

RESEARCH ARTICLE | MAY 23 2023

Rapid quench piston cylinder apparatus: An improved design for the recovery of volatile-rich geological glasses from experiments at 0.5–2.5 GPa

Isra S. Ezad ; Svyatoslav S. Shcheka ; Stephan Buhre ; Andreas Buhre; Lauren R. Gorjovsky ; Joshua J. Shea ; Michael W. Förster ; Stephen F. Foley 



Rev. Sci. Instrum. 94, 055107 (2023)

<https://doi.org/10.1063/5.0129417>



Optimize
Your
Research

Our Vacuum Gauges Provide
More Process Control
and Operational Reliability



PFEIFFER  VACUUM

Rapid quench piston cylinder apparatus: An improved design for the recovery of volatile-rich geological glasses from experiments at 0.5–2.5 GPa

Cite as: Rev. Sci. Instrum. 94, 055107 (2023); doi: 10.1063/5.0129417

Submitted: 4 October 2022 • Accepted: 18 April 2023 •

Published Online: 23 May 2023



View Online



Export Citation



CrossMark

Isra S. Ezad,^{1,a)} Svyatoslav S. Shcheka,¹ Stephan Buhre,² Andreas Buhre,³ Lauren R. Gorojovsky,¹ Joshua J. Shea,¹ Michael W. Förster,¹ and Stephen F. Foley^{1,4}

AFFILIATIONS

¹ School of Natural Sciences, Macquarie University, North Ryde, Sydney, NSW, 2109, Australia

² Institute of Geosciences, Johannes Gutenberg University of Mainz, Mainz, Germany

³ GUKO Sondermaschinenbau GmbH, Am Mühlensiek 4, 37170 Uslar, Germany

⁴ Research School of Earth Sciences, Australian National University, Canberra, ACT 2601, Australia

^{a)} Author to whom correspondence should be addressed: isra.ezad@mq.edu.au

ABSTRACT

The accurate and precise determination of the compositions of silicate glasses formed from melts containing volatile components H₂O and CO₂ recovered from high-pressure, high-temperature experiments is essential to our understanding of geodynamic processes taking place within the planet. Silicate melts are often difficult to analyze chemically because the formation of quench crystals and overgrowths on silicate phases is rapid and widespread upon quenching of experiments, preventing the formation of glasses in low-SiO₂ and volatile-rich compositions. Here, we present experiments conducted in a novel rapid quench piston cylinder apparatus on a series of partially molten low-silica alkaline rock compositions (lamproite, basanite, and calc-alkaline basalt) with a range of water contents between 3.5 and 10 wt %. Quench modification of the volatile-bearing silicate glasses is significantly reduced compared to those produced in older piston cylinder apparatuses. The recovered glasses are almost completely free of quench modification and facilitate the determination of precise chemical compositions. We illustrate significantly improved quench textures and provide an analytical protocol that recovers accurate chemical compositions from both poorly quenched and well-quenched silicate glasses.

© 2023 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). <https://doi.org/10.1063/5.0129417>

INTRODUCTION

Experimental petrology has advanced our understanding of the planet's interior by allowing access to the pressures and temperatures of formation and equilibration of rocks. The success of experimental petrology has relied on the continued development of high-pressure, high-temperature techniques including internally heated pressure vessels, piston cylinder and multi-anvil apparatuses, and diamond-anvil cells (Boyd and England, 1960; Kawai and Endo, 1970; Walker *et al.*, 1990). These high-pressure techniques are now able to investigate conditions up to 500 GPa, covering the entire pressure–temperature space within the Earth and other planetary bodies (Ishii *et al.*, 2019; Jenei *et al.*, 2018; Masotta *et al.*, 2012).

Melting within the Earth's mantle is restricted largely to a “magmatic zone” at depths between 40 and 250 km (Foley and Pintér, 2018), with most melting occurring in the uppermost 140 km (equivalent to ≈ 4.4 GPa). This makes piston cylinder apparatus especially useful due to their pressure range (0.5–4.0 GPa) and excellent temperature control.

The characterization of melt compositions by analyzing quenched glasses from experiments has led to a good understanding of fairly dry melt compositions derived from the mantle and crust, but the addition of water leads to rapid, uncontrolled, and abundant growth of crystals, both as individual crystals and as overgrowths on equilibrium crystals, during the short quenching period between run temperature and the solidus of the rock. This quench modification

can falsify melt compositions considerably due to the growth of thin rims around minerals (Green, 1976), and little glass may remain to analyze in water-rich, and particularly CO₂-rich, experiments. During the quenching of an experiment, the inevitable contraction of the capsule assembly usually leads to a pressure drop and may lead to the formation of low-pressure phases that are not stable at nominal run conditions.

Uncertainties surrounding the interpretation of quench textures has fueled considerable controversy around the identification of equilibrium crystals, melts, and fluids in water-rich experiments, which carry over into the interpretation of melting points and melt compositions (Grove *et al.*, 2006; Till *et al.*, 2012; Green *et al.*, 2014). These problems are especially relevant to low-SiO₂ alkaline silicate melts with low viscosities and depolymerized melt structures (Hess, 1977; Mysen *et al.*, 1982) such as nephelinites, basanites, melilitites and lamproites, which have long been known to require H₂O in their source regions, so that no meaningful models for their origin can be drawn from dry experiments.

Many igneous melts are thought to require mixed COH volatiles, either as H₂O + CO₂ in relatively oxidized conditions or H₂O + CH₄ in more reduced natural conditions (Green and Falloon, 1998), which further complicate quenching behavior. Here, we concentrate on the investigation of quenching behavior in water-bearing melts and glasses and include a comparison with mixed H₂O + CH₄ volatiles but do not consider H₂O + CO₂ mixtures.

Several intricate, time-consuming, and expensive methods have been introduced in an attempt to better characterize the compositions of high-pressure melts. These include (1) a series of “sandwich” experiments in which the analyzed melt composition is run in additional experiments together with its source rock (Wallace and Green, 1988; Davis *et al.*, 2011); (2) melt traps consisting of vitreous carbon

or diamond that separate the melt from the rock during the experiment and before the quenching procedure (Hirose and Kushiro, 1993); and (3) volume integration of microprobe analyses achieved by re-polishing and analyzing several levels through quenched melt pockets (Pintér *et al.*, 2021).

However, these methods have circumvented the quench issue rather than attempting to solve it. Here, we introduce a novel rapid quench piston cylinder (RQPC) apparatus, which improves the preservation of melts as glasses by increasing the rate of temperature reduction by 10%–20% compared to conventional apparatuses.

We demonstrate that the RQPC apparatus produces better quenched glasses for a series of low-SiO₂ rock compositions with added water that are directly relevant to the origin of alkaline rocks. This obviates the need for the expense of multiple experiments and complicated experimental designs. We present results for tests of the RQPC apparatus using anhydrous and hydrous silicate melts and compare the results to those from traditional end-loaded piston cylinder apparatus.

