

Article

Quantification of Feldspar and Quartz Nucleation Delay in a Hydrous Peraluminous Granitic Melt

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Abstract: A modified model based on classical nucleation theory was applied to a natural hydrous peraluminous pegmatite composition and tested against crystallization experiments in order to further investigate the quantification of nucleation delay in felsic melts. Crystallization experiments were performed in a piston-cylinder apparatus at 630 MPa and temperatures between 650 and 1000 °C for durations ranging from 0.3 to 211 h. Experimental run products were investigated by scanning electron microscopy paired with energy dispersive spectroscopy analyses of both crystalline and quenched liquid phases, the results of which were compared to an established theoretical nucleation delay model from the literature. The experiments showed good agreement (within a factor of 5) with the model for quartz, while it showed moderate agreement (within a factor of 10) with the model for sodic feldspar. Other crystals also nucleated, demonstrating abundant features of disequilibrium. Our research further demonstrates the potential of the model to predict nucleation delay, showing promising results for the quantification of the nucleation delay of quartz and feldspar in natural felsic melts, thus adding to previously published studies on hydrous, metaluminous, felsic melts and dry basaltic melts.

Keywords: crystallization kinetics; nucleation delay; quartz crystallization; feldspar crystallization; peraluminous granite; pegmatite; mullite stability; corundum stability



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1. Introduction

Nucleation is a key process in crystallization as it is the first step of crystal growth. Nucleation is defined as the formation of a nanoscopic, thermodynamically stable product phase, called the nucleus, resulting from the rearrangement of atoms (or molecules) initially present in a reactant phase (e.g., [1,2]). This first-order phase transition theoretically occurs once a specific set of pressure, temperature, and composition conditions are reached, but in nature, that is not always the case. The rearrangement of atoms triggering a phase transition is a process arising from fluctuations in density, composition, and concentration randomly occurring within the initial phase [1,3], and therefore, stable nuclei do not form as soon as a new phase is thermodynamically stable in the melt. Indeed, there is a delay before nucleation starts and the steady state rates of the new phase's growth are reached.

Nucleation has important impacts on rock textures, fabrics, and mineral shapes and can also explain how magmas of similar compositions can generate rocks with very different textures and mineral assemblages when crystallized at the same pressure and temperature (e.g., [4]). An extreme example of the effect of delayed nucleation would be the contrast between rhyolitic obsidian flows, which are glassy, and granitic pegmatites emplaced in the shallow crust, which can display meter-scaled crystals, even though both rock types may have had similar cooling time scales [5]. The crystallization of quartz and feldspar from peraluminous felsic melts and, more precisely, the nucleation delay prior to the crystallization of these phases is investigated in this study.

The concept of nucleation delay has been known since the beginning of the last century, which also coincides with the beginning of experimental petrology when Bowen [6,7]

described plagioclase crystals forming well below their liquidus temperatures. In the last 50 years, multiple attempts have been made to improve our understanding of crystallization in felsic melts through dynamic crystallization experiments [5,8–18]. However, many of these studies used simplified granitic melts as opposed to natural compositions [8,16,19–21], which may limit their application to natural rocks.

There is a lack of quantifiable nucleation delay measurements on natural granitic compositions and, more precisely, on common peraluminous granitic compositions. This contribution investigates nucleation delay in a peraluminous granitic melt composition to complement Rusiecka et al. [5], who performed quartz and feldspar nucleation delay experiments on a hydrous, metaluminous granitic composition and applied a modified Classical Nucleation Theory (CNT) model based on Fokin et al. [2]. We apply Rusiecka et al.'s [5] experimental and theoretical methodology to quartz and feldspar nucleation in a supercooled, natural, hydrous, peraluminous pegmatitic melt, comparing and evaluating the efficacy of the same theoretical model. The goal of this study was not to reproduce the natural mineralogy of the selected peraluminous composition and, therefore, the discussion of the natural rock was deemed out of the scope of this research and was kept to a minimum. As stated, most previous studies used haplogranite compositions to investigate the nucleation of feldspar and quartz, but we are interested in how nucleation delay functions in a natural composition to further investigate how the addition of other cations into granitic melts affects their kinetic properties (cf., [10,19,22]). Studying nucleation delay in peraluminous melts, similar in composition to most common pegmatites [23], is of particular importance because, in addition to the degree of undercooling, this parameter plays a key role in the formation of diagnostic pegmatite textures [24]. This paper reports on kinetic experiments on the nucleation of quartz and feldspar, the dominant minerals in peraluminous granitic pegmatites, and tests if the CNT model is able to accurately describe and predict nucleation delays over a range of felsic melt compositions. This research on nucleation delay improves our understanding of granitic systems, providing quantitative and qualitative models that describe the magmatic timescales and crystallization mechanisms responsible for their formation. Furthermore, additional knowledge of nucleation delay can also help constrain the timescales of magma ascent rates and volcanic eruptions [25].

2. Materials and Methods

2.1. Experimental Methods

The aim of this study was to investigate the nucleation delay of quartz and feldspar in a peraluminous granitic melt by studying the crystallization sequence of a natural pegmatite composition (MM45B) with an alumina saturation index (ASI) of 1.45 from Mt. Mica, Oxford County, ME, USA [26], at water-undersaturated conditions. Due to the heterogeneity of the Mt. Mica pegmatite, it was not possible to obtain a representative composition of the entire pegmatitic body from traditional whole rock analyses. Simmons et al. [26] obtained the representative bulk chemical composition by combining thorough mapping of the Mt. Mica pegmatite to estimate volumes of pegmatites and lepidolite pods with ICP-OES, ICP-MS and DCP analyses of 45 drill cores to obtain the major and minor element concentrations of the pegmatite (Table 1).

The MM45B glass powder used in the crystallization experiments was synthesized by melting rock powder in air at 1575 °C for 5 h in a 1 atm furnace and then grinding under ethanol, resulting in a crystal-free glass. Gold palladium (Au₇₅Pd₂₅) capsules of 2 mm diameter and 8 mm length were loaded with MM45B glass and 3.3 ± 0.1 wt% water. The capsules were welded in a water bath to prevent water loss. The capsules were then weighed and heated for at least an hour in an oven at 110 °C and weighed again to verify the absence of leaks.

Table 1. Composition of the 9 major element oxides in natural rock Mt Mica MM45B (normalized to a P-, Li- and LOI-free total of 100%) from Simmons et al. [26] and our EDS analyses of the quenched glass made from MM45B rock powder melted at 1575 °C, 1 atm., for 5 h followed by melting at 1070 °C, 630 MPa, for 96 h. The standard deviation was calculated by the EDS software (Oxford Aztec v. 3.3) and was based on seven analyses.

Oxide	wt% (Simmons et al., 2016)	Glass Mean wt% (EDS Analyses)	Standard Deviation on EDS Analyses
SiO ₂	72.99	73.61	0.17
TiO ₂	0.07	0.00	0.00
Al ₂ O ₃	17.55	17.41	0.22
FeO ^T *	1.22	1.06	0.06
MnO	0.04	0.26	0.02
MgO	0.16	0.13	0.04
CaO	0.48	0.50	0.02
Na ₂ O	5.42	5.03	0.11
K ₂ O	2.10	2.00	0.05

* Total iron as FeO.

All experiments were performed in a piston-cylinder apparatus. The assembly was composed of crushible alumina pieces inside a graphite furnace, which was surrounded by a Pyrex sleeve, NaCl cylinders (salt cells) and a lead sheet [27]. Repeat experiments were performed at every run condition by placing two or three identical capsules into drilled holes in the same assembly. To minimize water loss and empty space between the alumina and the capsules, the holes were filled with aluminum hydroxide powder. Temperatures were recorded using a tungsten rhenium (type C) thermocouple inserted in the middle of the assembly.

Melting experiments using the natural MM45B rock powder + 3.3 wt% water were used to constrain the melting temperatures of each crystalline phase found in the experiments for comparison with the crystallization experiments. Melting experiments were pressurized and simultaneously heated directly to the experimental temperature at a rate of 100 °C/minute. These experiments were performed at temperatures from 850 to 1070 °C, 630 MPa, for durations between 96 and 115 h. After isobaric quenching, the experimental run products were analyzed. These experiments (discussed in more detail in the Results section below) demonstrated that the liquidus of the bulk rock was below 1070 °C at the studied conditions.

