

1 **Plagioclase nucleation and growth kinetics in a hydrous basaltic melt by decompression experiments**

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32        **Abstract**

33        Isothermal single-step decompression experiments (at temperature of 1075 °C and pressure between 5 and 50 MPa)  
34 were used to study the crystallization kinetics of plagioclase in hydrous high-K basaltic melts as a function of pressure,  
35 effective undercooling ( $\Delta T_{\text{eff}}$ ) and time. Single-step decompression causes water exsolution and a consequent increase  
36 in the plagioclase liquidus, thus imposing an effective undercooling ( $\Delta T_{\text{eff}}$ ), accompanied by increased melt viscosity.  
37 Here we show that the decompression process acts directly on viscosity and thermodynamic energy barriers (such as  
38 interfacial-free energy), controlling the nucleation process and favoring the formation of homogeneous nuclei also at  
39 high pressure (low effective undercoolings). In fact, this study shows that similar crystal number densities ( $N_a$ ) can be  
40 obtained both at low and high pressure (between 5 and 50 MPa), whereas crystal growth processes are favored at low  
41 pressures (5 - 10 MPa).

42        The main evidence of this study is that the crystallization of plagioclase in decompressed high-K basalts is more  
43 rapid than that in rhyolitic melts on similar timescales. The onset of the crystallization process during experiments was  
44 characterized by an initial nucleation event within the first hour of the experiment, which produced the largest amount  
45 of plagioclase. This nucleation event, at short experimental duration, can produce a dramatic change in crystal number  
46 density ( $N_a$ ) and crystal fraction ( $\phi$ ), triggering a significant textural evolution in only 1 h. In natural systems, this may  
47 affect the magma rheology and eruptive dynamics on very short time scales.

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## 63 1. Introduction

64 The kinetics of magma crystallization may be influenced by melt composition, crystal types, temperature (T),  
65 pressure (P), undercooling ( $\Delta T = T_{\text{liquidus}} - T_{\text{experimental}}$ ), time, melt water content, oxygen fugacity ( $fO_2$ ), and cooling and  
66 decompression rates (e.g. Fenn 1977; Swanson 1977; Lofgren 1983; Cashman 1993; Toplis and Carroll 1995; Couch et  
67 al. 2003; Martel and Schmidt 2003; Hammer 2006; Brugger and Hammer 2010; Mollard et al. 2012; Martel 2012; Shea  
68 and Hammer 2013; Arzilli and Carroll 2013). Therefore, many variables play a role during magma crystallization at  
69 depth or in a volcanic conduit, and through experimentally derived constraints we can better understand pre- and syn-  
70 eruptive magma crystallization behavior. The thermodynamic properties of magmas have been extensively investigated  
71 as a function of T, P,  $fO_2$  and magma composition (e.g. Ghiorso 1997), and this allows estimation of the stability of  
72 equilibrium phases and physical parameters (e.g., density, viscosity). However, many natural igneous rocks contain  
73 geochemical, mineralogical and textural evidence of disequilibrium, suggesting that magmas frequently follow non-  
74 equilibrium, time-dependent pathways that are recorded in the geochemical and petrographic characteristics of the rocks  
75 (Muncill and Lasaga 1987). There are currently no suitable theoretical models capable of calculating nucleation and  
76 growth rates in disequilibrium conditions without experimental constraints.

77 The main aim of this study is to investigate crystallization kinetics of plagioclase in a hydrous HK-basalt (HK =  
78 high  $K_2O$ ) using the decompression experiments performed by Agostini et al. (2013). The HK-basalt used by Agostini  
79 et al. (2013) was erupted during the present day activity of Stromboli (Aeolian Islands, Italy). HK-basalts are commonly  
80 associated with the development of island arcs and orogenic volcanism (Jakeš and White 1971; Barberi et al. 1974;  
81 Morrison 1980; Stern et al. 1988). Therefore, studying kinetics and texture development during crystallization can help  
82 improve our understanding of eruption dynamics.

83 Equilibrium experiments using HK-basalts from Stromboli have previously been performed between atmospheric  
84 pressure and 400 MPa (Di Carlo et al. 2006; Pichavant et al. 2009; Agostini et al. 2013). Crystallization kinetics of  
85 plagioclase were experimentally studied in simple systems with 2 components by Kirkpatrick (1976) and Kirkpatrick et  
86 al. (1979). Crystallization kinetics in various basaltic melt compositions have also been extensively studied by several  
87 authors through cooling (Lofgren 1974; Lofgren et al. 1974; Donaldson et al. 1975; Kirkpatrick 1977; Lofgren 1983;  
88 Muncill and Lasaga 1987; Muncill and Lasaga 1988; Toplis et al. 1994; Burkhard 2005; Hammer 2006; Conte et al.  
89 2006; Orlando et al. 2008; Pupier et al. 2008; Szrámek et al. 2010; Vona et al. 2011; Shea and Hammer 2013; Vetere et  
90 al. 2013; Vona and Romano 2013), through heating experiments (Burkhard 2002) and at ambient pressure through *in*  
91 *situ* experiments (Schiavi et al. 2009; Ni et al. 2014). In these experimental studies, mainly plagioclase crystallization  
92 kinetics and the development of its morphology were investigated as a function of undercooling (e.g., Lofgren 1974).  
93 Crystallization of plagioclase in basaltic magma has been little studied through decompression experiments (Nicholis

94 and Rutherford 2004; Agostini et al. 2013). Instead, crystallization kinetics and textural evolution of intermediate and  
95 felsic magmas focusing mostly on feldspar crystallization have been largely investigated through decompression  
96 experiments (Geschwind and Rutherford 1995; Hammer and Rutherford 2002; Couch et al. 2003; Couch, 2003; Martel  
97 and Schmidt 2003; Nicholis and Rutherford 2004; Szramek et al. 2006; Suzuki et al. 2007; Castro and Gardner 2008;  
98 Calzolaio et al. 2010; Brugger and Hammer 2010; Mollard et al. 2012; Martel 2012; Shea and Hammer 2013; Arzilli  
99 and Carroll 2013). These experimental works highlight that the decrease in pressure causes water exsolution,  
100 accompanied by an increase in plagioclase liquidus temperatures. The undercooling resulting from this increase in  
101 liquidus temperature provides the driving force for crystallization. Unlike isobaric cooling, which imposes a  
102 conventional "undercooling" ( $\Delta T$ ) through a temperature variation, the isothermal decompression imposes an "effective  
103 undercooling" ( $\Delta T_{\text{eff}}$ ) through the decreasing of pressure.  $\Delta T_{\text{eff}}$  is defined as the difference between equilibrium  
104 plagioclase liquidus temperature and the run temperature at the final pressure (reached after the decompression)  
105 (Hammer and Rutherford 2002).

