

1 **Amphibole growth from a primitive alkaline basalt at 0.8 GPa: time-dependent**
2 **compositional evolution, growth rate and competition with clinopyroxene**

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4 Barbara Bonechi¹, Cristina Perinelli¹, Mario Gaeta¹, Vanni Tecchiato¹, Alessandro Fabbrizio²

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6 1: Dipartimento di Scienze della Terra, Sapienza Università di Roma, P.le Aldo Moro 5, 00185,

7 Rome, Italy

8 2: Institute of Petrology and Structural Geology, Faculty of Science, Charles University, Albertov 6,

9 12843 Prague, Czech Republic

10

11 Corresponding author:

12 Barbara Bonechi

13 Dipartimento Scienze della Terra,

14 Sapienza Università di Roma,

15 P.le Aldo Moro, 5

16 00185 Rome, Italy

17 Tel. (+39)064991 4156

18 E-mail: barbara.bonechi@uniroma1.it

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26 **Amphibole growth from a primitive alkaline basalt at 0.8 GPa: time-dependent compositional**
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30

31 **Abstract**

32 Amphibole growth rates were experimentally determined at hydrous (3.3-4.2 wt% H₂O), isobaric
33 (0.8 GPa) conditions, variable temperature (1030 and 1080 °C) and dwell time (0.25, 3, 6, and 9 h),
34 using as starting material a primitive alkaline basalt from Procida island (Campi Flegrei Volcanic
35 District, south Italy). Amphibole growth rates decrease from $1.5 \cdot 10^{-7}$ to $2.9 \cdot 10^{-8}$ cm·s⁻¹ as the
36 duration of our experiments increase from 0.25 to 9 hours. Moreover, increasing both temperature
37 and water content leads to similar growth rate increase at constant dwell time. The comparison
38 between amphibole and clinopyroxene growth rates determined at the same experimental conditions
39 reveals for amphibole a faster growth relatively to the coexisting clinopyroxene, regardless of the
40 dwell time. Furthermore, the experimental time appears to be a critical parameter for the
41 composition of synthetic amphiboles; specifically, edenite is the dominant composition in short
42 experiments (≤ 3 h), particularly, at low temperature (1030 °C), whereas the magnesiohastingsitic
43 amphibole becomes progressively more important shifting towards longer duration and higher
44 temperature run conditions. The magnesiohastingsite, on the basis of the amphibole-liquid Fe-Mg
45 exchange coefficient values, results to be the compositional term representative of amphibole-melt
46 equilibrium at the investigated *P-T-H₂O* conditions. Finally, experimental growth rates from this
47 study have been used to investigate the crystallization time of natural amphiboles and
48 clinopyroxenes from the Oligo-Miocene cumulates of north-western Sardinia (i.e. Capo Marargiu
49 Volcanic District, Italy), yielding crystallization times of 1.46-3.12 yr.

50

51 **Keywords:** amphibole growth rate; high pressure; primitive alkaline basalt; Campi Flegrei.

53 **1. Introduction**

54 Amphibole is a typical phase of mafic to felsic hydrous magmas (Arculus and Wills, 1980;
55 Cawthorn et al., 1973; Davidson et al., 2007). By virtue of the high physico-chemical sensitivity of
56 amphibole texture and composition, magmatic crystallization pressure and temperature as well as
57 magma storage, mixing and ascent processes have been qualitatively and quantitatively inferred in a
58 number of studies (e.g. Bachmann and Dungan, 2002; De Angelis et al., 2013; Ridolfi et al., 2010,
59 2008; Rutherford and Devine, 2008; Rutherford and Hill, 1993; Shane and Smith, 2013; Thornber
60 et al., 2004; Turner et al., 2013; Zhang et al., 2017). It is also widely documented that amphibole is
61 stable in hydrous basalts stalling at the roots of arc crust, influencing the chemical evolution of
62 derivative liquids obtained by fractionation of amphibole-bearing cumulates (e.g. Abd El-Rahman
63 et al., 2012; Davidson et al., 2007; Foden and Green, 1992; Green and Ringwood, 1968; Larocque
64 and Canil, 2010; Li et al., 2017; Melekhova et al., 2015). However, investigations on the kinetics of
65 amphibole crystallization (e.g. growth rate) from siliceous liquids are scarce and all addressed to
66 investigate calc-alkaline rocks affinity (i.e. Shea and Hammer, 2013; Simakin et al., 2009; Zhang et
67 al., 2019), implying negligible or misleading interpretation of the timescales on which magmatic
68 processes act at depth. Indeed, the only experimentally determined growth rates for amphibole were
69 obtained at 0.1-2.7 GPa and 860-970 °C from hydrous basaltic to andesitic melts (i.e. Shea and
70 Hammer, 2013; Simakin et al., 2009; Zhang et al., 2019). In this framework, using as starting
71 material a primitive alkaline basalt from Procida island (Campi Flegrei Volcanic District; south
72 Italy), we investigated the amphibole crystal growth rate at a pressure corresponding to the crustal-
73 mantle boundary in this area (~25 km of depth; Fedi et al., 2018). Aimed to this, we performed
74 hydrous (3.3-4.2 wt% H₂O), isobaric (0.8 GPa), time-series (dwell time 0.25, 3, 6, 9 h) experiments
75 at temperatures of 1030 and 1080 °C. These *T* were chosen on the basis of previous high pressure
76 experimental investigations on the APR16GL composition (Bonechi et al., 2019, 2017; Perinelli et
77 al., 2019) demonstrating that for an initial water content in the system of ~4 wt%, amphibole is

78 stable at $T < 1100$ °C. At the selected temperatures the undercooling, expressed as the difference
79 between liquidus and experimental temperatures ($\Delta T = T_{\text{liquidus}} - T_{\text{experiment}}$), is of ~ 200 and ~ 150 °C,
80 respectively. The imposed ΔT coupled to the variable time at isothermal conditions will also allow
81 to highlight how, after an early stage of significant undercooling, the equilibration processes affect
82 the amphibole crystal growth with increasing the dwell time (i.e. relaxation kinetics; Arzilli et al.,
83 2018; Mollo et al., 2012; Pontesilli et al., 2019).