EXPERIMENTS AND ANALYTICAL METHODS

The GUKO rapid quench piston cylinder apparatus: Technical aspects

The rapid quench piston cylinder apparatus manufactured by GUKO Sondermaschinen-bau GmbH, Uslar, Germany, is installed in the School of Natural Sciences at Macquarie University, Sydney, Australia. Major design changes relative to traditional piston cylinder apparatus (Boyd and England, 1960) include a 2.4 MN lightweight frame consisting of several plates rather than a single



FIG. 1. The rapid quench piston cylinder apparatus at Macquarie University. (a) Laboratory with two RQPC apparatuses; (b) close-up of one RQPC apparatus with experiment running; (c) control panel with touch-screen programmable ramps for temperature and pressure; (d) Strecon pressure vessel with additional cooling channels close to the tungsten carbide core, which improve cooling rate and core lifetime.

massive steel frame [Figs. 1(a) and 1(b)], a novel pressure stabilization controller. The rapid quench facility is supported by the use of internally cooled half-inch Strecon[®] pressure vessels [Fig. 1(d)]. Twelve extra vertical cooling channels around the tungsten core draw heat away radially from the tungsten carbide core. Along with massive coolers (and circulation of pre-cooled water) connected to the hydraulic bridge and top plate. This results in more rapid cooling of the sample and also prolongs the lifetime of the core.

Pressure and temperature controls are fully integrated into a powerful Siemens programmable logic controller system.

A novel pressure control system was developed to compensate instantly for any volume change inside the pressurized volume. This is achieved by a constant oil stream bypassing the primary end of the pressure intensifier. In this setup, the displacement of the hydraulic cylinders does not affect the prevailing pressure.

Calibration of the rapid quench piston cylinder apparatus

Calibration of pressure and temperature in the GUKO RQPC apparatus is similar to that in other piston cylinder apparatuses and all experiments were performed using an assembly with natural

CaF₂ as pressure-transmitting medium (Fig. 2), with MgO spacers and a standard graphite heater. These internal parts are not yet optimized for rapid quench, so that further improvements are possible. Temperature was monitored with Type B (Pt₃₀Rh₇₀–Pt₆Rh₉₄) thermocouples placed directly above the sample, and pressure was calibrated using the albite = jadeite + quartz reaction (Holland, 1980).

Experimental tests of quenching ability

We have tested the ability of the GUKO rapid quench piston cylinder (RQPC) apparatus to produce well-quenched experimental run products with a series of experiments on low-SiO₂ and alkaline melt compositions with different water contents and compare results to equivalent experiments in an older piston cylinder apparatus.

The starting materials include three synthetic oxide mixtures and three powdered natural rock samples, the compositions of which are presented in Table 1. Three [Gaussberg lamproite (GL), Leucite lamproite (LL), and Lake cargelligo (LC)] are potassic compositions, one is a basanite (BK-75115), and the others a tholeiitic basalt and a calc-alkaline dacite. The purpose of producing well-quenched glasses in the experiments differed, and included (i) the optimization of mineral/melt partition coefficients in lamproite melts

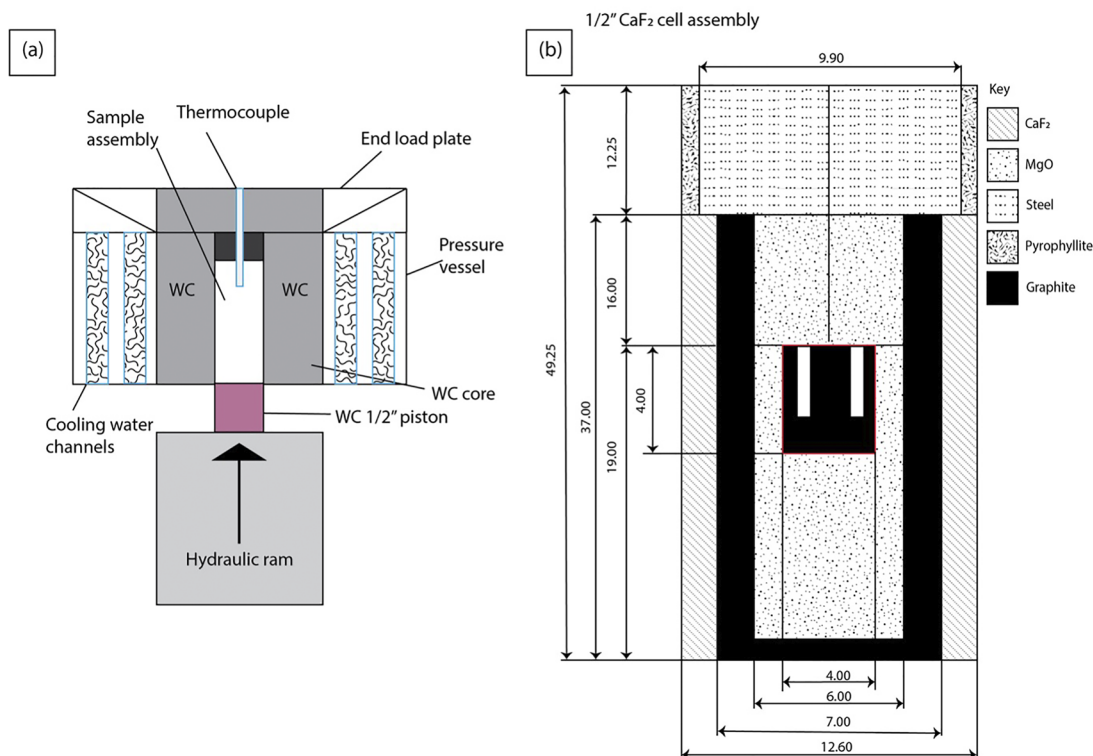


FIG. 2. Schematic drawings of the RQPC pressure vessel and CaF₂ cell assembly used in high-pressure, high-temperature experiments. (a) Cross section of the pressure vessel with additional cooling water channels, which help to rapidly cool the tungsten carbide core, rapidly quenching melts to glass upon cutting power to the furnace. (b) The standard 1/2" CaF₂ cell assembly used for experiments in the RQPC apparatus, graphite capsules wrapped in noble metals such as platinum are used with dual sample chambers to prevent iron loss. In some fluid bearing experiments, welded Pt capsules are used to prevent fluid loss at high temperatures. The Pt capsules are pre-enriched in Fe to prevent iron loss during the experiments.

TABLE I. Composition of starting materials (wt %), determined by whole rock XRF. * asterisk denotes synthetic oxide mix.

	Gaussberg leucite lamproite (GL)	Leucite lamproite (LL)*	Lake cargelligo (LC)	Calc-alkaline dacite*	Tholeiite basalt*	Buckland basanite (BK-75115)
SiO ₂	50.7	51.4	43.0	66.45	49.83	41.52
TiO ₂	2.38	3.45	3.67	0.72	1.83	2.36
Al ₂ O ₃	9.9	9.95	7.53	13.95	13.52	12.33
Cr ₂ O ₃	0.08	0.1		0.0044	0.004	0.0226
FeO _{TOT}	5.97	6.1	8.97	4.75	14.85	13.85
MnO	0.09	0.09	0.14	0.13	0.230	0.21
NiO	0.03	0.03		0.00	0.430	0.0217
MgO	8.12	8.03	13.5	1.18	5.29	11.71
CaO	4.75	4.67	9.15	3.38	9.62	9.57
Na ₂ O	1.71	1.67	1.22	4.75	2.68	4.05
K ₂ O	11.53	11.76	7.39	1.66	0.093	1.65
BaO		0.63	0.65			
P ₂ O ₅	1.45	1.5	0.86			1.34
F		0.33				
TE				2.30	0.930	
Sum	96.7	99.71	96.1	99.3	99.3	98.6

(Ezad and Foley, 2022) and (ii) synthetic calc-alkaline and basaltic silicate glasses were used to test the solubility of sulfur species in basaltic melts at varying fO_2 conditions. These experimental applications require precise and accurately determined chemical compositions of melts in equilibrium with their surrounding mineral phases and were therefore ideal projects to test the improvement of the rapid quenching ability of the GUKO apparatus press relative to earlier apparatuses.