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## 107 **2. The aim and strategy of this study**

108 The aim of this contribution is to study the nucleation and growth processes of plagioclase, induced by  
109 decompression, in a water-saturated HK-basaltic melt as a function of  $\Delta T_{\text{eff}}$ , pressure (P), H<sub>2</sub>O content, melt viscosity  
110 and time. Experimental data about plagioclase nucleation in basalt are typically obtained from cooling experiments at  
111 atmospheric pressure (e.g., Lofgren 1983; Conte et al. 2006; Vetere et al. 2013). In this study, we analyze the texture of  
112 plagioclase-bearing samples obtained from isothermal single-step decompression experiments (5-50 MPa) performed by  
113 Agostini et al. (2013).

114 The experimental study of Agostini et al. (2013) was focused on defining the crystallization of plagioclase and  
115 magma residence times in the shallow part of the Stromboli magma system. All decompression experiments were done  
116 using vertically mounted rapid-quench cold-seal pressure vessels (TZM alloy, pressurized with Ar) at the Bayerisches  
117 Geoinstitut in Bayreuth (Germany). The starting material used by Agostini et al. (2013) was the PST-9 sample (Table  
118 1), which comes from a fall-out layer of pumiceous, scoriaceous and mingled lapilli and bombs. PST-9 is representative  
119 of the pumiceous fraction (Pichavant et al., 2011) and it represents one of the most primitive sample compositions  
120 obtained from Stromboli (Di Carlo et al. 2006; Agostini et al. 2013). Modal proportions, determined by point counting  
121 (vol.%, vesicle-free basis) are 89 % glass, 8 % clinopyroxene, 1 – 2 % olivine and 1 – 2 % plagioclase (Di Carlo et al.  
122 2006). The groundmass composition (Table 1) is also distinctive, being the highest in MgO, CaO/Al<sub>2</sub>O<sub>3</sub> and Mg-  
123 number, and the lowest in FeO of all known pumice samples erupted from Stromboli in the past centuries (Pichavant et  
124 al. 2011).

125 Agostini et al. (2013) used the PST-9 powder to perform experiments in order to constrain the liquidus of  
126 plagioclase and plagioclase growth rates under conditions corresponding to those in the conduit system feeding volcanic  
127 activity at Stromboli volcano. They chose the conditions for decompression experiments on the basis of the plagioclase  
128 liquidus of PST-9 at water-saturated conditions. The decompression-induced crystallization experiments were done  
129 using isothermal single-step decompression. Samples were first held at 100 MPa and 1075 °C for 4 h (melting time),  
130 then rapidly (<1 minute) isothermally decompressed to final pressures ( $P_f$ ) between 50 and 5 MPa, and left to crystallize  
131 for experimental time ( $t_{exp}$ ) between 0.5 and 8 h before quenching. During the initial melting at 100 MPa and 1075 °C  
132 for 4 h, some clinopyroxenes and Fe-Ti oxides (~15 vol.%) were present in the sample and the melt had HK-basaltic  
133 composition (Table 1). The chemical composition of the glass obtained after the melting time that preceded all the  
134 decompression experiments is shown in Table 1. Water saturation was calculated using the solubility model from  
135 Moore et al. (1998) (Table 2) (for more details on experimental strategy see Agostini et al. 2013).

136 Experimental conditions of the decompression experiments were used to investigate the effect of  $P_f$ ,  $\Delta T_{eff}$  and time  
137 on the crystallization of plagioclase (5 to 50 MPa final pressure, 0.5 to 8 h at final pressure are reported in Table 2). The  
138 values of  $\Delta T_{eff}$  were calculated by Agostini et al. (2013) and they are shown in Table 2. In this study we measured,  
139 through the textures of the samples, the kinetics of nucleation and growth of plagioclase. The obtained results allow us  
140 to study the progressive crystallization, characterizing qualitatively the evolution of plagioclase morphology with  
141 applied  $\Delta T_{eff}$ . We study with a particular emphasis the nucleation process of plagioclase as a function of  $P_f$ , viscosity,  
142  $\Delta T_{eff}$  and time. In the discussion,  $\Delta T_{eff}$  will be considered independent of experimental duration even if the magnitude  
143 of  $\Delta T_{eff}$  should change through time as crystallization progresses. Furthermore, we discuss and compare the nucleation  
144 and growth kinetics of plagioclase with those of more evolved melts. In fact, we demonstrate that almost all of the  
145 sample crystallization occurs within the first 1-2 hours of the experiments.

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### 147 **3. Crystallization theory and the interfacial free energy**

148 In the classical theory of nucleation (CNT), the bulk free energy of a system changes during the formation of a cluster  
149 of atoms (Kirkpatrick 1981; James 1985). For a small cluster radius the interfacial free energy term ( $\sigma$ ) dominates and  
150 the nucleation does not occur (Kirkpatrick 1981; James 1985). There is an intermediate size, known as the critical size,  
151 at which the kinetic free energy barrier to nucleation ( $\Delta G^*$ ) decreases if the nucleus grows or dissolves, in agreement  
152 with the Gibbs-Thomson effect (Perez 2005). As a consequence, at very small size, the nucleus is unstable.  $\Delta G^*$  of the  
153 crystal phase increases with increasing the radius ( $r$ ) of the nucleus. If  $\Delta G^*$  is sufficiently high with respect to the  
154 interfacial free energy ( $\sigma$ ), the nucleus will be stable. Once the nucleus is large enough,  $\Delta G^*$  decreases as crystal growth  
155 progresses, and each addition of an atom to the lattice reduces the kinetic free energy barrier to nucleation ( $\Delta G^*$ ) (bulk

156 properties dominate over surface effects). The steady state rate equation for homogeneous crystal nucleation ( $I$ ,  $\text{m}^{-3}\text{s}^{-1}$ )  
 157 is related to absolute temperature according to the CNT and it is defined by following equation (James 1985):

$$158 \quad I = A \exp\left[\frac{-(\Delta G^* + \Delta G_D)}{k_B T}\right]; \quad A = \left[\frac{n_v k_B T}{h}\right]; \quad \Delta G^* = \left[\frac{16\pi\sigma^3}{3\Delta G_V^2}\right] S \quad \text{Eq. 1}$$