Crystallization experiments using the MM45B glass + 3.3 wt% water as starting materials were performed by heating the sample above the liquidus temperature to 1100 °C at a rate of 100 °C/minute while simultaneously increasing the pressure to 630 MPa. These pressure and temperature conditions were maintained for 24 h to homogenize the melt composition. The homogenization temperature was chosen to be above the liquidus temperature to ensure the absence of crystals when starting the nucleation experiments. After this 24 h homogenization step, the capsules were cooled at a rate of 30 °C/minute to the desired crystallization temperature, which varied between 650 and 1000 °C, and remained at the chosen temperature for 0.5 to 211 h. All experiments were then isobarically quenched and analyzed.

2.2. Analytical Methods

Melting experiments MB43, 45 and 33 were only analyzed under a petrographic microscope in oil immersion mounts to investigate the presence or absence of crystals in the run products. The other melting experiments (MB72, 74, 127, 129, and 131) were mounted in epoxy and analyzed on a scanning electron microscope—following the same

methodology used for the crystallization experiments—as described in the subsequent paragraph.

After each experiment, the unopened capsules for the crystallization experiments were immersed in epoxy, ground, and polished. They were analyzed using a Hitachi SU5000 scanning electron microscope (SEM) at McGill University with an accelerating voltage of either 10 or 15 kV to obtain backscattered-electron (BSE) images in order to characterize the run products formed in the experiments. Qualitative and quantitative analyses were performed using an Oxford Instruments SDD energy dispersive spectroscopy (EDS) detector (Oxford Instruments, Abingdon, UK) coupled with Aztec software (v. 3.3). The EDS analyses of the quenched glass produced in experiments above the liquidus temperature agree with the published composition of the MM45B glass, demonstrating the accuracy of this method of analysis (Table 1).

The analysis of crystalline phases in the experiments was hampered by the small size of most crystals, resulting in analyses of more than a single phase and making some determinations of the crystal's identity difficult. Attempts to use X-ray diffraction for supplemental crystal identification failed.

Measurements, annotations, and image alterations (only increasing contrast and brightness) of the backscattered electron images (BSE) were performed using ImageJ software (v. 1.54j) [28,29].

The water concentrations in glasses quenched from a few experiments were determined by Raman spectroscopy following the method of Behrens et al. [30] and Fortin et al. [31]. Raman spectra were collected at McGill University using a Renishaw InVia confocal micro-Raman spectrometer (Renishaw, Wotton-under-Edge, UK) with a 532 nm laser and 100× Leica microscope objective (Leica Microsystems, Wetzlar, Germany). The power was set to 10% (50 mW), and a 2400 L/mm grating system with a 50 µm slit was used. The spectra were recorded using Wire 4.2 software. The acquisition time was set to 40 s and repeated 5 times. The spectra were quantified using a set of hydrous rhyolitic glass standards [31].

3. Results

3.1. Melting Experiments

The EDS analysis of experiments using the ground MM45B rock powder (Table 2) demonstrated that melt (glass), plagioclase, quartz, an aluminum silicate that we identify as mullite, and corundum were present in the run products at 630 MPa and temperatures up to 900 °C.

Table 2. Melting experiments run table with results at 630 MPa for the MM45B rock. Total water represents the amount of water added to the rock powder and the water content initially present in MM45B, 0.94 wt%. Mul: Mullite, Crn: corundum, Gl: glass, Qz: quartz, Pl: plagioclase, crystals discussed in text.

Expt.	Final T (°C)	Time (h)	Total H ₂ O (wt%)	Phases	Total % Crystals
MB43	1070	96	4.3	Gl *	0
MB45	1040	96	3.7	Gl,crystals (Mul?,Crn?) *	trace
MB33	1015	96	3.8	Gl,crystals (Mul?,Crn?) *	trace
MB72	1000	110	4.2	Gl,Mul,Crn	20
MB131	950	94	4.3	Gl,Mul,Crn,Qz (stable?)	
MB129	900	115	4.3	Gl,Mul,Crn,Qz,Pl	
MB127	900	115	4.3	Gl,Mul,Crn,Qz,Pl	
MB74	850	115	3.6	Gl,Mul,Crn,Qz,Pl	80

* These experiments were not analyzed on the SEM but only in oil immersion mounts under a petrographic microscope. The minerals seen under the petrographic microscope are presumed to be the same as in the experiments at the temperatures below these experiments.

At 950 °C, mullite and corundum appeared stable, plagioclase was not present, and the small amounts of quartz observed in the run products appeared to be fragments of crushed crystals from the rock powder. We infer from the habit of the quartz crystals that they may be residual and not part of the equilibrium assemblage at 950 °C. At temperatures from 1000 to 1040 °C, melt, mullite, and corundum were present, and at 1070 °C, all crystalline phases had melted. Mullite and corundum in the 1000 °C experiment display, respectively, prismatic lath-like and anhedral rounded and elongated habits of similar length. Both mullite and corundum occurred homogeneously in the melt, but large clusters mainly composed of mullite seem to follow the outline of larger (at least one order of magnitude larger) remnant crystals (Figure 1).

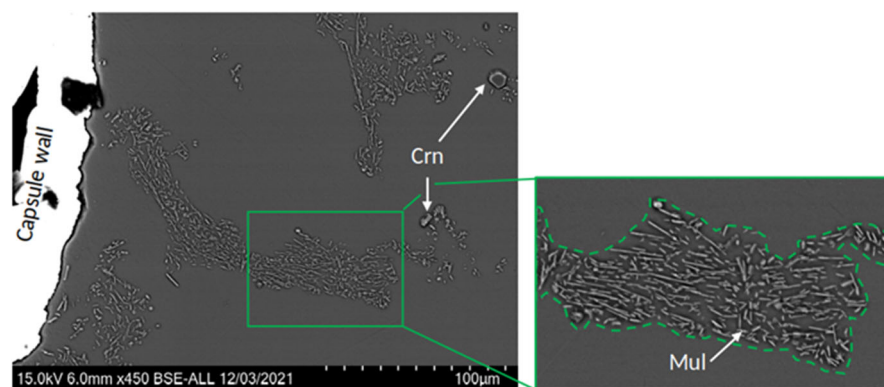


Figure 1. Backscattered electron images of the melting experimental run products, with the contrast and brightness adjusted in ImageJ; 1000 °C, 630 MPa, 110 h; Mullite (Mul) and corundum (Crn) crystals nucleating homogeneously; close-up of mullite occurring in a cluster and following the outline of a remnant larger-scaled crystal fragment.

3.2. Nucleation Delay Results

Crystallization experiments were performed at 1000, 900, 850, 800, 750, and 650 °C at 630 MPa for durations ranging between 0.3 and 211 h (Table 3). Images of the mineral phases and textures produced in the crystallization experiments are presented in Figures 2–6. Experimental conditions, total H₂O in the capsules, phases present, and percent crystallization are summarized in Table 3.

Table 3. Crystallization experimental conditions and the phases produced at 630 MPa following melting of the MM45B glass starting material at 1100 °C for 24 h; Ox: iron-oxide, Mul: Mullite, Crn: corundum, Gl: glass, Qz: quartz, Pl: plagioclase, dPrI: dehydroxylated pyrophyllite that formed halos around corundum, and UnkP: unknown phase interpreted as petalite.

Expt.	Final T (°C)	ΔT (°C)	Duration (h)	H ₂ O (wt%)	Phases	Percent Crystallized
MB52	1000	−55	6	3.3	Gl	0
MB53	1000	−55	6	3.2	Gl	0
MB58	1000	−55	44	3.3	Gl,Mul,Crn,ox	2
MB60	1000	−55	44	3.2	Gl,Mul,Crn,ox	2
MB67	900	−155	0.5	3.3	Gl,Mul,Crn	2
MB68	900	−155	0.5	3.2	Gl,Mul,Crn	2
MB61	900	−155	5	3.2	Gl,Mul	4
MB62	900	−155	5	3.3	Gl,Mul	4
MB64	900	−155	29	3.3	Gl,Mul,Crn *	2
MB69	900	−155	211	3.3	Gl,Mul,Crn	<1
MB70	900	−155	211	3.3	Gl,Mul,Crn	<1
MB105	850	−205	5	3.3	Gl,Mul,Crn,ox,dPrI	3
MB106	850	−205	5	3.3	Gl,Mul,Crn,ox,dPrI	2

Table 3. Cont.