All experiments used the same natural CaF_2 assemblies and thermocouples as in the calibration experiments (Fig. 2). Capsule design varied between experimental projects to allow for flexibility from running several compositions in the same experiment, to ensuring fluid was not lost during the generation of hydrous melts with added free water. Capsule configurations are described in Table II. Graphite capsules with dual sample chambers wrapped in 25 μm Pt foil were used for calc-alkaline and basaltic silicate glasses, whereas welded Pt capsules enriched in iron to minimize further iron loss were used for mineral/melt partitioning experiments (Ezad and Foley, 2022).

Experimental runs are automated by the GUKO-software [Fig. 1(c)], with which users are able to program complex “recipes” consisting of several ramps and ramping rates for compression and heating, hold for specified durations, quenching and decompression. Quenching to room temperature from temperatures of 1300 °C is achieved in ~15 s once power is cut to the transformer. To compare the quenching rate quantitatively, we conducted identical experiments in a traditional piston cylinder apparatus and the RQPC apparatus, recording the quench rate from 1200 °C to room temperature (Fig. 3). The RQPC apparatus has a cooling rate of 160 °C/S and is 20% more efficient than conventional piston cylinder apparatuses, which have cooling rates of ~130 °C/S (Bondar *et al.*, 2020), reaching temperatures below the glass transition (750 °C, Deubener *et al.*, 2003), required for solidification of melts (Fig. 3).

The advantage of the GUKO RQPC apparatus lies in the extra cooling power in combination with internally cooled Strecon® pres-

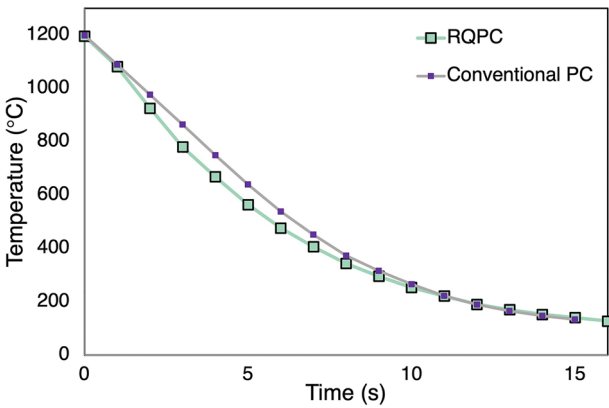


FIG. 3. Quench rates determined for rapid quenching piston cylinder (green squares) compared to a conventional piston cylinder apparatus. Identical cell assemblies were used in both apparatuses, and both experiments were quenched from 1200 °C to room temperature.

sure vessels, which facilitate more rapid initial cooling from run temperature to subsolidus temperatures.

For experiments designed to determine mineral/melt partition coefficients, experimental charges were first brought to the desired pressure before being rapidly heated at 41 °C per minute to above-liquidus conditions and then slowly cooled at a rate of 10 °C per minute until the final run temperature was achieved. This optimizes the growth of a few large crystals that can more easily be analyzed for trace elements by Laser-ICP-MS or SIMS by initiating crystallization in conditions with low nucleation rates (Tiepolo *et al.*, 2000). Experiments typically lasted 15–24 h to ensure the growth of large primary minerals including phlogopite and olivine, after which they were quenched to room temperature. Full results of the partitioning study are given in the work of Ezad and Foley (2022).

TABLE II. Experimental compositions and run conditions. Annealing temperature refers to overheating of mineral/melt partitioning experiments above the liquidus, before slow cooling to target temperature and holding for the experimental duration.

Run No.	Composition	Annealing		Duration (h)	Water added (wt %)	Phases	Press type	Experimental aim	Capsule type
		Pressure (GPa)	temperature (°C)						
T1863	LL	2.5	1150	24	^a	Phl, Opx, Glass	Boyd and England	Melting experiments with controlled fluid	Dual graphite sample and buffer capsules in outer welded Pt
OLD-PC 212	GL	1.5	...	0.5	5	Glass	Boyd and England	Glassing experiment	Welded Fe doped Pt capsule
M21-059	GL	1.5	1350	24	5	Phl, Cpx, Glass	RQPC	Mineral-melt partitioning	Welded Fe doped Pt capsule
A21-063	GL	1.5	1400	24	0	Glass	RQPC	Mineral-melt partitioning	Welded Fe doped Pt capsule
A21-028-A	Calc-alkaline	1	...	8	0	Glass	RQPC	Sulfur solubility	Dual sample chamber graphite capsule wrapped in Pt
A21-028-B	Tholeiite basalt	1	...	8	0	Glass	RQPC	Sulfur solubility	Dual sample chamber graphite capsule wrapped in Pt
M21-104-B	BK-75115	1	1200	24	10	Amph, Phl, Ap, Glass	RQPC	Mineral-melt partitioning	Welded Fe doped Pt capsule
A21-035-A	Calc-alkaline	1	...	8	5	Glass	RQPC	Sulfur solubility	Dual sample chamber graphite capsule wrapped in Pt
A21-035-B	Tholeiite basalt	1	...	8	3.5	Glass	RQPC	Sulfur solubility	Dual sample chamber graphite capsule wrapped in Pt
M22-027	LC	1	1400	24	0	Ol, Phl, Glass	RQPC	Mineral-melt partitioning	Dual sample chamber graphite capsule wrapped in Pt

^a Experiment contained a mixed CH₄-H₂O fluid consisting of 80% H₂O and 20% CH₄.

The experiments presented here allow several comparisons of the quenchability of melts to be made: The calc-alkaline dacite and tholeiitic basalts were run with and without added water, and basanite (BK-75115) and a low-SiO₂ lamproite (LC) were run with added water to widen the compositional scope of melts studied.

The SiO₂-richer Gaussberg lamproite composition (GL and LL) was used to compare quench textures with experiments conducted in older piston cylinder apparatus. The fluid-saturated experiment T-1863 was conducted in Tasmania with a mixed H₂O + CH₄ fluid under reducing conditions in a Boyd-England end-loaded 1/2" piston cylinder apparatus. The fluid was analyzed by GCMS as 80% H₂O (Foley, 1989) but the amount of H₂O in the melt is not known (but surely higher than that of other experiments reported here). Furthermore, an additional experiment (OLD-PC 212; Table II) was performed using a Boyd and England-type end-loaded 1/2" piston cylinder apparatus at Macquarie University with the same lamproite composition (GL in Tables I and II) as in the work of Ezad and Foley (2022) and Foley (1989). Run conditions for all experiments are presented in Table II.

Analytical methods

All samples recovered from high-pressure experiments were sliced using a diamond wire saw to expose the sample, after which

capsules were embedded in epoxy resin and polished to a 1 μ m diamond finish.

High-resolution imaging was conducted at Macquarie University using an FEI—Field Emission Scanning Electron Microscope (FE-SEM) operating at 15 kV, 11 nA beam current, calibrated to specimen current of 13 nA using a Faraday cup on the sample stage, with a spot size of 14.8 μ m and a working distance of $\sim$ 10 mm. Example BSE images are shown in Figs. 4, 6 and 7.

Chemical compositions of melts were quantitatively determined by wavelength-dispersive spectroscopy (WDS) using a 5 spectrometer Field Emission Electron Micro Probe Analyser (FE-EMPA) JEOL JXA 8530F at the University of Tasmania, operating at 15 kV and 10 nA. Acquisition positions were selected by pre-programming positions on glasses with a minimum of five analyses per sample; a defocused beam was used on all experimental charges with a spot size of 10–20 μ m to minimize beam damage and alkali loss. Times for the acquisition of background were also adjusted to minimize beam damage and improve detection of minor elements at low concentrations; 10/10 s respectively was used for Ca; 20/20 for Mg, Si, K, Na, Ti, Mn, Fe, Cl, Cr, Ba, Ni; 40/40 for P, and 70/70 for F.

