1   # REVISION 2

2   # Crystallization experiments in rhyolitic systems: the effect of

3   # temperature cycling and starting material on crystal size

4   # distribution

5   **Marize Muniz da Silva[1,2*], Francois Holtz[1] and Olivier Namur[1]**

6   [1] Leibniz Universität Hannover, Institut of Mineralogy, Callinstr. 3, 30167, Hannover, Germany;

7   [2] Departamento de Geologia, Instituto de Geociências, Universidade Federal do Rio de

8   Janeiro, Cidade Universitária, 21949-900 Ilha do Fundão, Rio de Janeiro, RJ, Brazil;

9   E-mail: muniz.marize@gmail.com; f.holtz@mineralogie.uni-hannover.de;

10   o.namur@mineralogie.uni-hannover.de

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12   ## Abstract

13   One of the various problems faced in experimental petrology is the fact that most

14   experimental products obtained by crystallization experiments are too small, making their

15   accurate identification by electron microprobe and laser ablation analyses very difficult. This

16   problem is magnified when a highly polymerized starting material is used for experiments at

17   low temperature (e.g. 700°C - 800°C). In this study, we present the results of crystallization

18   experiments performed using a rhyolitic starting glass in which we test the potential of

19   temperature cycling and pre-hydrated starting material to increase crystal size and discuss the

20   effect of those variables on the attainment of chemical equilibrium. Experiments were

21   performed at different temperatures (725 to 815°C) and pressures (1 and 2 kbar), under water-

22   saturated conditions (aH$_2$O = 1; with aH$_2$O being the water activity). During the experiments,

23   temperature was either constant or cycled to ± 15°C around the target temperature during the

24   first half of the runs. We used either a pre-hydrated (7 wt.% H$_2$O) rhyolitic glass or a dry

25   rhyolitic glass to which 7 wt.% H$_2$O was added during capsule preparation.

26 Our results differ between 1 and 2 kbar experiments. At 1 kbar, plagioclase and

27 orthopyroxene were the main crystalline phases affected and temperature cycling (±15°C) did

28 not increase the crystal size of these phases. In contrast, if only the nature of the starting

29 material is considered (dry glass vs. pre-hydrated), the use of a pre-hydrated starting material

30 successfully increased the overall crystal size and decreased the crystal number density. At 2

31 kbar, plagioclase and amphibole were the main phases and the largest crystals were also

32 obtained when pre-hydrated starting material was used. Contrary to experiments at 1 kbar,

33 temperature cycling also increased the overall crystal size. The different effects of

34 temperature cycling at 1 and 2 kbar are attributed (1) to the different cation diffusivities at 1

35 and 2 kbar caused by different melt water concentrations and (2) the negligible effect of

36 temperature cycling at 1 kbar (±15°C) is explained by little dissolution of phases, so that

37 small crystals were already too large to be completely consumed by the dissolution process in

38 the high temperature interval. The results demonstrate that temperature oscillation (depending

39 on the amplitude) and the nature of the starting material (pre-hydrated vs. dry glass + water)

40 are two parameters that can contribute to increase crystal sizes in experiments with rhyolitic

41 melts. However, we also observed that the use of a pre-hydrated starting material increased

42 the occurrence of zoned plagioclase crystals which may indicate that chemical equilibrium

43 was not perfectly reached.

44 **Keywords:** Crystallization experiment, Temperature cycling, Crystal size distribution,

45 Rhyolite

46   **Introduction**

47 Experimental petrology and high pressure technologies have been widely used in the last

48 century to understand the crystallization history of magmatic systems. In addition, all

49 thermodynamic models predicting liquid lines of descent are based on experimental

50 databases. The pre-requisite for accurate models is that equilibrium between solid phases,

51 fluids and silicate melts is reached. However, attaining complete equilibrium between highly

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52   polymerized melts and silica-rich crystals, such as feldspar, is difficult and becomes even

53   more complicated when crystallization experiments are performed under low temperature

54   conditions (700 – 800°C). This is mainly due to the high viscosity of the melt that makes

55   diffusion of chemical components very slow and extremely long experimental durations are

56   thus needed to obtain complete chemical equilibration between crystals and melt (e.g.

57   Pichavant et al. 2007; Fenn 1977).

58   Two fundamentally different methods to experimentally constrain phase equilibria in

59   magmatic systems are generally used: crystallization experiments (e.g. Scaillet et al. 2016)

60   and melting experiments (e.g., Rushmer 1995; Patino Douce et al. 1996; Patino Douce and

61   Harris 1998). Phase equilibria experiments in dacitic to rhyolitic systems need to be

62   conducted at low temperature (700°C – 900°C). At these conditions melting experiments

63   usually fail to reach bulk equilibrium due to slow diffusion of chemical components. For

64   melting experiments, if a natural rock powder with grain sizes of 30 – 60 μm is used as

65   starting material, there will be a large proportion of minerals that may not reach complete

66   equilibrium. This is commonly observed when using plutonic rock powders as starting

67   material as well as volcanic rock powders, which contain microlites or phenocrysts (e.g,

68   Venezky and Rutherford 1999; Shea and Hammer 2013). For crystallization experiments,

69   synthetic oxide powders are often used (e.g. Charlier and Grove 2012; Nandedkar et al. 2014)

70   and succeed in reaching equilibrium in high temperature experiments with basaltic systems.

71   They can however lead to the formation of meta-stable phases in experiments with high

72   viscosity melts (e.g. formation of mullite from Al_2O_3, for example; Holtz et al., 1992). The

73   use of an amorphous phase such as a gel (e.g., Tuttle and Bowen 1958; James and Hamilton

74   1969) or a glass (e.g., Pichavant 1987; Scaillet et al. 2016) is therefore better suited for phase

75   equilibria experiments in silicic systems. With an amorphous starting material, equilibrium

76   conditions are easier to reach in rhyolitic and dacitic systems, but experimental products

77   usually contain extremely small crystals. These small crystals represent a severe limitation in

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78   experimental petrology because they very often cannot be identified or accurately measured

79   by methods such as electron microprobe or laser ablation inductively coupled plasma mass

80   spectrometry (LA-ICPMS).

81   Temperature cycling during experiments has recently been proven extremely helpful

82   to increase the size of crystals in basaltic systems at 1 atm (Mills & Glazner 2013) or under

83   pressure (Erdmann & Koepke 2016), but the benefit of this approach has never been

84   quantitatively tested in rhyolitic systems. Crystal nucleation and growth strongly depend on

85   the degree of undercooling with low undercooling resulting in larger crystals (Lofgren, 1974;

86   Fenn 1977). Thermal cycling provides another opportunity to form large crystals because

87   components can be redistributed among phases. Melting the small crystals during heating

88   episodes of a temperature oscillation may lead to the formation of larger crystals during the

89   cooling episodes. Here we tested the potential of temperature cycling to increase crystal and

90   melt pool sizes in a highly polymerized rhyolitic system at low temperature (725°C - 815°C)

91   and moderate pressure (1 and 2 kbar). We also investigated the effect of temperature cycling

92   on the attainment of chemical equilibrium. We used two different approaches to perform our

93   crystallization experiments. The first approach, which is the most commonly applied in

94   experimental petrology, is to use a dry glass powder to which we add water (or other

95   volatiles) during capsule preparation. The second approach, which is less commonly used, is

96   to pre-saturate the glass with volatiles using high pressure vessels. In the first case, the

97   hydrous glass is produced during the experimental run by diffusion of H_2O from a vapor

98   phase into an initially dry glass. This implies that when the experiment starts, the fluid phase

99   is heterogeneously distributed in the capsule. In the second approach, crystals grow from a

100   melt in which volatiles are already distributed homogeneously. Our experiments show that

101   temperature cycling does not affect phase relationships or composition of the crystals but may

102   significantly increase crystal sizes, as does the use of pre-hydrated starting material.

103   **Methodology**

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General experimental strategy

The general methodology and the experimental conditions applied in this study are shown schematically in Fig. 1 and are designed to compare four types of experimental approaches: crystallization from a dry powder plus added water during capsule preparation, with and without temperature cycling and crystallization from a pre-hydrated glass powder, with and without temperature cycling. We performed a total of 14 crystallization experiments on a single composition, at temperatures between 700°C and 815°C and pressures of 1 and 2 kbar.