84 The calculated growth rates were used to investigate the crystallization process of natural products
85 from Sardinia. Our findings may be useful to correctly interpret the textural features of amphibole-
86 bearing mafic cumulates and rocks, and for a better constraining of the timescales of magmatic
87 processes at upper mantle-lower crustal depths.

88

89 **2. Methods**

90 *2.1. Starting material*

91 The APR16 sample (Table 1) is a primitive alkaline basalt found as scoria clast in the deposits of
92 the Solchiaro hydromagmatic centre located in Procida island (Campi Flegrei, Italy). Detailed
93 textural and compositional information about this product are provided by D'Antonio et al. (1999).
94 The starting material is an anhydrous glass (APR16GL; Table 1) prepared by first crushing pieces
95 of the natural APR16 sample in a mortar under ethanol, then by melting the resulting powder at
96 1400 °C and atmospheric pressure for 15 min and oxygen fugacity buffered at Nickel-Nickel Oxide
97 level by means of a CO/CO₂ gas mixture fluxed inside the furnace at the Bayerisches Geoinstitut,
98 Germany. The melting temperature (i.e. 1400 °C) was chosen so as to be above the liquidus
99 temperature of the APR16 natural sample (i.e. 1290 °C) at 0.8 GPa as calculated using MELTS
100 program (Asimow and Ghiorso, 1998; Ghiorso and Sack, 1995) and verified experimentally in the
101 work of Perinelli et al. (2019). Instead, the imposed fO_2 conditions for starting material preparation
102 take into account that at the experimental conditions (1080-1030 °C and 0.8 GPa) the initial oxygen

103 fugacity is \sim NNO -1, close to in the range of fO_2 previous estimates from runs performed with the
104 same kind of CaF_2 cell assemblages (Conte et al., 2009; Weaver et al., 2013).

105

106 2.2. Experimental techniques

107 Experiments were performed at isobaric conditions (\sim 0.8 GPa) as function of temperature and time
108 by using the $\frac{1}{2}$ inch end loaded piston cylinder apparatus at the HP-HT Laboratory of the Earth
109 Sciences Department, Sapienza University of Rome. Assemblies consist of an outer CaF_2 cell, a
110 graphite furnace and MgO crushable spacers. The experimental charges were prepared loading
111 $Au_{75}Pd_{25}$ capsules with \sim 40 mg of APR16GL powder after that appropriate water amount was added
112 into the capsules by using a microsyringe. The H_2O /rock ratio was of 1:25 (\sim 4 wt% of H_2O added to
113 the starting material; Table 2). Then the capsule was arc welded while keeping it cooled to avoid
114 loss of water. The welded capsule was weighed, stored in a furnace at 110 °C, and then weighed
115 again to confirm the absence of water leaks. Moreover, to prevent possible loss of H_2 the charges
116 were surrounded by pyrophyllite powder (Freda et al., 2001). The \sim 0.8 GPa experiments were
117 carried out at 1030 and 1080 °C (i.e. APR16-C3A and APR16-C3B series, respectively) for
118 different dwell time (0.25, 3, 6 and 9 hours). The choice of the temperature conditions is based on
119 the phase diagram obtained by Perinelli et al. (2019). The temperature was measured using a type D
120 $W_3Re_{97}-W_{25}Re_{75}$ thermocouple and maintained with an estimated accuracy of \pm 5 °C.

121 We performed a total of 8 experiments, whose experimental conditions are reported in Table 2.

122 The experimental assembly was first pressurized to the target pressure by piston-out procedure
123 (Johannes et al., 1971; Presnall et al., 1978), that consists in applying an overpressure of \sim 10 % of
124 the run pressure gradually increasing the temperature up to the working temperature, and correcting
125 for pressure drops due to stress relaxation within the assembly during heating. The sample is
126 maintained at the pressure and temperature for a given duration (nominal duration), and then
127 quenched down by turning off the power. The temperature drop below 500 °C was of $<$ 5 seconds
128 (average cooling rate of 150 °C/s). The oxygen fugacity (fO_2) was not controlled, however, an

129 estimation of experimental fO_2 was made using the theoretical model of Barr and Grove (2010)
130 which is based on the temperature-and fO_2 -dependent partitioning of Fe between the AuPd capsule
131 and coexisting melt. Thus, we measured the post-run Fe content in the sample-holder as closer as
132 possible to the capsule-sample boundary of a near-liquidus anhydrous experiment (1295 °C; see
133 Table 2 of Perinelli et al., 2019) and of 1080-1030 °C longest experiments. Applying the Barr and
134 Grove (2010) approach the calculated fO_2 were of NNO -0.5 for the near-liquidus run and NNO -0.8
135 and NNO -1.1 for the longest runs of this study.

136 Finally, being the undercooling a parameter that influence the kinetics of magma crystallization, for
137 both amphibole and clinopyroxene we determined also the effective undercooling (ΔT_{eff}) defined as
138 the difference between the equilibrium amphibole (clinopyroxene) liquidus temperature (T_L) and the
139 experimental temperature (Hammer and Rutherford, 2002). Using as starting material the
140 APR16GL composition we performed the Rhyolite-MELTS equilibrium crystallization calculations
141 to determine the T_L value of clinopyroxene and amphibole. However, for amphibole the
142 thermodynamic modelling provided dubious results. This is probably due to the poor reliability of
143 Rhyolite-MELTS in dealing with hydrous phases, therefore, we extrapolated the T_L value (1095 °C)
144 on the basis of T vs. H_2O in melt phase diagram of Perinelli et al. (2019) reported in Figure A1 in
145 the supplementary materials. T_L and ΔT_{eff} are listed in the Table 2.

