STUDY OF GROWTH RATE OF ALKALI FELDSPAR IN PHLEGRAEAN FIELDS TRACHYTES

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INTRODUCTION

In this thesis my purpose is to study the crystallization kinetics of phlegraean trachytic magmas, reproducing pre-eruptive conditions and through a combined study of textural and mineralogical features of the samples, trying to define magma behavior during the ascent towards the earth surface that is during eruption. The results of this study will allow the increase of specific knowledge of pre- and sin-eruptive processes of the Phlegraean Fields, with the aim of monitoring and forecasting the kind and the evolution of future eruptions, to create evacuation and first-aid plans. Experimental data on nucleation and growth kinetics are lacking now, for shoshonitic and trachytic melts are totally absent and the existing data for different kind of magmas vary of several order of magnitude, due to variations in the chemical composition of the melt, kind of minerals and undercooling degree. In this thesis cooling (at constant P) and decompression (at constant T) experiments on phlegraean natural samples have been performed. The results obtained after this experimental work will be compared with those obtained by Piochi *et al.* (2005) after the study of CSD in natural samples from Monte Nuovo, Phlegraean Fields.

STARTING MATERIAL AND ANALYTICAL METHODS

The starting material used in the present experimental work is a trachytic obsidian, from the basal unit of the Breccia Museo Member, Phlegraean Fields. This obsidian is subaphiric and contains less than 10% in volume of crystals; phenocrysts are mostly alkaline feldspars and secondarily plagioclase, clinopyroxenes, biotite and magnetite, with decreasing abundance, and as accessory phases apatite and titanite (Civetta *et al.*, 1997). This composition has been chosen because the phase relations are well known (Fabbrizio & Carroll, 2008; Calzolaio, 2005) and the composition is very similar to the Monte Nuovo products, both from a chemical and a petrographical point of view. The powder was introduced in Ag_{70}-Pd_{30} capsules with distilled and deionized water. The experiments in H_2O supersaturated condition have been carried out in vertical Cold Seal Pressure Vessels (CSPV, with Nimonic 105 composition) at the Earth Science Department of Camerino University. The oxidation condition of this apparatus is ~ 0.8 log fO$_2$ units above the NNO buffer (Di Matteo *et al.*, 2004).

Cooling experiments

In this kind of experiments, samples were at first heated above the alkali feldspar liquidus, at a temperature of 850°C (starting temperature, T*i*) and at the experimental pressure, to allow the homogenization of the starting materials contained in the capsules (annealing). After an hour of annealing, water-saturated samples were cooled to the experimental temperature (T*f* = 750, 775, 800, 825 °C) and let crystallize for different time durations (7200, 14400, 21600, 28800, 57600 seconds), to allow the study of the influence on crystal growth of the crystallization time, defined as the time that the sample spends in the alkali feldspar stability field (Fenn, 1977). All the experiments and with a ten-minutes-long quench. In Table 1 the experimental conditions are summarized.

Table 1: Experimental conditions for cooling experiments.

Sample	T (°C)	P (MPa)	ΔT (°C)	theoretical H_2O (wt.%)	time (s)
D1	750	200	15,24	8,00%	14400
D2	750	200	15,24	8,00%	7200
D3	800	100	18,1	6,00%	14400
D4	800	100	18,1	6,00%	7200
D5	800	100	18,1	6,00%	28800
D6	800	100	18,1	6,00%	21600
D7	750	200	15,24	8,00%	57600
D8	750	200	15,24	8,00%	28800
D9	825	50	20	4,00%	57600
D10	825	50	20	4,00%	28800
D11	825	50	20	4,00%	7200
D12	825	50	20	4,00%	14400
D13	775	150	16,19	7,00%	28800
D14	775	150	16,19	7,00%	57600
D15	775	150	16,19	7,00%	7200
D16	775	150	16,19	7,00%	14400
D20	750	200	15,24	8,00%	28800
D23	800	100	18,1	6,00%	21600
D24	800	100	18,1	6,00%	57600
D28	860	50	20	4,00%	14400
D33	840	50	20	4,00%	14400
D34	840	50	20	4,00%	7200

Decompression experiments

Decompression experiments were divided in three series, on the basis of the starting pressure (P_i). Experiments with P_i = 100 MPa belong to the Series A, with P_i = 150 MPa belong to the Series B, with P_i = 200 MPa belong to the Series C.

Water-saturated samples were lead to 850°C (starting temperature, T_i), above the alkali feldspar liquidus, and at the same time at the starting pressure. After an annealing time of an hour, temperature was decreased to 750°C (final temperature, T_f) and pressure was lead to the run value (P_f), to allow sample crystallization in the different condition of P_f (150, 100, 50, 30 MPa).

