AN EXPERIMENTAL CRYSTALLIZATION OF THE MACUSANI OBSIDIAN IN A THERMAL GRADIENT WITH APPLICATIONS TO LITHIUM-RICH GRANITIC PEGMATITES

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Abstract

Drilled cores of Macusani green obsidian pebbles from Peru were hydrated and melted above their liquidus temperatures at 200 MPa to a single column ~ 4 cm in length and then undercooled in a thermal gradient > 150°C along the length of the cores. Despite thousands of hours at subliquidus temperatures, the crystallinity of the products ranged from ~ 30 vol.% to ~ 5 vol.%. Mineral assemblages varied along the length of the cores but not in relation to the thermal gradients in all cases. Oscillations in the abundances of plagioclase, K-feldspar, and quartz were observed across the crystallization fronts and along the lengths of the cores. The originally homogeneous melts became heterogeneous in response to crystallization and to thermal gradients. Chemical gradients in the glasses included sharp boundary layer pile-up of F and B adjacent to the crystallization fronts, as well as linear gradients among several of the elements spanning the entire lengths of the melt columns. Values of molar K/(K+Na) in the glasses, plotted as K*, varied positively with Si, inversely with Al and F, and positively with the domains of K-feldspar that formed at maximum distance from the plagioclase-rich regions. Overall, the results are marked by sharply bounded textural domains, by the spatial segregation of mineral assemblages, by oscillations in mineral assemblages at multiple scales, and by monominerallic crystal aggregates that are hallmarks of pegmatite bodies. Temperatures recorded by feldspars closely approached the actual temperature gradient down to ~ 500°C, and the solvus on the alkali
feldspar join has been delineated for the first time by the simultaneous crystallization of feldspars from an undercooled melt.

Key words: experimental petrology, granite, pegmatite, feldspar, thermometry

Introduction

Over the history of experimentation in igneous systems, only a handful of studies have attempted to document the crystallization of melts in response to cooling, despite the fact that cooling is the principal driver of crystallization in natural melts. Thermal models of thin granitic dikes that form pegmatites predict that they would experience sharp thermal gradients from their margin to center. The few experimental programs that have been meant to simulate the pegmatite-forming environment, however, have been conducted at an isothermal state throughout the charges. This study reports on the crystallization response of the Macusani obsidian (U.S. National Museum specimens catalogued as #2143), a close analogue to the compositions of lithium-rich pegmatites (Table 1), in thermal gradients that were meant to mimic those across half of a pegmatite dike from margin to center. The principal contributions of these experiments include a validation of the feldspar solvus algorithms to low, subsolidus temperatures, an experimentally determined solvus for the alkali feldspars attained through the crystallization of undercooled melt at low temperature, records of chemical gradients along and across the melt volumes, and documentation of the spatial zonation of crystalline assemblages and their textures.

Geological Context

These experiments arise from the following observations, which served as the premise for the approach:
(1) Pegmatites solidify by the fractional crystallization of granitic melts from the margins of bodies to center (e.g., Cameron et al., 1949; Jahns, 1953a). Additional components of lithium, boron, fluorine, and phosphorus that act as fluxes in the melt constitute less than a couple of weight percent in total, even in the most fractionated of igneous bodies (e.g., Jahns and Ewing, 1977; Stilling et al., 2006). The rare-element pegmatites comprise far less than 1% of all pegmatites of a given pegmatite group or district (Norton and Redden, 1990; Černý, 1991). The vast majority are mineralogically ordinary granites close to their thermal minimum composition (Norton, 1966).

(2) The outer zones of pegmatites possess surface nucleation textures including skeletal intergrowths of quartz with tourmaline, beryl, albite, and K-feldspar (graphic granite), prominently oriented unidirectional crystal growth inward, and radial aggregates. These textures are indicative of crystal growth from a melt of high viscosity that is highly supersaturated with respect to mineral-forming components as a result of a large magnitude of liquidus undercooling prior to the onset of crystallization (e.g., London, 2008, 2009). The immediate contacts of pegmatites, thick and thin, are marked by granophyric intergrowths, an igneous quench texture, of quartz with plagioclase (London et al., 2020).

(3) Assemblages that can be reasonably construed as the products of hydrothermal recrystallization of earlier-formed minerals constitute less than 5 volume percent of pegmatites, even those that are rare-element rich (e.g., Heinrich, 1953; Jahns, 1953b). Miarolitic cavities, which represent incontrovertible evidence for the evolution of an aqueous solution at the end of consolidation of pegmatites, represent only a minute fraction (far less than 1%) of all granitic pegmatites (e.g., Černý, 2000). In contrast, the crystallization of a haplogranite melt that is saturated in H₂O (6.6 wt.%) at 200 MPa leads to an increase in volume of 21%, of which the
aqueous solution occupies 25% of the total volume (London, 2008). That calculation has been confirmed by experiment (Figure 5 of London and Morgan, 2017). In that context, the absence of miarolitic cavities in pegmatites and the lack of adjacent host rock alteration are significant (Bowen, 1928).

(4) Primary solvus feldspars record temperatures of ~ 400°C along the margins to ~ 450°C at centers of thin dikes (London et al., 2020, 2021). The cesium content of primary K-feldspars in pegmatites serves as a measure of the extent to which the feldspars have preserved their original igneous compositions. Rayleigh models based on the Cs content of the unaltered K-feldspars in pegmatites reflect their crystallization from melt in the absence of an aqueous solution until the ends stages of crystallization (London, 2022).

(5) Numerical simulations of conductive heat flow indicate that intrusive pegmatite bodies should cool quickly to ~ 400°C-450°C at their margins with the ingress of a sharp thermal gradient from margin to center (e.g., London, 2008). The crystallization of the feldspars appears to keep pace with the advance of an isotherm of ~ 400°C (London et al., 2019, 2020).

Background

At the inception of experimentation on rock-forming igneous systems, Bowen (1913) observed that the products of melting crystalline aggregates were not reproducible by cooling liquids of the same composition. In the plagioclase system, Bowen (1913) found that crystal-free melts had to be cooled to temperatures well below the liquidus conditions observed in the crystalline melting experiments, and many compositions failed to crystallize at all. He deduced that the undercooled melts persisted metastably below their liquidus temperature because their high viscosity impeded the nucleation of crystals. From that point on, liquidus experimentation
entailed thermally prograde (also known as forward-direction) experiments that involved the melting of crystalline aggregates, or less commonly the forward-direction crystallization from glasses. For the most part, these were partial melting experiments in which little or nothing actually crystallized, yet the liquidus relations that were derived from them were related to the crystallization of geologic melts upon cooling. Experiments in which silicate compositions were fully melted above their liquidus temperatures, then cooled below the liquidus temperatures (thermally retrograde or reverse-direction) to induce crystallization, were abandoned for decades.

The first significant attempts to quantify the crystallization response of high-silica melts as a function of liquidus undercooling were conducted in the alkali feldspar system (Fenn, 1977) and with synthetic granitic and granodioritic rock compositions (Swanson, 1977). Both authors plotted crystal growth rates (the single largest dimension of a crystal grown entirely within melt over the duration of an experiment) and crystal nucleation rates (actually, crystal density, the number of crystals per unit volume as a function of the duration of an experiment) against the magnitude of liquidus undercooling, $\Delta T$. The magnitude of $\Delta T$ correlates with the magnitude of the Gibbs Free Energy change of reaction for the crystallization of a chemical component of a mineral from its components in the melt: $\Delta \bar{G}_{\text{rxn}} = \bar{G}_{i,\text{crystal}} - \bar{G}_{i,\text{liquid}}$ where $i$ is the chemical composition of a mineral-forming component, e.g., $i\text{NaAlSi}_3\text{O}_8$. Values of $\Delta \bar{G}_{\text{rxn}}$ become increasingly negative, favoring the formation of crystals, with increasing $\Delta T$.

**Simulation Experiments**

Though Fenn (1977) and Swanson (1977) aimed to produce quantitative measures of crystallization in felsic melts, they took the approach of simulating crystallization upon cooling, and they related their results to the textures of igneous rocks that form at different rates of cooling. They regarded their experiments, therefore, as simulations of the natural igneous
environment to a first approximation. The first experiment that was explicitly treated as a simulation of a natural process of crystallization in a granitic composition, however, was published by Wyllie (1963; reproduced as Figure 6 of London, 1992). He attributed that single experiment to R.H. Jahns and C.W. Burnham. Jahns and Burnham never published the experiment, nor did they provide details of it in any other publication. Jahns (1982) described it as a perfect simulation and replication of the pegmatite-forming process following the Jahns-Burnham (1969) model, though he did not depict or take credit for the experiment. Wyllie (1963) attributed the same textural variations in two domains of the run product to a thermal gradient across the capsule, not along its length.