Starting material

Dry glasses: All experiments were performed using a synthetic glass of rhyolitic composition prepared from a mixture of pure oxide (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO) and carbonate ($CaCO_3$, Na_2CO_3, K_2CO_3) powders, mixed using an agate ball mill. The starting material was melted twice in a platinum crucible at a temperature of 1600°C and 1 atm for 4 hours, followed by immersion of the crucible in water for rapid quench. Between the two melting procedures, the sample was crushed and ground in a rotary mortar. The composition and homogeneity of the glass were determined by electron microprobe analyses (Table 1).

Pre-hydrated glasses: A total of three capsule were prepared where 93 wt.% of dry glass (400, 400 and 700 mg) and 7% wt.% of H_2O were loaded in gold/palladium ($Au_{80}Pd_{20}$) capsules (to avoid Fe loss). Capsules were then run in an internally heated pressure vessel (IHPV) at 1200°C and at a pressure of 3 kbar for 24 hours. After the runs, the water content in the quenched glass was measured by Karl-Fischer titration (see details in Behrens et al. 1996). Measurements were performed on 10 to 24 mg of pre-hydrated material, which is sufficient to obtain reliable results with an uncertainty smaller than 0.15 wt.% H_2O. To check the homogeneity of the samples, the analyzed aliquots were taken from the top and the bottom of

129 each gold/palladium capsule. Measured water concentrations range from 6.86 to 7.02 wt.%

130 H_2O and we did not find any obvious vertical variability.

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132 **Capsule preparation for crystallization experiments:** (1) pre-hydrated starting material was

133 crushed in a mortar and ~30 mg of this material were loaded in 12 mm long Au capsules (3.2

134 mm outer diameter and 0.2 mm wall thickness) that were welded shut or (2) dry glass powder

135 (93 wt.%; 30 mg) and 7 wt.% of deionized H_2O were loaded into Au capsules (same size as

136 before) and welded shut. To ensure that no fluid escaped during welding, the weight of the

137 loaded capsule was measured before and after the welding procedure.

138

139 **Experimental Apparatus**

140 Crystallization experiments were performed at the Leibniz Universität Hannover (LUH) in

141 Renee-41 cold-seal pressure vessels (CSPV). The CSPVs are arranged horizontally and water

142 is used as the pressure medium. The temperature during the experiments was continuously

143 recorded by an external sheathed K-type thermocouple, placed in a borehole at the end of the

144 autoclave near the hot zone. The CSPVs are equipped with a ramp/soak temperature

145 controller REX-P24 that allows automatic temperature oscillation as a function of time. The

146 relation between the measured temperature (external thermocouple) and the temperature at the

147 sample position was calibrated at: (1) atmospheric pressure in the temperature interval of 200

148 to 850°C using a self-made calibration device and a certified thermocouple and (2) at 1 kbar

149 over the same temperature interval using the self-made calibration device. This device

150 consists of three K-type thermocouples positioned side by side, with three different lengths

151 (positions A, B and C) covering the hot zone of the CSPV. Positions A, B and C are at 7, 27

152 and 46 mm respectively from the end of the borehole of the vessel. The uncertainties of the

153 thermocouples is ±1.3°C for temperatures > 700°C and ±0.6°C for temperatures < 700°C.

154 During calibration, temperature fluctuations (in each position) were not higher than ±2°C and

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155   we estimated that the uncertainty of the temperature measured during experiments is ±5°C.

156   We found that the temperature gradient along the hot zone of the CSPV is variable and may

157   reach up to 60°C. To minimize temperature variation during experiments, our capsules did not

158   exceed 12 mm in length in order to fit in the position closest to the external thermocouple

159   (position A). Water pressure was monitored with a transducer calibrated against a strain gauge

160   monometer, with an uncertainty of ±0.03 kbar. The amount of water needed to increase the

161   pressure from 0 to 2 kbar is 300 ml. The intrinsic oxygen fugacity of the CSPV is close to

162   NNO (Ni-NiO) oxygen fugacity buffer (Gardner et al. 1995).

163

164   **Experimental procedure**

165   In each experimental run, two capsules were inserted into each CSPV and placed side by side

166   in position A. For each run, one capsule contained a dry glass with 7 wt.% H_2O while the

167   other one contained the pre-hydrated glass. The pressure vessel was then inserted into a pre-

168   heated furnace and 20 to 30 minutes were sufficient to reach the target temperature. Run

169   durations were 21 days for twelve experiments and 14 days for two experiments (Table 2). As

170   shown in Fig. 1, we applied temperature cycling to some experiments. For cycled

171   experiments, the temperature path was as follows: temperature oscillation was started at the

172   beginning of the experiment, with a amplitude of +15°C above and then -15 °C below the

173   final equilibrium temperature (e.g., 725°C, 750°C, 775 °C and 815°C). The variation of 30°C

174   between the high and low temperatures was attained within two hours (0.5°C/min). The upper

175   and lower temperatures were held constant for one hour (Supplementary Dataset A). No

176   significant pressure change (< 0.07 kbar) was observed as a result of the temperature

177   variation. Temperature cycling was conducted for 14 days (only 7 days for one of the

178   experiments) and the temperature was then kept constant for another 7 days. At the end of the

179   experiments, the products were quenched by cooling the autoclave with a stream of

180 compressed air for 30 to 40 minutes. During quenching, the pressure was kept constant until

181 the autoclave reached ~20°C. Pressure was then released.

182

183 **Analytical techniques**

184 Run products were mounted in epoxy and polished for analysis. Experiments were analyzed

185 with an electron microprobe (Cameca SX100) at LUH. For mineral analysis, we used a

186 focused beam with a current of 15 nA. For glasses, we used a beam current of 4 nA and a spot

187 size of 10 μm. Minerals and glasses were analyzed with an acceleration voltage of 15 kV.

188 Counting times were 10 s on peaks and 5 s for background on both sides. Calibration of the

189 electron microprobe was based on natural and synthetic standards: albite for Na; wollastonite

190 for Ca and Si; orthoclase for K, Durango apatite for P; Al_2O_3 for Al; Mn_2O_3 for Mn; TiO_2 for

191 Ti; MgO for Mg; and Fe_2O_3 for Fe. Calibrations were independently checked against external

192 natural mineral standards: plagioclase (Labradorite) Lake County (USNM 115900);

193 hornblende, Kakanui, New Zealand (USNM 143965); augite, Kakanui, New Zealand (USNM

194 122142; Jarosewich et al. (1980), and glasses: rhyolite from Yellowstone, USA (Nash 1992)

195 and Ja-rhyolite (USNM72857 VG-568; Jarosewich et al. 1980).

196

197 **Crystal size distribution analysis**

198 Crystal size distribution (CSD) analyses of plagioclase, amphibole or pyroxene were

199 performed using back-scattered electron (BSE) images acquired with the electron microprobe.

200 The analysis consisted of the measurement of two-dimensional parameters corresponding to

201 the longer axis and the orthogonal short axis (length and width respectively) of each crystal

202 using the open source computer program *ImageJ (*Schneider et al. 2012*;*

203 *http://imagej.nih.gov/ij/)*. For the characterization of the crystal sizes, at least seven BSE

204 pictures at the same magnifications (1600X, 800X or 400X) were analyzed for each sample.

205 The magnifications were chosen based on the average size and number of crystals to ensure

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206   that a minimum of 90 crystals could be measured for each experiment. The magnifications

207   translate to sample area per image of 0.27 mm^2 (400X) and 0.02 mm^2 (1600X). The crystal

208   size measurement was manual and each crystal in the image was measured individually. The

209   data (length and width) were used to calculate the approximate area of the surface of each

210   crystal, their frequency distribution, crystal area fraction (ϕ) and crystal number density. The

211   crystal number density (N_A) is the frequency, for each size interval (bins), divided by the total

212   area measured (Higgins 2000) while the crystal surface area was calculated by multiplying

213   length and width and was used to obtain crystal area fraction. The crystal area fraction was

214   calculated by dividing the total crystal area by the total area measured. The ϕ and N_A were

215   then used to calculate a characteristic crystal size ($S_N = (\phi/N_A)^{0.5}$) and volume crystal density

216   ($N_v = N_A/S_N$) (Blundy and Cashman 2008).