The experiments belonging to the A series (P_i = 100 MPa) were lead to final pressure of 50 and 30 MPa, while B series experiments (P_i = 150 MPa) were lead to 100 and 50 MPa and C series experiments (P_i = 200 MPa) were lead to 150 and 100 MPa. Samples were left at the final conditions for 2, 6 and 14 hrs (7200, 21600 and 50400 seconds, respectively) to study how the growth rate is influenced by the time available for crystallization, that is that time that the sample spends in the alkali feldspar stability field, starting from the moment in which decompression is performed (Fenn, 1977). All the experiments end with a ten-minutes-long quench. In Table 2 the experimental conditions are summarized.

Growth rate calculation

Sample textural analysis is useful to determine crystals dimensions and thus their growth rate. Starting from SEM images of the samples after the runs, crystal dimensions were measured by Adobe Photoshop 7.0. In every sample only the 10 longest feldspar crystals were considered.

From the collected images is evident the presence of many crystalline phases, among which, of course, alkali feldspars, many in crystalline radial aggregates, from which was impossible to gain any

Table 2: Experimental conditions for decompression experiments.

Sample	T (°C)	Pi (MPa)	Pf MPa)	time (s)	ΔT (°C)	theoretical H_2O (wt.%)
D39	750	200	150	50400	42,86	8,00%
D55	750	200	150	7200	42,86	8,00%
D37	750	200	150	21600	42,86	8,00%
D51	750	150	100	21600	69,52	6,00%
D53	750	150	100	50400	69,52	8,00%
D38	750	200	100	21600	69,52	8,00%
D40	750	150	100	7200	69,52	7,00%
D42	750	200	100	7200	69,52	8,00%
D27	750	200	100	50400	69,52	8,00%
D49	750	100	50	50400	94,55	5,00%
D46	750	100	50	21600	94,55	5,00%
D45	750	150	50	50400	94,55	6,00%
D43	750	100	50	7200	94,55	6,00%
D50	750	150	50	21600	94,55	6,00%
D30	750	150	50	7200	94,55	7,00%
D47	750	100	30	50400	106,36	5,00%
D48	750	100	30	21600	106,36	5,00%
D44	750	100	30	7200	106,36	6,00%

information on crystallization kinetics, as it was not possible to define the exact dimensions of the minerals. In fact, only K-feldspar single crystals were taken into account to measure their length (L).

In the calculation of the growth rate we referred to Couch (2003). To calculate maximum growth rate on the longest side of the crystal (G_L) was used the relation:

$$G_L = (0.5\ L)\ /\ t$$

where L is the length of the crystal and t is the duration of the experiment.

RESULTS

The crystallization process is strongly affected by the undercooling degree (ΔT) and by the pressure decrease in the system, implying variations in texture, on bubble percentage, on abundance and dimension of the present phases.

In the sample analyzed with the SEM, the prevalent phases are:

- Alkali Feldspar, with intermediate composition between albite and orthoclase (Ab_{60-90} - Or_{40-10}, anorthoclase). This is evident even in the K-feldspars from natural samples from Monte Nuovo.

- Clino-pyroxenes, as shown in the semi-quantitative analysis.

- Glass, with a composition similar to that of the alkali feldspar.

DISCUSSION

The graphs "G_L *vs.* ΔT" correlates undercooling, experiment duration and growth rate (inferred from the longest direction of the crystal, G_L) for cooling (Fig. 1) and decompression experiments (Fig. 2). For low ΔT growth is more helped than for high ΔT where G_L is reduced. With increasing experiment duration there is an apparent growth rate reduction, of about an order of magnitude. Error bars (standard deviation of the growth rate of the 10 alkali-feldspar crystals measured for every sample) are quite large.