Expt.	Final T (°C)	ΔT (°C)	Duration (h)	H ₂ O (wt%)	Phases	Percent Crystallized
MB80	850	−205	115	3.3	Gl,Mul,Crn,ox,dPrI,Qz	3
MB81	850	−205	115	3.3	Gl,Mul,Crn,ox,dPrI,Qz	2~1
MB114	800	−255	0.3	3.3	Gl,Crn,ox	2
MB115	800	−255	0.3	3.3	Gl,Crn,ox,dPrI (only 1)	2
MB118	800	−255	4	3.3	Gl,Mul,Crn,ox,dPrI	4
MB119	800	−255	4	3.3	Gl,Mul,Crn,ox,dPrI	6
MB87	800	−255	115	3.3	Gl,Mul,Crn,ox,dPrI,Qz,Pl	25
MB88	800	−255	115	3.3	Gl,Mul,Crn,ox,dPrI,Qz,Pl	25
MB110	800	−255	120	3.3	Gl,Mul,Crn,ox,dPrI,Qz,Pl	35
MB111	800	−255	120	3.3	Gl,Mul,Crn,ox,dPrI,Qz,Pl	35
MB94	750	−305	2	3.3	Gl,Mul,Crn,	5
MB95	750	−305	2	3.3	Gl,Mul	5
MB89	750	−305	5	3.3	Gl,Mul	2
MB90	750	−305	5	3.3	Gl,Mul	2
MB91	750	−305	28	3.3	Gl,Mul,cr,ox,dPrI,Qz,UnkP	15
MB92	750	−305	28	3.3	Gl,Mul,Crn,ox,dPrI,Qz,UnkP	15
MB120	650	−405	115	3.3	Gl,Mul,Crn,ox,dPrI,Qz,Pl,UnkP	34
MB123	650	−405	115	3.3	Gl,Mul,Crn,ox,dPrI,Qz,Pl,UnkP	28

* Duplicate experiment failed.

Glass (melt), mullite, corundum, iron oxides, quartz, feldspar, what we interpret to be dehydroxylated pyrophyllite, and an unknown phase believed to possibly be petalite (Table 4, discussed below) were present in the crystallization run products. All experiments are dominated by glass (quenched melt), with the highest degree of crystallinity (35%) achieved at 800 °C. These crystals were identified by semi-quantitative EDS spectra; because of the small size of the crystals in the run products, analytical points were frequently composed of crystals and glass, and the apparent stoichiometry of the crystals differed from their ideal composition (Table 4).

Table 4. Representative mean phase compositions in crystallization experiments normalized to 100.

Oxide (wt %)	Mullite n = 7 ¹	Corundum n = 10	Quartz n = 12	Feldspar 800 °C n = 4	Feldspar 650 °C n = 1	Glass n = 35	Dehydroxylated Pyrophyllite (Halos) n = 5	Unknown Phase Petalite? n = 5
SiO ₂	28.46 (1.19) ²	2.38 (1.16)	97.01 (1.54)	66.95 (1.14)	70.54	75.9 (0.8)	68.65 (1.04)	82.11 (0.55)
Al ₂ O ₃	68.58 (3.86)	96.82 (1.63)	2.40 (1.27)	20.95 (0.64)	16.07	16.5 (0.6)	30.36 (2.19)	16.18 (0.97)
Fe ₂ O ₃	2.80 (3.63)	0.77 (0.80)	0.13 (0.11)	0	0	0.94 (0.21)	0.80 (1.60)	1.33 (0.29)
CaO	0.00	0.01 (0.03)	0.04 (0.06)	1.41 (0.24)	0	0.52 (0.06)	0.00	0
Na ₂ O	0.16 (0.28)	0.01 (0.03)	0.28 (0.22)	9.86 (0.56)	13.39	4.21 (0.40)	0.38 (0.47)	0.27 (0.41)
K ₂ O	0.00	0.01 (0.02)	0.13 (0.02)	0.82 (0.30)	0	1.98 (0.12)	0.00 (0.00)	0
Cations								
Si	2.039	0.040	0.976	2.934	3.093		3.928	4.010
Al	5.790	1.936	0.028	1.082	0.830		2.047	0.931
Fe	0.153	0.010	0.001	0.000	0.000			0.049
Ca	0.000	0.000	0.000	0.066	0.000		0.034	0.000
Na	0.011	0.000	0.005	0.838	1.138		0	0.013
K	0.000	0.000	0.002	0.046	0.000		0.043	0.000
Li (assumed)							1	1.000
Sum cations	7.994	1.987	1.013	4.967	5.061		6.052	6.004
No. Oxygens	13	3	2	8	8		11	10.000

¹ n is the number of analyses used for calculation of the mean and standard deviation. ² mean concentration is followed by the standard deviation in parentheses for each oxide.

For example, some of the quartz crystals analyzed by EDS were pure SiO_2 , whereas others appeared to contain minor amounts of Na and Al. Unfortunately, the latter crystals were small, and we could not be certain that we were only analyzing the quartz crystal and not a mixture of melt and crystal. However, in most cases, one or two of the analyses of each type of crystal used to compile the mean compositions in Table 4 were stoichiometric (see Supplemental Materials Table S1). The major-element-oxide melt composition is homogeneous within each run product, even in the vicinity of crystals, and inter-experimental variability in the melt composition is so small, often below analytical uncertainty, that the mean of melt analyses from multiple experiments is presented in Table 4. Raman analyses of water concentration showed significant variability in the run products analyzed, and in a single experiment, it could vary from less than 1 wt% up to 7 wt%. The variability is attributed to the difficulty in avoiding crystals during Raman analysis and the disequilibrium nature of the nucleation experiments. Because of these difficulties, we used Raman spectroscopy in only a few experiments to verify that water was present in the quenched glasses. Except for a few rare occasions, the duplicate capsules from the same experiment contained the identical phase assemblage (see Table 3) and only slightly varied in total percent crystallization and modal abundance of each phase.

Corundum, quartz, and feldspar were easily identifiable by their EDS spectra, even when small amounts of glass were included in the analytical spots. The identification of mullite was more challenging because its composition is similar to sillimanite—the common, stable aluminum silicate that is expected at the pressure and temperatures of the experiments [32] in natural granitic compositions. However, the stoichiometry of this crystalline phase in the experiments (Table 4) was more consistent with mullite than sillimanite. Furthermore, mullite has been seen previously in high pressure experiments on the melting of aluminous felsic compositions [33–36].

The crystalline phase we label as dehydroxylated pyrophyllite was identified by its atomic ratio of Si/Al, 3.928/2.047 (Table 4), which is close to the pyrophyllite and dehydroxylated pyrophyllite ideal Si/Al ratio of 4/2, and because our best analyses of this phase indicated that its major element composition was composed of only Si, Al, and O. The identification as dehydroxylated pyrophyllite is based upon the better cation stoichiometry when 11 oxygen atoms are used in the formula (cation sum = 6.052, Table 4), as in dehydroxylated pyrophyllite [37]. We were unable to obtain a Raman spectrum of this individual phase but did obtain a spectrum (from ~ 50 to 1300 cm^{-1}) that is interpreted to represent a mixture of quartz, pyrophyllite (or dehydroxylated pyrophyllite) and glass. A second spectrum (from ~ 3400 to 4100 cm^{-1}) at the same spot that spanned the $\sim 3675\text{ cm}^{-1}$ location of the hydroxyl peak in pyrophyllite [38] only displayed the broad peaks seen in hydrous glasses. The lack of a sharp peak is, however, not diagnostic evidence of dehydroxylated pyrophyllite because the previous analysis on the same spot might have damaged the sample. We refer to this phase in subsequent paragraphs as dehydroxylated pyrophyllite but recognize the possibility that it may be pyrophyllite or another mineral. Most of the lower-temperature, longer duration experiments contained radial aggregates of dehydroxylated pyrophyllite (Table 4) surrounding corundum (denoted as “halos” in this work), whose texture implies a reaction relationship between corundum and the melt. Dehydroxylated pyrophyllite was also found as individual crystals in some experiments.

At $1000\text{ }^\circ\text{C}$, no crystals were detected after 6 h. After 44 h, iron oxide, mullite, and corundum (Table 4) crystals nucleated (Figure 2a). The mullite crystals were euhedral, displaying rhombic habits (Figure 2a). Corundum mostly displayed highly anhedral habits (Figure 2a), except in some instances where corundum crystallized as small needles (between 3 and $103\text{ }\mu\text{m}$ in length) and possibly fibrous crystals. These aluminum-rich fibrous crystals are similar in habit to the abundant mullite needles in the experiments described by Holtz et al. [33]. Both corundum and mullite preferentially nucleated near the capsule walls; the centre of the capsule was almost free of any crystals. Iron oxide crystals were subhedral and nucleated both homogeneously and heterogeneously, with

larger crystals ($\sim 5\text{ }\mu\text{m}$) mainly nucleating with corundum and mullite, while smaller crystals ($<0.5\text{ }\mu\text{m}$) nucleated homogeneously in other regions of the capsule.