Experimental charges from traditional piston cylinder apparatus have texturally complex quenched glass mats [Figs. 4(a)–4(d)] and contain quenched minerals including phlogopite and other minor phases. Despite the challenging texture, FE-EMPA

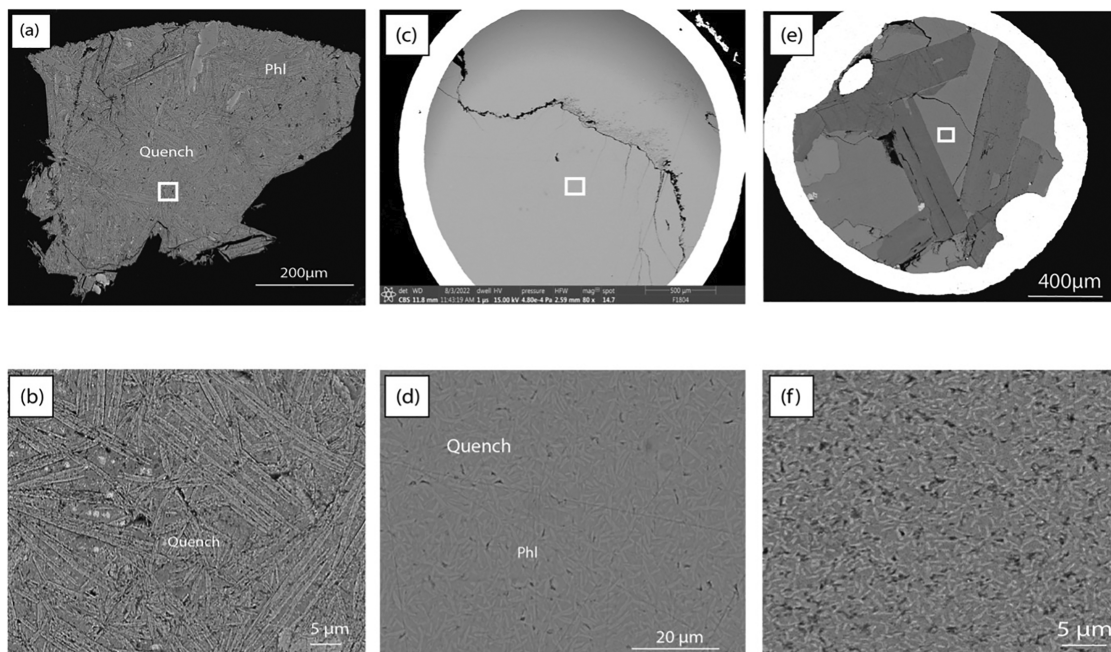


FIG. 4. Back-scattered images of experimental charges recovered from high-pressure, high-temperature experiments on a synthetic hydrous leucite lamproite: Panels (a)–(d) correspond to experiments run in traditional piston cylinder apparatus while panels (e) and (f) are those recovered from the rapid quench apparatus. (a) Experiment T1863 2.5 GPa, 1150 °C with a CH₄ < H₂O fluid. (b) High-magnification image of the area in the white box in (a). Substantial growth of quench phlogopite and orthopyroxene are present. (c) Experiment OLD-PC-212, 1.5 GPa, 1200 °C with 5 wt % water. (d): Large, $\sim$ 100 μ m, phlogopites that grew during the quench are present within the glass. (e) Experiment M21-059, 1.5 GPa, 1100 °C, 5 wt % H₂O, recovered from the rapid quench apparatus. Large phlogopites and clinopyroxenes were grown to facilitate a mineral-melt partitioning study (Ezad and Foley, 2022). (f) High-magnification image of the quenched glass in the area in the white box in (e), needles of quench crystals are dramatically smaller (<1 μ m) compared to those in (d).

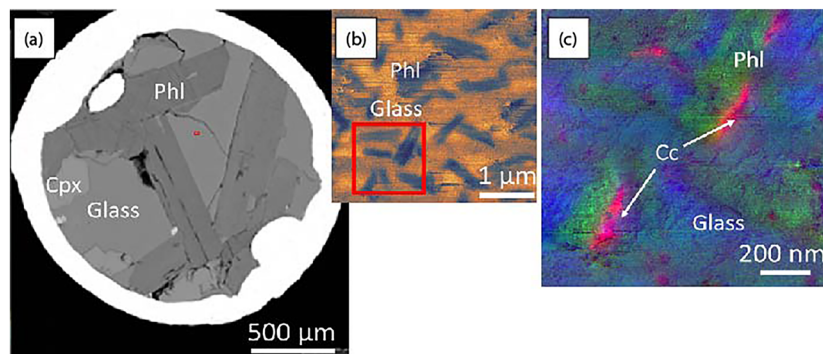


FIG. 5. PiFM images of experiment M21-059 (synthetic lamproite with 5 wt % H₂O). (a) Back-scattered image of experimental charge M21-059 showing position of PiFM images as red box. (b) PiFM map collected at wavenumber 1150 cm⁻¹, characterizing silicate glass. Higher PiFM response is denoted by orange color, with dark regions highlighting quenched phlogopite, which are only 200 nm in size. (c) PiFM map combining maps collected at 1000 cm⁻¹ (ν₃ stretching vibration of Si–O of mica), 1150 cm⁻¹ (ν₃ stretching vibration of Si–O of glass), and 1400–1450 cm⁻¹ (ν₃ stretching vibration of C–O of carbonate) wavenumbers. The quenched melt (glass; blue) contains tiny quench phlogopite (Phl; green) and associated calcite (Cc; red), which demonstrates limited volatile loss from the melt during quenching. There are no other visible quench phases in experiment M21-059.

measurements were acquired using a large 20 μm defocused beam to homogenize the quenched regions in a grid covering an area of 100 μm².

Additional high-resolution imaging and chemical characterization of a single high-pressure experiment recovered from the RQPC were conducted by Photo-induced Force Microscopy (PiFM) (Otter *et al.*, 2021) at the Research School of Earth Sciences, Australian National University. PiFM combines atomic force microscopy with infrared spectrometry, allowing for the collection of FTIR maps at sub-micron scale. PiFM maps were acquired on a small 256 × 256 pixel² area at known infrared wavenumbers chosen to correspond to the ν₃ stretching vibration of C–O of carbonate (1450 cm⁻¹) and the ν₃ stretching vibration of Si–O of silicate melt (1150 cm⁻¹) and mica (1000 cm⁻¹) (Fig. 5).

RESULTS

The size of quench crystals and the textures and homogeneity of glasses in experimental run products from both RQPC experiments and those from older piston cylinder apparatus is illustrated in Figs. 4–7.

Figure 4 depicts run products on the same rock compositions but with different volatile mixes and in different apparatus. The starting composition for each of these experiments was a hydrous synthetic leucite lamproite based on lavas of the Gaussberg volcano in eastern Antarctica. The RQPC experiment M21-059 [Figs. 4(e) and 4(f)] was designed to constrain partition coefficients between minerals and the melt (presented in Ezad and Foley, 2022). Experiment T-1863 [Figs. 4(a) and 4(b)] was conducted at the University of Tasmania in the mid-1980s and is a fluid-saturated run with a mixed fluid consisting of 80% H₂O and 20% CH₄ (Foley, 1989). Experiment OLD-PC 212 [Figs. 4(c) and 4(d)] is a control run in an old piston cylinder apparatus at Macquarie University with the same starting materials and water content as in M21-059: The only difference between the experiments is quench duration. Figures 4(c)–4(f) show the stark difference in quenched glass texture, with quench

crystals reduced in size by an order of magnitude in the RQPC apparatus. Experiments conducted using the rapid quench piston cylinder have large regions of silicate glass that appear to be quench-free [Figs. 4(e) and 4(f)]. Only at high magnification (×6500) are small quench needles on the order of 1 μm visible.

