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THE EFFECT OF F AND Cl ON THE KINETICS OF ALBITE CRYSTALLIZATION: A MODEL FOR GRANITIC PEGMATITES?

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ABSTRACT

Crystallization kinetics of albite from melts in the system $NaAlSi_3O_8$–H_2O are not dramatically changed by the addition of 1–2 wt.% F or Cl. Vapor-undersaturated liquidus temperatures in the hydrous system are lowered 25 to 50°C in the presence of F, whereas Cl does not appreciably change the temperature of the hydrous liquidus. A Cl-rich vapor phase is found in the Cl-bearing systems. At 900°C and undercoolings of 40 to 70°C, rates of albite growth range from 1.4 to 2.2 X 10^{-6} cm/s in the F-bearing hydrous system (compared to 1.4 to 3.2 X 10^{-6} cm/s in the F-free hydrous system at similar undercoolings). The growth rate of albite in the presence of about 1 wt.% Cl (and 2 wt.% H_2O) at an undercooling of 90°C is 0.6 X 10^{-6} cm/s. Nucleation lag is 0–10 hours in the F-bearing hydrous system, 10–24 hours in the hydrous system, and 38 hours in the Cl-bearing hydrous system. Growth rates at 850°C are highest in the hydrous system (71.1 X 10^{-6} cm/s), but are elevated (relative to rates at 900°C) for both the F-bearing (2.1-6.3 X 10^{-6} cm/s) and Cl-bearing (1.2 X 10^{-6} cm/s) hydrous systems. Lag times for nucleation at 850°C in the Cl-bearing system (20 hours) are longer than in the hydrous or F-bearing systems (0–9 hours). The presence of a Cl-rich vapor phase seems to delay albite nucleation. Large crystals in pegmatites are not formed by high rates of crystal growth induced by elevated F or Cl contents. They may be related to a prolonged interval of crystallization coupled with a reduced viscosity promoted by the fluxing action of components such as F and a range of nucleation events related to delayed nucleation in the presence of a vapor phase.

Keywords: albite, fluorine, chlorine, crystal growth, granitic pegmatite, experimental petrology.

SOMMAIRE

La cinétique de cristallisation de l'albite à partir d'un bain fondu dans le système $NaAlSi_3O_8$–H_2O n'est pas sérieusement modifiée par l'addition de 1 à 2% (en poids) de F ou Cl. La température du liquidus dans le système $NaAlSi_3O_8$–H_2O sous-saturé en phase volatile est abaissée de 25 à 50°C en présence de fluor, tandis qu'elle reste à peu près la même avec l'addition de chlore. Une phase fluide riche en Cl est présente dans tout système porteur de chlore. Avec des refroidissements de 40 à 70°C au dessous d'un point de départ à 900°C, les taux de croissance de l'albite vont de 1.4 à 2.2 X 10^{-6} cm/s dans un système contenant F et H_2O; ils vont de 1.4 à 3.2 X 10^{-6} cm/s dans le système hydraté sans fluor à des conditions semblables. Le taux de croissance de l'albite en présence d'environ 1% de Cl et 2% d'eau (base pondérale) à 90°C au-dessous du liquidus est 0.6 X 10^{-6} cm/s. Le délai jusqu'au point de nucléation est entre 0 et 10 heures dans le système fluoré et hydraté, entre 10 et 24 heures dans le système hydraté, et 38 heures dans le système hydraté avec chlore. Les taux de croissance à 850°C sont les plus élevés dans le système hydraté (71.1 X 10^{-6} cm/s), mais ils sont élevés, en comparaison des taux à 900°C, pour les systèmes hydratés fluoré (2.1-6.3 X 10^{-6} cm/s) et chloré (1.2 X 10^{-6} cm/s). Le temps d'éclosion des nucléus à 850°C dans le système chloré (20 heures) dépasse ceux dans les systèmes hydratés avec ou sans fluor (0–9 heures). La présence d'une phase fluide chlorée semble retarder la nucléation de l'albite. Les mégacristaux des pegmatites granitiques ne seraient pas dus à un taux élevé de croissance cristalline causé par des teneurs élevées de F ou Cl. Ils pourraient résulter d'un intervalle de cristallisation prolongé, d'une viscosité réduite à cause de la présence de composants tels le fluor, et enfin d'une multitude d'événements de nucléation, qu'aurait retardé la présence d'une phase fluide.

(Traduit par la Rédaction)

Mots-clés: albite, fluor, chlore, croissance cristalline, pegmatite granitique, pétrologie expérimentale.