146

147 *2.3 Analytical methods*

148 The recovered samples have been mounted in epoxy resin, ground flat and polished. Textural aspect
149 of the recovered samples was analysed by Scanning Electron Microscopy (SEM) using a FEI-
150 quanta 400 equipped for microanalysis with an EDAX Genesis system at the Earth Sciences
151 Department, Sapienza University of Rome and a TESCAN Vega equipped with EDS (energy
152 dispersive X-ray spectrometry) system at the Institute of Petrology and Structural Geology (Charles
153 University in Prague). Phase compositions were analysed at the CNR-Istituto di Geologia
154 Ambientale e Geingegneria di Roma, with a Cameca SX50 electron microprobe equipped with

155 five wavelength dispersive spectrometers (WDS) and at the Institute of Petrology and Structural
156 Geology (Charles University in Prague) with a Jeol JXA-8530F equipped with five WDS.
157 Quantitative analyses were performed using 15 kV accelerating voltage and 15 nA beam current. As
158 standards we employed metals for Mn and Cr, Jadeite for Na, Wollastonite for Si and Ca,
159 Orthoclase for K, Corundum for Al, Magnetite for Fe, Rutile for Ti and Periclase for Mg. Counting
160 times were 20 s per element and 10 s for backgrounds. Light elements were counted first to prevent
161 loss by volatilization. The PAP correction method was used. Minerals were analysed using a beam
162 diameter of 1 μm whereas for glasses a defocused electron beam from 10 to 15 μm was used. Water
163 contents of experimental glasses were estimated according to the *by-difference* method of Devine et
164 al. (1995). Due to the uncertainty (± 0.5 wt% H_2O) of this approach, the water content of those
165 glasses with ≤ 1 wt% H_2O has been more accurately measured (± 0.15 wt% H_2O) by micro-Raman
166 spectroscopy (Di Genova et al., 2017; Le Losq et al., 2012; Table 2). Raman spectra were acquired
167 from mineral- and/or bubble-free glass portions large enough to be analysed with a Horiba Lab Ram
168 HR 800 spectrometer at the Department of Science, Roma Tre University. Data were collected
169 using a 600 grooves/mm spectrometer grating and CCD detector.

170

171 2.4. Growth rate calculation

172 In the collected SEM images, crystal dimensions were measured using the *measure tool* in ImageJ®
173 software. Because we are interested in determining the maximum growth rate following a method
174 reported in the literature (Couch, 2003, and reference therein), the length (L , cm) and the width (W ,
175 cm) of the 10 largest crystals of amphibole from each experimental products were measured. The
176 maximum growth rate (G_L , $\text{cm}\cdot\text{s}^{-1}$) values were calculated using the following formula (Hammer
177 and Rutherford, 2002 and reference therein):

$$178 \quad (1)$$

179 where t (s) is the duration of the experiments.

180

181 3. Experimental results

182 3.1. Crystal abundance, shape and growth rates

183 All the experimental products show a high crystallinity (Fig. 1 and Table 2) as a result of the
184 imposed undercooling ($\Delta T = 150\text{-}200\text{ }^{\circ}\text{C}$). Indeed, this produces strong supersaturation conditions
185 in the K-basaltic melt and enhances the nucleation kinetics in the sample during the early stage of
186 experiments (e.g. Cashman, 1993; Hammer, 2008; Hammer and Rutherford, 2002; Iezzi et al.,
187 2011; Lofgren, 1983; Shea et al., 2015; Simakin et al., 2003) possibly influencing also the phase
188 modal proportions. Amphibole (Amph) occurs in seven of the eight experiments, followed by
189 clinopyroxene (Cpx), orthopyroxene (Opx) and oxide (Ox). Moreover, Amph is always the most
190 abundant phase, even in the highest temperature experiments ($1080\text{ }^{\circ}\text{C}$) despite its low ΔT_{eff} of ~ 15
191 $^{\circ}\text{C}$ (Table 2) that would suggest abundances significantly lower than those of Cpx ($\Delta T_{\text{eff}} \sim 140\text{ }^{\circ}\text{C}$).
192 The large experimental undercooling can account for this discrepancy considering that reached the
193 target experimental temperature, it triggered an important nucleation phenomenon in the sample
194 causing an “instantaneous” increase of the water content in the system, establishing the conditions
195 suitable for the amphibole crystallization. Notably, the APR16-C3Ac experiment ($1080\text{ }^{\circ}\text{C} - 6\text{ h}$
196 run), in which Amph does not crystallize, the different phase relations obtained (Gl + Cpx + Ol;
197 Table 2) with respect to the other experiments performed at the same P - T - H_2O_i ($\text{H}_2\text{O}_i = \text{nominal}$
198 content of water added to the charge) conditions, can be explained considering the lower final water
199 content in the melt (H_2O_f). Indeed, in this run the residual melt contains $\sim 6.5\text{ wt}\%$ of H_2O_f , whereas
200 the residual melt of the APR16-C3Ad experiment, performed at the same P - T - H_2O_i conditions and
201 showing a comparable crystallization degree, has a H_2O_f amount of $\sim 10.2\text{ wt}\%$. This indicates that
202 probably the H_2O in the APR16-C3Ac charge is partially lost, resulting in insufficient water for the
203 crystallization of amphibole (Table 3), as also observed in the phase relation diagram of Perinelli et
204 al. (2019). Glass is present in all the experimental runs, but it was analysed only in those with glass
205 portions large enough to be examined.