London et al. (1989) approached experimentation with the Macusani obsidian, a rhyolitic glass that is highly enriched in F, P, B, Li, Rb, and Cs (Table 1), in the same manner as did Fenn and Swanson. Powdered Macusani glass was devitrified at 400°C and 200 MPa H2O prior to forward-direction melting steps. A succession of experiments led to a liquidus diagram (Figure 1) as functions of temperature and H2O content of the experimental charge at 200 MPa total pressure (nominally anhydrous\(^1\) glass to H2O-oversaturated). A subsequent suite of experiments with powdered glass and variable H2O content was run to temperatures above the liquidus (determined in relation to the amount of added H2O) to produce a homogeneous melt, then cooled below the liquidus temperature. The majority of experiments entailed isobaric single-step cooling (Figure 1), and the results were related to the initial magnitude of undercooling, \(\Delta T\), as a function of the H2O content of the experiment up to saturation (10-11 wt.% H2O). The relationship of crystallization to H2O content was complex and unexpected: the nominally anhydrous Macusani obsidian powder crystallized immediately and completely at run conditions,

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\(^{1}\) London et al. (2012) pointed out that powdered (micronized) starting materials adsorb from 1 to 4 wt% of their weight in H2O from atmospheric moisture in the brief times they are exposed to air, even if stored under desiccation.
but as the content of H$_2$O added increased past 4 wt.%, no crystallization ensued until the experiments were oversaturated in an aqueous solution\textsuperscript{2}. In that state, crystallization occurred solely by deposition along the capsule walls from the aqueous solution, and the melt remained entirely crystal-free.

The H$_2$O-undersaturated powder experiments reproduced pegmatitic features in most respects, whereas the initially H$_2$O-oversaturated experiments did not. Undersaturated experiments recorded sequential crystallization, unidirectional solidification textures (UST), graphic feldspar-quartz intergrowths, and sharp spatial zonation of mineral assemblages from margins to center of the melt volumes. With crystallization in the vapor space, oversaturated experiments produced euhedral crystals in a spatially random assemblage with voids between crystals in the spaces of the aqueous solution. The texture resembled that of crystals found in miarolitic cavities of some pegmatites (e.g., London, 2013). At comparable degrees of crystallization, the H$_2$O-undersaturated melt showed progressive fractionation of the melt in terms of increasing concentrations of incompatible and fluxing components, whereas the melt in H$_2$O-oversaturated showed little or no fractionation at all (Table 8 of London et al., 1989).

In a similar study of the kinetics of crystallization upon liquidus undercooling of a hydrous haplogranite liquid of minimum composition at 200 MPa H$_2$O, Evensen (2001) observed that starting materials of glass powder crystallized partially but readily along the interface between aqueous solution and melt, but identical replications with solid glass cores failed to crystallize at all. The experimental study by Evensen (2001) and continued by London (2008) entailed 275 experiments, but it was never published because its goal was to assess the intrinsic

\textsuperscript{2} Swanson (1977) noted that the granitic composition failed to nucleate crystals for any combination of time and undercooling temperature with more than 3.5 wt% H$_2$O added to the charge (p. 969).
crystallization response of hydrous granitic liquid to cooling. The results turned out to be highly extrinsic, determined by the experimental methods as much as by the composition and its conditions. Results varied based on the starting state at the undercooling step, whether from melted glass powder, devitrified and remelted glass powder, or melted glass core. Recently, however, Devineau et al. (2020) have relied on seven undercooled experiments with granitic powder to account for the textural crystallization of pegmatites.

The observations from the study of hydrous haplogranite powder versus cored glass (Evensen, 2001), therefore, led London and Morgan (2017) to replicated experiments with the Macusani obsidian using solid glass cores instead of powders in order to produce a better simulation of a natural magma. To improve the simulation, London and Morgan (2017) added powdered amphibolite to one end of some capsules and completely surrounding some glass cores, such that the glass cores were in contact with a rock that might be regarded as a natural host. As in the study by Evensen (2001), London and Morgan (2017, p. 1025-1026) reported significant differences between powdered and isothermal core glass experiments of otherwise identical design. Their conclusion was that core experiments, which excluded a large quantity of air from the run material, provided a three-dimensional volume in contrast to the flattened two-dimensional products of powders, and which avoided possible contamination or other lab-induced effects from grinding and adsorption of moisture or solvents, represented a better simulation of the natural process of crystallization. The addition of amphibolite powder to one end of a capsule served the purpose of initiating crystallization of the melt there, as if along the contact of a likely host rock, which led to the spatial separation of mineral assemblages across the melt volume. London and Morgan (2017) deemed powders as unsuitable starting materials if the experimentation is meant to simulate a natural igneous process.
The simulation experiments that have been conducted to date were isothermal throughout their volume following the undercooling step. To this extent they are not adequate replications of a natural dike-forming melt that might crystallize in a thermal gradient from margins to center. A few new experiments with solid cores of the Macusani obsidian have started to address this deficiency.

Methods

Experimental Method 1 (MAC 246 and 247)

Cores of ~ 4-5 mm (L) by 2.5 mm (W) were drilled from an obsidian pebble of the Macusani obsidian (USNM 2143) obtained from the U.S. National Museum of Natural History. The cores were beveled slightly along their ends to prevent their edges from cutting the Au tubing, rinsed in technical grade HF for 3 seconds to remove any traces of abrasives, then washed in ultrafiltered deionized water. Eight cores in MAC 246, and six cores in MAC 247, totaling ~ 4 cm in length, were loaded into Au capsules along with ultrafiltered deionized water (Table 2), frozen at the end with water, and sealed with a TIG DC arc welder. Capsules were checked for leakage by heating to 100°C in air for 2 hrs. Capsules were pressurized to 198 MPa in water-pressurized cold seal reaction vessels and taken up to temperature above the liquidus for the composition. The final pressure was adjusted to 200 MPa at temperature with reference to a Bourdon-tube gauge. The controller temperature was set to 800°C, which was measured by an internal Chromel-Alumel thermocouple to be within 10°-15°C of that value at the hot end of the capsule. The temperature measured by the thermocouple, which was within 8-10 mm of the core at the cooler end of the capsule, was 755°C. The fugacity of O₂ in the experimental system, previously calibrated with respect to the solubility of cassiterite in melt (Taylor and Wall, 1992), was 1 log unit below NNO at pressure and temperatures, which resulted in a proportion of
Fe$^{3+}$/Fe$^{2+}$ of < 10% (Moore et al., 1995). Cores were preconditioned for 144 hrs. Based on a control experiment quenched from the preconditioning step, this procedure was sufficient to completely melt and homogenize the glass. Following the preconditioning step, the reaction vessel was repositioned outward toward the cool end of the furnace, such that the thermocouple temperature at the cool end of the capsule was read at 400°C or 450°C (Table 2). Because the crimped end of the capsule created an 8-10 mm gap between the end of the thermocouple and the end of the core, the likely temperatures at the cold end of the cores are taken as 410° and 460°C respectively. The hot ends of the capsules in the final run position were calibrated prior to the experiments with a thermocouple located where the hot end of the capsule would lie. That value was 610°C (MAC 246) and 585°C (MAC 247) with an uncertainty of ± 15°C (Table 2) because there was no thermocouple in place at the hot end during a run. End-to-end, the temperature gradients were ~ 160°C along MAC 246 and ~ 185°C along MAC 247.

**Experimental Method 2 (MAC 244)**

Eight cores for MAC 244 were prepared as described above with 4 wt.% H$_2$O and run at a set point temperature of 800°C at 200 MPa linking them into a single glass column ~ 4 cm long. Prior calibrations of the furnace gradient put the hot end temperature at 785°C (set to 800°C, read at thermocouple). The duration of the preconditioning of the core (96 hrs) was sufficient to hydrate it without inducing crystallization at the cold end (verified by inspection). The run was quenched, the cooler end of that experiment was cut off (glass examined optically for crystals), and that end placed against powdered amphibolite plus water in an outer capsule (a total of 6 wt.% H$_2$O added and in hydrated glass). The inner Au capsule, in which the cores were hydrated, prevented any chemical exchange between the melt core and the amphibolite except at the open end. The MAC 244 run was reloaded with the vessel repositioned in the furnace such as to give
an initial temperature of 785°C (the liquidus temperature for a melt with 4 wt% H2O is 750°C) at the hot end ("T Hot", Figure 2) and 540°C at the "Read T Cold" end of the experiment (Figure 2) to establish an initial gradient of 245°C along the length of the core. In contrast to MAC 246 and MAC 247, in which the thermal gradient of the undercooled melt remained constant over distance and time, MAC 244 was cooled in a stepwise fashion to simulate the loss of heat and decreasing temperature of a pegmatite body in contact with a cold host (Figure 2). MAC 244 was conducted for 2,064 hrs below the liquidus temperature. The cold end of the MAC 244 core was at or near a glass-forming state throughout the experiment. The hot end of the core approached the glass state, assuming that was at ~ 550°C (London and Morgan, 2017), after 1,000 hrs.