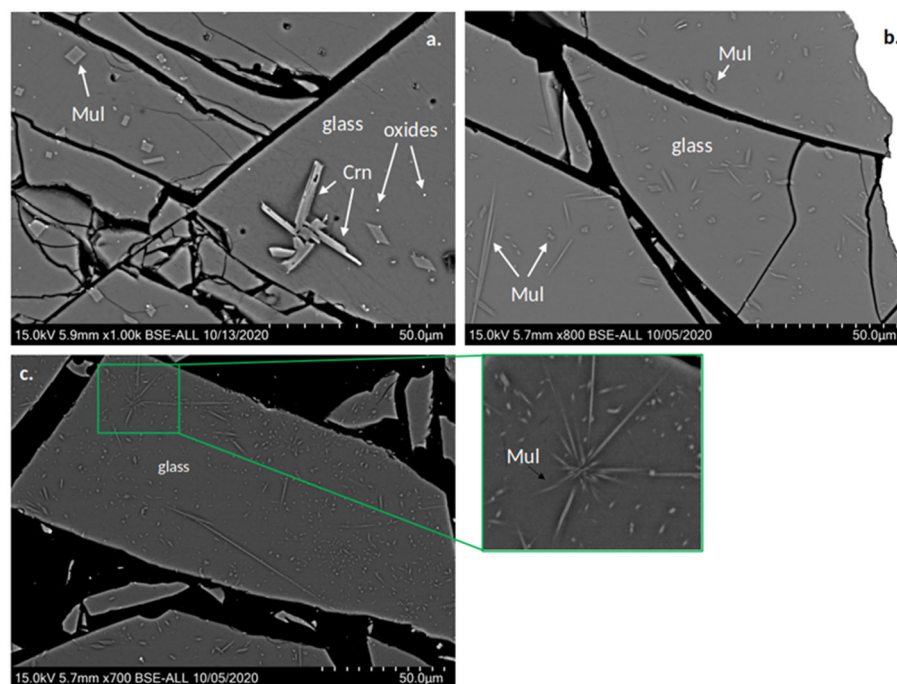


Figure 2. Backscattered electron images of the crystallization experimental run products with enhanced contrast and brightness: (a) 1000 °C, 630 MPa, 44 h; mullite and corundum crystals displaying rhombic and anhedral habits, respectively. Small oxides nucleated both homogeneously and heterogeneously with mullite and corundum crystals. Most of the capsule is occupied by the remaining melt, which becomes glass after being quenched. (b) 900 °C, 630 MPa, 5 h; mullite crystals randomly nucleating homogeneously in the entire capsule. (c) 900 °C, 630 MPa, 5 h; mullite crystals randomly nucleating homogeneously in the entire capsule; close-up of a radial aggregate of mullite crystals.

At 900 °C, after 0.5 h, both mullite and corundum crystals were present in the experiment, displaying the same habit as crystals present at 1000 °C (Figure 2b,c). In the 5-h experiment, only mullite crystals were found. They had rhombic habits with variable grain sizes (between 0.3 and 61 μm , Figure 2b). Mullite nucleated homogeneously everywhere in the capsules, but the degree of crystallinity varied randomly along the length of the capsule. Radial, crystalline aggregates were found in regions with higher crystallinity (Figure 2c), whereas in other regions, mullite crystals were randomly arranged (Figure 2b). In the 29-h experiment at 900 °C, mullite and corundum nucleated. Most crystals nucleated near the capsule walls, while the centre of the capsule was nearly free of crystals. Mullite crystals varied in size (between 1 and 54 μm), had rhombic habits, and some crystals were hollow. All corundum crystals are euhedral and have an acicular habit, unlike the corundum crystals produced at 1000 °C. The majority of crystals appear to have grown parallel to the walls of the capsules, most notably the corundum crystals. The 211 h-long experiment displayed the same mineralogy and texture as the 29-h experiment.

At 850 °C, after 5 h, mullite and corundum both nucleated homogeneously. Mullite crystals have rhombic habits (Figure 3a). The corundum crystals are most commonly anhedral, but some show elongated or rounded habits; the elongated crystals vary in size between 2 and 33 μm and the rounded crystals between 9 and 26 μm (Figure 3a). The corundum crystals are also systematically surrounded by halos of smaller crystals of dehydroxylated pyrophyllite that are richer in silicon and poorer in aluminum than the corundum crystals at the centres of the halos (Figure 3a,b). Oxides nucleated at the edge of the corundum and are also, when present, enclosed in the halos.

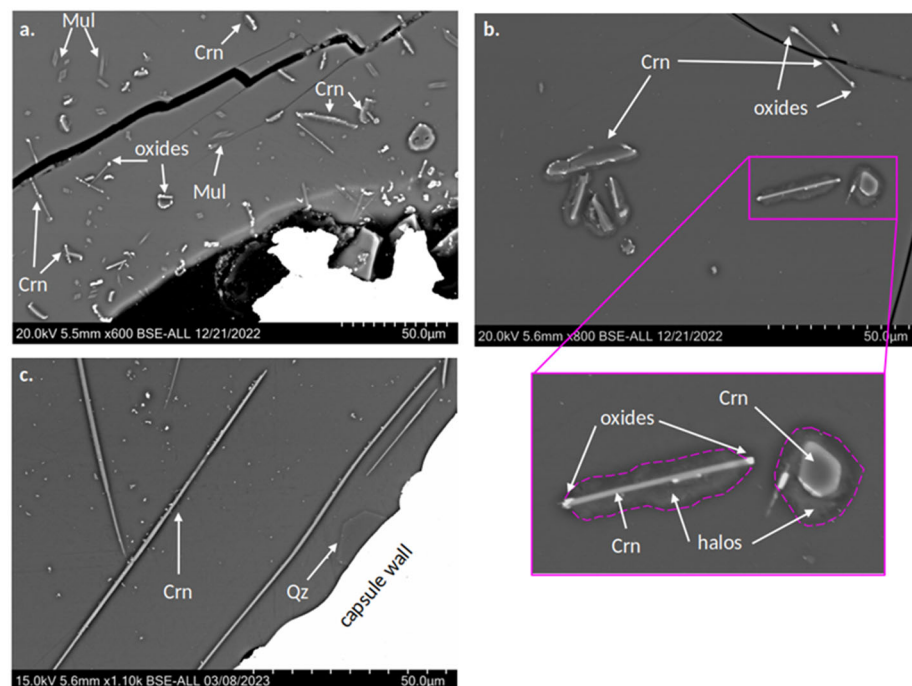


Figure 3. Backscattered electron images of the crystallization experimental run products with enhanced contrast and brightness: (a) 850 °C, 630 MPa, 5 h; mullite crystals displaying rhombic habits and corundum crystals displaying anhedral, elongated or rounded habits. Iron oxides nucleated heterogeneously at the edge of the corundum crystals. (b) 850 °C, 630 MPa, 5 h; close-up of the halos surrounding corundum crystals and iron oxides. (c) 850 °C, 630 MPa, 115 h; long acicular corundum crystals nucleating parallel to the capsule wall and euhedral quartz (Qz) crystals nucleating on the capsule wall.

In the 850 °C, 115-h experiment, rhombic mullite crystals, which are sometimes hollow, nucleated. They are an order of magnitude larger than mullite that crystallized at higher temperatures. Long acicular corundum crystals (between 23 and 103 µm) are also present and appear to mainly have nucleated parallel to the capsule walls (Figure 3c). A few dehydroxylated pyrophyllite crystals were found, but they did not form halos around corundum. Corundum crystals mainly nucleated in the vicinity of the capsule walls (Figure 3c), while mullite nucleated homogeneously everywhere in the capsule. Quartz nucleated heterogeneously on the capsule wall, often as euhedral crystals (Figure 3c). In other instances, quartz crystals have rounded irregular habits and completely enclose small needle-like crystals, creating a texture similar to fibrolite. Due to the small size of the needles, it was not possible to obtain EDS analyses without analyzing the glass or the surrounding quartz, but based on qualitative analysis of elemental EDS maps, these needles appear to only be composed of Al_2O_3 and are most probably corundum crystals. Iron oxides were present in all experiments performed at 850 °C. No feldspar was found in any experiments at 850 °C.