159 where  $A$  is the pre-exponential factor that includes the frequency of attachment attempts,  $k_B$  is the Boltzman constant,  $T$   
 160 is temperature,  $n_v$  is the volumetric concentration of reactant atoms and  $h$  is Planck's constant. Furthermore,  $\Delta G_V$  is the  
 161 volume free energy and it is defined as  $\Delta G_V = \Delta G/V_M$  where  $V_M$  is the molar volume of the crystallizing phase and  $\Delta G$   
 162 is the bulk free energy decrease driving crystallization. If the nucleation is homogeneous,  $S=1$ , then the thermodynamic  
 163 barrier to crystal nucleation is a function of the difference in volumetric free energies of the liquid and solid (James  
 164 1985).  $\Delta G$  is the thermodynamic driving force for crystallization (Turnbull 1952):  $\Delta G = (\Delta H_f \Delta T)/T_L$ , where  $\Delta H_f$  is the  
 165 enthalpy of fusion,  $\Delta T$  is the undercooling and  $T_L$  is the liquidus temperature. During the nucleation process, the  
 166 activation energy ( $\Delta G_D$ ), another energetic barrier, plays an important role in the genesis of nuclei in that it must be  
 167 overcome every time an atom is added to a cluster (Kirkpatrick 1983). The activation energy ( $\Delta G_D$ ) for the formation of  
 168 a crystalline nucleus decreases with decreasing  $\sigma$ , increasing enthalpy of fusion ( $\Delta H_f$ ), and increasing undercooling  
 169 (Kirkpatrick 1983). Since a combination of experimental data and the CNT is needed to determine the nucleation  
 170 rate, several simplifying assumptions are introduced in the calculation. For instance, the activation energy ( $\Delta G_D$ ) of  
 171 atomic jumps across the liquid-nucleus interface is the same as that of shear relaxation of the liquid (i.e., the Stokes-  
 172 Einstein approximation; Ree and Eyring 1958; Dingwell and Webb 1989), allowing  $\Delta G_D$  to be expressed in terms of  
 173 viscosity ( $\eta$ ).  $\Delta G_D$  is described by following equation (Christian 1965):

$$174 \quad \Delta G_D = -k_B T \ln\left(\frac{h}{\lambda^3 3\pi\eta}\right) \quad \text{Eq. 2}$$

175 where  $\lambda$  is the atomic jump distance and  $\eta$  is the viscosity.  $\Delta G_D$  is combined with the pre-exponential factor  $A$  (see Eq.  
 176 1) in order to obtain the equation for homogeneous nucleation rate:

$$177 \quad I = \frac{n_v k_B}{3\pi\lambda^3\eta} T \exp\left[\frac{-\Delta G^*}{k_B T}\right] \quad \text{Eq. 3}$$

178 The calculation of energies involved in the nucleation process and comparisons between natural and experimental  
 179 data can help us to better understand the crystallization kinetics of multiphase systems (Davids et al 1997; Fokin and  
 180 Zanotto 2000, Ikeda et al. 2002, Hammer 2004). Interfacial free energy ( $\sigma$ ) is crucial parameter for the nucleation and it  
 181 is extremely difficult to determine independently from nucleation rate and viscosity (Hammer 2004). Interfacial free  
 182 energy can be calculated rearranging Eq. 3 and the following equation describes  $\sigma$  for homogeneous crystal nucleation:

$$\sigma = \sqrt[3]{\frac{3k_B T}{\pi} \left( \frac{\Delta H_f \Delta T}{4T_L V_M} \right)^2 \ln \left( \frac{n_v k_B T}{3\pi \lambda^3 \eta l} \right)} \quad \text{Eq. 4}$$

184

#### 185 4. Image analysis

186 In this study, crystallization kinetics of plagioclase were measured through textural analysis, collecting a larger  
 187 number of back scattered electron (BSE) images in comparison to those used by Agostini et al. (2013). 10 BSE images  
 188 were acquired for each sample in order to accurately measure the nucleation of plagioclase, including at least 50 crystals  
 189 of plagioclase per sample (Hammer et al. 2000; Couch et al. 2003; Clarke et al. 2007). BSE images were collected with  
 190 a ZEISS EVO-MAV10 scanning electron microscope (SEM) at Istituto Nazionale di Geofisica e Vulcanologia of Pisa  
 191 (Italy), using an acceleration voltage of 15 kV and sample current of  $\sim 5$  nA. Textural analyses of the run products were  
 192 performed on BSE images using ImageJ, an open-source software (NIH Image; Abramoff et al. 2004; Schneider et al.  
 193 2012). Because of the high number of adjacent plagioclase grains on several samples, manual separation of the crystals  
 194 was necessary before conversion into binary images.

195 The number of plagioclase crystals ( $n_{\text{plg}}$ ) was measured to calculate the crystal number density ( $N_a$ , crystals/cm<sup>2</sup>) of  
 196 the plagioclase.  $N_a$  and crystal area fraction ( $\phi$ ) of plagioclase were calculated on a vesicle-free basis. We refer to the  
 197 vesicle-corrected sample area as the “reference area” ( $A_r$ ), and this was obtained by subtracting vesicle areas from the  
 198 total image area (Hammer et al. 1999), accordingly:

$$199 \quad N_a = \frac{n_{\text{plg}}}{A_r} \quad \text{Eq. 5}$$

$$200 \quad \phi = \frac{A_{\text{plg}}}{A_r} \quad \text{Eq. 6}$$

201 where  $A_{\text{plg}}$  is the area of the plagioclase. Because of their similar average atomic number, plagioclase crystals and the  
 202 surrounding glass were often difficult to distinguish in BSE images. Thus, to measure areas of both glass and  
 203 plagioclase, the latter phase was segmented manually. The areas of clinopyroxenes, oxides and bubbles were measured  
 204 using a single threshold because their grey tones were clearly distinguishable. The uncertainty in the area measurements  
 205 was estimated on the basis of 10 images per sample.

206 Mean crystal size ( $s_n$ ) was also estimated:

$$207 \quad s_n = \sqrt{\frac{\phi}{N_a}} \quad \text{Eq. 7}$$

208 The volumetric number density  $N_v$  ( $N_v = N_a/s_n$ ) was calculated using a standard method for correcting the two-  
 209 dimensional data to volumetric nucleation density (Cheng and Lemlich 1983; Couch 2003). The minimum nucleation

210 rate,  $I_m$  (Couch 2003) was calculated dividing  $N_v$  by the experimental duration time ( $I_m=N_v/t$ ). The incremental  
 211 nucleation rate,  $I_i$  (Couch 2003), is estimated from:

$$212 \quad I = \frac{N_{v2} - N_{v1}}{t_2 - t_1} \quad \text{Eq. 8}$$

213 where  $N_{v2}$  and  $N_{v1}$  are the volumetric number densities measured at experimental times  $t_2$  and  $t_1$  respectively, for two  
 214 experiments with the same  $P_f$  but different durations. Stereological corrections and further details can be found in  
 215 Hammer et al. (1999) and citations therein. The incremental nucleation rate ( $I_i$ ) was calculated to highlight the influence  
 216 of time, step by step, on the nucleation process.

217 Crystal dimensions were also measured through back-scattered electron (BSE) images. Typically, only the largest 10  
 218 crystals in each image were measured (e.g., Couch 2003) because of the interest in determining the maximum growth  
 219 rate. Growth rate ( $G_L$ ) was calculated using only the longest dimension of each crystal (e.g., Fenn 1977; Hammer and  
 220 Rutherford 2003; Couch et al. 2003). The uncertainty for sizes and growth rate measurements was estimated on the  
 221 basis of the 10 largest crystals observed in each sample. According to Couch (2003) and Calzolaio et al. (2010) we used  
 222 the following relationship:

$$223 \quad G_L = \frac{0.5L}{t} \quad \text{Eq. 9}$$

224 where  $t$  is the duration of the experiment. Furthermore, incremental growth rate ( $G_{Li}$ ) was calculated to study the  
 225 influence of time on growth process, using the following relationship:

$$226 \quad G_{Li} = \frac{(0.5L_2 - 0.5L_1)}{(t_2 - t_1)} \quad \text{Eq. 10}$$

227 where  $L_2$  and  $L_1$  are the maximum lengths measured at experimental times  $t_2$  and  $t_1$ , respectively, for two experiments  
 228 with the same  $P_f$  but different durations.