217   The number of crystals analyzed per photo mosaic was variable: plagioclase from 210 to

218   2017; amphibole from 115 to 605; and pyroxene from 98 to 370. In all experimental samples,

219   amphibole or pyroxene crystals have lower crystal number densities than plagioclase.

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Experimental results

Dry powder vs. pre-hydrated melt

223   Plagioclase and pyroxene were used for two-dimension crystal size analyses for experiments

224   performed at 1 kbar while plagioclase and amphibole were used for experiments performed at

225   2 kbar (their compositions can be found in Supplementary Datasets B, C and D). All

226   experiments with pre-hydrated glass as starting material (Ex11, Ex13 at 1 kbar and Ex44 at 2

227   kbar; Fig. 1) have larger plagioclase (Figs. 2A and 3A), pyroxene (Figs. 2B) or amphibole

228   crystals (Fig. 3B) than those found in experiments with dry glass and H$_2$O as starting material

229   (Ex12 and Ex14 at 1 kbar and Ex45 at 2 kbar).

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230   At 1 kbar, when we compare crystal sizes in the runs in which temperature was kept constant

231   (Ex11 and Ex12), we observe that the experiment with pre-hydrated glass (Ex11) exhibits

232   plagioclase and pyroxene crystals up to a maximum of four times larger than those found in

233   the experiment where dry glass and water was used (Ex12) (Figs. 2A and 2B). In experiments

234   where temperature was cycled (Ex13 and Ex 14) plagioclase and pyroxene are only slightly

235   larger in the pre-hydrated experiments (Ex13) than in experiments with dry glass plus water

236   (Ex14) (Supplementary Dataset E). Similar crystal size distributions are observed in

237   experiments performed at 2 kbar. Plagioclase and amphibole present a maximum crystal size

238   up to two times larger in the experiments performed with pre-hydrated starting material

239   (Ex44) than in the one with dry glass (Ex45) (Fig. 3A and 3B).

240   In experiments performed at static temperature, we observe that in the charges with dry glass

241   and water (Ex12 and Ex45) plagioclase and pyroxene are respectively 50% to 90% and 20%

242   to 30% more abundant in number of crystals than in experiments where pre-hydrated starting

243   material (Ex14 and Ex44) was used, considering the same area. For experiments in which

244   temperature was cycled, we observe that only the number of plagioclase crystals was more

245   abundant using dry glass rather than pre-hydrated starting material. In contrast, the pyroxene

246   crystal number was found to be lower.

247   Qualitative analyses of crystal morphology (Lofgren, 1974) show that plagioclase crystal

248   shape was strongly affected by changing the nature of the starting material. In runs performed

249   with pre-hydrated glass, skeletal crystals dominate. In contrast, when dry starting material and

250   water was used tabular crystals prevail (see Figs. 4 and 5).

251   Concerning mineral compositions, no chemical zoning was observed in plagioclase, pyroxene

252   or amphibole crystals in Ex11, Ex12, Ex13, Ex14 (1 kbar) and in Ex44, Ex45 (2 kbar).

253   However, a significant variability of the plagioclase An (anorthite) content is observed

254   between crystals of individual experiments (see Supplementary Dataset A; Fig. 6). This

255   variability is usually larger for experiments performed on dry glass plus water than on pre-

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256   hydrated glass. Pyroxene compositions equivalent in Ex13 and Ex14, while in Ex12 this

257   mineral is slightly enriched in Fe in comparison to Ex11 (Fig. 7). Amphibole composition

258   also present small variation between experiments and Ex44 shows higher amphibole Mg

259   number [Mg/(MA+Fe^{2+})] than Ex45 (see Supplementary Dataset B; Fig. 8). Residual melt

260   composition present small variability with Ex11 (pre-hydrated; 1 kbar), Ex14 (dry glass; 1)

261   and Ex45 (dry glass; 2 kbar) showing higher Na_2O than Ex12 (dry glass; 1), Ex13 (pre-

262   hydrated; 1 kbar), and Ex44 (pre-hydrated; 2 kbar). In addition, Ex14 exhibits higher K_2O

263   content than Ex13 (Table 3).

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265   1 kbar vs. 2 kbar experiments

266   At 1 kbar orthopyroxene is the dominant mafic phase but amphibole and biotite are observed

267   in experiments performed at 2 kbar. Plagioclase, ilmenite and magnetite were identified at

268   both pressures. Plagioclase is the only mineral that can be used to estimate the effect of

269   pressure on crystal sizes. Experiments performed at 2 kbar (Ex30 and Ex43) produced larger

270   crystals than experiments performed at 1 kbar (Ex12 and Ex14). When dry starting material

271   was used under static temperature, the maximum size of plagioclase crystals was up to three

272   times larger in the 2 kbar experiment (Ex30) than in the 1 kbar experiment (Ex12) (Fig. 9A).

273   When temperature was cycled, the maximum size of plagioclase crystals was up to five times

274   larger at 2 kbar (Ex43) than at 1 kbar (Ex14) (Fig. 9B).

275   Regardless of the temperature path (cycling vs. static temperature), experiments at 2 kbar

276   exhibit a lower plagioclase density than experiments at 1 kbar. For experiments with

277   temperature cycling, considering the same area, Ex14 (1 kbar) has 99% more plagioclase

278   crystals in number than Ex43 (2 kbar). For experiments at constant temperature, Ex12 (1

279   kbar) exhibits only 6% more plagioclase crystals than Ex30 (2 kbar). No change of crystal

280   morphology is observed by changing pressure, and plagioclase at 2 kbar is more enriched in

281   An-component compared to plagioclase at 1 kbar (Fig. 6). A slight change of residual melt

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282 composition is observed when comparing experiments at 2 kbar (Ex30 and Ex43) and 1 kbar

283 (Ex12 and Ex14) with higher Al_2O_3, CaO, Na_2O and lower K_2O content at high pressure (Tab.

284 3).

285

Constant temperature vs. temperature cycling

287 *1 kbar experiments* – Crystal size analyses were performed for plagioclase and pyroxene.

288 Comparing experiments performed with dry glass plus 7% of water, the experiment at static

289 temperature (Ex12) with very small plagioclase crystals (≤ 3 μm^2) presents a higher crystal

290 number density than the experiment in which temperature was cycled (Ex14) (Fig. 10A).

291 However, both experiments show a similar crystal number density of large plagioclase

292 crystals (~13 μm^2) with Ex14 having slightly larger plagioclase crystals than Ex12 (Fig. 10A).

293 For pyroxene, temperature cycling did not effectively influence crystal growth and the static

294 experiment (Ex12) resulted in larger crystals than the cycled one (Ex14) (Fig. 10B). Based on

295 analyses of BSE images, we conclude that, considering the same area, Ex12 (constant

296 temperature) displays ~24% more plagioclase and ~17% more pyroxene (Fig. 4) crystals than

297 Ex14 (cycled temperature).

298 When pre-hydrated starting material is used, experiments with temperature cycling (Ex13 and

299 Ex46) exhibit higher crystal number density of small plagioclase crystals than the static ones

300 (Ex9 and Ex11) (Fig. 10A). For pyroxene, the experiment with temperature cycling performed

301 at 775°C (Ex13) presents higher crystal number density of small crystals (≤ 3 μm^2) than the

302 static one (Ex11) (Fig. 10B). However, in the experiment performed at 815°C the static

303 experiment (Ex9) presents a slightly higher crystal number density of small crystals (≤ 3

304 μm^2) than the one with temperature cycling (Ex46) (Supplementary Dataset F). All static

305 experiments resulted in larger plagioclase and pyroxene crystals than the cycled ones. In

306 terms of crystal fractions, BSE image analyses show that considering the same area, the

307 cycling experiment with dry powder (Ex13) contains, in number of crystals, ~89% more

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plagioclase and ~67% more pyroxene crystals than the corresponding static one (Ex11) while Ex46 (cycling; pre-hydrated melt) contains ~66% more plagioclase and ~17% less pyroxene crystals than the static one (Ex9). No changes in crystal morphology are observed when only the temperature oscillation is taken into account (Fig. 4).

Plagioclase from experiments using pre-hydrated starting material and temperature cycling (Ex13 and Ex46) show a smaller An range than plagioclases from experiments at constant temperatures (Ex11 and Ex9). In contrast, when dry glass and water is used, the plagioclase from the experiment at constant temperature (Ex14) exhibits a larger variation in An-content than its conjugate run with cycling temperature (Ex12) (Fig. 6). Pyroxene shows a very homogenous composition within individual samples but small compositional differences are observed between static and cycling experiments (Fig. 7).