At 800 °C, after 0.3 h, anhedral crystals of corundum and oxides are present. Corundum crystals nucleated homogeneously in the melt, and oxides nucleated both heterogeneously on the capsule walls and on corundum crystals and homogeneously in the melt. One of the two experiments at 800 °C, 0.3 h, had halos around the corundum. In the 4-h experiment, mullite, corundum, and oxide crystals nucleated homogeneously. Mullite crystals occurred mainly as acicular or hollowed rhombic crystals, while corundum crystals had anhedral elongated habits and were surrounded by halos. In some cases, multiple corundum crystals are clustered inside a single halo that encapsulates all of them.

The 800 °C, 115-h, experiment contained mullite and corundum crystals that nucleated homogeneously. Corundum crystals were mainly elongated or rounded, and the oxides systematically nucleated at the edges of the crystals. Similar to the 4-h experiment, clusters

of corundum also occurred inside halos. Mullite crystals were present as rhombic and acicular crystals. Rounded and irregular quartz nucleated heterogeneously with mullite and corundum crystals and on the capsule walls (Figure 4). Large skeletal feldspar spherulites also formed heterogeneously on the capsule walls (identified as “spherulite” in Figure 4a).

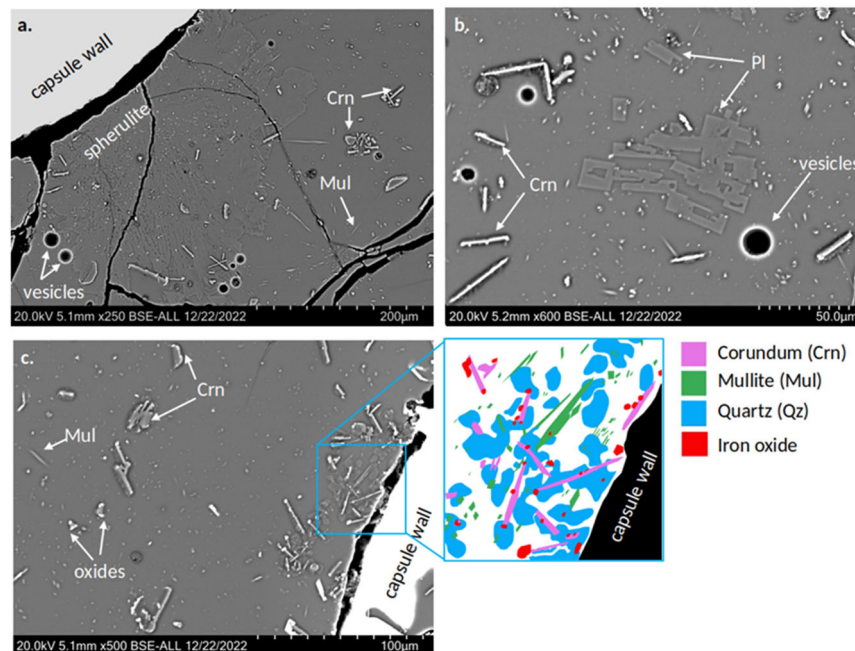


Figure 4. Backscattered electron images of the crystallization experimental run products, with the contrast and brightness, increased in ImageJ: (a) 800 °C, 630 MPa, 120 h; Skeletal spherulite of plagioclase surrounded by epoxy-filled vesicles; the crack between the spherulite and the capsule wall (black region) formed during quenching or sample preparation for analysis. Mullite crystals occur as radial aggregates. (b) 800 °C, 630 MPa, 120 h; isolated skeletal crystal of plagioclase (Pl) surrounded by epoxy-filled vesicles. Elongated anhedral corundum crystals are surrounded by halos previously described. (c) 800 °C, 630 MPa, 120 h; close-up showing the order of crystallization of the crystalline phases, with rounded irregular quartz enclosing corundum, mullite and iron oxides.

The feldspar in the spherulites reached sizes up to 600 μm . Most spherulites nucleated heterogeneously on the capsule wall, but there are also instances where smaller spherulites nucleated homogeneously. These isolated spherulites were one order of magnitude smaller than the spherulites that nucleated on the capsule wall. All spherulites were highly skeletal and contained melt inclusions. The average feldspar composition was $\text{Ab}_{88}\text{An}_7\text{Or}_5$. The relatively high An concentration suggests that these are plagioclase crystals (Table 4). Mullite and corundum crystallized before quartz and feldspar, as indicated by the latter minerals enclosing the former (Figure 4c). It is, however, not possible to determine the relative order of crystallization of quartz and feldspar because they are never in direct contact with one another. In the 120-h experiment, the same phases are present as in the 115-h experiment. However, acicular crystals of mullite are arranged in radial aggregates, corundum crystals are enclosed by halos, and the feldspar spherulites are present in higher modal abundance and form more regular rims. The feldspar spherulites mainly nucleate heterogeneously on the capsule wall, but a few smaller spherulites also nucleate homogeneously (Figure 4b). Vesicles are present in the vicinity of isolated plagioclase crystals and spherulites (Figure 4a,b). The vesicles do not perfectly follow the edges of crystals; some occur directly on the crystal, whereas others are found further away in the melt. The quantity of vesicles also seems to increase with the size and the quantity of spherulites present, with 2–3 vesicles around isolated crystals of 50 μm and approximately 30 around large 700 μm spherulites. These vesicles were only observed in the 120-h experiment, and they are similar to those described in previous studies (e.g., [5,16,39]).

At 750 °C, 2 h, the two capsules are not consistent; one crystallizes only mullite and the other, mullite and corundum. In both capsules, mullite is rhombic and nucleated homogeneously and randomly in the capsule. Corundum crystals also nucleated homogeneously, and the crystals are anhedral and elongated. In the 5-h experiment at 750 °C, only mullite nucleated, and most crystals displayed a subhedral rhombic habit; a few bladed mullite crystals were also present. After 28 h (Figure 5), mullite, corundum, quartz and iron oxides were present, displaying the same morphology as at 800 °C for 120 h (Figure 5b,c). Moreover, the fibrous corundum seen in the 850 °C, 115-h experiment was also present, enclosed by irregular, rounded quartz crystals (Figure 5c); dehydroxylated pyrophyllite and iron oxides were present after 28 h. No feldspar was found in any experiments at 750 °C.

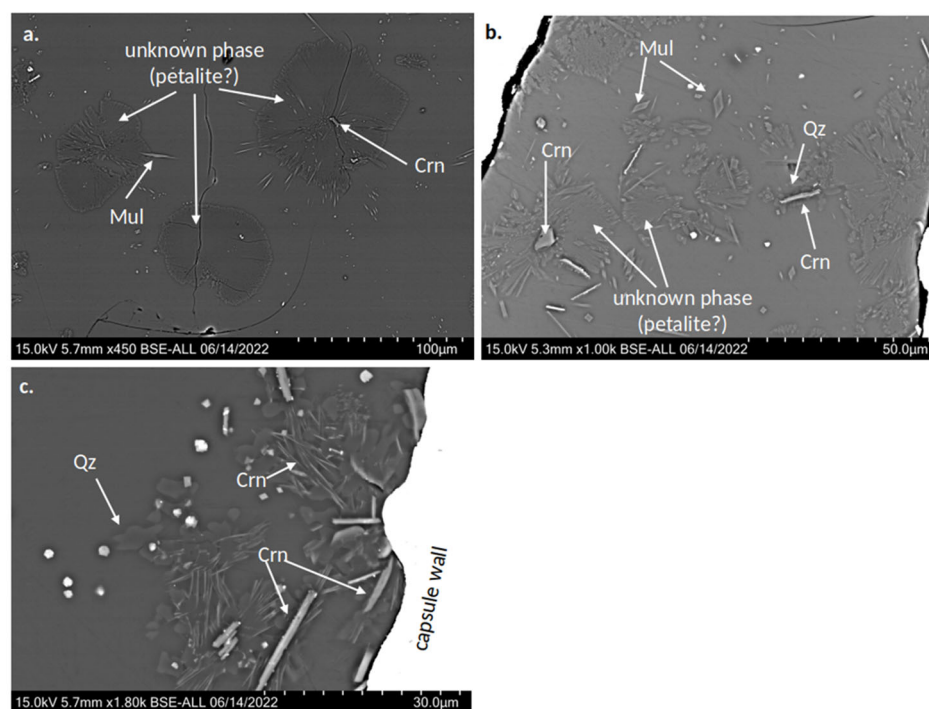


Figure 5. Backscattered electron images of the crystallization experimental run products, with the contrast and brightness enhanced; 750 °C, 630 MPa, 28 h: (a) Spherulites of the unknown phase (petalite?) nucleating homogeneously in the melt, enclosing mullite and corundum crystals; (b) Fan, bowtie and spherical spherulites of the unknown phase (petalite?) nucleating both homogeneously and heterogeneously around corundum crystals and on the capsule wall; (c) Rounded irregular quartz crystals nucleating around elongated and fibrous corundum crystals. Iron oxides nucleate both homogeneously and heterogeneously.