229

## 230 **5. Experimental results**

### 231 5.1 Morphology and crystallization kinetics of plagioclase

232 Experiments containing plagioclase crystals show a systematic variation of crystal morphology with a gradual  
 233 transition from tabular to prismatic elongated to hopper and skeletal shapes as final pressure ( $P_f$ ) decreases (see Table 3,  
 234 Fig. 1). Tabular and prismatic elongated crystals up to  $6.11 \cdot 10^{-3}$  cm were found at 25 and 50 MPa. At shorter  
 235 experimental durations tabular shapes are more abundant, whereas at longer durations crystals tend to become more  
 236 prismatic. Hopper and skeletal crystals up to  $1.63 \cdot 10^{-2}$  cm are dominant for a range of  $P$  that varies from 5 to 10 MPa.

237 The characteristics of plagioclase nucleation and growth are hereafter described as a function of  $t_{exp}$ ,  $P_f$  and  $\Delta T_{eff}$ .



238 Experiments performed at 25 and 50 MPa showed a plagioclase nucleation delay of at least 0.5 h, whereas no delay was  
239 observed for runs at 5 and 10 MPa (see Table 3). In our experiments crystal number density ( $N_a$ ) varies between  $10^5$  and  
240  $10^4 \text{ cm}^{-2}$  and no relationship is evident with  $P_f$  and  $t_{\text{exp}}$  (Fig. 2, Table 3). In fact, Fig. 2 suggest that time has no  
241 resolvable influence on nucleation, particularly at longer experimental durations. During the first hour of the  
242 experiment, the minimum nucleation rate ( $I_m$ ) range between  $10^2$  to  $10^5 \text{ cm}^{-3} \text{ s}^{-1}$  and  $I_m$  increases with increasing  $P_f$  (Fig.  
243 3, Table 3). Considering the incremental nucleation rate ( $I_i$ ), values range from  $10^5$  to  $10^0 \text{ cm}^{-3}/\text{s}$ , decreasing with  
244 increasing  $t_{\text{exp}}$  (Fig. 4 and Table 3). These results strongly suggest that the main event of nucleation occurred during the  
245 first hour following decompression.

246 The plagioclase sizes ( $L$ ) tend to increase slightly with decreasing  $P_f$  (Fig. 5a and Table 3). The incremental growth  
247 rate ( $G_{Li}$ ) ranges between  $10^{-7}$ - $10^{-9} \text{ cm/s}$  (Fig. 5b and Table 3), depending on the experimental duration and  $P_f$ . These  
248 incremental growth rates show that the majority of crystal growth is completed within the first hour or two following  
249 decompression.

250

## 251 6. Discussion

### 252 6.1 The effect of time

253 Time plays a crucial role in the crystallization processes of silicate melts (e.g. Couch 2003; Hammer and Rutherford  
254 2002; Arzilli and Carroll 2013). Fig. 4 shows that the incremental nucleation rate ( $I_i$ ) decreases with increasing time.  $I_i$   
255 is relatively high during the initial nucleation event ( $t_{\text{exp}} = 0.5$  and 1 h), from  $10^4$  to  $10^5 \text{ cm}^{-3}\text{s}^{-1}$ , and rapidly decreases  
256 during the following time steps (2, 4 and 8 h). The value of  $I_i$  shows minor fluctuation with increasing time, and at  $t_{\text{exp}}$   
257 higher than 1 hour  $I_i$  remains in the interval between 1 and  $10^1 \text{ cm}^{-3}\text{s}^{-1}$  (Fig. 4). This suggests that the main event of  
258 nucleation occurred during the first hour or the first half hour of the experiment, depending on nucleation delay, and  
259 that the system is able to progress towards equilibrium conditions quickly (reaching the equilibrium crystal fraction for  
260 each given pressure in 1-2 h). The two samples quenched at higher pressures took longer to begin crystallizing (~1  
261 hour) compared to the samples quenched at low pressure (~30 minutes), which suggests that higher  $P_f$  is associated with  
262 a slight nucleation delay.

263 The maximum dimensions of the crystals ( $L$ ) are obtained at low  $P_f$  (5 and 10 MPa), however the crystal sizes range  
264 in the same order of magnitude (Fig. 5a). Furthermore,  $L$  is quite constant with time (Fig. 5a).  $G_{Li}$  values range from 0  
265 cm/s (essentially no measurable growth and no changes in average crystal size) to  $10^{-6}$  -  $10^{-7} \text{ cm/s}$  (maximum growth).  
266 The  $G_{Li}$ , after the first hour, changes from 0 to  $10^{-6} \text{ cm/s}$ , and crystals show either no growth or size increments of 10-80  
267  $\mu\text{m}$ . Thus, also the main growth event occurred at the beginning of the experiment, during the first hour (Fig. 5b),  
268 followed by an apparent decrease in  $G_{Li}$  while time increases. Our results are in agreement with the results of Couch et

269 al. (2003) and by Couch (2003), which show that diffusion- or interface-controlled growth should display lower  
270 incremental growth rates as the system approaches equilibrium for rhyolitic and haplogranitic melts. Coarsening is also  
271 a growth process that may influence crystallization kinetics. However, on the basis of our results (see Figs 2 and 5b) we  
272 find no evidence to suggest that coarsening occurred over the time scale investigated; coarsening implies that the  
273 nucleation density ( $N_a$ ) should decrease with time, which is not observed. Furthermore, if coarsening occurred in our  
274 samples, incremental growth rates ( $G_{Li}$ ) should increase with time, instead it decreases after 1 h. In conclusion, the  
275 results of this study suggest that time has no resolvable influence at longer experimental durations than 1 - 2 h  
276 essentially because the crystal-melt system closely approaches a near-equilibrium state on these timescales. As shown  
277 in Figs 4, 5 and 6 the crystallization of plagioclase is so rapid that the majority of nucleation and growth occurred  
278 within the first two hours, determining the final texture of the samples (Fig. 6a) and the compositions of plagioclases  
279 (Fig. 6b) and melts (Fig. 6c, d). Therefore, future studies should investigate the crystallization kinetics of plagioclase in  
280 hydrous basaltic melts at durations less than 1 h to better understand the nucleation and growth processes in  
281 disequilibrium conditions.