INTRODUCTION

Most geologists characterize granitic pegmatites as being extremely coarse-grained (Carmichael *et al.* 1974, Bates & Jackson 1987). However, it is really the variability in grain size that distinguishes the texture of a granitic pegmatite from other granitic rocks (Jahns 1955). The range in grain size in granitic pegmatites (millimeters to meters, a variation of 4 to 5 orders of magnitude) is similar to that found in volcanic rocks (micrometers to millimeters, a range of 4 to 5 orders of magnitude). Rapid quenching of silicate melt during eruption results in a large range in temperature of crystallization for volcanic rocks and a corresponding large range of grain size. Pegmatitic systems may also undergo quenching, but in this case the quench is compositional, associated with the loss of a vapor phase (Jahns & Burnham 1969). Quenching either by eruption or loss of a vapor phase greatly undercools the melt. An increase in undercooling (ΔT, temperature interval between liquidus and crystallization) results in a dramatic increase in the number of nuclei (*i.e.*, in nucleation density) in silicate melts (*e.g.*, Swanson 1977). Crystallization with a high density of nuclei accounts for the finer grain-size in volcanic and pegmatitic systems. It is the juxtaposition of giant crystals with fine-grained fractions that accounts for the large range of grain size in granitic pegmatites.

REVIEW OF F AND Cl IN GRANITIC SYSTEMS

The abundance of fluorine in granitic rocks and magmas has been reviewed by Bailey (1977), who proposed an average of 800 ppm F in granite. Alkaline granites and granitic pegmatites may contain up to 3000 ppm F, but in general the "normal" granitic rocks contain between 100 and 1000 ppm F. Estimation of Cl contents is complicated by the apparent low solubility of Cl in granitic melts. Zunkel & Hempel (1917) reported a solubility of 860 ppm NaCl in an obsidian melt at 1200°C and 1 bar. Kuroda & Sandell (1953) reported an average of only 22 ppm Cl in crystalline granitic rocks, whereas Roedder (1972) reported Cl contents as high as 110,700 ppm in fluid inclusions from granitic rocks. Chlorine clearly is fractionated into the vapor phase, and an appreciable amount may be lost during crystallization, a result confirmed by experimental studies (Kilinc & Burnham 1972). Thus the estimation of an initial Cl content of a typical granitic magma is difficult, but may be on the order of 1000 to 2000 ppm.

The effect of excess H_2O on melting in granitic systems has been well documented, beginning with the studies of Goranson (1932) on the melting of the Stone Mountain granite and the classic study of Tuttle & Bowen (1958) on liquidus relationships in the system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2–H_2O. Some attention has also been given to conditions under which the system is undersaturated with respect to H_2O (Robertson & Wyllie 1971, Steiner *et al.* 1975, Whitney 1975). The effect of H_2O on the kinetics of crystallization in both H_2O-saturated and H_2O-undersaturated granitic systems has been discussed by Fenn (1977) and Swanson (1977).

The halogens F and Cl are prominently mentioned as facilitating crystallization of silicate melts (Buerger 1948). The fluxing action of F in controlling the melting point and viscosity of silicate glasses has been well documented (Manning 1981, Dingwell *et al.* 1985). Solidus temperatures for F-bearing granites (Weymouth & Williamson 1957, Weidner & Martin 1987) are 30–60°C lower than in F-free granitic systems (*e.g.*, Tuttle & Bowen 1958). In the system Ab–NaF, Koster van Groos & Wyllie (1968) were able to form homogeneous melts at temperatures as low as 860°C at 1 bar. Chlorine, on the other hand, has little effect on melting in the system Ab–NaCl and in compositions containing more than 5 wt.% NaCl in silicate melts (Koster van Groos & Wyllie 1969). To our knowledge, there are no available data on the effect of either F or Cl on the crystallization kinetics of geologically meaningful silicate melts.

Combinations of H_2O and halogen-bearing components have been shown to have varying effects on melting and crystallization of silicate systems. Addition of HF (Wyllie & Tuttle 1961) or NaF (Koster van Groos & Wyllie 1968) to Ab–H_2O or granite–H_2O systems depresses solidus and liquidus temperatures to a greater degree than either H_2O or F alone. Both sets of investigators reported that the growth of albite was enhanced by the presence of a fluoride component in the melt. Liquidus compositions of the minimum in the water-saturated system Ab–Or–Q are enriched in the Ab-component and shifted to lower temperatures owing to the addition of F (Manning 1981). Addition of HCl (Wyllie & Tuttle 1964) or NaCl (Koster van Groos & Wyllie 1969) to Ab–H_2O depresses the solidus and liquidus temperatures only slightly, whereas the addition of HCl to a granite–H_2O system apparently increases the solidus temperature (Wyllie & Tuttle 1964). The relative ease of crystallization of albite in the presence of chloride components was not discussed in either study. In a system of silicate melt + aqueous vapor, Cl is strongly partitioned into the vapor phase (Kilinc & Burnham 1972). Based on these results, it can be concluded that F is quite soluble in silicate melts, whereas Cl is relatively insoluble and, in the presence of H_2O, is strongly partitioned into the vapor phase (Wyllie & Tuttle 1964, Kilinc & Burnham 1972).

The system Ab - H_2O - second volatile is a satisfactory model for more complex granitic systems (Wyllie & Tuttle 1961). An interpretation of phase equilibria in this system is complicated by the presence of "extra" components (H: Wyllie & Tuttle 1961, 1964; Na: Koster van Groos & Wyllie 1968, 1969) added with the second volatile component (HF, NaF, NaCl). The presence of Na in excess of albite stoichiometry lowers the liquidus temperature in the dry system (Schairer & Bowen 1956). The effect of excess H has not been investigated in detail, but the increased solubility of albite in increasingly acidic solutions suggests that pH may be a significant factor. Thus the presence of excess Na or H in the previous studies may have had significant effects on the phase relations observed, and these effects are not easily separable from the influence of F or Cl.