206 *Amphibole*. In the runs with short duration (0.25-3 h), Amph are clustered (Fig. 1a-b) with L and W
207 sizes up to 10 μm . In the 6 h run, Amph shows frequently well-formed outer faces and occurs as \leq
208 20 μm sized isolated grains. Finally, in the 9 h experiments, Amph is euhedral with maximum L and
209 W size of ~ 40 and 20 μm , respectively (Fig. 1c), sometimes hosting small Cpx in the inner region of
210 the crystal (Fig. 1d).

211 *Other mineral phases*. All the observed pyroxene and oxide crystals have, respectively, euhedral
212 habit with sizes up to ~ 5 and 40 μm , in agreement with the experimental results of Bonechi et al.
213 (2019) obtained from the same starting material at $P = 0.8$ GPa, $T = 1170$ -1250 $^{\circ}\text{C}$ ($\Delta T_{\text{eff}} = 45$ -100
214 $^{\circ}\text{C}$) and $\text{H}_2\text{O}_f \leq 5$ wt%. Olivine crystallized only in the run APR16-C3Ac and it is characterized by
215 euhedral habit and maximum size of 30 μm . Finally, in the 0.25-3 h run with high degree of
216 crystallization (Table 2), subhedral to euhedral plagioclase with dimension ≤ 10 μm occurs.

217 Amphibole growth rates calculated by using equation (1) are reported in Table 3, together with Cpx
218 and Ox growth rates determined by Bonechi et al. (2019). Amph- G_L vary between $1.5 \cdot 10^{-7}$ $\text{cm} \cdot \text{s}^{-1}$
219 (APR16-C3Aa, 0.25 h) to $2.9 \cdot 10^{-8}$ $\text{cm} \cdot \text{s}^{-1}$ (APR16-C3Bd, 9 h), showing an inverse correlation with
220 time.

221

222 3.2. Phases composition and approach to equilibrium

223 *Amphibole*. Chemical compositions of Amph are reported in Table 4. According to the Hawthorne
224 et al. (2012) classification, all the crystallized Amph is calcic and its composition varies from
225 magnesiohornblende and edenite (Fig. 2a, b) to pargasite and magnesiohastingsite (Fig. 2b, c) with
226 increasing time.

227 *Other phases*. Chemical compositions of the other phases crystallized in the experimental runs are
228 reported in Table A1. Clinopyroxene compositions are augitic ($\text{Wo}_{42}\text{-En}_{41}\text{-Fs}_{18}$) and diopsidic
229 ($\text{Wo}_{47}\text{-En}_{43}\text{-Fs}_{10}$), whereas the orthopyroxene crystals found in the APR16-C3Bc run is enstatitic
230 ($\text{Wo}_4\text{-En}_{73}\text{-Fs}_{23}$). Oxide crystals are generally hercynites, while in the APR16-C3Aa run Cr-rich
231 spinels also occur. Olivine is present only in the run APR16-C3Ac and is characterized by

232 compositions of Fo₈₄ while plagioclase grains occurring in the shorter runs (0.25-3 h) are bytownitic
233 and labradoritic in composition.

234 Where possible we calculated the equilibrium conditions between the mineral phases crystallized in
235 the investigated runs (i.e. Amph, Cpx, Plg and Ol) and the corresponding melts (Table 4 and A1).
236 As regards Amph, the calculated Amph-melt Fe-Mg exchange coefficient (i.e. $K_{D_{Fe-Mg}}^{Amph-liq} =$
237 $(FeO/MgO)^{Amph}/(FeO/MgO)^{liq}$) varies between ~0.3 and ~1, showing an almost linear decrease with
238 increasing time (Fig. 3). According to the Putirka (2016) $K_{D_{Fe-Mg}}^{Amph-liq}$ value (i.e. 0.28 ± 0.11), only
239 the magnesiohastingsites crystallized in the runs at 9 h (APR16-C3Ad and APR16-C3Bd),
240 characterized by the lowest $K_{D_{Fe-Mg}}^{Amph-liq}$ values (0.34 and 0.40, respectively) attained Amph-liquid
241 equilibrium conditions. Similar $K_{D_{Fe-Mg}}$ trend towards equilibrium with increasing run times has
242 been observed by Mollo et al. (2013) also for clinopyroxene phase.

243 As regards the other phases, instead, Cpx and Plg results to be always in disequilibrium conditions.
244 Particularly, since Cpx-melt Fe-Mg exchange coefficient (i.e. $K_{D_{Fe-Mg}}^{Cpx-liq} = (FeO/MgO)^{Cpx}/$
245 $(FeO/MgO)^{liq}$) is 0.41 ± 0.01 and 0.43 ± 0.02 in the APR16-C3Ad and APR16-C3Bb runs,
246 respectively, Cpx result to be in disequilibrium with the melt, according to the Putirka (2008) $K_{D_{Fe-Mg}}^{Cpx-}$
247 liq value (i.e. 0.28 ± 0.08). Similarly, Plg are not in equilibrium with the melt according to the
248 (Putirka, 2008) $K_D(An-Ab)^{Plg-liq}$ value (0.1 ± 0.05 for $T < 1050$ °C). Indeed, plagioclase-liquid
249 equilibrium (i.e. $K_D(An-Ab)^{Plg-liq}$) is 0.46 and 0.47 ± 0.02 in the APR16-C3Ba and APR16-C3Bb runs,
250 respectively. Different case is the APR16-C3Ac run (1080 °C, 6 h), in which both Ol and Cpx
251 results to be in equilibrium with the melt. In this run, indeed, both $K_{D_{Fe-Mg}}^{Cpx-liq}$ (0.36 ± 0.04) and $K_{D_{Fe-Mg}}^{Ol-}$
252 liq (0.30 ± 0.01) are in agreement with the Putirka (2008) reference values (0.28 ± 0.08 and
253 0.29 ± 0.06 , respectively).