Analytical Methods

Electron beam microanalysis included backscattered electron imaging (BSE), energy-dispersive x-ray analysis (EDXA) of rastered areas, and spot analyses of minerals and glasses by wavelength-dispersive x-ray spectrometry (WDS) on CAMECA SX50 and SX100 instruments at the University of Oklahoma. Imaging was conducted using 15 kV acceleration and 20 nA sample current (measured at the Faraday cup). Analyses by WDS also were performed using 15 kV acceleration. Crystalline phases were analyzed using 20 nA current, a spot size of 2 μm, and counting times of 30s on peak for major elements and 30-60s for minor and trace elements yielding minimum detection levels of ~0.02-0.07 wt.% for all components except F (~0.23 wt.% using a TAP diffractor) and B (~ 0.2-0.4 wt.% B2O3 using an LSM device with 2d = 200Å: e.g., Morgan, 2015). To further investigate the potential incorporation of boron, selected feldspars were analyzed using 8 kV acceleration, and beam current of 20 nA, and 5 μm spot size; counting times were 30s for Na and Al, 60s for Si, and 75s for K, Ca, and B yielding minimum detection levels of 0.01 to 0.02 wt.% for all elements except B (0.15 wt.%). Following the protocols of
Morgan and London (1996, 2005a), glasses were analyzed using two beam conditions to minimize the effects of alkali volatilization. Both conditions utilized 15 kV acceleration and a defocused 20 μm spot size; a 2 nA beam current was first used for analyzing Na, Al, Si, K, and Ca (30s counting times, Na and Al measured first and concurrently), followed by a second 40 nA condition (30-60s counting times) for all other minor and trace elements. Minimum detection levels for glasses were similar to those obtained for crystalline phases. EDXA-based x-ray beam-scanned mapping of selected samples was performed by spectral imaging on the CAMECA SX100 using a Thermo Ultra-Dry SDD and Noran System Seven automation. Images were acquired into 1024 x 768 pixel arrays, using 15 kV acceleration and 20 nA sample current; maps were acquired using 200-300 frames acquired at 200s per frame. Phase analysis on the maps was performed using the COMPASS principal components analysis model within the Noran automation.

Solvus temperatures were calculated for pairs of plagioclase and K-feldspar using the Margules-corrected fits to the solvus by Elkins and Grove (1990) in the software package SOLVCALC (Wen and Nekvasil, 1994). Feldspar pairings were between adjacent (touching) plagioclase and K-feldspar crystals. The uncertainty associated with each analysis was set at 2 mol.% deviation from the mean for each component in plagioclase and K-feldspar. Values as mole fractions were input to the fourth decimal place in order to include the low An content of K-feldspar, which was close to the detection limit for most of the analyses (Electronic Appendix I). Using that accuracy, temperatures were calculated for 40 pairs of touching feldspars; among those, only 9 failed to converge on a temperature for all three feldspar components.

Crystallization in a Thermal Gradient

Textures and Mineralogy of MAC 246
Figure 3 presents backscattered electron images of the core from MAC 246. A visual estimate over the entire core from BSE imagery indicates that ~ 70 vol.% of the core remained as glass. Segment 1 contained a sharply defined, very fine-grained vesicular border zone up to 125 $\mu$m thick (Figure 3a) that consisted of an intergrowth of skeletal lamellar crystals too fine to analyze individually. Energy-dispersive x-ray analyses of the region were consistent with mostly plagioclase. The border zone was followed inwardly by a layer of skeletal K-feldspar, then coarse plagioclase to 500 $\mu$m in length tipped with more potassic K-feldspar at the crystallization front. The sharply coarse-grained layer with inward UST will be referred to here as a wall zone; the mineralogy and textures of the two zones, border and wall, are characteristic of the same units in the same structural position in zoned pegmatites (Cameron et al., 1949). Radial sprays of micas, whose cores of zinnwaldite evolved to lepidolite at the rims, were encased within large quartz crystals to 250 $\mu$m across (see London and Morgan, 2017, for analyses of similar intergrowths). The quartz-mica intergrowths shown in Figure 3a appear to have truncated, and hence preceded, the terminus of the wall zone. Vesiculation caused by crystallization created vesicles that are immediately adjacent to the crystallization front (Figure 3a). The extent of vesiculation along the entire core was proportional to the amount of crystallization. Segments 2 through 6 contained a few minute vesicles, and segments 7 and 8, which were nearly free of crystals, were equally devoid of vesicles. Along the margin of segments 3 and 4, the border zone was ~ 10-20 $\mu$m wide. Large skeletal crystals of K-feldspar-plagioclase intergrowth radiated off of this surface (Figure 3b), and at the contact with the glass, single euhedral crystals of K-feldspar with plagioclase formed patchy intergrowths that have been observed in prior experiments with the obsidian. Quartz formed small anhedral crystals within the skeletal branches of the K-feldspar intergrowth and in an association with blocky albite in domains.
between branching K-feldspars. Skeletal sprays of micas dotted the glass; some were encased in quartz overgrowths, and some not (Figure 3c). Segments 5 and 6 were similar in that the border zone was practically gone, and the crystallization front consisted mostly of skeletal K-feldspar with interstitial albite and small anhedral grains of quartz; quartz constituted less than 15 vol.% of the intergrowth. Segments 7 and 8 were entirely vitreous except for traces of patchy feldspar intergrowths along their margins. In the glass of segment 8, thin blades of a stannous iron oxide (unique to this run) were present along with other thin skeletal crystals too narrow to analyze, but which resembled micas (Figure 3d).

**Feldspar Solvus Thermometry in MAC 246**

Figure 4 plots the convergent three-component (An-Ab-Or) temperatures (solid diamonds) derived from the solvus thermometry program SOLVCAL against position within the experimental core. The average temperature among the three components that did not converge within the assigned error is shown as gray squares. A black line denotes the probable temperature profile over the length of the core as extrapolated between calibrations at the hot and the cold ends (open diamonds). The temperature of the hot end carried a larger uncertainty because there was no thermocouple to record it. The uncertainty at the cold end was ~ 5°C. The liquidus temperature of the Macusani obsidian containing 6 wt.% H₂O at 200 MPa (dotted line) is 725°C (London et al., 1989). Upon positioning the vessel outward for the duration of the run, the resultant instantaneous liquidus undercooling of melt (ΔT) varied from ~ 115°C at the hot end to ~ 235°C at the cold end.

The calculated solvus temperatures in MAC 246 exhibit scatter but generally conform to the decreasing temperature profile across the melt column. For all feldspar components in plagioclase and K-feldspar, the convergence was better at low temperature than at the high end.
Many of the calculated temperatures for the Ab and An components are identical, and the equilibration temperatures of the Ab and An components of the feldspars more closely approached the temperature profile than did Or. The average calculated temperatures for the Or component of K-feldspar exhibited an increasing deviation from the thermal profile of the experiment with increasing temperature, which likely accounts for many of the convergent values to deviate from the thermal profile along the capsule.