282

## 283 6.2 The effect of pressure and $\Delta T_{\text{eff}}$ on nucleation and growth mechanism

284 Effective undercooling ( $\Delta T_{\text{eff}}$ ), as imposed by isothermal decompression, acts as the driving force for crystallization  
285 in water-saturated melts.  $\Delta T_{\text{eff}}$  varies with pressure ( $P_f$ ) and  $H_2O$  content, increasing as  $P_f$  decreases. Although the melt  
286 is saturated with water, decompression reduces the amount of  $H_2O$ , increasing the viscosity of the melt. Variations in  
287 pressure, effective undercooling, water content and viscosity are not independent but all can strongly affect the  
288 nucleation and growth processes; unfortunately the interdependence of these variables can render difficult the  
289 evaluation their individual contributions to magma crystallization kinetics. To do so would require new experiments  
290 designed to closely investigate the 10 - 120 minute time interval following decompression.

291 Crystallinity (Fig. 6a), plagioclase and residual glass compositions (Fig. 6b, c, d) depend on the value of  $P_f$ . Crystal  
292 fraction increases with decreasing  $P_f$  (corresponding to increasing  $\Delta T_{\text{eff}}$ ; Fig. 6a). Anorthite content in plagioclase is  
293 >70 mol% (up to 83 mol%) in experiments at 25 and 50 MPa, and decreases to as low as  $An_{65}$  in experiments at 5 and  
294 10 MPa (Fig. 6b). The plagioclase compositions obtained in our experiments at 25 and 50 MPa are close to those  
295 obtained by Di Carlo et al. (2006) through equilibrium experiments at the same pressures. The presence of lower An  
296 plagioclase at lower  $P(H_2O)$  is consistent with results from many other studies (e.g., Couch, 2003; Couch et al., 2003;  
297 Mollard et al., 2012). Experimental glass compositions rapidly evolve towards higher  $K_2O$  and lower  $CaO$  with  
298 decreasing  $P_f$  (see Fig. 6c, d and Online Resource 1). The  $SiO_2$  in the residual glass changes from ~50 wt % (starting  
299 glass) to 50-56 wt % (residual glass) in a few hours (Online Resource 1). These chemical variations are strongly

300 associated with the crystal fraction of plagioclase, the most abundant mineral phase in all experiments and capable of  
301 dramatically modifying both rock texture and the composition of the residual glass as a function of  $P_f$  and  $\Delta T_{\text{eff}}$  (Fig. 6c,  
302 d and Online Resource 1). The experimental duration has only a minor effect on the chemical composition of residual  
303 glass and plagioclase compared to  $P_f$ , suggesting that nucleation and crystal growth, which control the chemical  
304 compositions of the system, are rapid at the beginning of the experiments. Furthermore, Fig. 6 (and Online Resource 1)  
305 also indicate that  $\Delta T_{\text{eff}}$  changes through time because the melt composition changes as a result of crystallization, thus,  
306 the values of  $\Delta T_{\text{eff}}$  show in this study are the instantaneous effective undercooling at the moment decompression occurs.

307 The nucleation density varies little between 5 and 50 MPa (Fig. 2). However, the plagioclase crystal fraction ( $\phi$ ) is  
308 higher at low  $P_f$  (5 and 10 MPa) (Fig. 6a), indicating that the growth process, over the same range of durations, is  
309 slightly favored at higher  $\Delta T_{\text{eff}}$  (lower  $P_f$ ). Fig. 3, considering only experiments of 1 h, also shows that nucleation rate  
310 ( $I_m$ ) is positively related with  $\Delta T_{\text{eff}}$ , while the growth rate ( $G_L$ ) is negatively related with  $\Delta T_{\text{eff}}$ , highlighting that the  
311 nucleation process is relatively slow at high  $\Delta T_{\text{eff}}$  in comparison with the growth process. This behavior is anomalous  
312 when compared with equilibrium and cooling experiments (e.g., Lofgren 1974; Nabelek et al. 1978; Lofgren et al. 1979;  
313 Shea and Hammer 2013; Vona and Romano 2013) but the crystallization process could be differently driven by  
314 conventional undercooling (imposed after a change in temperature) in comparison with effective undercooling ( $\Delta T_{\text{eff}}$ ),  
315 which is related to a change in pressure and water content. In contrast, several authors have observed that conventional  
316 undercooling and  $\Delta T_{\text{eff}}$  have similar influence on nucleation and growth rates of feldspar in basaltic andesite and  
317 trachyte (Shea and Hammer 2013; Arzilli and Carroll 2013). So far, this aspect is still an open question and near-  
318 eutectic melt compositions (rhyolitic, phonolitic) may behave differently from melt compositions far removed from  
319 eutectic-like conditions. In addition for more mafic melts with extended temperature intervals for crystallization, the  
320  $\Delta T_{\text{eff}}$  must decrease through time as crystallization progresses, affecting the nucleation and growth processes. In fact,  
321 after the initial step of nucleation most of the crystallization may be completed within the first 2 hours (see Fig. 4).

322 The decrease in melt water content with decreasing pressure ( $P_f = P_{\text{H}_2\text{O}}$  in water-saturated conditions) has a strong  
323 influence on the melt viscosity and on the rates of element diffusion during crystallization (Kirkpatrick 1981). Fig. 7a  
324 shows the effect of melt viscosity ( $\eta$ ) on the minimum nucleation rate ( $I_m$ ) during the initial event of nucleation for each  
325 investigated  $P_f$  (only 1 h experiments are considered in Fig. 7a). The viscosity ( $\eta$ ) of the starting melt, before the initial  
326 event of nucleation, was calculated using the model of Giordano et al. (2008), the chemical composition of the starting  
327 glass (obtained after the melting time; see Table 1), water content at  $P_f$  (calculated using Moore et al. 1998) and  
328 experimental temperature of 1075 °C. Figure 7a shows that for otherwise comparable conditions, the nucleation rate  
329 decreases as melt viscosity increases. As a result, in our experiments, the increasing viscosity at lower  $P_f$  reduces  
330 nucleation rate and the effect of  $\Delta T_{\text{eff}}$  may be overpowered by that of viscosity. The strong relationship between

331 viscosity and the nucleation process can be also seen as an important effect of the water content on the crystallization  
332 kinetics. High water content de-polymerizes the melt, reducing the viscosity and increasing the rate of diffusion, thereby  
333 facilitating nuclei formation (Kirkpatrick 1983).

334 The high nucleation rate obtained at low  $\Delta T_{\text{eff}}$  and short experimental duration can be explained also in terms of  
335 plagioclase-melt interfacial free energy ( $\sigma$ ). Nucleation process is hindered by energy barriers that can be thought of as  
336 the activation energy for nucleation. In theory, the activation energy decreases considerably as the undercooling  
337 increases, favoring the nucleation process. In this study, the Interfacial free energy ( $\sigma$ ) was calculated through Eq. 4  
338 based on nucleation rates ( $I_m$ ) obtained from experiments. Figure 7b shows the relation between the calculated  
339 interfacial free energy and the viscosity of the melt ( $\eta$ ), as a function of  $\Delta T_{\text{eff}}$  and H<sub>2</sub>O content (see Online Resource 2).  
340 Data reported in Fig. 7b show the relation between viscosity ( $\eta$ ) and interfacial free energy, considering 1 h  
341 experiments with different  $\Delta T_{\text{eff}}$  and  $P_f$  (see Online Resource 2). The interfacial free energy increases with increasing  
342 viscosity (Fig. 7b), therefore with increasing  $\Delta T_{\text{eff}}$  and decreasing  $P_f$  and water content (in agreement with the results of  
343 Hammer 2004). Figure 7b shows a negative correlation between  $I_m$  and the interfacial free energy: at lower  $\Delta T_{\text{eff}}$  (higher  
344  $P_f$ ) the nucleation process is favored due to low interfacial free energy and a lower viscosity, depolymerized melt.  
345 Furthermore, the nucleation rate increases as  $P_f$  increases (Figs 3 and 7a), showing that nucleation process can produce  
346 more nuclei at lower viscosity, even if the nucleation delay is shorter at low  $P_f$  (at 5 and 10 MPa) than high  $P_f$  (25 and  
347 50 MPa). According to the classical nucleation theory, high melt viscosity suppresses nucleation (e.g., Hammer 2008),  
348 thus viscosity may play a crucial role during nucleation processes.