254

255 4. Discussion

256 4.1. Amphibole growth rate dependence on time and temperature

257 Studies of amphibole growth rate at high-pressure conditions are scarce in the literature. The only
258 data available are obtained at 0.1-2.7 GPa, 860-970 °C, undercooling between 100 and 600 °C from
259 hydrous basaltic to andesitic melts (i.e. Shea and Hammer, 2013; Simakin et al., 2019, 2009; Zhang
260 et al., 2019) and range from 10^{-5} to 10^{-8} $\text{cm}\cdot\text{s}^{-1}$. Amphibole growth rates from this study decrease
261 from $1.5\cdot 10^{-7}$ to $2.9\cdot 10^{-8}$ $\text{cm}\cdot\text{s}^{-1}$ with increasing the duration of the experiments (Fig. 4), since longer
262 runs allow to attain conditions close to equilibrium under which kinetic processes (i.e. growth) slow
263 down. Notably, textural variations, observed starting from 6 h of dwell time, that from widely
264 dispersed cluster of tiny amphiboles (< 10 μm in size Fig. 1a-b) change in well-formed to euhedral
265 isolated grains (Fig. 1c-d), point out the recrystallization of the set of small crystals with decreasing
266 of the crystal density number and increasing of the average and maximum size over time. This
267 dissolution-precipitation process may be induced from small temperature fluctuations unavoidable
268 in experiments of long durations (Simakin and Bindeman, 2008) and therefore, the G_L determined
269 for long-lasting experiments may be apparent or reflect a recrystallization process (Simakin et al.,
270 2019). However, it should be emphasized that the Amph growth rate calculated in this work varies
271 of about an order of magnitude between the runs with the shortest duration and those with the
272 longest one (Table 3).

273 Concerning the effect of water in the system on the Amph growth rate, Figure 5 shows that the G_L
274 value of Amph in run 1080 °C (APR16-C3Ad) with 10.2 wt% H_2O_f (i.e. water content dissolved in
275 the melt) is higher than that of crystals in 1030 °C run (APR16-C3Bd) with 8.3 wt% H_2O_f ,
276 testifying that melt depolymerization, viscosity reduction, and element diffusivity increase by
277 increasing both temperature and water content. Since Zhang et al. (2019) also show that amphibole
278 growth rate depend upon time and temperature, we applied their regression equation calibrated on 1
279 to 100 hours long experiments, to calculate amphibole growth rate (G_{CSD}) as a function of
280 temperature and (also) pressure:

$$281 \quad G_{\text{CSD}}(T, P) = 7.4(\pm 3.8) \cdot 10^{-10} \cdot T + 1.4(\pm 0.2) \cdot 10^{-7} \cdot P - 7.0(\pm 3.5) \cdot 10^{-7} \quad (2)$$

282 At the isobaric conditions of 0.8 GPa, this method yields growth rate values of $2.11 \cdot 10^{-8} \text{ cm} \cdot \text{s}^{-1}$ at
283 $1080 \text{ }^\circ\text{C}$ and $1.74 \cdot 10^{-8} \text{ cm} \cdot \text{s}^{-1}$ at $1030 \text{ }^\circ\text{C}$, keeping in line with those experimentally obtained from 3-
284 9 hours long experiments ($2.9\text{-}6.4 \cdot 10^{-8} \text{ cm} \cdot \text{s}^{-1}$) mismatching instead the G values determined for the
285 shortest experiments ($1.5 \cdot 10^{-7} \text{ cm} \cdot \text{s}^{-1}$). The quite good correspondence of G values between our
286 medium-long experiments and those calculated by Zhang et al. (2019) equation probably reflects
287 the action of textural equilibration process driven by surface energy reduction, that affected our 3-9
288 hours experiments. Indeed, as stated by Zhang et al. (2019) their experiments have time for crystals
289 to undergo textural maturation (Ostwald ripening; Voorhees, 1992) or coarsening (Marsh, 1988)
290 during which smaller crystals, with higher surface energy, dissolve and larger crystals grow.
291 However, it should be emphasized that in our study only the longest experiments approach also to
292 the chemical equilibrium.

293

294 4.2. Antagonism with clinopyroxene

295 As for amphibole, clinopyroxene growth rate determined at the same experimental conditions
296 (Bonechi et al., 2019) decrease from $2.0 \cdot 10^{-8}$ to $8.2 \cdot 10^{-9} \text{ cm} \cdot \text{s}^{-1}$ with increasing time (Fig. 6; Table
297 3), paralleling the trend described by data of Bonechi et al. (2019) for synthetic clinopyroxene
298 crystallized from the same starting material at $P = 0.8 \text{ GPa}$, $T = 1170\text{-}1250 \text{ }^\circ\text{C}$ and $\text{H}_2\text{O}_f \leq 5 \text{ wt}\%$.
299 However, these Cpx- G_L values are in general slightly higher than those determined in this study
300 (e.g. $\sim 2.0 \cdot 10^{-8}$ and $\sim 0.8 \cdot 10^{-8} \text{ cm} \cdot \text{s}^{-1}$ for a same dwell time), but it should be noted that the
301 temperatures and the H_2O -melt contents of Bonechi et al. (2019) experiments are, respectively,
302 higher and lower than our investigated conditions and not suitable for Amph formation. Thus, the
303 above small differences in Cpx- G_L values can be explained by the contemporary amphibole-
304 clinopyroxene crystallization in our experiments and by the strikingly evidences of the faster
305 growth of amphibole relatively to clinopyroxene (Fig. 7). Such phenomenon is readily explained by
306 the chemical and structural similarities of these minerals (e.g. Kennedy, 1935; Wones and Gilbert,
307 1982), that compete for Mg, Fe, Ca and to a lesser extent Al and Na. The occurrence of amphibole

308 at high water content, therefore, not only reduces the abundance of clinopyroxene (Fig. 8), but also
309 the rates of clinopyroxene nucleation and growth (Fig. 7), as previously observed by Shea and
310 Hammer (2013).