Notably, the 750 °C, 28 h experimental run products contain fan, bowtie and spherical spherulites, following Lofgren's [40] terminology, that appear to be formed by small fibres of an unknown phase. The spherulites occur both homogeneously in the melt and heterogeneously on the capsule wall or around corundum and mullite crystals. The latter indicates that the spherulites formed after corundum and mullite. In BSE images, this phase was darker than corundum, mullite, quartz and feldspars, indicating a lower mean atomic weight than any of these other crystals observed in the experiments. Qualitative EDS elemental maps indicate that they are richer in silicon and poorer in sodium compared to the melt. Due to the darker colour of this phase in the BSE images, we suspected that it might be a lithium-bearing mineral and considered the stoichiometry of spodumene ($\text{LiAlSi}_2\text{O}_6$), virgilite ($\text{LiAl}_x\text{Si}_{3-x}\text{O}_6$), and petalite ($\text{LiAlSi}_4\text{O}_{10}$). Due to the small size of the fibres in the spherulites, the EDS quantitative analyses of the unknown phase were difficult as they almost certainly contained both the crystals and the glass, and we could not analyze

for lithium. However, the best analyses (Table 4) indicate a Si:Al molar ratio of ~ 4 , and if the cations are calculated on the basis of 10 oxygens, with the assumption of 1 lithium cation, the cation total is 6.004 (Table 4). This calculation suggests that these spherulites may possibly be petalite. However, further investigation of these spherulites is beyond the scope of this work and was not performed.

Mullite, corundum, dehydroxylated pyrophyllite, plagioclase, quartz and iron oxides were found in the 115 h experiment at 650 °C (Figure 6). Halos surrounding corundum and mullite were larger than seen in higher-temperature experiments. This experiment also crystallized halos around the iron-oxide crystals, but EDS analysis of these small crystals, ~ 1 micrometre in their maximum dimension, was inconclusive.

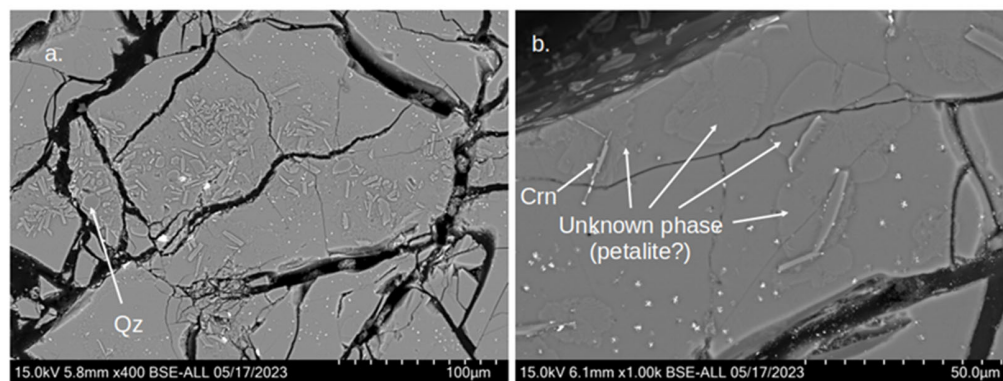


Figure 6. Backscattered electron images of the crystallization experimental run products, with the contrast and brightness enhanced; 650 °C, 630 MPa, 115 h: (a) Aggregate of quartz (identified), plagioclase, mullite, corundum, and the unknown phase crystals (petalite?) in melt. (b) Corundum surrounded by halos and the unknown phase (petalite?).

4. Discussion

4.1. The Presence of Mullite Instead of Sillimanite in the Experiments

The finding of mullite in both our melting and crystallization experiments was surprising because this phase is not seen in the natural pegmatite from which our sample was taken, and we are unaware of any report of mullite in granitic rocks. On the other hand, stable magmatic sillimanite has been reported in granitic rocks (e.g., [41–43]) and is associated with earlier periods of crystallization at high temperatures and low water activity [42,44], similar to the experimental conditions in our study. We suspect that the mullite in the experiments is metastable, that it formed instead of sillimanite at the experimental conditions and is possibly a transition phase as the system evolves toward equilibrium following the Ostwald step rule (p. 375 ff. in [45], [46]) because of the similar formulas and structures of these two minerals (e.g., [47]). We hypothesize that given enough time, far beyond that available for our experiments, the mullite would evolve into sillimanite at the pressure and temperature conditions used in this study.

4.2. Halos Surrounding Corundum

The observation of halos of dehydroxylated pyrophyllite surrounding corundum seen in crystallization experiments below 900 °C is inferred to indicate a reaction relationship between corundum and the melt, resulting in the production of a new phase. Because dehydroxylated pyrophyllite is not a mineral in granites and the stability of pyrophyllite in the Al_2O_3 - SiO_2 - H_2O system is hundreds of degrees below our experiments [48], we do not think that pyrophyllite or dehydroxylated pyrophyllite is stable in these experiments. Indeed, we interpret these crystals as metastable products of the reaction relationship between corundum and melt; we think that they, too, are an example of the Ostwald step rule [45,46] rather than the final crystalline phase that should be present at equilibrium.

On the basis of the complex melting reactions of plagioclase that result in the crystallization of corundum [36], we suggest that these halos may be the transition phase of a reaction between corundum and melt that leads to the crystallization of plagioclase. However, we cannot rule out the possibility that the dehydroxylated pyrophyllite is pyrophyllite and possibly a transition phase in a reaction relationship between corundum and melt to produce another mineral such as biotite, a mineral with a similar structure to pyrophyllite whose stability can extend to above 800 °C in granitic bulk compositions at the pressures of the experiments (e.g., [9,49,50]).

4.3. Calculation of Nucleation Delay Using Classical Nucleation Theory

For a crystal nucleus to form and grow, elements must diffuse into the growing nucleus. The nucleus must be larger than a certain size, called the critical size, in order to be stable and grow to macroscopic dimensions (e.g., [1,2,19]). But, stable nuclei do not form as soon as a new phase is thermodynamically favoured in the melt; there is a delay before nucleation starts, and steady state rates of the new phase's growth are reached. Classical nucleation theory (CNT) provides a key to understanding the origins of this delay and predicting its duration.

Classical nucleation theory is based upon J. Willard Gibbs' early work on the thermodynamic description of heterogeneous systems where the parent phase and the new nucleating crystalline phase (the nucleus) are described as two homogeneous phases separated by a sharp planar interface of zero thickness (e.g., [1,2,13]). Assuming a spherical shape, the thermodynamic barrier for the formation of a nucleus can be described by

$$W^* = \frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \sigma \quad (1)$$

where W^* is made up of two terms, namely the volume-free energy (the first term on the right-hand side composed of the radius of the nucleus, r , and the Gibbs free energy of the reaction per unit volume, ΔG_V) and surface free energy (the second term on the right-hand side composed of the radius and the interfacial energy per unit area, σ). The volume-free energy term describes the decrease of free energy of the system associated with the formation of a new, thermodynamically favoured, crystalline phase, while the interfacial free energy term describes the increase in free energy due to the formation of an interface between the new phase and the parent phase (e.g., [51,52]). The volume-free energy contributes to the stabilization of a nucleus, whereas the interfacial free energy is a positive value, and it destabilizes the nucleus. At small radii, the surface free energy term dominates, and at this point, the nucleus will be unstable and tend to dissolve. At the critical radius size, the nucleus becomes large enough that the volume term dominates, and the growth of the nucleus decreases the total free energy of the system (e.g., [51,52]). After reaching the critical nucleus size, the probability of decay is smaller than the probability of growth, and nucleus will be able to grow to macroscopic crystals (e.g., [3]).