349 Another way to explain the high nucleation rate at low effective undercooling concerns pre-existing phases which  
350 may influence crystal nucleation, favoring the heterogeneous regime (e.g. Fokin et al. 1999). In the starting material of  
351 our experiments, clinopyroxenes are present before samples are decompressed and they may be nuclei for plagioclase  
352 growth. Generally, nucleation is thought to occur heterogeneously at low undercoolings as the energy barrier required  
353 by homogeneous nucleation is high near the phase liquidus (Lofgren 1983). However, the lack of clustering of  
354 plagioclase around pre-existing nuclei and textures observed in BSE images suggest that nucleation of plagioclase  
355 occurred homogeneously throughout the melt.

356 It is well known in the literature that crystal shape is closely linked to the growth rate, and thus to undercooling.  
357 Plagioclase forms tabular and prismatic elongated crystals (Fig. 1) at lower  $\Delta T_{\text{eff}}$  ( $\leq 46$  °C) in agreement with Lofgren  
358 (1974; 1983), Fenn (1977) and Muncil and Lasaga (1987; 1988). This suggests that the growth of tabular crystal at  
359 lower  $\Delta T_{\text{eff}}$  is facilitated by crystal-melt interface controlled growth. Whereas, the growth is controlled by diffusion at  
360 high  $\Delta T_{\text{eff}}$  (84 and 97°C), favoring the formation of hopper and skeletal shapes (Fig. 1). This is coherent with results of  
361 Conte et al. (2006) who observed crystal shapes changing from euhedral to granular to skeletal to dendritic as cooling

362 rate increased and quenching temperature decreased. In agreement with previous studies (Lofgren 1974; Lofgren 1983;  
363 Hammer and Rutherford 2002; Couch et al. 2003; Martel and Schmidt 2003; Brugger and Hammer 2010; Mollard et al  
364 2012; Martel 2012; Shea and Hammer 2013), these results confirm that effective undercooling, notwithstanding  
365 changes through time, plays a crucial role in the morphological evolution of plagioclase.

366

### 367 6.3 Comparison with previous studies

368 The aim of this section is to compare the crystallization kinetics of plagioclase obtained within our hydrous basaltic  
369 single step decompression experiments with those produced in experimental investigations employing similar and more  
370 evolved melt compositions (basaltic-andesitic, rhyodacitic and rhyolitic) (Hammer and Rutherford 2002; Couch 2003;  
371 Couch et al. 2003; Brugger and Hammer 2010; Mollard et al. 2012; Shea and Hammer 2013). This comparison  
372 considers kinetic data (i.e., nucleation and growth rates) retrieved from single-step or very fast decompression  
373 experiments, where the effective undercooling is imposed in a near instantaneous fashion. All the kinetic data are  
374 compared in terms of effective undercooling ( $\Delta T_{\text{eff}}$ ) with respect to plagioclase (Fig. 8a, b). Figure 8a shows a  
375 comparison of plagioclase nucleation rates as documented in a variety of experimental studies on water-saturated  
376 compositions ranging from basaltic through rhyolitic. Results from this study for 1 h duration experiments show that  
377 plagioclase crystals in basalt have high nucleation rates ( $I_m$ ; between  $10^4$  and  $\sim 10^5 \text{ cm}^{-3} \text{ s}^{-1}$ ) and  $I_m$  shows a general  
378 decrease with increasing  $\Delta T_{\text{eff}}$ . This is in contrast with the results of several other studies, which suggest that the  
379 nucleation process is favored at higher effective undercooling (Couch et al. 2003; Couch 2003; Hammer and Rutherford  
380 2002; Brugger and Hammer 2010; Mollard et al. 2012; Shea and Hammer 2013) and the nucleation rate should be faster  
381 in a less polymerized melt (Kirkpatrick 1983). Much of our knowledge concerning crystallization kinetics of  
382 plagioclase derives from studies of near-eutectic melt compositions and they may not be applicable to melts with a  
383 considerable temperature interval between the liquidus and the solidus. The nucleation rates of plagioclase in basalt are  
384 higher than those in basaltic andesite (Fig. 8a); this could be due to the different experimental durations investigated. In  
385 fact, this study shows that the nucleation could be completed within 2 h, therefore, the nucleation of plagioclase in  
386 basaltic andesite may have similar timescales. Shea and Hammer (2013) performed experiments with durations  $>12$  h,  
387 thus they could have underestimated the maximum  $I_m$  as times  $< 12$  h have not been investigated. Nucleation rates,  
388 estimated from Shea and Hammer (2013), increase with increasing  $\Delta T_{\text{eff}}$  (Fig. 8a); this behavior is similar to the trend of  
389 8 h runs in basaltic melts, whereas it is the opposite compared to 1 h runs (Fig. 8a). This evidence highlights that more  
390 experiments with basaltic and andesitic melts are needed at short durations ( $< 2$  h) because disequilibrium processes that  
391 drive the initial step of nucleation are still poorly constrained. When considering 8 h duration experiments, the  
392 nucleation rates of plagioclase in basaltic compositions range between  $10^2$  and  $10^3 \text{ (cm}^{-3} \text{ s}^{-1})$  and  $I_m$  shows a general