311

312 *4.3. Chemical evolution of amphibole with time*

313 Synthetic amphibole from this study shows compositional variability from edenite to
314 magnesiohastingsite with increasing time (Fig. 2). According to our chemical data (Table 4), the
315 percentage of amphibole species at different dwell time (Fig. 9a) shows that edenite is the dominant
316 term in short (≤ 3 h), low-temperature (1030 °C) runs, whereas the magnesiohastingsite abundance
317 progressively increases shifting towards longer experimental duration and higher temperature.
318 Coherently with the amphibole-liquid Fe-Mg exchange coefficient values (Fig. 3),
319 magnesiohastingsite is therefore identified as the compositional term representative of amphibole-
320 melt equilibrium at the investigated P - T - H_2O conditions. Specifically, we consider the formation of
321 magnesiohastingsitic amphibole as the final product of a reaction process that begins with the
322 crystallization of metastable edenite, whose early nucleation is probably promoted by the pressure
323 conditions. Indeed, the formation of Na-Ca amphiboles is favored by the increase of pressure but
324 hampered by the elevated temperatures that stabilize the pargasite amphibole type (Ernst and Liu,
325 1998 and reference therein). Therefore, the variation of Si and Al^{IV} in the tetrahedral site with time
326 (Fig. 9b) depicts the overall tendency of amphibole to preferably incorporate Al rather than Si in
327 four-fold coordination, mirroring the time-dependent chemical evolution from more siliceous (i.e.
328 edenite) to more aluminous (i.e. magnesiohastingsite) species. At the same time, the SiO_2/Al_2O_3
329 ratio of amphibole keeps always constant around the value of 3 (Fig. 9c), suggesting that the
330 transition from metastable edenite to magnesiohastingsite is not driven by any change of Si and Al
331 activities in the melt. Graham and Navrotsky (1986) observe that a reduction of albite activity from
332 1.0 to 0.5, corresponding to a change in plagioclase composition from albite to andesine, is
333 responsible for the compositional deviation of coexisting amphibole from edenite to tremolite.

334 Alternatively, under equilibrium conditions, the crystallochemistry of coexisting experimental
335 phases potentially acts as a buffer for cation exchange substitutions between the different amphibole
336 structural sites (Graham and Navrotsky, 1986; Holland and Blundy, 1994; Spear, 1981). On this
337 basis, by exemplifying the edenite and magnesiohastingsite activity as a function of the exchange
338 reaction



340 where the subscripts indicate the A, M and T sites of amphibole structure, we can qualitatively
341 conclude that the absence of plagioclase (Table 2) and the minor abundance of clinopyroxene (Fig.
342 8) in the 6-9 h experiments drive the reaction to the right, stabilizing magnesiohastingsite.

343

344 *4.4. Crystallization timing for Capo Marargiu Oligo-Miocene igneous products*

345 Experimental growth rates from this study have been applied to investigate the crystallization time
346 of natural amphiboles and clinopyroxenes from the Oligo-Miocene products of north-western
347 Sardinia (i.e. Capo Marargiu Volcanic District; CMVD). According to Tecchiato et al. (2018b),
348 these minerals crystallize at $P = 0.2\text{--}0.7$ GPa, $T = 960\text{--}1140$ °C and $\text{H}_2\text{O} = 5\text{--}6$ wt% during the
349 polybaric differentiation of a primitive basalt towards andesitic terms by olivine + Cr-spinel +
350 clinopyroxene + amphibole + plagioclase (i.e. crystallization sequence) fractionation. Intriguingly,
351 amphibole crystals are found as millimetre- to centimetre- sized relicts either dispersed in the
352 groundmass of porphyritic, magmatic enclaves (Fig. 10a) entrapped in basaltic andesitic domes, or
353 as plutonic-textured, plagioclase-bearing crystal clots disrupted within andesitic dikes, representing
354 the lower (enclave amphibole) and upper (crystal clots) levels of a crustal-scale cumulitic pile
355 variably sampled and disaggregated upon eruption of basaltic andesitic to andesitic magmas
356 (Tecchiato et al., 2018b, 2018a). Therefore, they always show coronas due to resorption under
357 crystal-melt disequilibrium conditions, where amphibole is replaced by an anhydrous paragenesis of
358 clinopyroxene + plagioclase + titanomagnetite/ilmenite \pm low-Ca pyroxene (Tecchiato et al.,
359 2018b). Based on Simakin and Shaposhnikova (2017), the bimodal distribution of amphibole from

360 enclaves and crystal clots in the $\text{Fe}^{3+}+\text{Ti}^{4+}$ vs. Al^{VI} diagram (Fig. 10b) implies the calculation of
361 different regression equations. The intercepts of these lines with the y-axis provide two $\text{Al}^{\text{VI}}_{\text{max}}$
362 parameters, that according to the Simakin and Shaposhnikova (2017) barometric formulation

$$363 \quad P = (-7.819 \pm 0.359) + (16.051 \pm 0.773) \cdot \text{Al}^{\text{VI}}_{\text{max}} \quad (3)$$