This can be explained with the Ostwald ripening theory that predicts that in disequilibrium conditions (short duration experiments) several dimensional classes can form, while approaching equilibrium (increasing experiment duration) there is a homogenization of the dimensions (Cabane *et al.*, 2005), with the reduction of error bars, as we can see from graph in Fig. 2.
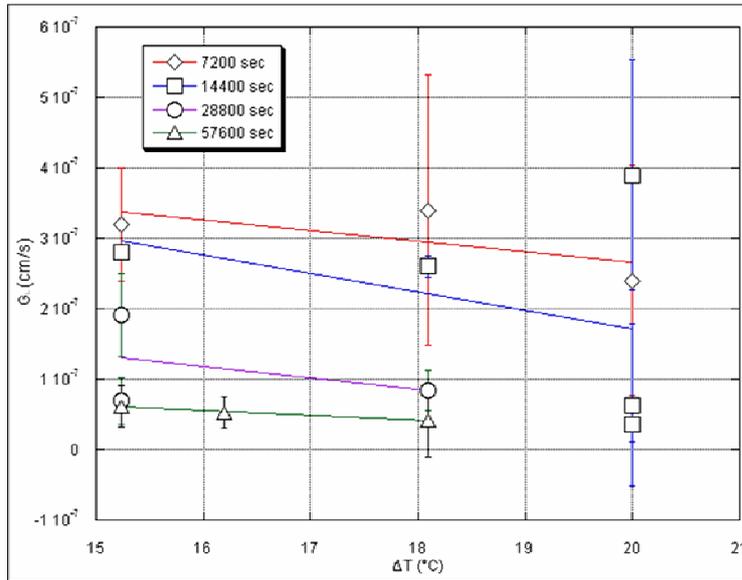

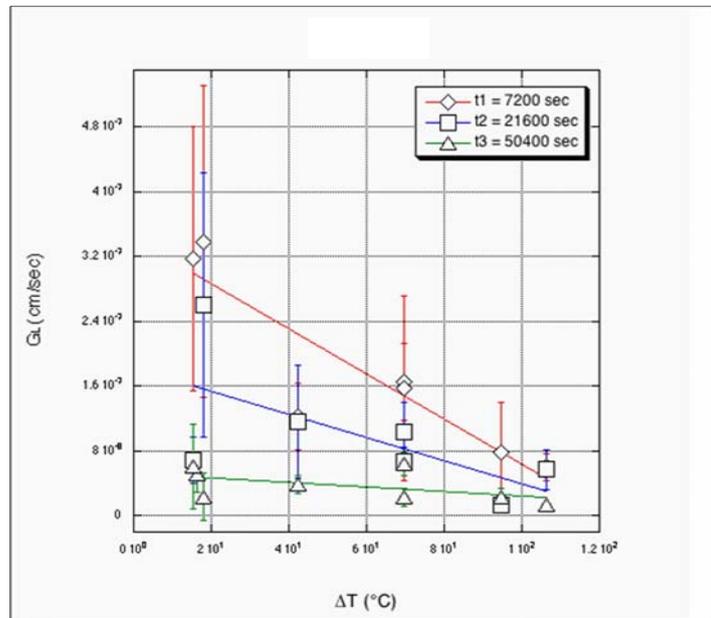Fig. 1 - Correlation between growth rate and undercooling for cooling experiments.

Fig. 2 - Correlation between growth rate and undercooling for decompression experiments.

The graphs "G_L *vs.* t" for cooling (Fig. 3) and decompression (Fig. 4) experiments show that crystal growth is high for short experimental duration, because in this condition the driving force for crystal growth is significant, while, with increasing experimental duration, G_L decreases because the system is approaching equilibrium. Between the shortest and the longest experiment durations there is a difference of about one order of magnitude.
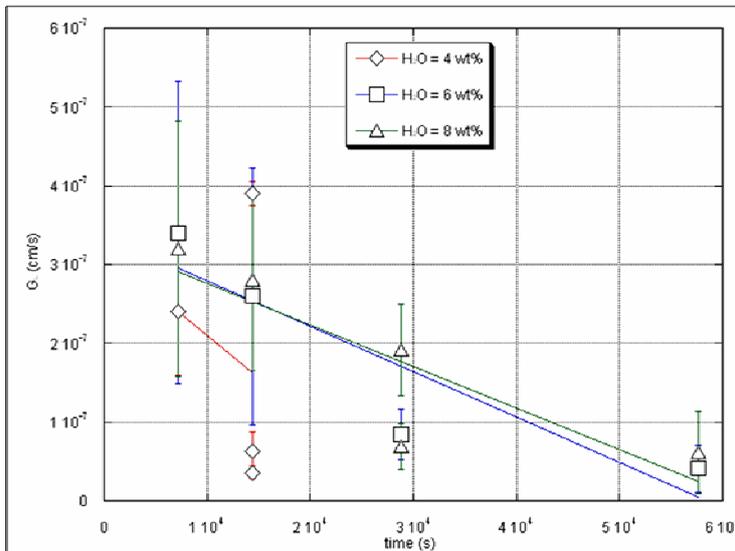