Normalized glass composition values do not show significant differences between the 815°C experiments (Ex9-Ex46). For the 775°C experiments (Ex11 and Ex13), glass composition in Ex11 is slightly more enriched in Al_2O_3, FeO, CaO and Na_2O than Ex13, at the expense of SiO_2 (Table 3).

2 kbar experiments – Under this condition plagioclase and amphibole were the phases used for crystal size analyses. Experiments with temperature cycling show consistently larger plagioclase crystals than the static ones (Fig. 11A). For amphibole, we obtained contrasting results. When dry starting material was used the largest amphibole crystals in cycling experiments are approximately four times larger than those of static experiments (Fig. 11B). When pre-hydrated starting material was used amphibole is slightly larger in experiments at constant temperature (Fig. 11B). However, in experiments performed at 725°C, temperature cycling (Ex21) resulted in a higher concentration of very small amphibole crystals (≤ 3 μm^2) than at static temperature (Ex44), while in experiments performed at 750°C we observe the opposite.

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334   In terms of number of crystals, experiments performed with static temperature always contain

335   more crystals that experiments performed with cycled temperature (Figs. 4 and 5). In most of

336   the experiments the morphology of plagioclase did not change when using temperature

337   cycling. However, in Ex22 (dry glass plus water) we observe the occurrence of tabular and

338   skeletal crystals while the corresponding static experiment (Ex45) only shows tabular crystals.

339   Plagioclase crystals do not display chemical zoning in most experiments performed at 2 kbar

340   with the exception of two charges (Ex20 and Ex21), with an compositional zoning varying

341   from ~38 mol% (core) to 32-34 mol% (rim) in An content. In addition to zoning, plagioclase

342   exhibits a significant compositional range of An within a single charge, with Ex15 (static

343   temperature) showing the largest range of An-content (An_{33} to An_{48}) of all experiments

344   performed at 2 kbar (Fig. 6). No significant compositional variability was observed in

345   amphibole in individual experiments, with the exception of Ex43, but the amphibole Mg

346   number [$Mg/(Mg+Fe^{2+})$] varies between experiments (Fig. 8). Melt compositions vary

347   slightly between cycling and static experiments. Ex21 and Ex22 (cycling temperature) exhibit

348   higher Na_2O and K_2O than Ex44 and Ex45, while Ex15 (static temperature) present higher

349   Na_2O and K_2O than Ex20 (cycling temperature) (Table 3).

350

351   **Discussion**

352   **Attainment of equilibrium**

353   Reaching complete equilibrium between crystals and melt is difficult in experimental

354   petrology, and even more so at low temperatures (700 to 800°C) for highly polymerized melts

355   (high Si content). To reach near-equilibrium conditions in these situations, long run duration

356   experiments (weeks to a month) and homogenous starting materials are required. In this study,

357   we performed experiments with a run duration of 14 to 21 days using crushed homogenous

358   glass as starting material and under water-saturated conditions, which should facilitate the

359   attainment of equilibrium.

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360   Classical evidences for equilibrium as mentioned in the literature are and identified in our

361   experiments are: (1) euhedral crystal shapes, without inclusions and evenly distributed

362   throughout the gold capsules and (2) chemically unzoned crystals, as well as homogeneous

363   melt composition. In our study, plagioclase crystals are usually euhedral, evenly distributed

364   throughout the capsules and unzoned in most of the experiments with exception of four runs

365   performed with pre-hydrated starting material (Ex9 and Ex46 at 1 kbar, and Ex20 and Ex21 at

366   2 kbar). However, when crystals from different locations within a single charge are analyzed,

367   they can present significant variations in anorthite content. The largest An range was observed

368   in Ex15 where plagioclase crystals show an An content ranging between An_{33} to An_{48}. This

369   relatively large compositional variation can be observed in many studies of phase equilibria in

370   felsic systems (e.g., Scaillet et al., 1995). However, in such studies, only few plagioclase

371   crystals from each experiment were usually analyzed, in contrast to the systematic in this

372   study. Previous studies interpreted the variation of plagioclase An-content within individual

373   experiments to be caused by heterogeneous distribution of water at the beginning of

374   experiments, where the more calcic plagioclase crystallized before the water-melt equilibrium

375   was attained (Scaillet & Evans 1999; Costa 2004). However, this explanation probably needs

376   to be reconsidered, at least for the experiments in which pre-hydrated glasses were used as

377   starting material. For example, in Ex15 which was conducted with pre-hydrated glass, the

378   results may indicate that although plagioclase is not in complete equilibrium at the sample

379   scale, local equilibrium was attained. Such local variations may be due to different

380   crystallization rates of plagioclase and other Ca-bearing minerals such as amphibole. If

381   amphibole crystallizes faster than plagioclase, the local environment of this mineral may be

382   depleted in constituents forming amphibole, and plagioclase growing in the vicinity may

383   record this local change of melt composition (e.g., Pichavant et al. 2007).

384   In two charges (Ex20 and Ex21) a few plagioclase crystals show zoning with a relatively large

385   variation in An content between the core (37-38 mol% An) and the rim (31-34 mol% An).

15

386 Both experiments were performed with temperature cycling and pre-hydrated starting

387 material. The zoned plagioclase crystals were usually larger than the average minerals. We

388 speculate that diffusion in pre-hydrated glass is faster than in dry glass in the first hours of

389 experiments which helped crystal growth and consequently increased the chances of forming

390 crystals with normal zoning.

391 We carried out an additional test to evaluate equilibrium conditions comparing the glass and

392 mineral compositions of experiments performed at the same pressure and temperature. We

393 observed that experiments run in the same vessel are similar in composition, while

394 experiments run in separate vessels at the same P and T conditions may present variations in

395 Fe and Mg content. For example, Ex11 and 12 were run together at constant T in a new vessel

396 of the laboratory while, Ex13 and Ex14 (cycling T) were run in one of the oldest vessels. We

397 assigned the difference in Fe and Mg content between one set of experiments and the other to

398 possible differences in fO_2 prevailing in the vessels, independently of temperature cycling.

399 The CSPVs are made of a Ni-based alloy and therefore, the intrinsic fO_2 may change.

400 According to the results presented here, with pyroxenes from the older vessel showing higher

401 Mg and lower Fe content than those from the newer vessel, we assume that the intrinsic fO_2

402 becomes slightly more oxidizing with time.

403

404 **The effect of starting material on crystal phases**

405 The experiment pairs conducted either at static temperature or with cycling temperature lead

406 to the same conclusions: (1) we observe the same mineral assemblages, and no systematic

407 change in mineral compositions between experiments performed with pre-hydrated glass and

408 dry glass. This means that the starting material does not influence phase relationships or

409 compositions; (2) most experiments conducted with pre-hydrated glass have larger and less

410 crystals than experiments conducted with dry powder. One possible explanation to this

411 observation is that the absence of fluid between the grains of the starting powder and the

16

412 homogeneous distribution of volatiles in the pre-hydrated starting glasses contribute to

413 reducing the nucleation of phases along grain boundaries during the initial stages of the

414 experiment. This observation also implies that fluid-absent experiments can be conducted at a

415 water activity which is controlled very accurately if pre-hydrated glasses with well-

416 characterized water concentrations are used. However, it should be noted that all strongly

417 zoned plagioclase crystals identified in this study are in experiments performed using pre-

418 hydrated starting material; (3) a possible inconvenience of using pre-hydrated starting

419 material is its strong effect on plagioclase crystal morphology. Skeletal, anhedral crystals with

420 rough surface are more common in such experiments than in those performed with a dry

421 glass.

422 Previous experimental studies demonstrated that plagioclase crystal morphology is strongly

423 dependent on the degree of supercooling (Lofgren, 1974; Corrigan, 1982). They showed that

424 the shape of plagioclase changes from tabular to skeletal with formation of dendrites and

425 spherulites when cooling rate increases. However, we obtained changes in plagioclase crystal

426 morphology from experiments with identical cooling rates, when we used a pre-hydrated

427 starting material (see Fig. 4 (Ex11 vs. Ex12); (Ex13 vs. Ex14) and Fig. 5 (Ex44 vs. Ex21)).