364 testifies to crystallization pressures of 0.91 ± 0.12 GPa and 0.32 ± 0.09 GPa, respectively, confirming
365 the polybaric nature of these minerals and providing a slightly higher crystallization pressure for
366 enclave crystals. Tecchiato et al. (2018a) also identify three types of clinopyroxenes into the CMVD
367 porphyritic enclaves, but only the first and the second population show disequilibrium dissolution
368 features (i.e. spongy texture and rounded corners) ascribable to crystal recycling and/or uptake from
369 a deep cumulate region. Specifically, while the $\text{Mg}\#_{83-93}$ Type 1 is a near-liquidus mineral
370 crystallizing along with early olivine and Cr-spinel, the $\text{Mg}\#_{75-84}$ Type 2 is texturally associated to
371 amphibole (Fig. 10a), representing a colder stage of the magmatic history (Tecchiato et al., 2018a).
372 An approximate estimation of the the minimum growth time and, then, a minimum residence time
373 of the Type 1 and Type 2 amphiboles can be obtained using a growth rate of $2.9 \cdot 10^{-8} \text{ cm} \cdot \text{s}^{-1}$ that is
374 the average experimental G_L from 9 h runs (Table 3), and that on the basis of $K_D(\text{Fe-Mg})^{\text{Cpx-liq}}$ fall in
375 the field representing equilibrium conditions. We aware that this G_L probably better represent a
376 recrystallization rate, however, it is in the order of the effective growth rate determined from
377 amphiboles in the 3 h runs (see *Amphibole growth rate dependence on time and temperature*
378 section) and can be confidently used to provide an estimation of the crystallization time of natural
379 Type 1 and Type 2 amphiboles. Thus, depending on the crystallographic orientation, the maximum
380 dimension of the five biggest amphibole crystals measurable from thin sections ranges from 1.340
381 to 2.850 cm (Table 5), translating to crystallization times of 1.5-3.1 yr at a growth rate of $2.9 \cdot 10^{-8}$
382 $\text{cm} \cdot \text{s}^{-1}$ (i.e. the average experimental growth rate from 9 h runs; Table 3). In turn, clinopyroxene
383 measurements yield maximum dimension of 1.375 cm for Type 1, and 0.380 cm for Type 2 crystals.
384 Crystallization time for Type 1 clinopyroxene (i.e. 2.18 yr) is comparable to that from enclave
385 amphibole (1.46-2.03 yr; Table 5) only when the $2.0 \cdot 10^{-8} \text{ cm} \cdot \text{s}^{-1}$ growth rate from amphibole-free

386 experiments of Bonechi et al. (2019) is adopted. In contrast, the lowest growth rate of $7.4 \cdot 10^{-9} \text{ cm} \cdot \text{s}^{-1}$
387 ¹ from amphibole-bearing runs (Table 3) is necessary to retrieve a consistent Type 2 crystallization
388 time (i.e. 1.62 yr). In conclusion, these results suggest that at the lower crustal pressures typical of
389 enclave paragenesis, the bigger, more primitive Type 1 population crystals coexisting with olivine
390 and Cr-spinel at higher temperature grow faster than the smaller, more evolved Type 2
391 clinopyroxene crystals associated with amphibole at colder conditions, reflecting the coupled effect
392 of amphibole crystallization and temperature on clinopyroxene growth rate.

393

394 **5. Conclusions**

395 New amphibole growth rate data from this study improve knowledge of amphibole growth kinetics
396 at high pressure ($\sim 0.8 \text{ GPa}$). At the investigated P - T - H_2O conditions, amphibole growth rate
397 decreases from $1.5 \cdot 10^{-7}$ to $2.9 \cdot 10^{-8} \text{ cm} \cdot \text{s}^{-1}$ with increasing time (from 0.25 to 9 h), temperature (from
398 1030 to 1080 °C) and water content in the melt (from 8.3 to 10.2 wt%), reflecting time-dependent
399 equilibration, melt depolymerization, viscosity reduction, and element diffusivity increase.
400 Comparison between amphibole and clinopyroxene growth rates provide evidence for the faster
401 growth of amphibole with respect to clinopyroxene, which we surmise is due to chemical and
402 structural similarities between these minerals that cause a “kinetic competition”. According to our
403 chemical data, edenite is the dominant term in short ($\leq 3 \text{ h}$), low temperature (1030 °C) runs,
404 whereas magnesiohastingsite is progressively more important in longer experimental duration and
405 higher temperature runs. Coherently with the amphibole-liquid Fe-Mg exchange coefficient values,
406 magnesiohastingsite is likely representative of amphibole-melt equilibrium at the investigated P - T -
407 H_2O conditions. The results obtained by applying our growth rate data to amphiboles and
408 clinopyroxenes from the Oligo-Miocene products of Capo Marargiu Volcanic District (Sardinia,
409 Italy) suggest that the biggest, more primitive Type 1 population of clinopyroxenes co-existing with
410 olivine and Cr-spinel at higher temperature grow over a longer period of time (2.18 yr) than the
411 smaller, more evolved Type 2 clinopyroxene (1.62 yr) associated to amphibole (1.46-3.12 yr) at

412 colder conditions, reflecting the coupled effect of amphibole crystallization and temperature on
413 clinopyroxene growth rate.

414

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425

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632

633 **FIGURE CAPTIONS**

634 **Figure 1** - Backscattered (BSE) images of selected run products, showing the textural variation as a
635 function of time and temperature. a) clustered Amph with sizes < 10 μm; b) clustered Amph and
636 isolated grains (sizes > 10 μm); c) euhedral Amph with maximum size of ~40 μm; d) euhedral
637 Amph hosting small Cpx in their inner region. Abbreviation: Cpx: clinopyroxene; Ox: oxide;
638 Amph: amphibole; Gl: glass.