In order to form a thermodynamically stable nucleus, the system must overcome a thermodynamic and a kinetic barrier, both of which can be described by the time lag before the onset of the steady state nucleation rate, I_{st} , which is given by the following:

$$I_{st} = I_0 \exp\left(\frac{-W^* + \Delta G_D}{k_B T}\right) \quad (2)$$

where I_{st} is the steady state nucleation rate, I_0 is a pre-exponential term depending on temperature, W^* is the change in Gibbs free energy associated with the formation of the critical cluster (Equation (1)), ΔG_D is the activation energy required to transfer structural units from the melt to the nucleus, i.e., the kinetic barrier, k_B is Boltzmann's constant, and T is the temperature [1,2,53,54].

Fokin et al. [2] derived an equation to calculate the time lag before the onset of steady state homogeneous nucleation, the nucleation delay, or τ :

$$\tau = \frac{16h}{\pi} \frac{\sigma}{\Delta G_D^2 a^4} \exp\left(\frac{\Delta G_D}{RT}\right) \quad (3)$$

where h is Planck's constant, R is the gas constant, T is temperature, and a is the size of the structural unit in the melt involved in the formation of the nucleus. The kinetic barrier, ΔG_D , can be expressed as the activation energy, E_a , required to transport structural units to the growing nucleus and represents the kinetic barriers to growth (e.g., attachment processes, transport, rearrangement of bonds, etc.); this value must be overcome for the nuclei to grow [13]. Multiple variations of Equation (3) have been derived; each variant of the equation provides a slightly different estimate of the nucleation delay (e.g., [55–58]). Equation (3) was chosen for this study because of its previously demonstrated success in the prediction of nucleation delay times [5,25,59].

For heterogeneous nucleation, a correction is added to Equation (3) due to the presence of a pre-existing surface that lowers the interfacial free energy:

$$\tau_{\text{heterogeneous}} = \tau \varphi^{\frac{1}{3}}, \text{ where } \varphi = \frac{1}{2} - \frac{3}{4} \cos \theta + \frac{1}{4} \cos^3 \theta \quad (4)$$

where θ is the interior contact angle between the nucleation surface and the nucleating phase [2].

The CNT assumes a sharp planar interface between the growing nucleus and the melt, regardless of the size of the nucleus, and that both the nucleating phase and the initial bulk phase have the same thermodynamic properties [13,60]. These assumptions are thought to explain why CNT fails to accurately describe nucleation by several orders of magnitude in multiple systems [13,60]. To account for this discrepancy, the CNT model used in this study was adjusted to qualitatively consider the diffuse interface theory (DIT) [60]. The DIT considers an interface between the nucleus and the melt with intermediate properties (i.e., enthalpy and entropy) between the two phases [60]. The solid nucleus has a structural influence on the melt interface, but that same interface has an atomic configuration more similar to that of a melt than a solid [13]. This interface is also size dependent [60]. The DIT was only qualitatively considered in this study, and we incorporated the concept of an interfacial region at the boundary between the nucleus and the melt in our nucleation delay calculations following Rusiecka et al. [5].

4.4. Calculation of the Nucleation Delays for Quartz, Plagioclase, Mullite/Sillimanite, and Corundum

Although the experimental results are complicated by the appearance of mullite and dehydroxylated pyrophyllite, which we argued above are metastable phases, the crystallization of quartz and plagioclase in selected experiments allows us to extend the application of the nucleation delay model presented above to the peraluminous granitic melt composition studied. In order to apply Equation (3) to the prediction of nucleation delay, we need to establish the values of each of the variables in that equation: the melt–crystal interfacial energy, the Gibbs Free Energy for the crystallization reaction, the size of the structural unit of growth, and the energy of the kinetic barrier to growth. Because we are directly comparing our results to those of Rusiecka et al. [5], we chose each of these values based upon the arguments and justifications presented in Rusiecka et al. [5].

The value of the interfacial energy (σ) was calculated from the relationship between the interfacial energy and the water concentration in the melt established by Hammer [13]:

$$\sigma = 0.0176 \times H_2O(\text{wt.}\%) + 0.1121 \quad (5)$$

where, once again following [5], we assume that the water concentration at the crystal–melt interface is not necessarily the same as the bulk water concentration in the melt.

The value of ΔG_v for plagioclase, quartz, corundum, and sillimanite (as a proxy for mullite because Rhyolite-MELTS does not model mullite) were calculated from the affinities given by Rhyolite-MELTS [61], version 1.0.2, run on the ENKI server, using the MM45B composition, and converting from molar free energies to volume free energies using the molar volumes of the minerals [62]. The saturation temperatures for plagioclase and quartz calculated by Rhyolite-MELTS were consistent with the melting experiments and were not adjusted. However, the experimental melting and crystallization temperatures of mullite and corundum were $\sim 300^\circ\text{C}$ above the saturation temperatures of sillimanite and corundum calculated by Rhyolite-MELTS, thus necessitating an upward shift in the saturation temperatures to match the experimental melting temperatures. Rusiecka et al. [5] found that similar shifts were necessary to fit the basaltic and granitic melt compositions they investigated, and this adjustment does not impact the accuracy of our results as they are reported and analyzed with respect to the ΔT values and not the absolute temperatures.

Following [5], the size of the structural unit (a) was taken as the radius of the Si^{4+} cation, $0.26 \times 10^{-10} \text{ m}$ [63], and the kinetic barrier (ΔG_D) is assumed equal to the activation energy of Si-Al diffusion calculated by fitting measurements in a dry and hydrated metaluminous rhyolitic melt [64,65].

Both the activation energy and the interfacial free energy are written in terms of the water content of the melt–nucleus interface (cf., [5]) and, therefore, only this one parameter, water concentration at the interface, is adjusted in Equation (3) to determine the fit between the calculated nucleation delay and our experimental data. Ideally, we would like to know the interfacial water concentration, but this value at the molecular-scale, nucleus–melt interface is unknown and cannot be measured, which is why we could not a priori assign a value to this variable and instead adjusted it to fit the experimental measurements.

4.5. Comparison of Modeled Homogeneous Nucleation Delay and Experimental Measurements

We calculated nucleation delay times for the MM45B melt composition with varying amounts of water at the crystal–melt interface and compared the models to our experimental results. For both quartz and plagioclase, an interfacial water concentration of $0.4 \pm 0.1 \text{ wt\%}$ resulted in the best fit between the measured and calculated nucleation delays (Figure 7). The fit is best between the calculated and measured nucleation delays for quartz, although we note that the difference between calculated and experimental constraints can reach a factor of 5 (Figure 7).

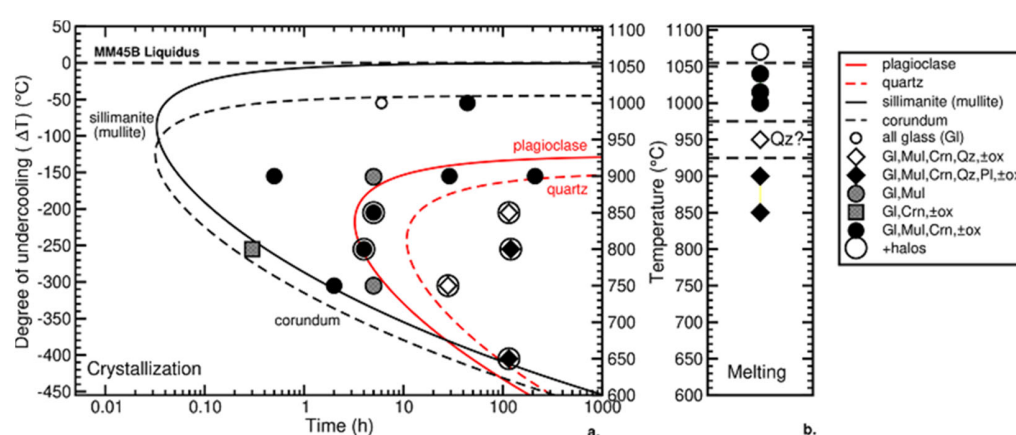


Figure 7. (a) Comparison of nucleation delay experiments during crystallization with theoretical calculations as discussed in the text. The nucleation delay curve for mullite was calculated using thermodynamic data for sillimanite. (b) Phase equilibria of the bulk composition studied based upon melting experiments. Note that the experiment at 900°C contained a few quartz crystals that were interpreted to be residual and not in equilibrium with the melt.

The match between the experimental results and the nucleation delay model for plagioclase with $0.4 \text{ wt\%}$ water at the interface is not as successful as seen for quartz (Figure 7).