428 We speculate that a change of the dominant process of crystal growth occurs from interface-

429 controlled when dry glass plus water is used to diffusion-controlled when pre-hydrated

430 starting material is used. Interface-controlled growth leads to planar, faceted morphology and

431 smooth surface (Kirkpatrick, 1975) while diffusion-controlled growth leads to cellular

432 morphology and skeletal shapes (Kirkpatrick, 1975; Hammer, 2008).

433

434 **The effect of pressure on crystal phases**

435 As already noted in several studies, variation of P in the range of 1 - 2 kbar can have a strong

436 effect on the stability of mafic phases. The mineral assemblage formed at 1 kbar is made up of

437 plagioclase, orthopyroxene, magnetite and ilmenite, while in 2 kbar experiments the

17

438 assemblage is integrated by plagioclase, amphibole, biotite, magnetite and ilmenite. Thus, this

439 study confirms that hydrous minerals such as amphibole and biotite are not stable at low

440 pressure when the water content of the melt is close to or below 4 wt% H_2O (e.g., Rutherford

441 and Hill 1993; Venezky and Rutherford 1999; Cichy et al. 2011).

442 Interestingly, temperature cycling (±15°C) at 2 kbar increased plagioclase crystal size, while

443 at 1 kbar we observed the opposite effect. These differences are interpreted as being due to

444 properties of the silicate melt such as viscosity and diffusivity that are influenced, among

445 other parameters, (e.g. degree of polymerization and temperature) by the amount of water

446 dissolved in the melt. As our experiments were conducted at nearly water-saturated

447 conditions, one major difference between 1 and 2 kbar runs is that the water content in the

448 melt was in the range of 3.5 - 4 wt% H_2O at 1 kbar and between 6 - 6.5 wt% H_2O at 2 kbar.

449 Assuming that small changes in temperature (25°C) do not affect water solubility significantly

450 (Holtz et al. 1995) and using the models of water solubility from Behrens and Jantos (2001)

451 and the the model of Hess and Dingwell (1996) for calculation of viscosity, we calculate that

452 the melt viscosity in our experiments perfomed at 1 and 2 kbar is of $10^{5.3}$ and $10^{4.6}$ Pa.s,

453 respectively. Additionally, at 1 kbar, orthopyroxene (Ca-free phase) dissolved at high

454 temperature and crystallized at low temperature together with plagioclase, while at 2 kbar,

455 amphibole (Ca-bearing phase) was the mineral affected. This change in Ca concentration in

456 the melt with temperature cycling will be different in the 1 and 2 kbar experiments, possibly

457 affecting the kinetics of dissolution and growth of plagioclase.

458

459 **The effect of temperature cycling on crystal phases**

460   **Experiments performed at 1 kbar.** One possible explanation for the small effect of

461 temperature cycling on the crystal size at 1 kbar may be that the cycling amplitude chosen

462 (±15°C) was not high enough to completely dissolve the small crystals during the high

463 temperature interval. In one series of experiments, the experiment in which the temperature

464   was cycled not only has smaller crystals, but also presents a higher crystal number density

465   than the counterpart experiment in which temperature was constant (see Fig. 3A and Fig. 3B).

466   This observation could indicate that new nuclei, together with the growth of crystals that

467   survived dissolution at high temperature, formed when temperature decreased. As a

468   consequence, the overall crystal number density increased and the crystal size decreased. The

469   results observed in experiments at 815 (±15°C) corroborate this interpretation, since the

470   minerals exhibit less prominent size differences than those in the experiments performed at

471   775°C (±15°C). We also observed that in the experiments performed at 775°C (±15°C) the

472   largest plagioclase and pyroxene crystals are ~3 times larger in the static experiments (Fig.

473   3A). At 815 °C (±15 °C) the largest plagioclase is only ~2 times larger (Fig. 6A) and

474   pyroxene just slightly larger (Fig. 6B) in static than in cycling experiments. We speculate that

475   at the high temperature stage of 815°C ±15°C (830°C) experiments, the conditions are closer

476   to the liquidus temperature of pyroxene and therefore small crystals start to completely

477   dissolve.

478   Mills & Glazner (2013) demonstrated that at atmospheric pressure, the amplitude is one of the

479   major parameters that directly control the degree of crystal coarsening. Our results show that

480   for a highly polymerized starting material at 1 kbar and temperature of $\leq$ 815°C, the

481   amplitude of ±15°C will not increase the crystal size. However, at the same conditions, pre-

482   hydrated starting material at constant temperature does indeed significantly increase crystal

483   size.

484   **Experiments performed at 2 kbar.** A large difference in the amount (number of

485   crystals considering the same surface area) of plagioclase and amphibole crystals was

486   observed between Ex30 (775°C) and Ex43 (775 ±15°C). Ex30 has ~99% more plagioclase

487   crystals and ~89% more amphibole crystals than Ex43. Approximately 97% of plagioclase

488   crystals in Ex30 (constant T) have a surface area of $\leq$ 0.00001 mm^2 while the smallest

489   plagioclase crystal in Ex43 (cycling) has an area of 0.00005 mm^2. A possible explanation for

19

490   this difference in crystal size and proportion is that with a temperature of 775°C and a cycling

491   amplitude of ±15°C, the maximum temperature reaches 790°C. The textures observed in Ex43

492   (Fig. 7) have lower crystal densities and larger and cleaner melt pools than other experiments,

493   indicating that this sample is close to liquidus temperature, therefore resulting in improved

494   dissolution of small crystals at the peak temperature and a smaller crystal number density.

495

496   **Implications**

497   This study shows that the best approach to increase plagioclase, pyroxene or amphibole

498   crystal sizes in crystallization experiments performed from highly polymerized melts, under

499   water-saturated conditions and at low temperatures (700°C − 800°C) is to use pre-hydrated

500   glass as starting material. However, the formation of zoned plagioclase crystals seems to be

501   favored by using pre-hydrated glass.

502   The effect of temperature cycling on crystal size changes between experiments at 1 kbar and

503   those performed at 2 kbar. Our explanation for this different behavior is that temperature

504   cycling is more effective if melt viscosities and cation diffusivities are low, which increases

505   the kinetics of crystal growth and dissolution. The temperature amplitude of cycling is also

506   important and cycling may have strong or minor effects, depending on the amount of phases

507   present during the high temperature stage of the temperature path. Finally, our methodological

508   study of crystallization processes indicates that the composition of plagioclase can vary by

509   nearly 10 mol% within one experiment, which may be due to small local compositional

510   variations related to the crystallization of other neighbor phases. This compositional range is

511   slightly lower in experiments with cycling temperature than in experiments performed at

512   static temperature (Fig. 6).

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600

Figure captions

601

602   **Figure 1.** Flow-chart of the experimental strategy.

603

604   **Figure 2.** Log-plot of crystal and population number density vs. square root of plagioclase

605   (N_A^{plag}) and pyroxene (N_A^{pyr}) surface area for Ex12 and Ex11. This figure illustrates the effect

606   of starting material on crystal size and on crystal number density. We observe that pre-

607   hydrated starting material greatly increases plagioclase (A) and pyroxene (B) crystal sizes.

608   Experiments performed with dry glass exhibit higher crystal number density of smaller

609   plagioclase and pyroxene crystals. Circles represent area number density (N_A, mm^{-2}) and

610   squares represent population number density (N_v, mm^{-3}).

611

612   **Figure 3.** Log-plot of crystal and population number density of plagioclase (N_A^{plag}) and

613   amphibole (N_A^{amph}) vs. the square root of the mineral surface area for Ex45 and Ex44. At 2

614   kbar experiments performed with pre-hydrated starting material (Ex44) also present larger

615   plagioclase (A) and amphibole (B) crystals than those performed with dry glass (Ex44). In

616   addition, the experiment with dry glass (Ex45) exhibits a higher crystal number density than

617   the pre-hydrated experiment (Ex44). Circles represent area number density (N_A, mm^{-2}) and

618   squares represent population number density (N_v, mm^{-3}).

619

620   **Figure 4.** Backscattered electron images (BSE) (see table 2 for run details) of experiments

621   performed at 1 kbar. The images show the differences in texture and in abundance of crystals

622   of different experiments. P.H.: Pre-hydrated and D.G.: Dry glass. Phase abbreviation: Pl,

623   plagioclase; OPX, orthopyroxene.