393 increases with increasing  $\Delta T_{\text{eff}}$  (Fig. 8a). Comparing 8 h runs, basaltic compositions have similar nucleation rates to the  
394 synthetic rhyolite of Couch et al. (2003) at low  $\Delta T_{\text{eff}}$ , whereas they are slightly lower than those in synthetic rhyolites at  
395 high  $\Delta T_{\text{eff}}$  (Fig. 8a). This could be due to the fact that basaltic melts are subjected to an initial annealing period above  
396 the liquidus of plagioclase in order to remove nuclei of this phase, whereas the pre-decompression conditions of  
397 synthetic rhyolite (Couch et al. 2003) were close to plagioclase-in curve (slightly below the liquidus) and 2 % of  
398 plagioclase crystals were present in the starting material. Despite the difference of viscosity between basaltic and  
399 rhyolitic melts, pre-existing plagioclase crystals and initial conditions below the liquidus could favor the nucleation  
400 process, whereas the superliquidus heating conditions should reduce nucleation efficiency (i.e., Tsuchiyama 1983;  
401 Donaldson 1985; Pupier et al. 2008). Furthermore, pre-existing plagioclases lead to adding  $\sim 40^\circ\text{C}$  to the  $\Delta T_{\text{eff}}$  values  
402 given by Couch et al. (2003), favoring a rapid nucleation in silica-rich magmas. The nucleation rates of haplogranite (8  
403 h durations; Couch 2003) are two orders of magnitude lower than basalt at low  $\Delta T_{\text{eff}}$ , whereas  $I_m$  increases as  $\Delta T_{\text{eff}}$   
404 increases reaching similar order of magnitude of basalt at high  $\Delta T_{\text{eff}}$  (Fig. 8a). The nucleation rates estimated from  
405 Couch (2003) are similar to those of Hammer and Rutherford (2002) and Brugger and Hammer (2010) and, they also  
406 show similar trends with  $\Delta T_{\text{eff}}$  (Fig. 8a). The nucleation rates of rhyolitic and rhyodacitic melts (with  $\text{SiO}_2$  between 71  
407 and 77 wt%) show a general increase with  $\Delta T_{\text{eff}}$ , in agreement with the trend of 8 h runs in basaltic melts (instead it is  
408 opposite our observations for 1 h runs; Fig. 8a). The nucleation rate of plagioclase in basalt (8 h experimental durations)  
409 is two orders of magnitude higher than those grown in synthetic rhyolite (48 h experimental durations; Mollard 2012);  
410 this could be due at longer experimental duration investigated by Mollard et al. (2012). However, the high viscosity of  
411 synthetic rhyolite ( $\text{SiO}_2 = 79$  wt. %; Mollard et al. 2012) and the absence of pre-existing crystals in the starting material  
412 at initial conditions above the liquidus of the plagioclase could inhibit the nucleation. Despite the experimental duration  
413 investigated by Mollard et al. (2012), being shorter than that of Hammer and Rutherford (2002) the nucleation rates are  
414 one order of magnitude lower than those of Hammer and Rutherford (2002). Furthermore, the silica content of rhyolite  
415 ( $\text{SiO}_2 = 79$  wt. %) used from Mollard et al. (2012) is similar to that of natural rhyolite ( $\text{SiO}_2 = 77$  wt. %) used from  
416 Hammer and Rutherford (2002) and both the starting compositions were annealed above the liquidus of plagioclase,  
417 therefore, the reason for the difference of  $I_m$  could be the presence of pre-existing crystals in the starting material used  
418 by Hammer and Rutherford (2002). However, it remains unclear the reason for the high nucleation rates observed in  
419 silica-rich magmas and low  $I_m$  obtained in basaltic-andesite. Another aspect is the delay to form nuclei as our basaltic  
420 experiments register a nucleation lag of 0.5 h at low  $\Delta T_{\text{eff}}$  (24 and 46  $^\circ\text{C}$ ). Synthetic rhyolites show higher nucleation  
421 delay than basalt, with a lag of 2-3 days for  $\Delta T_{\text{eff}} < 25^\circ\text{C}$  (Mollard et al. 2012) and of 4-8h for  $\Delta T_{\text{eff}} \sim 38^\circ\text{C}$  (Couch et  
422 al. 2003; Couch 2003). Instead, nucleation delay is not shown from plagioclase in natural rhyolite (Hammer and  
423 Rutherford 2002), rhyodacite (Brugger and Hammer 2010) and basaltic-andesite (Shea and Hammer 2013), probably

424 because their experiments were never brief enough to document a nucleation delay. Therefore, the comparison of  
425 nucleation rates of different silicate melts at similar effective undercoolings shows that melt viscosity, superliquidus  
426 heating conditions and pre-existent phases (heterogeneous nucleation) could have the major control on the nucleation  
427 delay of plagioclase.

428 The growth rate ( $G_L$ ) of plagioclase crystals, considering several melt compositions, shows a general increase as  
429 viscosity increases (Fig. 8b). Some differences are present in the way of determining growth rates, for instance 10  
430 largest crystals were measured in each sample by Couch et al. (2003), Couch (2003), Hammer and Rutherford (2002),  
431 Mollard et al. (2012) and Shea and Hammer (2013), whereas total crystallinity was used to estimate  $G_L$  by Brugger and  
432 Hammer (2010). However, growth rates obtained from these studies can be compared because both approaches give  
433 similar order of magnitude results. Considering crystal growth rates (Fig. 8b), short duration experiments (1 h) show  
434 that growth of plagioclase in basalt is rapid, reaching  $10^{-6}$  cm/s. The growth rate of plagioclase in basalt ranges between  
435  $10^{-6}$  and  $10^{-7}$  cm/s and it is up to two orders of magnitude higher than that of plagioclase in rhyolite ( $10^{-8}$  cm/s; Hammer  
436 and Rutherford 2002) (see Fig. 8b). Instead, at 8 h the apparent growth rates in basalt are similar to basaltic-andesite  
437 (12 h, Shea and Hammer 2013) and synthetic rhyolite (4 h, Couch et al. 2003). The growth rates of plagioclase in  
438 synthetic rhyolite (Couch et al. 2003) and in haplogranite (Couch 2003) after 8 h are slightly slower than plagioclase in  
439 basalt (Fig. 8b). This is due to the fact that growth requires transportation of the plagioclase-forming components,  
440 which is controlled by diffusion (diffusion is slower in more viscous melts than basaltic ones). The kinetics of growth  
441 estimated by Mollard et al. (2012) and Hammer and Rutherford (2002) are up to three orders of magnitude lower than  
442 those of plagioclase in basalt estimated in this study (Fig. 8b). This could be due to long experimental durations used  
443 from Mollard et al. (2012) and Hammer and Rutherford (2002) which could provide an underestimation of the growth  
444 rates (i.e., much growth occurs in early part of experiment, and longer durations give lower apparent growth rates).

445 The main evidence of this comparison is that the basaltic melts could produce a significantly higher number of  
446 plagioclase crystals much more rapidly than rhyolitic melts within the first 4 hours of the experiment. This shows that  
447 the nucleation delay of plagioclase in rhyolite is higher than that in basalt. However, after 8 h, there are no more  
448 significant differences in nucleation between the basalt and the rhyolite. In all of this discussion it must be remembered  
449 that kinetic studies inherently imply an imposition of disequilibrium conditions on a system, and the measurements  
450 relate to how fast the system tries to return to equilibrium via crystal growth. Thus, parameters such as  $\Delta T_{\text{eff}}$  or  $\Delta T$  are  
451 actually transient, time dependent parameters, that change as the system crystallizes (approaches equilibrium).