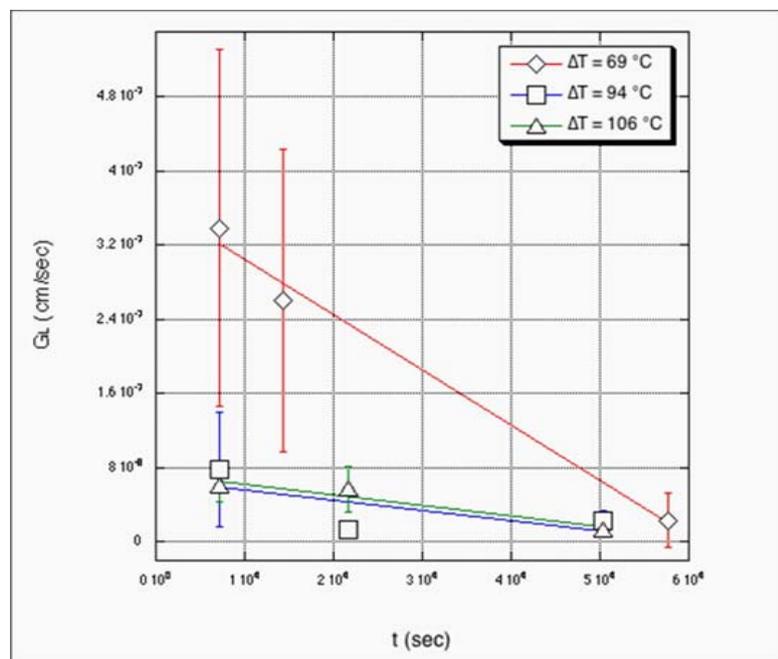Fig. 3 - Correlation between growth rate and experimental duration for cooling experiments.

Fig. 4 - Correlation between growth rate and experimental duration for decompression experiments

Comparison between cooling and decompression experiments

Graph "G_L *vs*. t" (Fig. 5) shows a reduction in growth rate (G_L) with increasing experimental duration. It can be highlighted that G_L is a little higher for cooling experiments at constant pressure with respect to the decompressed ones. This behavior is due both to lower ΔT in cooling experiments (that helps growth) and to the exsolution of water during decompression that slows down the diffusivity of the elements inside the melt.
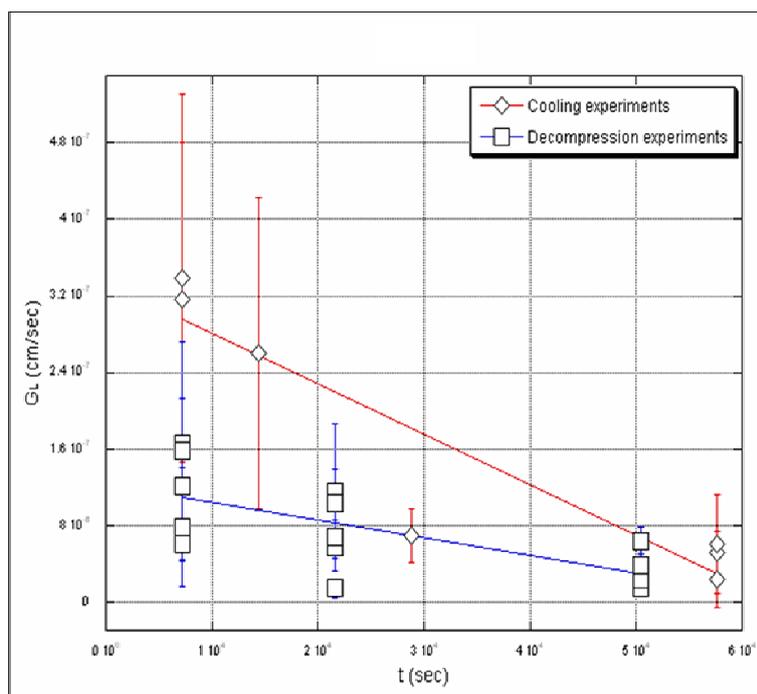

Fig. 5 - Comparison of crystal growth rate obtained in decompression and cooling experiments.

Comparison with previous studies

Studies about K-feldspar growth rate are scarce in the scientific literature: the only ones that calculated G for alkaline feldspars are Swanson (1977) in synthetic granitic melts and Fenn (1977) in an albite ($NaAlSi_3O_8$), orthoclase ($KAlSi_3O_8$) and H_2O mixture.

To allow this comparison between the growth rates obtained in this work and those obtained by Swanson and Fenn through cooling experiments at constant pressure, we considered the values of G obtained at the same experimental temperature (750°C). The order of magnitude of K-feldspar growth rate estimated by Swanson varies between 10^{-8} and 10^{-6} cm/s; in Fenn's results, G has an order of magnitude of 10^{-6} cm/s; in the end in this thesis G varies between 10^{-8} and 10^{-7} cm/s both for decompression and cooling experiments.