624

24

625 **Figure 5.** Backscattered electron (BSE) images (see table 2 for run details) of 2 kbar

626 experiments showing the differences in texture and crystal abundance between experiments

627 performed under constant or cycling temperature. P.H.: Pre-hydrated and D.G.: Dry glass.

628 Phase abbreviations: Pl, plagioclase; Amph, amphibole, Bt, biotite.

629

630 **Figure 6.** Ternary diagram of plagioclase composition. (A) Plagioclase chemical variation in

631 experiments performed at 1 kbar and (B) plagioclase compositional variation of experiments

632 performed and 2 kbar. Experiments performed at 2 kbar show a larger variation of An

633 (anorthite) content than experiments performed at 1 kbar.

634

635 **Figure 7**. Ternary diagram of orthopyroxene for experiments performed at 1 kbar. Pyroxene

636 crystals exhibit a homogenous composition within the same charge.

637

638 **Figure 8**. Amphibole compositional diagram for experiments performed at 2 kbar. Amphibole

639 Mg number [$Mg/(Mg+Fe^{2+})$] does not show a significant variation present within individual

640 charges in almost all experiments with the exception of Ex43. It is however variable between

641 experiments.

642

643 **Figure 9.** Log-plot of crystal and population number density of plagioclase (N_A^{plag}) vs. the

644 square root of the mineral area for Ex12 and Ex30, Ex14 and Ex43. Experiments performed at

645 2 kbar present larger plagioclase crystals than those performed at 1 kbar. Circles represent

646 area number density (N_A, mm^{-2}) and squares represent population number density (N_v, mm^{-3}).

647

648 **Figure 10.** Log-plot of crystal number density and population number density of plagioclase

649 (N_A^{plag}) and pyroxene (N_A^{pyr}) vs. the square root of the mineral surface area. (A) Ex12

650 presents a higher concentration of small plagioclase crystals (≤ 3 µm^2) than Ex14, while both

25

651   experiments present very similar crystal number densities of the larger ($\sim$13 μm^2) crystals.

652   Ex11 (static T) present larger plagioclase crystal number density than Ex13 (cycling T).

653   (B) Ex12 and 11 (static T) presents larger pyroxene crystals than Ex14 and Ex13 (cycling).

654   Circles represent area number density (N_A, mm^{-2}) and squares represent population number

655   density (N_v, mm^{-3}).

656

657   **Figure 11.** Log-plot of the crystal number density of plagioclase ($N_A{}^{plag}$) and amphibole

658   ($N_A{}^{amph}$) plotted against the square root of the mineral surface area for Ex21, Ex22, Ex44 and

659   Ex45. (A) Ex21 and Ex22, performed with temperature cycling, presents larger plagioclase

660   crystals than Ex 44 and Ex45 performed with static temperature. (B) Amphibole was greatly

661   affected by temperature cycling when dry starting material was used and the largest

662   amphibole crystal in Ex22 is $\sim$4 times larger than the largest crystal in E45. In another hand,

663   when pre-hydrated starting material was used, amphibole is slight larger in the static T

664   experiment (Ex44) in comparison with the cycling one (Ex21). The circles represent area

665   number density (N_A, mm^{-2}) and the squares represent population number density (N_v, mm^{-3}).

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667

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Table 1. Starting composition (wt%)

Sample	Pre-hydrated starting material	Dry glass starting material
n:[1]	15	24
SiO_2	70.83[4] (0.45)[3]	70.63 (0.46)
TiO_2	0.42 (0.03)	0.45 (0.04)
Al_2O_3	14.87 (0.23)	15.23 (0.50)
FeO	3.07 (0.17)	3.02 (0.20)
MnO	b.d[2]	b.d
MgO	0.93 (0.06)	1.01 (0.06)
CaO	2.71 (0.15)	2.83 (0.12)
Na_2O	3.54 (0.23)	3.77 (0.23)
K_2O	3.61 (0.09)	3.48 (0.12)
Total[5]	92.15	100.41

Notes: [1]Number of analyses

[2]Below detection limit

[3]Number in parentheses indicates one standard deviation of replicate analyses

[4]Pre-hydrated analyses values were normalized to 100%

[5]Original total

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Table 2. Experimental conditions, durations and run products

Run	P [kbar]	P. H.[2] or D. G.[3]	T [°C]	Cycling or constant T	Duration [Days]	Results
Ex 11	1	P.H	775	constant	21	Pl, Opx, Ox
Ex 13	1	P.H	775± 15	cycling	21	Pl, Opx, Ox
Ex 12	1	D.G	775	constant	21	Pl, Opx, Ox
Ex14	1	D.G	775± 15	cycling	21	Pl, Opx, Ox
Ex 9	1	P.H	815	constant	21	Pl, Opx, Ox
Ex 46	1	P.H	815± 15	cycling	21	Pl, Opx, Ox
Ex 45	2	D.G	725	constant	21	Pl, Amph, Bt, Ox
Ex 22	2	D.G	725± 15	cycling	21	Pl, Amph, Bt, Ox
Ex 44	2	P.H	725	constant	21	Pl, Amph, Bt, Ox
Ex 21	2	P.H	725± 15	cycling	21	Pl, Amph, Bt, Ox
Ex 15	2	P.H	750	constant	21	Pl, Amph, Bt, Ox
Ex 20	2	P.H	750± 15	cycling	21	Pl, Amph, Bt, Ox
Ex 30	2	D.G	775	constant	14	Pl, Amph, Bt, Ox
Ex 43	2	D.G	775± 15	cycling	14	Pl, Amph, Bt, Ox

Notes: All experiments were run with 7 wt% of H_2O contend

[2]Pre-hydrated starting material

[3]Dry starting material

Phase abbreviation: Pl, plagioclase; OPX, orthopyroxene; Amph, amphibole; Bt, biotite; Ox, oxides.

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Table 3. Composition of residual melt

Run	Ex 11	Ex 13	Ex 12	Ex14	Ex 9	Ex 46	Ex 45	Ex 22	Ex 44	Ex 21	Ex 15	Ex 20	Ex 30	Ex 43
T [°C]	775	775 ±15	775	775 ±15	815	815 ±15	725	725 ±15	725	725 ±15	750	750 ±15	775	775 ±15
P [kbar]	1	1	1	1	1	1	2	2	2	2	2	2	2	2
n^1	14	8	20	14	11	9	13	13	8	18	13	11	13	9
P. H[2]. or D. G[3]	P.H	P.H	D.G	D.G	P.H	P.H	D.G	D.G	P.H	P.H	P.H	P.H	D.G	D.G
SiO_2	71.72 (0.69)[4]	74.18 (0.72)	70.94 (0.32)	72.58 (0.58)	71.16 (0.32)	71.24 (0.74)	70.57 (0.67)	72.69 (0.37)	71.59 (0.57)	72.34 (0.30)	68.88 (0.55)	71.37 (0.49)	69.12 (0.50)	68.04 (0.39)
TiO2	0.21 (0.03)	0.13 (0.03)	0.21 (0.04)	0.16 (0.02)	0.25 (0.03)	0.22 (0.03)	0.12 (0.06)	0.12 (0.04)	0.15 (0.05)	0.12 (0.04)	0.20 (0.04)	0.09 (0.04)	0.17 (0.06)	0.20 (0.02)
Al_2O_3	12.73 (0.22)	11.77 (0.27)	12.16 (0.28)	12.04 (0.23)	12.61 (0.23)	12.60 (0.24)	12.32 (0.36)	12.23 (0.26)	11.88 (0.25)	12.10 (0.14)	13.28 (0.08)	12.57 (0.18)	13.20 (0.25)	13.94 (0.34)
FeO	1.24 (0.22)	1.09 (0.31)	1.43 (0.20)	1.11 (0.31)	1.38 (0.12)	1.37 (0.22)	1.06 (0.31)	0.89 (0.15)	1.11 (0.38)	0.90 (0.05)	0.95 (0.20)	0.92 (0.16)	1.10 (0.25)	1.63 (0.22)
MnO	b.d[5]	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d	b.d
MgO	0.18 (0.05)	0.45 (0.20)	0.49(0.19)	0.59 (0.18)	0.22 (0.04)	0.40 (0.16)	0.63 (0.25)	0.16 (0.09)	0.30 (0.14)	0.18 (0.07)	0.49 (0.22)	0.15 (0.04)	0.61 (0.18)	0.65 (0.25)
CaO	1.09 (0.08)	0.96 (0.16)	1.17 (0.11)	0.96 (0.07)	1.19 (0.14)	1.23 (0.06)	1.37 (0.13)	1.22 (0.05)	1.28 (0.13)	1.24 (0.09)	1.73 (0.09)	1.36 (0.09)	1.63 (0.10)	1.83 (0.1)
Na_2O	2.92 (0.23)	2.57 (0.39)	2.22 (0.46)	2.74 (0.16)	3.12 (0.34)	2.99 (0.17)	2.60 (0.17)	2.83 (0.11)	2.49 (0.22)	2.71 (0.11)	3.07 (0.18)	2.80 (0.15)	2.73 (0.10)	2.99 (0.09)
K_2O	4.45 (0.12)	4.54 (0.16)	4.05 (0.17)	4.44 (0.08)	4.37 (0.15)	4.12 (0.11)	3.63 (0.10)	3.82 (0.11)	3.65 (0.11)	3.78 (0.06)	3.73 (0.15)	3.57 (0.12)	3.50 (0.07)	3.48 (0.13)
Total[6]	94.54	95.69	92.66	94.61	94.3	94.17	92.31	91.19	92.45	93.36	92.34	91.19	92.06	92.76