PiFM maps (Fig. 5) show that tiny (200 nm) quenched phlogopite and calcite are the only phases present in the glass in the hydrous lamproite experiment from the RQPC (M21-059) experiment. Despite the imaging of quenched phlogopites using FE-SEM, the 200 nm long and <40 nm wide calcite quench crystals were not identified until PiFM maps were collected. This indicates that volatiles are not lost during quenching and that the use of large defocused beams is essential to ensure these small phases are reconciled within glass compositions to arrive at an accurate, homogenized melt composition.

Figure 6 compares BSE images of RQPC run products with different rock compositions and different water contents, each together with a high-magnification image of a small glass area shown by the white rectangles. Figures 6(a) and 6(b) show an experiment on the low-SiO₂ Lake Cargelligo lamproite with high CaO (9.5 wt %), MgO (13.5 wt %), and 3 wt % H₂O. These are compared to a dry calc-alkaline dacite [66.5 wt % SiO₂, 1.2 wt % MgO; Figs. 6(c)–6(d)] and a basanite (41.5 wt % SiO₂, 11.7 wt % MgO) with 10 wt % added H₂O [Figs. 5(e) and 5(f)]. The exceptionally well-quenched glass in the dacite is expected for SiO₂-rich and dry compositions [Figs. 6(c) and 6(d)] and known from many experimental studies (Melekhova *et al.*, 2017; Parat *et al.*, 2014), whereas a similarly well-quenched glass from an alkaline, low-SiO₂ composition with 3 wt % H₂O [Figs. 6(a) and 6(b)] is made possible by the RQPC apparatus. The higher H₂O content (10 wt %) in the low-SiO₂ basanite leads to discernible quench crystals even in the RQPC experiment, but these are only 2–3 μm long [Figs. 6(e) and 6(f)]. This is a major improvement over the large, continuous, and heterogeneously distributed mats of quench crystals from water-rich experiments conducted in traditional piston cylinder apparatus [Figs. 4(a) and 4(b)]. Quench phases in these experiments are tens of micrometers across and

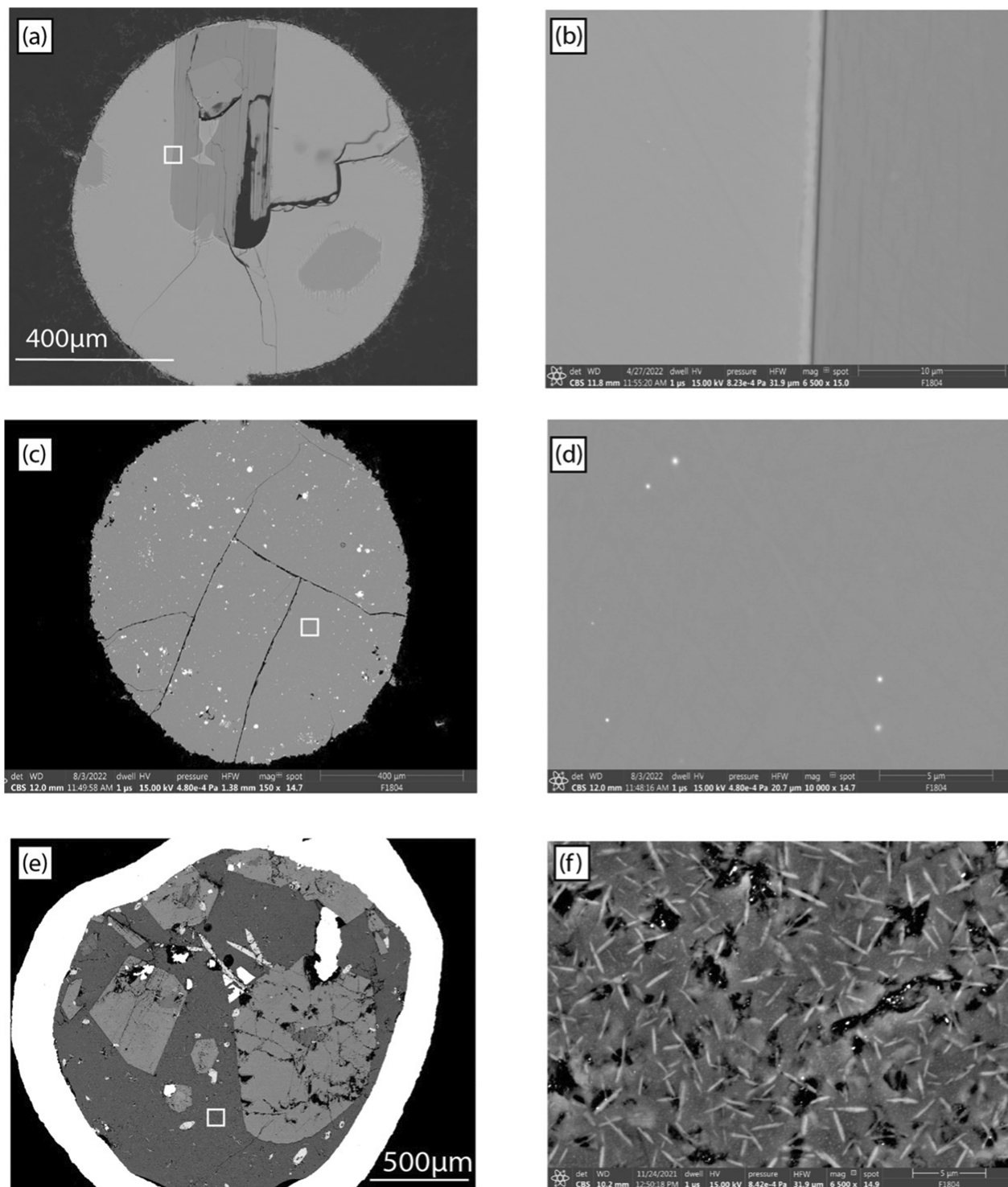


FIG. 6. High-pressure, high-temperature experiments recovered from the rapid quench piston cylinder apparatus for a variety of compositions, pressures, and temperatures. All experiments have large regions of silicate glasses with little to no visible quench crystal growth. (a) Experiment M22-027, low-Si lamproite, 1 GPa, 1200 °C, 3 wt % H₂O. (b) High-magnification image of quenched glass from the white box in (a). There are no visible quench needles in this hydrous lamproite glass. (c) Experiment A21-028-A, tholeiite, 1 GPa, 1280 °C. (d) High-magnification image of quenched glass in (c). (e) Experiment M21-104-B, basanite, 1 GPa, 975 °C, 10 wt % H₂O. (f) High-magnification image of quenched glass in (e): Only small (<1 μm) phlogopite needles are present within the glass despite the high water content.