452

## 453 **7. Final remarks and implications**

454 Single-step decompression experiments performed by Agostini et al. (2013) show that the crystallization of

455 plagioclase in decompressed high-K basalts is rapid. The order of magnitude of the crystal number density ( $N_a$ ) is  
456 determined at the beginning of the crystallization process. Therefore the textural evolution and the chemical  
457 compositions of plagioclase may be strongly influenced by the initial plagioclase nucleation event (within first 2 h).  
458 After the first hour, the nucleation rate decreases as duration increases.

459 Decompression imposes an effective undercooling ( $\Delta T_{\text{eff}}$ ), reducing water content in the melt and increasing its  
460 viscosity. Nevertheless, the values of effective undercooling ( $\Delta T_{\text{eff}}$ ) at low  $P_f$  were sufficient to overcome the  
461 sluggishness, resulting in crystallization (growth-dominated; as shown also by Couch 2003). Instead, high water content  
462 supports the nucleation process by lowering the melt viscosity and thus de-polymerizing the melt, in agreement with  
463 Kirkpatrick (1983). These isothermal single step decompression experiments show also that the low viscosity and  
464 interfacial-free energy ( $\sigma$ ) play a crucial role during crystallization process, favoring nucleation even at high final  
465 pressure ( $P_f$ ) and low effective undercoolings ( $\Delta T_{\text{eff}}$ ).

466 In comparison with previous studies of decompression-induced crystallization (e.g., Hammer and Rutherford 2002;  
467 Couch 2003; Couch et al. 2003; Brugger and Hammer 2010; Mollard et al. 2012; Shea and Hammer 2013), our results  
468 indicate that kinetic processes could be so rapid as to have a significant effect on magma rheology in the conduit during  
469 magma ascent. Our data show that degassing and crystallization kinetics may be established entirely within the volcanic  
470 conduit and their rapidity may have strong implications for magma rheology; for example, the increase in viscosity of  
471 Stromboli basalt is substantial during the first hours of subliquidus conditions, as also shown by Vona et al. (2011) and  
472 Vona and Romano (2013). A substantial amount of crystallization can take place due to a small quantity of water  
473 degassing on short timescales (1-2 hours). The consequences of degassing-driven crystallization are potentially more  
474 serious for basaltic systems than for systems with more silicic melt composition because the crystallization process of  
475 hydrous basaltic melts is rapid, triggering dramatic crystallinity changes in 2 hours.

476

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states as a function of experimental duration, final pressure and effective undercooling. (a-c) Textures  
MPa ( $P_2$ ) as a function of experimental duration: 1 h (a - sample 7), 4 h (b - sample Cap13), 8 h (c -  
f) Textures obtained at 25 MPa ( $P_2$ ) as a function of experimental duration: 1 h (d - sample 13), 2 h (e -  
r (f - sample Cap16), 8 h (g - sample 12), (h-k) Textures obtained at 10 MPa ( $P_2$ ) as a function of  
uration: 1 h (h - sample Cap9), 2 h (i - sample Cap12), 4 h (j - sample Cap17), 8 h (k - sample Cap19)  
obtained at 5 MPa ( $P_2$ ) as a function of experimental duration: 1 h (l - sample Cap10), 2 h (m - sample  
- sample Cap13), 8 h (n - sample Cap20) p16 = polyacrylate, cps = dioxepanone, gl = glass, on =

tion between nucleation density ( $N_0$ ) and  $P_2$ . The uncertainties of  $N_0$  were estimated on the basis of 10  
spic.

relation of nucleation rate ( $I_n$ ) and growth rate ( $G_n$ ) of polyacrylate with the  $\Delta T_{eff}$  at  $t_{sp}$  = 1 h. The  
 $I_n$  were estimated on the basis of 10 images per sample. The uncertainties for growth rate  
were estimated on the basis of the 10 largest crystals observed in each sample.

tion between the incremental nucleation rate of polyacrylate ( $I_n$ ) and  $t_{sp}$ .

relation between the maximum length of polyacrylate (L2) and  $t_{sp}$ . (b) Relation between incremental  
polyacrylate ( $G_n$ ) and  $t_{sp}$ . For the data at  $P_2 = 10$  MPa, the diagram shows the average value of  $G_n$   
at 7 and 14. The uncertainties for sizes were estimated on the basis of the 10 largest crystals observed in

relation between polyacrylate crystal fraction and the chemical compositions of polyacrylate and residual  
intrinsic crystal fraction (a) vs experimental duration ( $t_{sp}$ ), (b) An content as a function of  $t_{sp}$ . (c) The  
wt % in residual glass as a function of  $t_{sp}$ . (d) K<sub>2</sub>O wt % content in glass as a function of  $t_{sp}$ .  
Data on polyacrylate and residual glass were taken from Agostini et al. (2013).

temperature of 1075°C. (b) Relation between plagioclase-melt interfacial free energy ( $\sigma$ ) and viscosity free energy ( $\eta$ ) was calculated by Eq. 4 (see also Online resource 2). Since decompression experiments melt plagioclase compositions ( $An_{60-65}$  and  $An_{50-55}$ ), we calculated free values of  $F_{pl}^* / F_m^* = 1.014 \cdot 10^{-7}$  instead for  $An_{60-65}$  (Klein 1994), whereas  $F_m^* = 1.108 \cdot 10^{-7}$  mol/mol was calculated for  $An_{50}$  (Klein 1977) m.  $\Delta G_f^*$  was calculated for each An content ( $An_{60-65}$ ) at ambient pressure as a linear combination of these values ( $\Delta G_f^*$  of albite was 64.5 kJ/mol, obtained by Tenner et al. 2007;  $\Delta G_f^*$  of anorthite was 133.0 kJ/mol by Rickett and Bottinga 1984). The volumetric concentration of reactant anorthite is defined:  $n_r = N_r / F_m^*$  (also constant). To calculate the interfacial free energy ( $\sigma$ ) in the Eq. 4,  $\Delta T_{pl}$  is used as value for  $\Delta T$ .

Comparison of experimental kinetic data for plagioclase (nucleation and growth rates) collected from the literature of effective undercooling, such composition (basaltic, basaltic andesitic, rhyolitic and starting material type (natural or synthetic)) (a) Relation between nucleation rates ( $I_{pl}$ ) of plagioclase and melt between growth rates ( $G_{pl}$ ) of plagioclase and  $\Delta T_{pl}$ . Crystallization kinetics in crushed natural (b) Hammer and Rutherford 2002; Bruggner and Hammer 2010; Shea and Hammer 2011) and in synthetic (c) Couch et al. 2003; Couch 2003; Molnar et al. 2012) are distinguished. For the comparison we used, experiments with durations between 1 and 12 hours, in order to investigate the initial periods of growth. The exceptions were the natural rhyolite (Hammer and Rutherford 2002), rhyolite (Bruggner 04) and synthetic rhyolite (Molnar et al. 2012) as experimental durations were 168, 966 and 48 h with the aim to show and compare the kinetics of plagioclase in silica-rich melts at long durations. HR = Hammer and Rutherford, 2002; C = Couch et al., 2003; C = Couch 2003; HB = Hammer and Bruggner and M = Molnar et al., 2012; SH = Shea and Hammer 2011.