Only two sets of experiments crystallized plagioclase, which makes comparison of the model and experiments difficult. Attempts to fit the experiments in which plagioclase nucleated with Equation (3) at any water concentration were unsuccessful unless the melting temperature of plagioclase in the MM45B composition was lowered below our experimental determination (Figure 7), which is an unrealistic modification to the model. Nevertheless, the fit at an interfacial water concentration of 0.4 ± 0.1 wt% is encouraging, with a difference between theory and experiment of a factor of ~ 10 at 800 °C. The water concentration at the quartz–melt and plagioclase–melt interfaces that best match the experimental measurements, 0.4 ± 0.1 wt%, is within uncertainty of the value in Rusiecka et al. [5], who found that an interfacial water content of 0.5 ± 0.1 wt% best fit both the feldspar and quartz nucleation curves. Rusiecka et al. [5] worked with a hydrous metaluminous granitic composition with an ASI = 0.96, and both quartz and plagioclase nucleated within 24 h at similar undercoolings to those in our study. The nucleation delays for peraluminous melts are, therefore, greater than for metaluminous melts, although the presence of twice as much K₂O in the metaluminous melt [5] may also affect the nucleation delay. These results demonstrate that compositional differences in high-silica melts can have an important influence on nucleation delay times that can substantially affect the magmatic evolution of granitic and pegmatitic melts.

Comparing the theoretical predictions for corundum and sillimanite (mullite) with the experiments is challenging because of the short nucleation times for these minerals in the experiments and the lack of the appropriate thermodynamic data for mullite. The best fit for the homogeneous nucleation delays of mullite and corundum was with an interfacial water concentration of 1.95 ± 0.1 wt%, far above the value used for quartz and feldspar. However, this fit deviated from the experimental results by $\sim 50^\circ$ and almost 3 orders of magnitude in time at temperatures near the liquidus (Figure 7). Furthermore, some experiments that would be expected to nucleate both corundum and mullite based upon experimental results and theoretical modelling did not (e.g., most notably the experimental pair at 900 °C, 5 h, in Figure 7).

The nucleation of metastable dehydroxylated pyrophyllite around corundum in selected experiments below 900 °C (Figure 7) is enigmatic because we do not know the stable, crystalline phase into which it would evolve. Because the appearance of this phase in the experiments is consistent with the nucleation delay predicted for feldspar (Figure 7), and corundum is known to form during feldspar melting [36], it is tempting to associate metastable dehydroxylated pyrophyllite with stable feldspar. If this association is correct, then feldspar nucleation delay calculations would be in better agreement with the experimental observations (Figure 7). However, this similarity may simply be a coincidence. Without experiments with durations of much longer time than feasible in our laboratory (most probably thousands of hours), we cannot be certain of the solution to this conundrum and must leave it to future studies.

The discrepancies between the theoretical model of homogeneous nucleation and experimental results could be potentially caused by the nature of our observations. Since we are surveying a 2D surface to extrapolate observation of a 3D volume, it is possible we overlooked some crystallizing phases. Moreover, nucleation remains a stochastic process, and nucleation theory is indeed a statistical prediction (e.g., [3,66]). It is, therefore, statistically possible that a run product fails to nucleate a phase even if it is favoured. This behaviour was plausibly exhibited by our 750 °C, 2-h run where the two capsules nucleated different mineral assemblages. The stochastic nature of nucleation could also explain the difference in percent crystallization observed between capsules of experiments at the same run conditions.

4.6. The Minor Effect of Heterogeneous Nucleation

Because the vast majority of mullite and corundum crystals nucleated homogeneously, the heterogeneous nucleation correction was not considered. However, quartz and most plagioclase crystals nucleated heterogeneously on the capsule wall or on previously nucle-

ated phases. The correction for heterogeneous nucleation requires the value of the inner contact angle (Equation (4)). Our experiments had a low modal abundance of feldspar and quartz, which made contact-angle measurements unreliable. Instead, we used the mean value determined by Rusiecka et al. [5] of $89 \pm 22^\circ$ (one standard deviation). This contact angle results in a reduction in the nucleation delay of only ~20% and is considered within the uncertainty of our measurements. Even if the contact angle is as low as 20° , the resulting decrease in the nucleation delay is only a factor of ~10. Thus, this weak dependence of the nucleation delay on the contact angle suggests that even when heterogeneous nucleation is ignored, nucleation delay calculations should predict the actual value to within a factor of approximately 10.

4.7. Why Are Water Concentrations at the Melt–Nucleus Interface Lower Than in the Bulk Melt?

Following the diffuse interface theory, the melt at the interface should be poorer in water than the bulk melt, which coincides with our results, as the adjusted interface water contents for corundum, mullite, quartz and feldspar are smaller than the bulk water content of 3.3 wt%. Surprisingly though, corundum and mullite have much higher (~5×) interfacial water concentrations than plagioclase and quartz. We speculate that these differences could be related to the differing abilities of these nominally anhydrous minerals to incorporate water into their structures. Although few measurements have been made, mullite can contain up to 200 µg/g water, while quartz can incorporate up to 82 µg/g [67]. Considering that the interface between the growing nucleus and the melt has intermediate properties between the crystal and melt [60], if mullite can incorporate more water into its structure, the mullite–melt interface’s water content could be higher than the quartz–melt interface, thus explaining the higher modelled water content at the interface between mullite and the melt than at the quartz–melt interface. We could not find similar data for corundum and plagioclase water incorporation but speculated similar behaviour to that of mullite and quartz.

We recognize that other studies (e.g., [21,24]) found water concentrations higher than the bulk water concentration in the vicinity of crystals, and, indeed, in some experiments, we observed vesicles near the melt–crystal interface, suggesting local water saturation at the growing crystal–melt interface. It is, however, important to stress that we are not discussing the same phenomenon. Indeed, the diffuse interface theory describes nucleus growth on the nanometre scale, and the interfacial water content denotes the water content at the interface of the nucleus during this pre-growth step of the crystallization process. In contrast, Devineau et al. [21] and London [24] discussed the water content adjacent to crystals that have grown to sizes many orders of magnitude larger than crystal nuclei.

5. Conclusions

The modified theoretical nucleation delay model based on Rusiecka et al. [5] is in good agreement with the experimentally determined quartz nucleation delay of a hydrous peraluminous felsic melt at 630 MPa and at temperatures between 650 and 1000 °C. And although the theoretical plagioclase nucleation delay for this bulk composition agrees less well with experiments, nucleation delay theory still can provide useful constraints on the crystallization timescales and temperatures of peraluminous granitic melts. The nucleation delay model even provides useful constraints on the nucleation delay of metastable mullite and corundum. This study represents a stepping-stone in improving our understanding of the quantification of nucleation delay, adding to the growing body of literature on the topic. Though further studies are required, particularly on the nucleation delay of common hydrous minerals as well as investigations of melts with differing water concentrations, this study shows promising results in the quantification of nucleation delay in felsic melts and demonstrates the potential of the theoretical model.

Despite the need for more validation of the model, it can calculate the nucleation delay of quartz, plagioclase, clinopyroxene, and olivine in anhydrous basaltic melts and hydrous felsic melts within a factor of approximately $10\times$ ([5,59] and this study). And although the

model has not yet been applied to intermediate composition melts, we predict that it will be successful in the calculation of nucleation delays in these compositions too. Indeed, we suggest that nucleation delay in many common magmatic melts can now be modeled by combining classical nucleation theory [2], thermodynamic models of plagioclase, quartz, olivine, and clinopyroxene crystallization [61], our knowledge of Si-Al interdiffusion in silicate melts, and silicate–melt interfacial energies [13]. Although these calculated delays may not be exact, a combination of the nucleation delay time with detailed petrographic observations may provide important constraints on the times available for crystallization during processes such as intrusion of a hot magma into cold country rocks, extrusion on to the surface of a planet, ascent and undercooling of hydrous magmas in magmatic conduits, and any other magmatic process where a magma is rapidly cooled to subliquidus conditions (e.g., [5,25]).

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/min14060611/s1>, Table S1: Individual phase analyses.

Author Contributions: This paper is based upon the M.Sc. Thesis of M.B.; Conceptualization, M.B. and D.R.B.; methodology, M.B. and D.R.B.; software, D.R.B. and M.B.; writing—original draft preparation, M.B.; writing—review and editing, M.B. and D.R.B. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: All acceptable analyses of the individual phases in the experimental run products used to construct Table 4 are included in the Supplementary Materials.

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