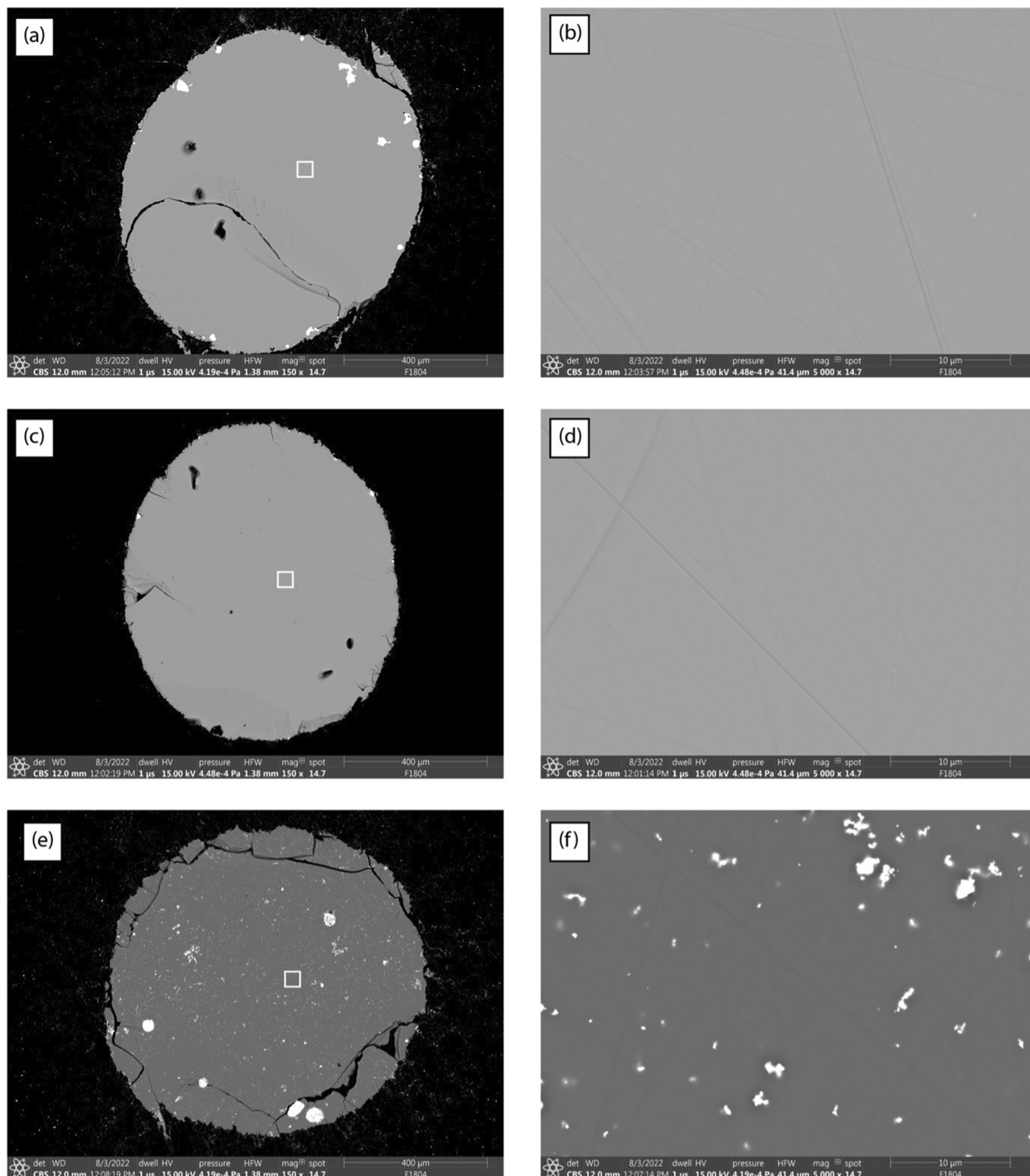


FIG. 7. High-pressure, high-temperature experiments recovered from the rapid quench piston cylinder on calc-alkaline and tholeiite basaltic melts, with and without water. (a) Experiment A21-028-B, 1 GPa, 1280 °C—anhydrous tholeiite basalt. (b) High-magnification image of (a). (c) A21-035-A, calc-alkaline dacite, 1 GPa, 1250 °C, 5 wt % H₂O. (d) High-magnification image of (c). (e) Experiment A21-035-B, tholeiite basalt, 1 GPa, 1250 °C, 3.5 wt % H₂O. (f) High-magnification image of (e). Panels (d) and (f) are the same scale as b and show no quench crystal growth despite the addition of water.

cause falsified glass compositions (Green, 1976), making accurate chemical analysis almost intractable.

Figure 7 illustrates the quench products in further experiments on a tholeiite basalt with and without water and the dacite with 5% added H₂O. The tholeiite quenches well to a glass both when dry [Figs. 7(a) and 7(b)] and with added water [Figs. 7(e) and 7(f)]; the highly reflective sulfide minerals are more dispersed and smaller in the hydrous experiment [Figs. 7(f) vs 7(b)] but the glass in the background contains no discernible quench crystals. The dacite containing 5 wt % H₂O [Figs. 7(c) and 7(d)] quenches to a glass as good as the dry experiment on the same composition [Fig. 6(d)].

Analysis of melt compositions

Volatile-rich melts generally quench poorly in piston cylinder experiments, leading to various textures, such as quench overgrowths on equilibrium crystals to complex mats of interlocked larger crystals, particularly when mixed volatile species are used [e.g., Fig. 4(a)]. For the analysis of melt compositions, the dramatic improvement in quench textures in the RQPC apparatus allows direct analysis of well-quenched glasses, which is preferable to elaborate systems of analysis, such as area analysis, averaging of numerous analytical points using defocussed microprobe beams, or re-polishing and re-analysis.

Chemical compositions for the experimental glasses are reported in Table III and can be compared to the starting compositions in Table I; the latter were obtained for the natural starting materials by X-ray fluorescence (XRF) spectroscopy major element analysis of whole rock powders prior to high-pressure, high-temperature experiments. This provides an independent quantitative check for melt compositions analyzed in the rapid quench piston

cylinder. The quench crystal-free glasses in the synthetic dacite and tholeiite compositions (Fig. 7) are successfully reproduced by rapid quenching of the glasses (Table III), showing consistent reproducibility across several high-pressure experiments. The quality and reproducibility of the analyses is high for water-bearing experiments, exemplified by basanite run A21-104B, which shows standard deviations less than the uncertainty of the microprobe for elements other than Na (Table III).

Similar comparisons for the series of lamproite experiments are less clearly defined, as the mineral phases phlogopite, clinopyroxene, and/or olivine grew during the partitioning experiments so that the melts reflect fractionated compositions that do not correspond to the whole experimental charge.

However, a glassing experiment with only melt and 5 wt % H₂O from the old Macquarie piston cylinder apparatus (OLD-PC-212) can be compared to A21-063 a glass-only experiment to which no additional water was added in the RQPC apparatus (Table IV). Despite the visibly coarser-grained quench texture produced by the traditional piston cylinder apparatus [Fig. 4(d)] the compositions determined by EPMA are similar, with the largest deviations between the two compositions in SiO₂ (1.76 wt % difference), Al₂O₃ (0.74 wt %), and CaO (2.1 wt %). For all other major elements, the difference between the two experimental glasses is less than 0.5 wt %. While not insignificant, the small differences between the two glass compositions fall within the standard deviations determined from the individual EMPA WDS measurements, suggesting that a careful EMPA approach to homogenizing glass compositions determined from quench products is satisfactory in reproducing accurate chemical compositions also in older piston cylinder experiments.

Our experiments demonstrate that while analyzing complex quench textures remains analytically challenging, the compositions

TABLE III. Major element compositions of recovered experimental glasses as determined by EMPA (wt %).