639 **Figure 2** - Classification diagram of calcic amphiboles (Hawthorne et al., 2012). Cation abundances
640 are calculated by using the Ridolfi et al. (2018) “AMFORM Calc” and expressed in apfu (atoms per
641 formula unit). Runs of APR16-C3A series are reported in green while those of APR16-C3B series
642 in yellow. Circle indicates 0.25 h runs, triangle 3 h runs, hexagon 6 h runs and square 9 h runs.
643 Orange arrow in b) shows the time-controlled equilibration trend from edenite to
644 magnesiohastingsite.

645 **Figure 3** - Amph-melt Fe-Mg exchange coefficient vs time diagram. Only the magnesiohastingsites
646 of the 9 h runs match the grey field representing the Putirka (2016) equilibrium range (0.28 ± 0.11).
647 Runs of APR16-C3A series are reported in green while those of APR16-C3B series in yellow.
648 Asterisk indicates edenite (Ed), plus pargasite (Par) and circle magnesiohastingsite (Mg-Hs). Grey
649 dashed line indicates the linear regression of the experimental data.

650 **Figure 4** - Amphibole growth rate ($\text{cm} \cdot \text{s}^{-1}$) vs dwell time (s) diagram. The yellow area shows
651 literature data: red crosses indicate Shea and Hammer (2013) growth rate values obtained for ΔT of
652 $\sim 115 - 155$ °C; light blue crosses indicate Zhang et al. (2019) growth rates obtained for ΔT of ~ 180
653 $- 300$ °C for runs at 0.6-1 GPa experiments and ΔT of $\sim 500 - 600$ °C at 2.1- 2.6 GPa; magenta
654 crosses indicate Simakin et al. (2019) growth rates obtained for ΔT of $\sim 130 - 180$ °C; and purple
655 cross indicates Simakin et al. (2009) one obtained for a ΔT of ~ 150 °C. Symbols for data from this
656 study are as in Figure 2.

657 **Figure 5** - Amphibole growth rate ($\text{cm} \cdot \text{s}^{-1}$) vs final water content in the melt (H_2O_f , wt%) and T (°C)
658 diagram, revealing that the positive correlation is possibly due to melt depolymerization, viscosity
659 reduction, and element diffusivity increase. Symbols are as in Figure 4.

660 **Figure 6** - The decrease of clinopyroxene growth rate ($\text{cm} \cdot \text{s}^{-1}$) with increasing dwell time (s).
661 Literature data from Bonechi et al. (2019). Symbols are as in Figure 4.

662 **Figure 7** - Clinopyroxene and amphibole growth rate ($\text{cm} \cdot \text{s}^{-1}$) vs dwell time (s) diagram, showing
663 the faster growth of amphibole (diamonds) relatively to coexisting clinopyroxene (circles).
664 Literature data (orange symbols) from Shea and Hammer (2013) are in agreement with our
665 observation.

666 **Figure 8** - Histogram showing the clinopyroxene (blue) and amphibole (red) modal percentage
667 variation from 0.25 to 9 h runs at both 1030 and 1080 °C. Amphibole becomes progressively more
668 abundant with increasing time at the expense of clinopyroxene.

669 **Figure 9** - a) Histogram showing the time-dependent variation of amphibole species percentage at
670 different temperature conditions, and b) variation of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, Si (apfu) and Al^{IV} (apfu)

671 against time (s). Edenite is reported in green, magnesiohornblende in light blue, pargasite in
672 yellow and magnesiohastingsite in orange.

673 **Figure 10** - a) A centimetre-sized amphibole crystal as appear in a porphyritic, magmatic enclave
674 from CMVD (Tecchiato et al., 2018a). Smaller Type 2 clinopyroxene is included in this amphibole
675 megacryst (see text for further details). Abbreviation are as in Figure 1. b) The bimodal distribution
676 of amphibole from enclaves and crystal clots in the $\text{Fe}^{3+}+\text{Ti}^{4+}$ vs. Al^{VI} diagram (Fig. 10b) testifies to
677 different crystallization pressures (cf. Simakin and Shaposhnikova, 2017), with enclave amphibole
678 belonging to lower crustal environments. Data from Tecchiato et al. (2018b).

679

680 **Figure A1** - T vs. H_2O_f in melt phase diagram from Perinelli et al. (2019) showing experimental
681 saturation curves (dashed when estimated), phase assemblages and stability fields for APR16,
682 APR16GL and SCE compositions. NWA solidus temperature of APR16 composition is from
683 Bonechi et al. (2017). Phase abbreviation Cpx, Ol, Ox and Amph as in Fig. 1. Liq: liquid; Plg:
684 plagioclase; Opx: orthopyroxene. Error bars are smaller than symbol size.

685

686

687 TABLE CAPTIONS

688 **Table 1** - Composition (wt%) of APR16 rock sample and APR16GL starting material.

689 **Table 2** - Experimental run conditions, melt water contents, phases assemblage and proportions in
690 run products.

691 **Table 3** - Growth rate calculations for amphibole, clinopyroxene and oxide.

692 **Table 4** - Electron-microprobe analyses and crystal-chemical formulas of amphibole crystallized in
693 the experimental runs.

694 **Table 5** - Crystal size and estimated crystallization time for natural amphibole and clinopyroxene
695 from the Oligo-Miocene Capo Marargiu Volcanic District (Sardinia, Italy; Tecchiato et al., 2018b).

696

697 **Table A1** - Electron-microprobe analyses of the other phases crystallized in the experimental runs.

698