Figure 5 traces the feldspar solvus as functions of temperature versus mole fraction of Or component in albite and K-feldspar for the convergent pairs only. It is the first known depiction of the alkali feldspar solvus as derived by the simultaneous crystallization of feldspar pairs from hydrous melt in response to cooling. The compositions of K-feldspar in MAC 246 lie on the binary join between Ab and Or. The compositions of albite lie off of the join by an average of ~5 mol.% An component (Electronic Appendix 1). Also shown on Figure 5 are the locations of the solvus curve as calculated at 500°C and 600°C from the Margules mixing model of Elkins and Grove (1990) as incorporated by Wen and Nekavasil (1994) into SOLVCALC. The calculated solvus for albitic plagioclase is projected to the Ab-Or join from the An apex in the ternary feldspar system through the solvus locations at 500°C and 600°C at An05. Figure 5 illustrates the correspondence between the calculated experimental temperatures and the calculated position of the solvus in relation to albitic plagioclase and K-feldspar. For both feldspars, deviations of the experimental data from the calculated solvus position increased with increasing temperature in the direction of an increased Ab component. The K-feldspars contained up to half a weight percent of Rb2O, and both feldspars contained upwards of 0.5 wt.% P2O5 (Electronic Appendix I). Both components, which were omitted from the solvus calculations, might have been sufficient to influence the solvus solutions.
The Chemical Composition of Glass in MAC 246

The Macusani obsidian is notably homogeneous (e.g., London et al., 1988), and the preconditioning step of melting insures that any minute crystals (except andalusite) or other potential variations in composition are eliminated. Over the length of the glass column in MAC 246, however, gradients were observed among several of the components measured (Electronic Appendix II). In Figure 6, thin dashed horizontal lines convey the initial elemental concentration or elemental ratio in atoms per 8 oxygens for a melt of the Macusani obsidian containing 5 wt.% H₂O. Vertical arrows in Figure 6 show the extent to which elements or ratios increased or decreased over their values in the starting hydrated obsidian. Data are regressed to a linear fit. Deviations along the length of profiles arise from the uneven distribution of crystal clusters along the margins of the core and their consequent chemical fractionation of adjacent melt. From cold to hot end, Si increased by 3% apfu based on 8 oxygens, and Al decreased by 7% Al apfu. Boron decreased by 51% B apfu and phosphorus by 17% P apfu over the same distance. Fluorine, however, fell by more than half, from 0.545 to 0.247 F apfu. The ratio of Rb/K fell 60% from the cold to hot end, but all measured values were greater than the initial ratio in the Macusani obsidian. The ratio of K to Na, measured as K*, apfu K/(K + Na), varied from 0.274 at the cold end to 0.334 at the hot end, an increase of 18%.

Textures and Mineralogy of MAC 247

Figure 7 depicts representative backscattered electron images of the core. A visual estimate over the entire core from BSE imagery indicated that ~ 95 vol.% of the core remained as glass. In segment 1 at the cold end (Figure 7a), a thin vesicular border zone ~ 40 µm wide consisted of a skeletal intergrowth of too fine to resolve, but EDXA are consistent with mostly plagioclase and subordinate dendritic K-feldspar. A wall zone ensued with skeletal K-feldspar crystals up to 400...
μm in length, followed by a layer of coarsely crystalline blocky plagioclase and quartz. A few radial clusters of mica were isolated in the glass. Segment 2 contained but one small cluster of crystals that repeated the plagioclase-rich border zone and the skeletal K-feldspar wall zone upon it. The curving trace of a crack in the glass was delineated by a mica-quartz intergrowth (Figure 7b). The margins of segments 3 and 4 were lined with a monophase layer of petalite (LiAlSi4O10) crystals ~ 20 μm in size with traces of skeletal K-feldspar at their junctions (Figure 8c). Otherwise, no feldspars or micas were present in the segments. Segment 5 was all glass except for a few minute dispersed crystals of mica (Figure 7d). Segment 6 at the hot end presented a fine-grained margin of plagioclase, followed inwardly by a mostly crystal-free zone dotted with micas, then a few clusters of radial feldspar and exceedingly fine-grained crystals that resembled micas dispersed in the “glass” (Figure 7e). Small vesicles were present in the crystal-bearing “glass”.

The Chemical Composition of Glass in MAC 247

The chemical attributes of the glass are displayed in Figure 8 and Electronic Appendix III. As in MAC 246, Si increased and Al apfu and ASI both decreased from cold to hot ends. Boron and phosphorus showed no significant variation across the glass, but F was highly enriched adjacent to the crystal front in segment 1 at the cold end. Within the same glass region, values of K* fell well below the initial ratio, and beyond segment 2, K* values exceeded the initial ratio. The glass was, therefore, more sodic where albite was most abundant in the adjacent crystalline zone, and more potassic where K-feldspar was the predominant feldspar (though the fraction of crystallization was minute toward the hot end).

Textures and Mineralogy of MAC 244
Figure 9 shows five composite BSE images of the 4-cm long experiment that was conducted with decreasing temperature with time along its thermal gradient (Figure 2). A polyphase crystallization front with mineralogically distinct domains occupied ~15 vol.% of the total core but did not surround the margins of the core completely or uniformly; the remaining 85 vol.% of the core was non-vesicular glass. Crystallization occurred along both ends of the composite core, decreasing toward the central segments 4 and 5. End segments 1 and 8 contained ~10 vol.% of a mineral dispersed through the glass that was too fine-grained for EMPA (labeled “glass” in Figure 9). In its morphology and BSE intensity, the dispersed crystalline phase resembled mica, but analyses of “glass” in these segments showed an increase in Si and a decrease in Al in this region. Minute vesicles were attached to many grains of the dispersed mineral. Segment 1 was likely in the glass state throughout its cooling. It possessed an exceedingly fine-grained border of plagioclase and quartz (Figure 9a). Segment 8 (Figure 9e) at the hot end was texturally similar to segment 1 despite its higher run temperatures from 785°C to 480°C). It presented a mineralogically complex border zone with three oscillations of layers rich in K-feldspar and of plagioclase plus quartz. Figure 10a illustrates the nature of the mineralogical variations both across and along the crystallization front. A layered sequence dominated by K-feldspar with lesser plagioclase plus quartz evolved to the opposite proportionality, dominated by plagioclase plus quartz, from the margin inward and toward the end of the segment. The detailed mineralogy at the end of segment 8 is revealed as a phase map based on a composite set of elemental x-ray images of the area (Figure 10b). The glass in segment 2 contained dispersed crystals of skeletal radial zinnwaldite included within quartz, and the same micas occurred in segment 3 but without quartz (Figure 9b). Segment 5 contained a curved crystal-bordered crack that resembled similar crystalline threads in the isothermal core experiments described in London and Morgan (2017),
and which they attributed to crystallization along fractures that developed on the cooling cycle of experiments. Crystallization along the margins of segments 4 and 5 began with an exceedingly fine-grained border zone dominated by plagioclase with minor mica, followed inwardly by a graphic K-feldspar-quartz intergrowth, and terminated inwardly by a monophase layer of K-feldspar at the melt interface (Figure 10d).

The compositions of entirely crystalline portions were analyzed by EDXA in 50 X 50 μm scan areas, and their compositions were recast as CIPW norms. Within each of the eight core segments, the crystallization front was divided into two domains based on texture: an exceedingly fine-grained and finely vesicular border zone adjacent to the interface with the Au tube, and a coarser wall zone displaying unidirectional crystal growth inward at the crystallization front.

Figure 11 presents normative mineral variation diagrams along the length of the core for the border and wall zones of the crystallization front. In the border and wall zones, normative quartz decreased from ~ 25 wt.% at the cold end to ~ 20 wt.% at the hot end, as compared to 35.7 wt.% CIPW normative quartz in the starting Macusani obsidian. Oscillations in normative albite and orthoclase occurred at the scale of millimeters along the length of the border zone, and K-feldspar was predominant in the central segments. The wall zone presented oscillations between quartz and albite at the scale of millimeters along its length, and the same prominently potassic region in the central segments. The normative corundum component of the CIPW norms, which was contained as a component of mica, varied irregularly from ~ 1 to 4 wt.% depending on whether a mica happened to be included in the analyzed area. A relatively constant normative

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3 CIPW normative analyses do not include lithium, which would be expressed as a lithium aluminosilicate. As a result, CIPW norms of Li-rich compositions overestimate the quartz and corundum components. For phosphorus-
hypersthene component (~ 1.4 wt.%) mirrored that of the starting obsidian, and was hosted as the ferrous component of the micas.

**The Chemical Composition of Glass in MAC 244**

The glass portion of MAC 244 was analyzed with two different transects: at the center line along the length of the core, and transects across each core segment (*Electronic Appendix IV*). Points were picked by hand where necessitated by crystals, but crystals were unavoidable in the “glass” domains of segments 1 and 8.

*Figure 12* displays five chemical attributes of the glass along its length. Silicon was elevated along the length of the glass core relative to the starting composition, a result that was dictated by the low normative quartz component of the crystalline margins. The Si content of the glass, however, increased within both end segments 1 and 8 of the core, and Al decreased in the same volume (*Figure 12a*). Those variations implied that the finely divided crystalline material was quartz, however as noted above, the morphology and BSE intensity of that crystalline material is more akin to mica. The vitreous domains of cores 2-7, however, were free of crystals except for a few large mica-quartz aggregates that were avoided. Potassium and K* increased from both ends toward the center of the glass column, where the normative K-feldspar component of the crystalline margins also attained a maximum and where the fraction of crystallization at the margins was at a minimum along the length of the core. In *Figure 12b*, boron and phosphorus were relatively unchanged from their starting concentrations and no gradients in their concentrations were evident along the length of the glass transect. Fluorine, however, exhibited rich compositions like the Macusani obsidian, CIPW norms also overestimate the apatite component, while the anorthite component typically becomes a negative value.
spikes in cores 2 and 7, which were the first fully vitreous domains inward from the more extensively crystallized end segments.

