*	45.71±*0.46*	4.51±*0.08*	48.93±*0.85*
SiO_2	50.44±*0.30*	39.34±*0.10*	50.61±*0.21*	38.83±*0.97*	50.12±*0.21*	40.09±*0.42*	52.19±*0.16*	40.24±*0.46*
Al_2O_3	17.82±*0.06*	0.05±*0.03*	17.69±*0.15*	0.07±*0.07*	17.62±*0.12*	0.07±*0.08*	17.83±*0.09*	0.05±*0.06*
FeO	7.72±*0.16*	17.1*0.38*	7.65±*0.06*	15.38±*0.27*	7.21±*0.15*	14.46±*0.13*	5.7±*0.06*	11.6±*0.26*
MnO	0.14±*0.03*	0.28±*0.02*	0.14±*0.02*	0.28±*0.02*	0.15±*0.04*	0.27±*0.03*	0.12±*0.03*	0.29±*0.02*
K_2O	0.93±*0.02*	0.00±*0.00*	0.96±*0.02*	0.01±*0.00*	0.94±*0.02*	0.01±*0.00*	0.98±*0.03*	0±*0.01*
P_2O_5	0.22±*0.04*	0.09±*0.05*	0.22±*0.03*	0.08±*0.07*	0.23±*0.02*	0.08±*0.1* 0	0.22±*0.03*	0.06±*0.08*
Total	100±*0.00*	100±*0.25*	100±*0.00*	98.4±*1.77*	94.4±*0.28*	100±*0.71*	93.9±*0.28*	101±*1.10*
Mg#	0.532±*0.007*	0.817±*0.004*	0.535±*0.004*	0.834±*0.003*	0.549±*0.012*	0.849±*0.002*	0.585±*0.005*	0.883±*0.003*

Experiment F14 at NNO + 2.73 did not crystallize olivine

Table 5: The Fe^{3+}/Fe_{tot} ratios of the melts from the experimental run products along with 1 σ error. Calculated based on the Fe-Mg exchange between olivine and melt

Shoshonite

Expt. no.	**Fe-Mg exchange between olivine and melt**	**Fe^{3+}/Fe_{total}**
F1	0.30±*0.02*	0.22±*0.07*
F15	0.29±*0.02*	0.32±*0.06*
F10	0.29±*0.02*	0.36±*0.06*
F11	0.28±*0.02*	0.45±*0.05*

Calc-alkaline basalt

Expt. no.	**Fe-Mg exchange between olivine and melt**	**Fe^{3+}/Fe_{total}**
F1	0.31±*0.02*	0.18±*0.06*
F15	0.31±*0.02*	0.25±*0.05*
F10	0.30±*0.02*	0.29±*0.05*
F11	0.30±*0.02*	0.37±*0.05*

Experiment F14 at NNO + 2.73 did not crystallize olivine

Table 6: The composition of magnetite crystals in the experimental run products (in wt%) along with 1 σ error

	F1		**F10**		**F11**		**F14**	
	calc-alkaline basalt	**shoshonite**	**calc-alkaline basalt**	**shoshonite**	**calc-alkaline basalt**	**shoshonite**	**calc-alkaline basalt**	**shoshonite**
FeO	86.27±*2.64*	81.86±*1.8*	85.55±*0.7*	0.88±*0.07*	81.08±*0.63*	85.28±*0.77*	76.66±*0.35*	79.39±*0.54*
MnO	0.01±*0.01*	0.30±*0.03*	0.01±*0.01*	6.48±*0.14*	0.33±*0.02*	0.01±*0.01*	0.4±*0.02*	0.05±*0.01*
Cr_2O_3	0.01±*0.01*	1.33±*1.15*	0.00±*0.01*	3.71±*0.14*	0.67±*0.18*	0.00±*0.01*	0.32±*0.04*	0.01±*0.01*
Na_2O	0.04±*0.04*	0.05±*0.04*	0.01±*0.02*	3.7±*0.19*	0.01±*0.02*	0.01±*0.02*	0.05±*0.03*	0.14±*0.03*
MgO	3.78±*0.86*	4.09±*0.47*	6.58±*0.16*	52±*0.12*	7.28±*0.26*	6.54±*0.15*	9.47±*0.09*	8.12±*0.42*
SiO_2	1.43±*1.93*	0.59±*0.34*	0.23±*0.3*	16.58±*0.1*	0.2±*0.14*	0.27±*0.26*	0.21±*0.14*	0.14±*0.03*
Al_2O_3	4.39±*0.25*	7.06±*0.87*	4.2±*0.15*	6.45±*0.12*	6.51±*0.21*	4.17±*0.15*	8.5±*0.11*	4.9±*0.16*
CaO	0.71±*0.92*	0.3±*0.07*	0.11±*0.14*	0.01±*0.01*	0.11±*0.05*	0.1±*0.12*	0.17±*0.04*	0.14±*0.04*
K_2O	0.05±*0.03*	0.02±*0.01*	0.03±*0.01*	3.98±*0.12*	0.01±*0.01*	0.03±*0.02*	0.02±*0.01*	0.04±*0.01*
TiO_2	5.1±*0.26*	5.7±*0.49*	2.9±*0.07*	0.57±*0.04*	2.4±*0.02*	2.9±*0.06*	1.9±*0.03*	2.2±*0.03*
Total	101±*0.83*	101±*0.98*	99.62±*0.46*	94.1±*0.23*	98.6±*0.83*	99.3±*0.71*	97.7±*0.35*	95.2±*0.57*

In experiment F15 at NNO + 0.33, it was not possible to analyze the composition of the magnetite crystals because of their small size.