Notes: [1]Number of analyses

[2]Pre-hydrated starting material

[3]Dry starting material

[4]Number in parentheses indicate one standard deviation of replicate analyses

[5]Below detection limit

[6]Original total

Figure 1

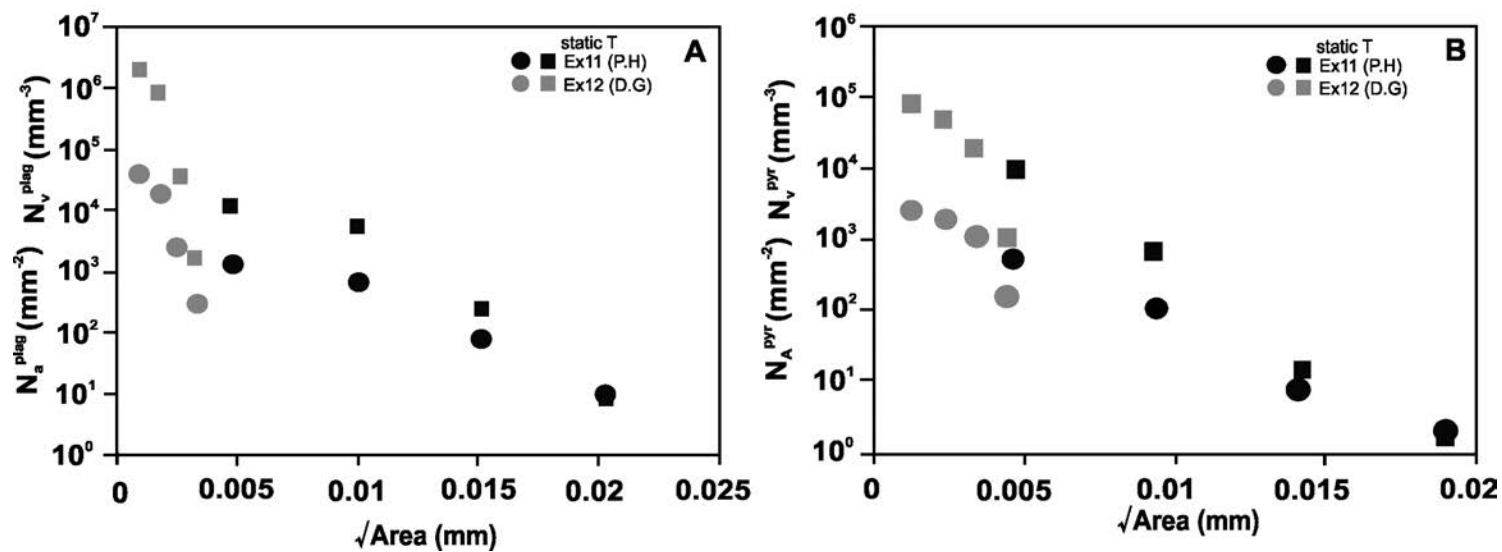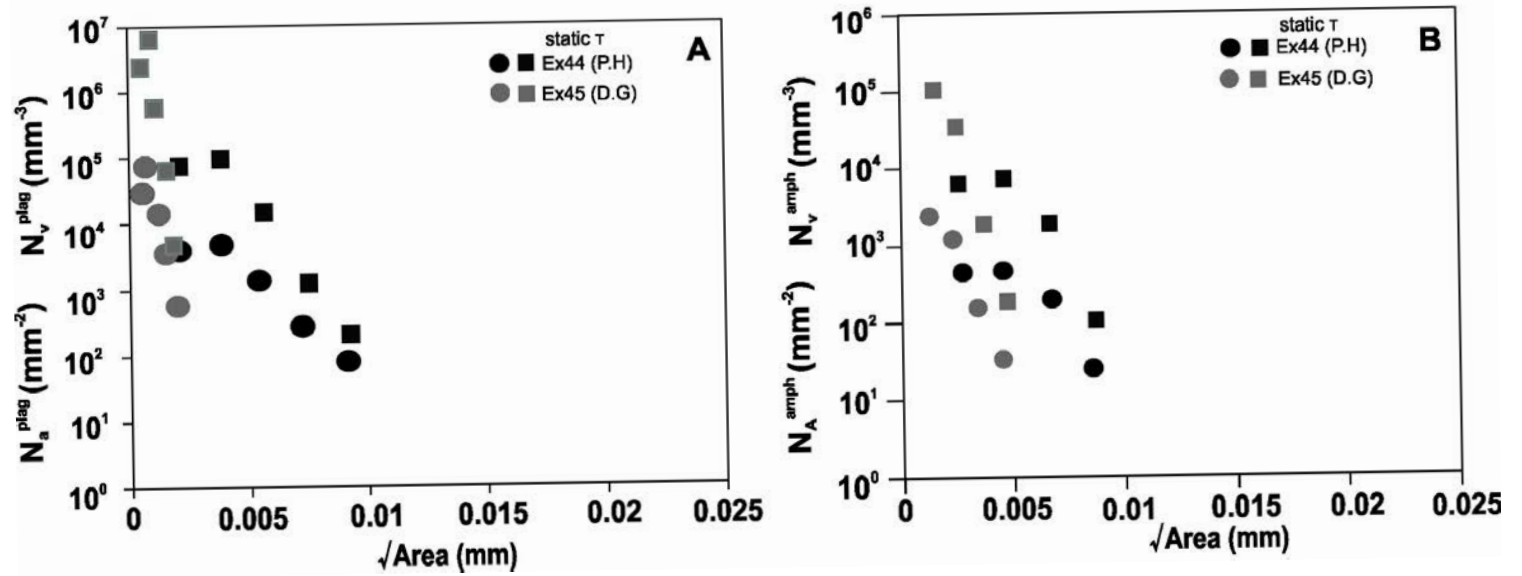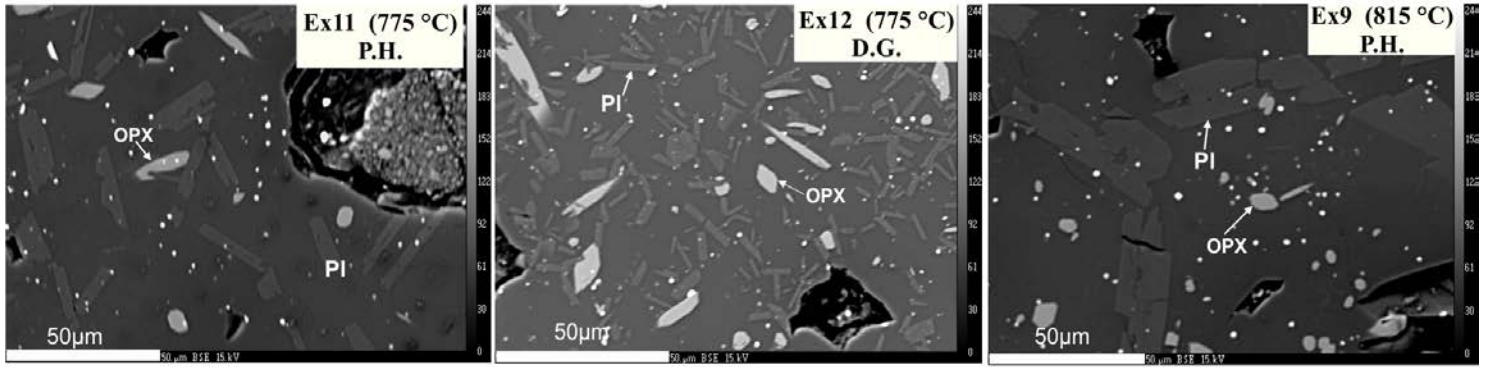|	Dry glass starting material plus H_2O		Pre-hydrated starting material	
	1 kbar	2 kbar	1 kbar	2 kbar
725 °C		Ex22 / Ex45		Ex21 / Ex44
750 °C				Ex20 / Ex15
775 °C	Ex14 / Ex12	Ex43 / Ex30	Ex13 / Ex11	
815 °C			Ex46 / Ex9	