Figure 13 plots a transect (yellow line in Figure 11) across the glass of segment 6 beginning at the crystalline margin. A pronounced enrichment of B and F was evident near the crystallization front. The concentration profile for P was flat, as it was in most other analyses of the glasses. Though the value of K* was elevated above the starting composition in this segment, there was no correlation between K* and F. Other transverse analyses were similar where a crystallization front was present at the margin. No compositional gradients were found where crystals were absent along the margins.

Discussion of Results

A Comparison of Experimental Methods and Results

Three experimental programs with the Macusani obsidian at 200 MPa (London et al, 1989; London and Morgan, 2017, and this study) shared similarities, which might be construed as intrinsic to the composition of the obsidian, and differences based on the experimental method. These results with the Macusani obsidian have been consistently observed in all experiments:

1) incipient crystallization at the margins produced a very fine-grained border zone dominated by plagioclase and lesser quartz. The An content of plagioclase fell from margin (~An08-12) to center (~ An02-05).

2) Inward of the border zone, a wall zone of coarse patchy or graphic intergrowth of K-feldspar with albite or with quartz that exhibited unidirectional solidification texture formed elongate crystals pointing toward the remaining melt pools. All crystalline phases coarsened by a factor of ~ 10^2 from margin to melt center.
Quartz formed overgrowths on the feldspar crystallization front and isolated crystals of quartz and quartz plus mica in the central domains of melt pools. Micas were present throughout the experiments, but they were abundant only in compositions with > 6 wt.% H\textsubscript{2}O added (core experiments only), or in which the H\textsubscript{2}O content of melt increased beyond this value by the fractional crystallization of feldspars and quartz along the margins.

To this extent, all three experimental programs replicated the spatial distributions of minerals and textures found in the vast majority of common granitic pegmatites that possess simple zonation, from plagioclase-quartz $\rightarrow$ K-feldspar $\rightarrow$ quartz $\pm$ mica (Cameron et al., 1949).

**Crystallinity, undercooling, and H\textsubscript{2}O content.**

The relationships among $\Delta T$ and H\textsubscript{2}O content on crystallization, vesiculation of the melt, the delay in crystal nucleation and growth, and the spatial distributions of the feldspars were different among the three studies cited here. These differences are primarily a function of the methods used.

The anhydrous obsidian powder crystallized immediately and completely upon approach to run conditions (700\textdegree-800\textdegree C, 200 MPa), but crystallization decreased with increasing H\textsubscript{2}O content of the melt, and crystallization ceased abruptly beyond 4 wt% H\textsubscript{2}O (London et al., 1989). In contrast, anhydrous obsidian cores did not crystallize at all; crystallinity increased principally as a non-linear function of time and liquidus undercooling (Figure 11 of London and Morgan, 2017). Though crystallization increased when H\textsubscript{2}O was added, there was no correlation between the percentage of crystallization and the initial H\textsubscript{2}O content added to the charges (Figure 12 of London and Morgan, 2017). At comparable compositions and undercooling, the experiments presented here showed far less crystallization than in the isothermal core results over longer run
durations. Portions of MAC 244, 246, and 247 that were held above 500°C for at least 1,000 hours produced almost no crystallization, whereas isothermal core experiments of similar temperature, duration, and H2O content crystallized abundantly.

Vesiculation. Vesicles were absent along the crystallization fronts in powder experiments, whereas vesicles were abundant at that interface in solid core runs. A continuous crystallization front completely surrounded the margins of the cores in the isothermal experiments, whereas crystal clusters in powder experiments left melt in contact with the precious metal tubing. The entrapment of vesicles, therefore, appears to have been a function of the experimental geometry: flattened charges (powder) with melt in contact with tubing allowed H2O to diffuse out of melt into the space around the melt body. Solidification fronts around cores appear to have inhibited that process, leading to the nucleation and retention of aqueous bubbles at the crystallization fronts.

The powder experiments, especially those of low initial H2O content, trapped abundant bubbles of air upon sintering, and air bubbles persisted throughout the runs. Air bubbles persist in viscous melts because although nitrogen is highly compressible, it is almost completely insoluble in silicic melts at elevated pressures (Mysen et al., 2008; London et al., 2012a). As a result, many such experiments are vapor saturated regardless of their H2O content, and the solubility of H2O in the air bubbles increases with the concentration of H2O added. Figure 2 of Burnham and Jahns (1962) illustrated the same trends in bubble entrapment in a series of three experiments, the first nearly opaque with air bubbles at low H2O content, culminating in nearly vesicle-free transparent glass at high H2O content. This observation is relevant to the proper interpretation of experimental products: it is a fact that powder starting materials of high silica content trap and
retain air bubbles at moderate pressures (several hundred MPa); hence, they are vapor-saturated whether the bulk composition is hydrous or not and H$_2$O-saturated or not.

In a geological context, the crystallization of highly undercooled and viscous melts should trap abundant vesicles upon crystallization if the melts are indeed saturated in H$_2$O, as Bowen (1928, p. 294) observed:

“...deep bodies have sent dikes into surrounding rocks at all stages of their careers and these dikes are often, at least at their margins, aphanitic or glassy. They have thus crystallized so rapidly that if the liquid were vesicular the aphanite would be vesicular as well. Yet vesicular dikes or dike selvages are exceedingly rare and are apparently always found in association with flows which indicate for them a shallow depth... It is very much to be doubted, therefore, that any process which involves vesiculation can be the principal or even an important process in igneous differentiation. But even on the supposition that vesiculation is a common condition in deep-seated magma and that for some reason its evidence is concealed from us, the quantitative adequacy of the process is seriously in doubt.”

**Sequential versus simultaneous crystallization.** In the powder experiments (London et al., 1989), crystallization from margins toward melt ensued with a single episode of sequential crystallization as described above. In the isothermal core experiments (London and Morgan, 2017), feldspar-dominant assemblages formed along the margins while quartz or quartz-mica intergrowths precipitated as isolated crystals in the centers of melt pools, as was the case in this study. The crystallization of feldspar-rich and quartz-rich domains appears to have been partly simultaneous (e.g., as in Figure 3), much as Jahns (1982) suggested for pegmatites, but not by the mechanism that he proposed. At the undercooled state of these experiments, feldspars exhibited a propensity for nucleation along the marginal surfaces of the melt, irrespective of the
capsule, aqueous solution, or rock in contact with melt, whereas quartz nucleated
homogeneously within the melt. Neither vesicles nor rare inherited phenocrysts of andalusite in
the obsidian fostered crystal nucleation within the melt in any of the experiments.

In the isothermal core experiments (London and Morgan, 2017), the addition of powdered
amphibolite to one end of the capsule led to a marked end-to-end segregation of minerals:
plagioclase plus quartz precipitated adjacent to amphibolite, and K-feldspar formed at the
opposite end. London and Morgan (2017) cited the identical compositions of first-formed
plagioclase in experiments (powder and core) without amphibolite as evidence that the locus of
incipient crystallization along the interface with amphibolite was not the result of chemical
contamination of the adjacent melt. The two mineralogical domains at the ends of cores
constituted the complementary portions of a single assemblage, and the feldspars were close to
thermal (chemical) equilibrium despite having crystallized hundreds of degrees below their
liquidus temperatures. London and Morgan (2017) inferred that the incipient crystallization of
plagioclase plus quartz along the amphibolite induced the crystallization of K-feldspar at the
opposite end of the melt column based on the clearly sequential nature of these two feldspars in
the powder experiments. In that case, the two components of the assemblage would have been
nearly simultaneous, but not exactly, one as a matter of cause, the other an effect.

In this study, only MAC 244 produced enough crystallization over its length to allow any
comparison. The notable feature of MAC 244 is the concentration of K-feldspar in the central
core segments, and a corresponding increase in K and K* of glass in the same region. Following
from the logic of London and Morgan (2017), that result would be interpreted in the same way:
after the initial crystallization of plagioclase-richer domains at the ends of MAC 244, enrichment
of the melt in K occurred in opposite directions toward the center, where K-feldspar was mostly
deposited.