Experiment Rock	T1863 High-Si lamproite H ₂ O + CH ₄	OLD-PC 212 High-Si lamproite 5% H ₂ O	M21-059 High-Si lamproite 5% H ₂ O	A21-028-A Dacite anhydrous	A21-028-B Tholeiite anhydrous
n	25	8	4	5	5
SiO ₂	50.88 (0.42)	48.69 (0.49)	52.36 (0.25)	66.27 (0.55)	49.06 (0.43)
TiO ₂	3.16 (0.07)	3.09 (0.03)	3.2 (0.01)	0.64 (0.10)	1.65 (0.04)
Al ₂ O ₃	10.20 (0.18)	8.95 (0.06)	9.34 (0.03)	14.35 (0.09)	13.86 (0.15)
Cr ₂ O ₃	0.09 (0.02)	0.05 (0.01)		0.11 (0.01)	0.13 (0.03)
FeO _{TOT}	5.17 (0.22)	4.44 (0.18)	2.57 (0.03)	3.79 (0.21)	12.61 (0.16)
MnO	0.07 (0.01)	0.09 (0.02)	0.12 (0/01)	0.11 (0.03)	0.22 (0.02)
NiO	0.02 (0.02)				0.06 (0.02)
MgO	6.59 (0.40)	9.3 (0.15)	4.61 (0.09)	1.68 (0.13)	6.95 (0.13)
CaO	4.24 (0.32)	4.17 (0.06)	3.24 (0.08)	3.31 (0.16)	8.75 (0.10)
Na ₂ O	0.70 (0.14)	1.42 (0.13)	1.96 (0.02)	4.55 (0.18)	2.34 (0.04)
K ₂ O	7.78 (0.46)	10.26 (0.08)	11.59 (0.12)	1.88 (0.05)	0.26 (0.01)
BaO	0.50 (0.06)	0.61 (0.03)	0.79 (0.03)		0.07 (0.01)
P ₂ O ₅	1.64 (0.07)	1.3 (0.02)	1.63 (0.03)		
Cl		0.09 (0.01)	0.13 (0.01)		
F	0.18 (0.02)	0.29 (0.01)	0.18 (0.01)		
H ₂ O ^a		7.25	8.28		
SO ₃				0.10 (0.03)	0.22 (0.02)
Sum	91.24	100	100	96.85	96.25

^aH₂O determined by difference from total.

TABLE IV. Major element compositions of recovered experimental glasses as determined by EMPA (wt %).

	T1863 High-Si lamproite H ₂ O + CH ₄	OLD-PC 212 High-Si lamproite 5% H ₂ O	A21-063 High-Si lamproite No additional water	Difference between OLD-PC 212 and A21-063 wt %
n	25	8	4	
SiO ₂	50.88 (0.42)	48.69 (0.49)	50.45 (0.59)	−1.76
TiO ₂	3.16 (0.07)	3.09 (0.03)	3.31 (0.09)	−0.22
Al ₂ O ₃	10.20 (0.18)	8.95 (0.06)	9.69 (0.17)	−0.74
Cr ₂ O ₃	0.09 (0.02)	0.05 (0.01)	0.08 (0.01)	−0.03
FeO _{TOT}	5.17 (0.22)	4.44 (0.18)	4.86 (0.14)	−0.42
MnO	0.07 (0.01)	0.09 (0.02)	0.09 (0.01)	0
NiO	0.02 (0.02)			
MgO	6.59 (0.40)	9.3 (0.15)	9.56 (0.21)	−0.26
CaO	4.24 (0.32)	4.17 (0.06)	6.27 (0.14)	−2.1
Na ₂ O	0.70 (0.14)	1.42 (0.13)	1.32 (0.03)	0.1
K ₂ O	7.78 (0.46)	10.26 (0.08)	9.56 (0.19)	0.7
BaO	0.50 (0.06)	0.61 (0.03)	0.61 (0.04)	0
P ₂ O ₅	1.64 (0.07)	1.3 (0.02)	1.26 (0.04)	−0.04
Cl		0.09 (0.01)	0.06 (0.01)	0.03
F	0.18 (0.02)	0.29 (0.01)	0.30 (0.02)	−0.01
H ₂ O ^a			7.25	2.62
SO ₃				
Sum		91.24	100	100

^aH₂O determined by difference in total.

determined by homogenizing large areas are robust and representative of the “true” composition when compared to clearly “cleaner” and therefore analytically simpler glasses produced by the RQPC.

IMPLICATIONS

We present the first experimental results comparing the structure and composition of quenched melts between a new “rapid quench” piston cylinder apparatus and traditional piston cylinder apparatus. Our preliminary findings demonstrate quenching rates of 160 °C/S, which facilitates a very rapid decrease from run temperatures at which melt is present to subsolidus conditions at 1100–900 °C to below the glass transition, which for these compositions is around 750 °C (Deubener *et al.*, 2003).

This rapid quenching, which is 20% better than convective piston cylinder apparatus (Bondar *et al.*, 2020), vastly improving quench structure for both hydrous and anhydrous silicate melts, allowing for improved quantification of melt compositions and facilitating better determination of the position of melting curves due to improved recognition of the presence of melts at low degrees of melting. This is particularly important for silica-undersaturated alkaline melts, such as basanites, nephelinites, melilitites, and kimberlites, which are known to originate in volatile-rich source regions. Crystals and overgrowths grown during the quench are minimized, lessening the confusion about interpretations of quenched melts, crystals, and vapor, which have in the past led to controversy in the identification of rock solidi (Mysen and Boettcher, 1975; Till *et al.*, 2012; Green *et al.*, 2014).

Despite the many improvements a rapid quench piston cylinder offers, access to them is currently limited as is the pressure–temperature range they can achieve. Our comparison of melt compositions between RQPC experiments and those run in older apparatus shows that accurate analyses can be achieved by EPMA analysis of quench-modified silicate glasses using defocussed beams of at least 20 μm or integration of WDS measurements collected in grid patterns covering a minimum area of 100 μm². The resulting homogenized large area measurements are in good agreement with chemical compositions determined from RQPC experiments and can therefore be routinely used when determining glass compositions from quench-modified glasses.

Despite these improvements in quenching rates, further challenges lie ahead, most notably for carbonate-rich melts, which usually produce complex intergrowths of quench crystals with little or no glass preserved (Weidendorfer *et al.*, 2020; Pintér *et al.*, 2021). For these, the development of the PiFM technique (Otter *et al.*, 2021) promises to make sense of nanoscale features and may be assisted by a greater understanding of the stabilization of amorphous carbonates as function of chemistry (e.g., Tester *et al.*, 2014).