☐ cycling T

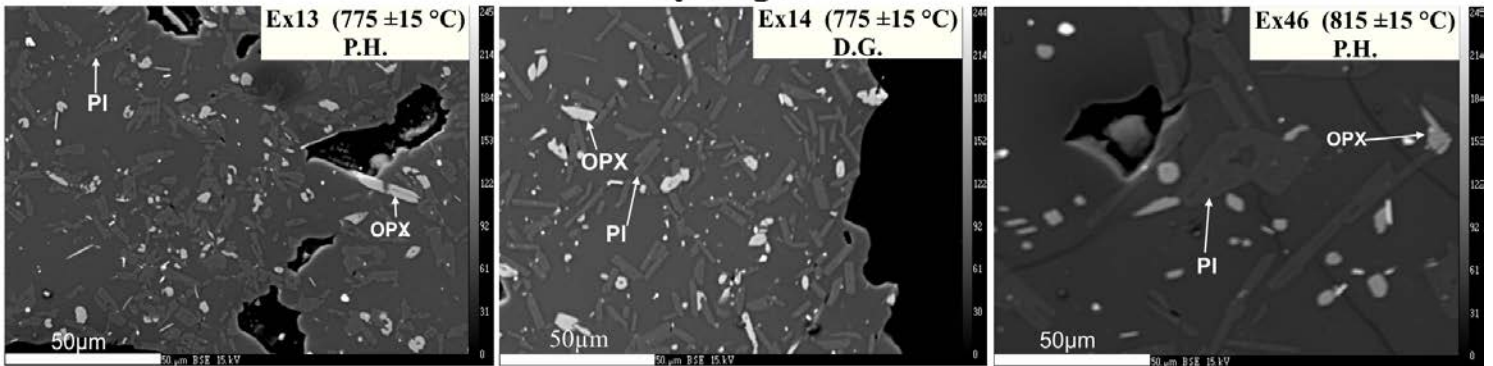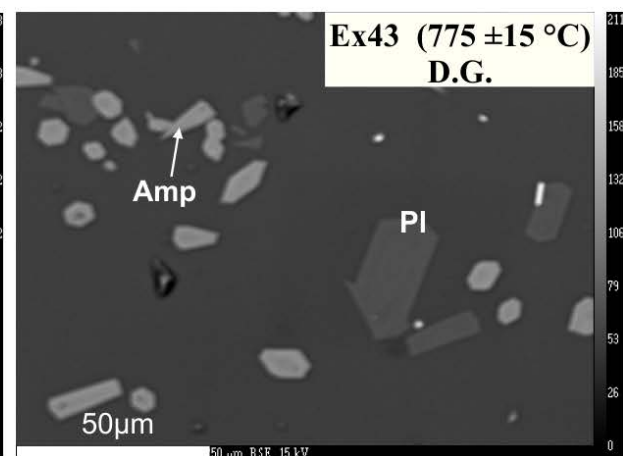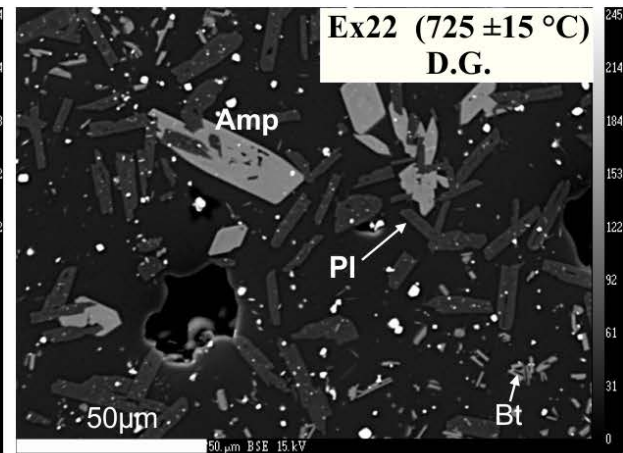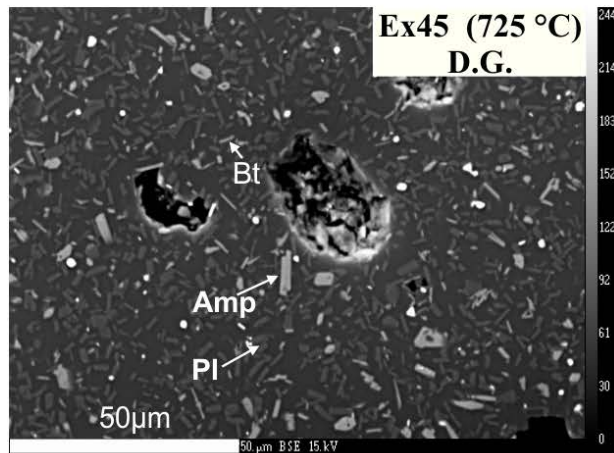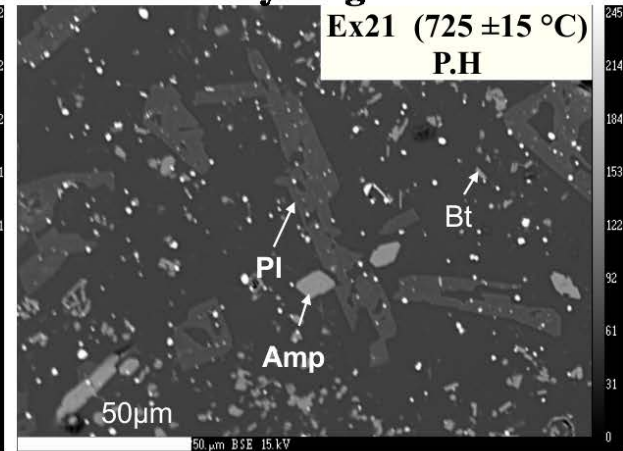▨ static T

Figure 2

Figure 3

Figure 4

Constant T

Cycling T

Figure 5

Constant T   **Cycling T**

Ex44 (725 °C) P.H.

Ex21 (725 ±15 °C) P.H

Ex45 (725 °C) D.G.

Ex22 (725 ±15 °C) D.G.

Ex15 (750 °C) P.H.

Ex20 (750 ±15 °C) P.H.

Ex30 (775 °C) D.G.

Ex43 (775 ±15 °C) D.G.

Figure A shows a plagioclase feldspar classification diagram with samples Ex9 (open circle), Ex11 (dark gray square), Ex12 (gray circle), Ex46 (triangle), Ex13 (plus), Ex14 (black square). The ternary-style classification includes fields: An 0-10% (Albite, NaAlSi₃O₈), An 10-30% (Oligoclase), An 30-50% (Andesine), Orthoclase KAlSi₃O₈, An 50-70% (Labradorite), An 70-90% (Bytownite), An 90-100% (Anorthite, CaAl₂Si₂O₈).

Figure B shows the same classification diagram with samples Ex30 (gray circle), Ex21 (plus), Ex43 (black square), Ex44 (open gray circle), Ex15 (open circle), Ex22 (dark gray circle), Ex20 (triangle).

Figure 7

Figure 8

Figure 9

Figure 10