The spatial segregation of co-crystallizing minerals as seen in both sets of core experiments
addresses a fundamental misunderstanding of pegmatite zonation. That is, aggregates of one or
two minerals, for example monominerallic crystallization fronts of petalite in PEG 46 (London
and Morgan, 2017) and here in MAC 247 (Figure 7c), have historically been interpreted as
hydrothermal deposits because any one- or two-phase crystalline domain is far from the
composition of the granite minimum. What these experiments reveal is that the various parts of
any given assemblage can and do crystallize simultaneously in separate regions of the melt body,
thereby preserving a near-minimum assemblage in spatially separate mineralogical domains.

The observed sequences of crystallization among plagioclase, K-feldspar, and quartz can be
rationalized in relation to the Gibbs Free Energy change attending their crystallization from melt
(the parameter $\Delta \bar{G}_{\text{rxn}}$ as defined above). At a highly undercooled state of the melt, the
crystallization of anorthite liberates more thermal energy per mole than K-feldspar, and K-
feldspar more than albite (Table 3). The feldspars release far more energy than does quartz on an
equimolar Si$_4$O$_8$ basis. In the absence of Ca, K-feldspar would be expected as the first-formed
crystalline phase based on the data of Table 3, as was observed in the experiments of London
(1999) and Evensen (2001). When Ca is present even in small amounts, the first-formed phase is
the most calcic plagioclase that the system can produce because the An component of plagioclase
releases a substantial quantity of heat from the melt (Table 3). From that An-rich composition
along the margins of charges, feldspars evolve with isothermal cooling to the final composition
of solvus pairs (Figure 2 of London, 2014b). The same evolutionary trends of feldspars are
typical of zoned pegmatites (Cameron et al., 1949; London et al., 2012b, 2020, 2021).
Oscillatory crystalline assemblages. Crystallization in the powder and isothermal core experiments produced one sequential episode of a ternary phase assemblage – plagioclase, K-feldspar, quartz, in that order – before crystallization ceased. In Ca-absent haplogranite minimum compositions, the single sequential episode of crystallization produced K-feldspar, plagioclase, then quartz (London, 1999; Evensen, 2001). Those differences in the mineralogical sequence can be rationalized by the data of Table 3, whereby the first-formed feldspar should be K-feldspar in highly undercooled, Ca-free melts, but plagioclase when the melt contains a small fraction of Ca. The normative mineral proportions and oscillations along the length of MAC 244 are remarkably similar to the modal oscillations in the texturally complex Swamp dike from Ramona, California (Figure 14). The normative quartz component of the feldspathic portions of MAC 244 is ~ 20-25%, similar to its modal abundance in the footwall section of the Swamp dike, which crystallized before most of the overlying pegmatite (London et al., 2012b). Those low quartz contents of the outer portions of experiments and early footwall portions of a natural pegmatite required that complementary quartz-rich portions of crystallization should follow sequentially in the centers of pegmatite bodies.

Metastable Persistence of Melt

A notable feature of these experiments, like those from prior studies (e.g., Swanson, 1977; Fenn, 1977, 1986; London et al., 1989; Evensen, 2001; London and Morgan, 2017), is that crystallization began but ceased over long durations in melts that remained highly undercooled, hence metastably supersaturated with respect to the equilibrium state of the system. Morgan and London (2005b) observed (but did not report) that the magnitudes of nucleation delay (time) and liquidus undercooling (ΔT) that were necessary to initiate crystallization increased as bulk compositions shifted from near the Or apex of the Ab-Or-Qz system toward the minimum
composition at 200 MPa. Fractionation attending liquidus undercooling within a single melt composition could be expected to behave similarly, which would mean that crystallization would cease as the composition of melt migrated toward the liquidus until sufficient undercooling restarted it.

The metastable persistence of melt of flux-poor hydrous haplogranite compositions (Swanson, 1977; Evensen, 2001) and of flux-rich Macusani obsidian on the duration of months at temperatures in the range of 450°-500°C is relevant to the cooling of thin pegmatite-forming dikes. Dikes of 1 to 2 meters thickness have been modeled to cool to this temperature range at their centers in days to weeks (e.g., London et al., 2012b, 2020, 2021). Feldspar solvus temperatures from the pegmatites recorded nearly isothermal crystallization at ~400° ± 15°C across their width (London et al., 2020, 2021). If the crystallization of feldspars in these pegmatites was coincident with the ingress of the cooling front, then the pegmatite bodies would have had to have begun their crystallization almost immediately upon emplacement, and the crystallization front would have had to have advanced at the rate of centimeters per day. Two hypotheses are immediately apparent to account for this disparity between the long delay of crystal nucleation and growth in experiments and the thermal models that predict rapid cooling and crystallization at the temperatures recorded by the feldspars in pegmatites: (1) the experiments are not an adequate simulation of the natural environment, or (2) feldspar crystallization in the pegmatites commenced after the cooling front of ~400°-450°C reached the dike center.

In the latter case, the crystallization of a dike would have ensued from glass, but the rate of cooling would have been much slower from that temperature, the duration of crystallization longer, and the temperatures would be nearly uniform across the body of melt (see examples in...
Chapter 16 of London, 2008). Skeletal habits and strongly anisotropic UST of highly elongate crystals found in pegmatites are akin to spherulites that crystallize in obsidian. The skeletal unidirectional intergrowth of feldspar and quartz in graphic granite (Figure 15), the defining texture of pegmatites that is also the only texture found in pegmatites that is not also present in hydrothermal veins⁴, is a similar one-dimensional linear growth pattern that, like spherulites, arises from a growth medium of high viscosity (London, 2008, 2009). In the case of graphic granite, the high viscosity of the melt impedes the diffusion of excess silica away from the interface, which leads to local saturation in quartz in troughs along the feldspar surface (Fenn, 1986). High viscosity of the melt also inhibits the lateral diffusion of high field strength ions (e.g., Si, Al) along the crystal front that is necessary to promote the two-dimensional expansion of the crystal surface to form large, single crystals (London, 2008, 2009). In most pegmatites, the graphic granite intergrowth begins with exceedingly fine-grained blebs of quartz in feldspar (Figure 15b) that coarsen inwardly to monophase K-feldspar crystals in massive quartz (Figure 15a), either because the rate of advance of the K-feldspar crystal slows, or because the diffusivity of ions along its growth surface increases (London, 2008, 2009). Though Fenn (1986) speculated that an aqueous solution might be implicated in the formation of graphic granite, London (2008, 2009) concluded that the growth medium for graphic intergrowths must be a highly viscous medium for the reasons given above, from Fenn’s (1986) work, and from hundreds of H₂O-undersaturated experiments with the Macusani obsidian and other granitic compositions that yielded graphic intergrowths. London (2018) presented experimental evidence in which the simultaneous crystallization of feldspar and quartz from a highly supersaturated aqueous solution

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⁴ Other textures found in pegmatites including unidirectional solidification from the margins, spatial zonation of mineral assemblages, layered assemblages, and increasing crystal size from margins to center are present in hydrothermal veins. Graphic mineral intergrowths are not found in hydrothermal veins because the intergrowth hinges upon high viscosity and low ionic diffusivity through its growth medium.
that was generated via undercooling of the Macusani obsidian produced a feldspar-quartz assemblage of euhedral crystals, not in a graphic intergrowth.

**Feldspar Solvus Thermometry at Low Temperatures**

London et al. (2020) noted that the experiments on which feldspar thermometry is based were performed at temperatures hundreds of degrees higher than the temperatures at which experiments such as these were conducted. All of the prior experimental calibrations of the alkali feldspar solvus entailed the subsolidus, forward direction recrystallization of starting crystalline compositions or glasses; none were crystallized from an undercooled melt. Fuhrman and Lindsley (1988) and Parsons et al. (2009) cautioned that the solvus method becomes highly inaccurate toward the alkali feldspar join of the system because of the steep slope of the solvus with respect to temperature at low anorthite content of the feldspars. The anorthite content of feldspars produced in these experiments, however, is so low (Electronic Appendix I) that their compositions are nearly binary on the alkali feldspar side.

London and Morgan (2017) reported that albite-K-feldspar pairs synthesized at the margins of melt pools consistently gave convergent solvus temperatures that were within $25\pm10^\circ$C of the actual run temperature down to $500^\circ$C. They cited this correlation as evidence that the solutions to the solvus surface were sufficiently accurate, even at low temperature and low anorthite content of the feldspars, as to be useful for thermometry in pegmatites if it could be demonstrated that the feldspars had preserved their igneous compositions. They noted, however, that the discrepancies between calculated and measured temperature were always on the high side of the run state, even for forward-direction experiments that never achieved the calculated temperature. London et al. (2020) concluded that in regard to the energy released by
crystallization to approach an equilibrium state, close is close enough for the feldspars, and they
approach that chemical equilibrium from a fictive higher temperature.