Swanson and Fenn studied growth rate in relation to ΔT (that goes from few degrees under the liquidus temperature to about 400°C). Maximum growth rate is obtained with ΔT between 200 and 250°C and trends to decrease with increasing or decreasing undercooling, while the data collected in this work show that growth rate is maximum for low ΔT, while decreases for increasing ΔT.

Besides, Fenn relates G with ΔT and melt dissolved water percentage and shows that for low ΔT (between 20 and 70°C), the increase of water causes an increase in alkali-feldspar growth rates. This

behavior was found in our data as well. The undercooling and the water percentages have similar value to those used in the decompression experiments of the present experimental work, while Fenn's G varies of one or two orders of magnitude with respect to the values of G obtained in this work.

Available application of the collected data

Growth rate is used both in the description of magmas crystallization kinetics and in the study of the Crystal Size Distribution (CSD), to determine residence and ascent times, to forecast future eruptive events and consequently realize an evacuation plan of the phlegraean area.

Crystal Size Distribution is the variation of the number of crystals for each size in natural samples. In a CSD graph [size *vs.* ln(population density)], the slope (s) of the linear regression obtained from the plot of natural samples is (-1/G·t) (after Higgins, 2000, 2002). Known G from experimental studies and s from the observation of natural samples, we can calculate t that is time needed for crystal growth.

Piochi *et al.* (2005) calculated residence and ascent rates during the Monte Nuovo eruption using two values of G:

- 10^{-9} cm/s is the value of G for the crystallization processes inside the magma chamber with low ΔT (Cashman, 1993) and was used to calculate the residence time of the magma;

- $2 \cdot 10^{-8}$ cm/s, on the contrary is the mean value of all the G estimated by Geschwind & Rutherford (1995) and by Couch *et al.* (2003), with no distinction between plagioclases and alkali feldspars. This value was used to calculate ascent time in the conduit towards surface, with consequent decrease of pressure and magma degassing.

The value of G used by Piochi *et al.* (2005) to determine the ascent time is quite similar (10^{-8} cm/s) to the decompression growth rates calculated in this thesis, differing at the most of an order of magnitude. This difference implies significant variations of the rising time. CSD studies on Monte Nuovo products carried out by Piochi *et al.* (2005) to investigate magma dynamics in sin-eruptive conditions, show rising time between 1 and 2 days. On the contrary, using the value of G obtained in this experimental work, we can obtain a new timing for magmatic processes: similar (using 10^{-8} cm/s) or lower (using 10^{-7} cm/s) duration than Piochi *et al.* (2005).

CONCLUSION

We performed two different kinds of crystallization experiments, cooling and decompression ones, to investigate how the kinetics of crystallization are affected by the different changing parameters. We found that for cooling experiments growth rate varies between $3.6 \cdot 10^{-8}$ and $3.9 \cdot 10^{-7}$ cm/s, while for decompression experiments it varies between $1.4 \cdot 10^{-8}$ and $1.7 \cdot 10^{-7}$ cm/s.

Crystal growth rate is higher in experiments with shorter duration, while it decreases with increasing experimental duration. The undercooling degree implies significant variation in the crystallization kinetics: for low ΔT growth is helped, in fact we find values of G higher than experiments with higher ΔT (where the growth slows down). This behavior differs from the theoretical relation between G and ΔT (see for example Peccerillo & Perugini, 2003), probably because the theoretical curve simply encloses all the experimental results, while in the present work different G values experimentally obtained were distinguished for experimental conditions. The percentage of dissolved water in the melt plays a fundamental role in helping growth, as well: collected data show an increase of crystal growth rate with increasing water content in the melt. This behavior is due to the depolymerizing effect of water that reduces magma viscosity and consequently helps atoms mobility inside the magma.

From the comparison between cooling and decompression growth rates we can see that the former are slightly faster than the latter. This is because the amount of dissolved water in the melt depends on the experimental starting pressure. In decompression experiments pressure is lowered and consequently the amount of dissolved water in the melt lowers as well, implying a lower mobility of cations and consequently a lower crystal growth rate.

The estimate of alkali feldspar growth rate together with the study of the CSD is useful to determine residence and rising time of trachytic phlegraean magmas to evaluate eruptive dynamics of volcanic events that can involve the area. The values of G presented here are the same (10^{-8} cm/s) or differ at the most of an order of magnitude (10^{-7} cm/s) from the growth rates used by Piochi *et al.* (2005) for Monte Nuovo, so the rising time that will be calculated will surely be similar or lower than those estimated by Piochi *et al.* (2005).

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