ACKNOWLEDGMENTS

The prototype RQPC, designed by Stephan and Andreas Buhre, was built at the Geocycles Earth System Science Research Centre of the Johannes Gutenberg University of Mainz, funded by the State of Rhineland-Palatinate. The Macquarie instrument was funded by Macquarie University in support of the Australian Research Council Laureate Fellowship to S.F.F. The authors wish to thank Sean Murray

for his help with imaging on the FE-SEM at Macquarie University and Sandrin Feig for his assistance with FE-EMPA data collection at the University of Tasmania. This work was funded by an ARC Laureate Fellowship (Grant No. FL 180100134) awarded to S.F.F.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Isra S. Ezad: Conceptualization (lead); Data curation (lead); Formal analysis (lead); Investigation (lead); Methodology (lead); Validation (lead); Visualization (lead); Writing - original draft (lead); Writing - review & editing (lead). **Svyatoslav S. Shcheka:** Formal analysis (supporting); Investigation (supporting); Methodology (supporting); Writing - review & editing (equal). **Stephan Buhre:** Conceptualization (equal); Investigation (equal); Methodology (equal); Writing - review & editing (equal). **Andreas Buhre:** Conceptualization (equal); Methodology (equal). **Lauren R. Gorjovsky:** Investigation (supporting); Resources (supporting); Writing - review & editing (supporting). **Joshua J. Shea:** Resources (supporting); Writing - review & editing (supporting). **Michael W. Förster:** Conceptualization (supporting); Methodology (supporting); Writing - original draft (supporting); Writing - review & editing (equal). **Stephen F. Foley:** Conceptualization (supporting); Funding acquisition (lead); Supervision (equal); Writing - original draft (equal); Writing - review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

REFERENCES

- Boyd, F. R. and England, J. L., "Apparatus for phase-equilibrium measurements at pressures up to 50 kilobars and temperatures up to 1750 °C," *J. Geophys. Res.* **65**, 741–748, <https://doi.org/10.1029/jz065i002p00741> (1960).
- Kawai, N. and Endo, S., "The generation of ultrahigh hydrostatic pressures by a split sphere apparatus," *Rev. Sci. Instrum.* **41**, 1178–1181 (1970).
- Walker, D., Carpenter, M. A., and Hitch, C. M., "Some simplifications to multi-anvil devices for high pressure experiments," *Am. Mineral.* **75**, 1020–1028 (1990).
- Ishii, T., Liu, Z., and Katsura, T., "A breakthrough in pressure generation by a Kawai-type multi-anvil apparatus with tungsten carbide anvils," *Engineering* **5**, 434 (2019).
- Jenei, Z., O'Bannon, E. F., Weir, S. T., Cynn, H., Lipp, M. J., and Evans, W. J., "Single crystal toroidal diamond anvils for high pressure experiments beyond 5 megabar," *Nat. Commun.* **9**, 3563 (2018).
- Masotta, M., Freda, C., Paul, T. A., Moore, G. M., Gaeta, M., Scarlato, P., and Troll, V. R., "Low pressure experiments in piston cylinder apparatus: Calibration of newly designed 25 mm furnace assemblies to P = 150 MPa," *Chem. Geol.* **312–313**, 74–79 (2012).
- Foley, S. F. and Pintér, Z., "Primary melt compositions in the Earth's mantle," in *Magma Under Pressure*, edited by Kono, Y. (Elsevier, Amsterdam, 2018), pp. 3–42.
- Green, D. H., "Experimental testing of "equilibrium" partial melting of peridotite under water-saturated, high-pressure conditions," *Can. Mineral.* **14**, 255–268 (1976).
- Grove, T., Chatterjee, N., Parman, S., and Médard, E., "The influence of H₂O on mantle wedge melting," *Earth Planet. Sci. Lett.* **249**, 74–89 (2006).
- Till, C. B., Grove, T. L., and Withers, A. C., "The beginnings of mantle wedge melting," *Contrib. Mineral. Petrol.* **163**, 669–688 (2012).
- Green, D. H., Hibberson, W. O., Rosenthal, A., Kovács, L., Yaxley, G. M., Falloon, T. J., and Brink, F., "Experimental study of the influence of water on melting and phase assemblages in the upper mantle," *J. Petrol.* **55**, 2067–2096 (2014).
- Hess, P. C., "Structure of silicate melts," *Can. Mineral.* **15**, 162–178 (1977).
- Mysen, B. O., Virgo, D., and Seifert, F. A., "The structure of silicate melts; implications for chemical and physical properties of natural magma," *Rev. Geophys.* **20**, 353–383, <https://doi.org/10.1029/rg020i003p00353> (1982).
- Green, D. H. and Falloon, T. J., "Pyrolite: A ringwood concept and its current expression," in *The Earth's Mantle: Composition, Structure and Evolution*, edited by Jackson, I. (Cambridge University Press, Cambridge, 1998), pp. 311–378.
- Wallace, M. E. and Green, D. H., "An experimental determination of primary carbonatite magma composition," *Nature* **335**, 343–346 (1988).
- Davis, F. A., Hirschmann, M. M., and Humayun, M., "The composition of the incipient partial melt of garnet peridotite at 3 GPa and the origin of OIB," *Earth Planet. Sci. Lett.* **308**, 380–390 (2011).
- Hirose, K. and Kushiro, I., "Partial melting of dry peridotites at high pressures: Determination of compositions of melts segregated from peridotite using aggregates of diamond," *Earth Planet. Sci. Lett.* **114**, 477–489 (1993).
- Pintér, Z., Foley, S. F., Yaxley, G. M., Rosenthal, A., Rapp, R. P., Lanati, A. W., and Rushmer T., "Experimental investigation of the composition of incipient melts in upper mantle peridotites in the presence of CO₂ and H₂O," *Lithos* **396–397**, 106224 (2021).
- Holland, T. J. B., "The reaction albite = jadeite + quartz determined experimentally in the range 600–1200 °C," *Am. Mineral.* **65**, 129–134 (1980).
- Ezad, I. S. and Foley, S. F., "Experimental partitioning of fluorine and barium in lamproites," *Am. Mineral.* **107**(11), 2008–2019 (2022).
- Bondar, D., Fei, H., Withers, A. C., and Katsura, T., "A rapid-quench technique for multi-anvil high-pressure-temperature experiments," *Rev. Sci. Instrum.* **91**, 065105 (2020).
- Deubener, J., Müller, R., Behrens, H., and Heide, G., "Water and the glass transition temperature of silicate melts," *J. Non-Cryst. Solids* **330**, 268–273 (2003).
- Tiepolo, M., Vannucci, R., Oberti, R., Foley, S., Bottazzi, P., and Zanetti, A., "Nb and Ta incorporation and fractionation in titanite, pargasite and kaersutite: Crystal-chemical constraints and implications for natural systems," *Earth Planet. Sci. Lett.* **176**, 185–201 (2000).
- Foley, S. F., "Experimental constraints on phlogopite chemistry in lamproites: 1. The effect of water activity and oxygen fugacity," *Eur. J. Mineral.* **1**, 411–426 (1989).
- Otter, L. M., Förster, M. W., Belousova, E., O'Reilly, P., Nowak, D., Park, S., Clark, S., Foley, S. F., and Jacob, D. E., "Nanoscale chemical imaging by photo-induced force microscopy: Technical aspects and application to the geosciences," *Geostand. Geoanal. Res.* **45**, 5–27 (2021).
- Melekhova, E., Blundy, J., Martin, R., Arculus, R., and Pichavant, M., "Petrological and experimental evidence for differentiation of water-rich magmas beneath St. Kitts, Lesser Antilles," *Contrib. Mineral. Petrol.* **172**, 98 (2017).
- Parat, F., Streck, M. J., Holtz, F., and Almeev, R., "Experimental study into the petrogenesis of crystal-rich basaltic to andesitic magmas at Arenal volcano," *Contrib. Mineral. Petrol.* **168**, 1040 (2014).
- Mysen, B. R. O. and Boettcher, A. L., "Melting of a hydrous mantle: I. Phase relations of a natural peridotite at high pressures and temperatures with controlled activities of water, carbon dioxide and hydrogen," *J. Petrol.* **16**, 520–548 (1975).
- Weidendorfer, D., Manning, C. E., and Schmidt, M. W., "Carbonate melts in the hydrous upper mantle," *Contrib. Mineral. Petrol.* **175**, 72 (2020).
- Tester, C. C., Whittaker, M. L., and Joester, D., "Controlling nucleation in giant liposomes," *Chem. Commun.* **50**, 5619 (2014).