The data from MAC 246 and from London and Morgan (2017) demonstrate that the feldspars
attain their near-equilibrium compositions even following instantaneous cooling by hundreds of
degrees below their liquidus temperatures and from melts of high viscosity that might have been
glass. Rapid equilibration of feldspars at such low temperatures requires rapid diffusion of the
alkalis through melt or glass. Acosta-Vigil et al. (2012) and Morgan and London (2005b)
documented that the diffusion of alkalis through hydrous haplogranite melt and glass is rapid and
coordinated down to 515°C at 200 MPa, which would facilitate the equilibration of the feldspars
at low temperatures through an exceedingly viscous growth medium. The experimental data base
that is now available validates the conclusion that feldspar thermometry can be a reliable method
for establishing temperatures of crystallization at low temperatures if other measures indicate
that the feldspars have preserved their original igneous compositions (London et al., 2020;

Glass Compositions

Boundary layer pile-up refers to an increase in the concentration of an incompatible element
along a crystallization front that results when the rate of advance of the crystalline front exceeds
the rate at which the incompatible element can diffuse away from that interface to erase its
chemical activity gradient. Among the principal fluxing components of pegmatite-forming melts,
H and F exhibit high diffusivity in flux-rich melts at high temperature, whereas the diffusion
coefficient of B is orders of magnitude smaller, similar to that of Al, and P diffuses even more
slowly than Si (Wolf and London, 1994; London, 2009, 2015). Boundary layer pile-up among F,
B, Rb, and Cs has been documented previously in the low-temperature experiments with the Macusani obsidian and other compositions (London, 1999; London and Morgan, 2012, 2017). The most prominent features of the glasses in this study were their chemical gradients among most components along the central length of the cores and across them, even at very low levels of crystallization. In some profiles, F and B possessed steep exponential gradients (Figures 8b and 13), in others they varied linearly along the entire length of a melt column (Figure 6b). The widths and magnitudes of the boundary layer pile-up of B relative to F in Figure 13 can be explained by the differences in their diffusivity. Phosphorus showed little variation in any analytical profiles of the glass, even though its diffusivity in granitic melt is exceedingly low (Wolf and London, 1994), and boundary-layer pile up of phosphorus is expected (e.g., Morgan and London, 2005b). The lack of variation in phosphorus in these experiments arose from the high ASI of the Macusani obsidian, which promoted the incorporation of P in alkali feldspars (London et al., 1993) to the extent that the bulk distribution coefficient for P was approximately unity (Electronic Appendix I).

The ratios of K and Na, expressed as K*, varied systematically along the lengths of the cores such that values of K* were mostly antithetical to those of F (Figure 8b) and to Al and to ASI but correlated positively with Si (Figure 6a). High concentrations of Na in glass (low values of K*) occurred adjacent to plagioclase-rich crystallization fronts, and high K* values developed in glass where mostly K-feldspar precipitated (Figure 12a). Normally, opposite gradients would have been expected: a K-enriched melt adjacent to a plagioclase crystallization front, and an Na-enriched melt adjacent to a K-feldspar-rich domain as a result of an accumulation of the excluded elements, Na or K (e.g., see Figures 7 and 9 of London, 2009). Sodium, Al, and F were positively correlated in the glass of segment 1 of MAC 247 (Figure 8). An association among
Na, Al, and F as a cryolite (Na₃AlF₆) component in melt has been noted from other experiments (e.g., Manning, 1981), and cryolite was observed as inclusions within quartz that crystallized from the Macusani obsidian melt (Figure 14 of London, 2014). London (2014) explained the cryolite as a precipitate from a boundary layer liquid because the bulk melt was undersaturated with respect to cryolite.

Growth steps that are evident in large, tapering crystals from pegmatites appear to result from cyclical episodes of crystallization (e.g., Figure 17-4 of London, 2008). The consequence of episodic growth is that abrupt boundary layer pile-up of incompatible elements in the melt adjacent to crystals would be erased over the interval of time in which growth has ceased, and diffusion would erase those gradients completely if no further crystallization ensued. In a time series of experiments, the chemical gradients in glass would therefore be transient as a function of the timing of quench in relation to the burst of crystallization.

The antithetical gradients between Si and Al that are evident along the cores of MAC 246 and MAC 247, however, are not likely the result of crystallization for the reasons that the proportion of crystallization was too low to affect the two most abundant cationic components of the melt, and the diffusivities of these components are exceedingly low even at the high temperatures (800°C) at which they have been measured (e.g., Acosta-Vigil et al., 2012). London (2009) observed, however, that gradients in slow-diffusing ions can be modified quickly by the diffusion of other components. In the experiments described in London (2009), the diffusion of alkalis, F, and B erased a chemical gradient of Si in the melt at a rate that was orders of magnitude faster than the rate at which Si diffused away from crystals of quartz as they dissolved into the melt. In MAC 246 and MAC 247, chemical gradients of Si and Al were created, however, not erased. It is possible, therefore, that the concentration profiles of Si and Al reflect a
reorganization of the melts in response to the temperature gradients, such that Al and its charge-balancing Na were concentrated at the cold ends of the melt columns, leaving Si and K enriched in the opposite direction. Such variations, however, appear to be small in relation to the chemical gradients in melt caused by crystallization.

Like MAC 246 and MAC 247, the thermal gradient along MAC 244 should have simulated the continuous cooling of half a dike, margin to center, with a decreasing fraction of crystals to melt from the cold to the hot end. However, MAC 244 resembles the zonation that would be expected across an entire dike: most crystallization occurred at both ends of the melt column and decreased toward the center of the core (Figure 10). The textures at the hot end of MAC 244 were the similar to the border zone at the cold end of the core and along the margins (Figures 10a,d). MAC 244, therefore, apparently did not begin to crystallize at its hot end until it had cooled into the low-temperature realm that produced the fine-grained textures of the other highly undercooled experiments (London et al., 1989; London and Morgan, 2017). If that interpretation is correct, then the result augments other evidence that the magnitude of liquidus undercooling is more important to initiate crystallization in high-viscosity granitic melts than the rate at which it is attained (London, 2008, 2014a, 2018).

**Implications of Liquidus Undercooling for the Crystallization of Granite-Pegmatite Melts**

London (2008) proposed that pegmatites are granitic in composition because the high viscosity of their melts inhibits the nucleation of crystals until liquidus undercooling by 150°-250°C (actual temperatures of ~ 400°-500°C) finally triggers the crystallization response. Pegmatitic textures are the result of crystallization of highly viscous melt at the undercooled state far from the equilibrium of the liquidus (London, 2008, 2014b). Mafic and alkaline melts, with their higher temperatures and lower melt viscosities, nucleate crystals more readily near the liquidus.
surface, and uniform textures and assemblages are the more common result. Now, however, the resistance to crystallization shown by undercooled liquidus experiments with granitic and flux-rich pegmatitic compositions poses a problem in relation to the modeled cooling histories of thin granitic dikes emplaced into much cooler host rocks. According to the numerical simulations of heat flow, a delay in crystal nucleation and growth by weeks to months would put the pegmatite-forming melts well below their glass transition temperature by the time crystallization commenced.

**Isothermal Powder Experiments.** The undercooled powder experiments with the Macusani obsidian (London et al., 1989) were the first such results that replicated the essential aspects of mineral zonation and texture in pegmatites. The increasing chemical fractionation of the H₂O-undersaturated melt also followed a trajectory that would, in pegmatites, lead to the precipitation of normally rare minerals. In that set of experiments, the sequence of crystallization in an undercooled granitic melt that contained measurable Ca conformed to expectations based on the calculated Gibbs Free Energy liberated by the feldspar- and quartz-forming components (Table 3).

**Isothermal Core Experiments.** London and Morgan (2017) documented the spatial separation of plagioclase-quartz and K-feldspar-rich assemblages on opposite ends of the melt column when a surface (powdered amphibolite) was present to initiate and localize the crystallization of plagioclase plus quartz. The spatial segregation of feldspars is a key aspect of zonation within pegmatites (e.g., Jahns and Tuttle, 1963). Though plagioclase plus quartz were the first-formed phases in the experiments, K-feldspar crystallized synchronously; thus, the actual mineral assemblage was the ternary assemblage that would have been expected from a granitic liquid at temperatures below the solidus and the solvus of the feldspar system. Feldspars were in chemical
and thermal equilibrium via the rapid diffusion of alkalis across the melt volume, which might have been glass in experiments of 550°C and below, even at the highly undercooled and metastable state of the glass. An aqueous solution played no part in the transfer of alkalis between the end domains (cf. Jahns, 1982).

**Polythermal Core Experiments.** The experiments presented here add a previously unseen component to the crystallization response of the Macusani obsidian, that of repeated oscillations of mineral phases from the margins to center of melt volumes and from cold to hot ends along the lengths of melt columns. The normative compositions of the border and wall zones of MAC 244 are a near-exact replication of the same features in the Swamp dike (Figure 14), which is typical of the more complexly zoned, subhorizontal, and layered pegmatites (Norton, 1983). The comprehensive sequence of mineral assemblages in pegmatites – 11 such zones from margin to center – is also characterized by oscillations in the abundances of plagioclase, K-feldspar, and quartz that culminate in pure quartz that constitutes the pegmatite core (Table 1 of Cameron et al., 1949).

The Macusani obsidian represents a close approximation to the compositions of highly fractionated lithium-rich pegmatites, but these constitute far less than 1% of all pegmatites (Černý, 1991). Otherwise, the compositions of pegmatites lie close to the thermal minimum in the granite system, they lack exotic mineralogy, they are non-miarolitic, and they have not generated metasomatic or other contact aureoles in their host rocks. Experiments likes the ones presented here with compositions closer to the simple hydrous haplogranite minimum would be more representative of pegmatites, but reverse-direction undercooled liquidus experiments starting with solid glass cores of that composition do not crystallize in a time frame on which academic geoscientists might be willing to stake their careers. Successful and complete
crystallization experiments that employ hydrous haplogranite glass cores would likely run into
many months or years.

Experimental simulations are not the ultimate means of understanding pegmatites, merely an
addition to the body of knowledge that comes from more traditional petrologic studies of the real
things. Nonetheless, the experimental crystallization of undercooled melts derived from the
Macusani obsidian has consistently produced textural attributes, mineral zoning, and chemical
fractionation trends that are the same as those found in natural pegmatites.

Acknowledgments

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NJ, 334 p.


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Revision 1


**Figures**

Figure 1. Phase boundary diagrams of temperature versus initial H₂O added for the Spruce Pine pegmatite (in gray: Burnham and Nekvasil, 1986) and the Macusani obsidian (in black: London et al., 1989). Black arrows denote the paths of liquidus undercooling of magnitude ΔT, followed
by increasing H$_2$O content of melt upon crystallization that ensued after an initial period of nucleation delay.

Figure 2. Cooling history of MAC 244. Green line segments and squares denote temperatures measured by the thermocouple near the cold end (Read T Cold) during the run. Blue line segments and squares denote the approximate temperatures at the hot end (T Hot) based on prior calibrations with the thermocouple at the location. Red line and squares (T Set) are temperature settings on the controller.

Figure 3. Representative backscattered electron images with locations in MAC 246. Refer to the text for explanations.

Figure 4. Convergent three-component (An-Ab-Or) temperatures (solid diamonds) derived from the solvus thermometry program SOLVCAL against position within the experimental core. The average temperatures among the three components that did not converge within the assigned error in nine of the pairs analyzed are shown as gray squares. Other elements of the figure are defined in the text.

Figure 5. Calculated temperatures and solvus boundaries versus the mole fractions of the orthoclase component ($X_{Or}$) in plagioclase (Pl) and K-feldspar (Kfs) from MAC 246 for feldspars that yielded a convergent temperature using the Margules mixing model of Elkins and Grove (1991) as incorporated into SOLVCAL (Wen and Nekvasil, 1994).

Figure 6. Plots of chemical components of glass versus distance from the cold end of MAC 246. ASI = molar Al/(Na+K+Ca); $K^*$ = molar K/(K+Na). Horizontal dashed lines convey the initial concentration of each parameter in the Macusani obsidian with 5 wt.% added H$_2$O.
Figure 7. Representative backscattered electron images with locations in MAC 247. Refer to the text for explanations.

Figure 8. Plots of chemical components of glass versus distance from the cold end of MAC 247. ASI = molar Al/(Na+K+Ca); K* = molar K/(K+Na). Horizontal dashed lines convey the initial concentration of each parameter in the Macusani obsidian with 5 wt.% added H₂O.

Figure 9. Representative backscattered electron images with locations in MAC 244. Refer to the text for explanations. The ranges of temperatures reflect the initial and final temperatures at each end of the core.

Figure 10. (a) A backscattered electron image toward the end of segment 6 at the hot end of MAC 244 shows the spatial variations between K-feldspar and albite from margin to center and with location along the length of the core. (b) A phase map at the end of segment 6 of MAC 244 that was constructed from co-added single-element x-ray maps. The phases are K-feldspar (orange), albite (blue), quartz (green), mica (pink), apatite (yellow), and void (black).

Figure 11. Normative mineral variation diagrams along the length of the core for the border and wall zones of the crystallization front, both scaled to a composite BSE image of the core. The yellow line in segment 6 denotes a cross section of glass that was analyzed for Figure 13.

Figure 12. Plots of chemical attributes of the glass in MAC 244 along its length. ASI = molar Al/(Na+K+Ca); K* = molar K/(K+Na). Horizontal dashed lines convey the initial concentration of each parameter in the Macusani obsidian with 5 wt.% added H₂O.

Figure 13. Analyses of elements across glass of segment 6 of MAC 244, starting near a margin dominated by K-feldspar and ending at the opposite margin that lacked crystallization. Refer to the yellow line in Figure 10.
Figure 14. Modal analysis by visual (1 square cm grid size) and microscopic point count (in aplite) across a complete dike cross section at the Little Three mine, Ramona, California, from London et al. (2012). Oscillations of mineral assemblages in the layered aplite are at a finer scale than the smoothed modal curves. Dark layers of aplite are mostly K-feldspar and tourmaline, light layers are plagioclase plus quartz.

Figure 15. (a) Crystallization upward across a vertical section perpendicular to the contact of the footwall half of the Phantom dike, Little Three mine, Ramona, California (Figure 17-7 of London, 2008). The faint dark blue horizontal bands across the feldspars are phantom layers of fine-grained tourmaline that were deposited along the crystallization front. The texture of graphic granite (quartz-feldspar skeletal intergrowth) coarsened upward and separated into monophase domains at the top. (b) A cross section parallel to the contact across the same dike illustrates the fine-textured scale of the quartz intergrowth in Manebach twins of K-feldspar.

Tables

Table 1. Compositions of the Macusani Obsidian and the Tanco Pegmatite, Canada

Table 2. Initial Experimental Conditions

Table 3. Gibbs Free Energy Change at 500°C, 200 MPa, for crystallization from melt
Spruce Pine pegmatite, $P = 500$ MPa from Burnham and Nekvasil (1986)

Macusani obsidian, $P = 200$ MPa from London et al. (1989)

Figure 1
Figure 2

MAC 244 furnace gradients

- Set T
- T Hot
- Read T Cold

Temperature (°C) vs. Time (hrs)
Figure 4
Figure 5

MAC246

Calculated equilibration temperature, °C

$X_{Or}$ in plagioclase and K-feldspar
Figure 6b

Chemical parameter

Distance from cold end, mm

460°C 610°C

F apfu/8O

B apfu/8O

P apfu/8O

Rb/K
Figure 7

4 cm

3 cm

2 cm

1 cm

0 cm

585°C

410°C

(a) K-feldspar

wall

quartz

albite

mica

glass

(b) quartz + mica

(c) glass petalite

(d) glass

(e) albite “glass”

500 μm

100 μm

200 μm
Figure 8b: Graph showing the chemical parameter trends for MAC247 at different temperatures (410°C and 585°C) with distance from the cold end (mm). The chemical parameters include F apfu/8 O, B apfu/8 O, and P apfu/8 O.
Figure 10
MAC 244

Si afpu/8 O

~ 10 vol.% crystalline

ASI

Al afpu/8 O

K* and K afpu/8 O

Chemical parameter

Distance from cold end, mm
Figure 12b

Distance from cold end, mm

Element apfu/8 O

MAC 244

F

B

P
Figure 13

Distance from edge, mm
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<th>Tanco</th>
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<td>SiO₂</td>
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1 London et al. (1988)
2 Stilling et al. (2006)
3 mol K(K+Na)
4 mol Al/(Li + Na + K + Rb + Cs + 2Ca)
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<tr>
<th></th>
<th>H₂O wt.%</th>
<th>Cold °C</th>
<th>ΔT&lt;sub&gt;Cold&lt;/sub&gt; °C</th>
<th>Hot °C</th>
<th>ΔT&lt;sub&gt;Hot&lt;/sub&gt; °C</th>
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<td>585</td>
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<td>750</td>
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Table 3. Gibbs Free Energy Change at 500°C, 200 MPa, for crystallization from melt

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1 from equations in Table 1 and 2 of Burnham and Nekvasil (1986)