The present study was designed to study the effects of F and Cl on crystallization kinetics of albite in the model silicate system Ab-H_2O-(F or Cl) without interference from "extra" components. In order to avoid adding "extra" components to the system Ab-H_2O, initial bulk compositions were prepared as Na-deficient Ab. The use of NaCl or NaF to remove the Na-deficiency results in a system of the type Ab-H_2O-X, where X is F or Cl.

EXPERIMENTAL METHODS

Starting materials

Starting materials were prepared as Na-deficient $NaAlSi_3O_8$ ($Na_{0.9}AlSi_3O_8$ A9F, $Na_{0.7}AlSi_3O_8$ A7F) using the coprecipitated gel technique (Luth & Ingamells 1965). Additional Na was added to the fired gels in the form of NaCl or NaF to make the final composition of $NaAlSi_3O_8$ plus F or Cl. Addition of NaF to A9 and A7 resulted in compositions of $NaAlSi_3O_8$ + 0.73 wt.% F (A9F) and $NaAlSi_3O_8$ + 2.20 wt.% F (A7F), respectively. If NaCl is added to A9, the result is a composition of $NaAlSi_3O_8$ + 1.35 wt.% Cl (A9Cl). These halogen contents are higher than expected concentrations in granitic magmas, but may be reasonable estimates for those that crystallize with a pegmatitic texture. This method of introducing F and Cl into the system does not result in excess amounts of Na (such as are produced when NaCl or NaF are added to $NaAlSi_3O_8$) or H (such as are produced when HCl or HF are added). The effect of F and Cl on phase equilibria or crystal nucleation and growth is easily studied in such systems without the complication of these "excess" components.

Apparatus and techniques

Gels were ground in a mill to an average grain-size of less than 5 μm and then mixed with NaF or NaCl and reground by hand. The mixtures were then loaded into platinum capsules (2.0 mm O.D.) that contained a known amount of freshly boiled, deionized water. Crystal-growth experiments and the phase-equilibria experiments above 800°C were made in internally heated pressure vessels (Holloway 1971). Phase-equilibria experiments below 800°C were made in externally heated cold-seal pressure vessels (Luth & Tuttle 1963). Temperature measurement and control were done with $Pt/Pt_{90}Rh_{10}$ or Chromel/Alumel thermocouples that were periodically calibrated against the melting points of NaCl and Au. Temperatures reported are considered to be accurate within 10°C. Argon was the pressure medium in both types of pressure vessels. Pressure was measured on both a Heise gauge and on a Carey–Foster bridge using manganin coils. Pressures are considered to be accurate to within 100 bars.

Two very different types of experiments were carried out in this study. Phase-equilibria experiments were done by adjusting the temperature and pressure on the capsules to the conditions of the experiment, maintaining these conditions for the duration of the experiment (72–168 hours), and then quenching to ambient conditions. These run times are believed to be adequate to obtain equilibrium, based on the results in similar systems using the same equipment (Whitney 1975, Swanson 1979). The use of finely divided gel in these phase-equilibria experiments provided a large number of potential sites for the nucleation of crystals. Crystals produced in phase-equilibria experiments are always less than 100 μm. A second type of experiment, called crystal growth, involved the nucleation and growth of crystals from a silicate melt. In these experiments, pressure and temperature on the capsules were adjusted to superliquidus conditions (1000°C, 2500 bars) and maintained for 72 hours to allow homogenization of the silicate liquid. Temperature was then isobarically lowered until the temperature of crystal growth was attained, then maintained for a period between 6 and 96 hours. At the end of both types of experiments, the power to the furnace was turned off, and the capsules were quenched to room temperature, the capsules were removed, checked for leaks, and opened to remove the charges. Thin sections were prepared of the crystal-growth experiments that produced crystals.

Measurement of crystals

The amount of crystal growth during the experiment was determined by measuring the largest crystal in an experiment with a micrometer on a petrographic microscope. Internally nucleated crystals and heterogeneously nucleated crystals (obvious nucleation on the edge of the charge or in the capsule crimp) were distinguished and measured separately. The total length of the heterogeneously nucleated crystals was taken as the amount of unidirectional growth during the experiment. For internally nucleated crystals, the total length was divided by 2 to allow for the possibility of symmetrical unidirectional growth. For charges that contain a radial arrangement of crystals, the amount of growth was measured from the center to the outer margin of the array.

EXPERIMENTAL RESULTS

Phase equilibria

Experimentally determined liquidus curves for the compositions A9F, A7F, and A9Cl as a function of water content at 2500 bars are shown in Figure 1. Also shown for comparison in the halogen-bearing systems is the liquidus in the system $NaAlSi_3O_8$–H_2O at 2500 bars. The addition of Cl does not change the liquidus (A9Cl, Fig. 1), within the limits of reproducibility of these

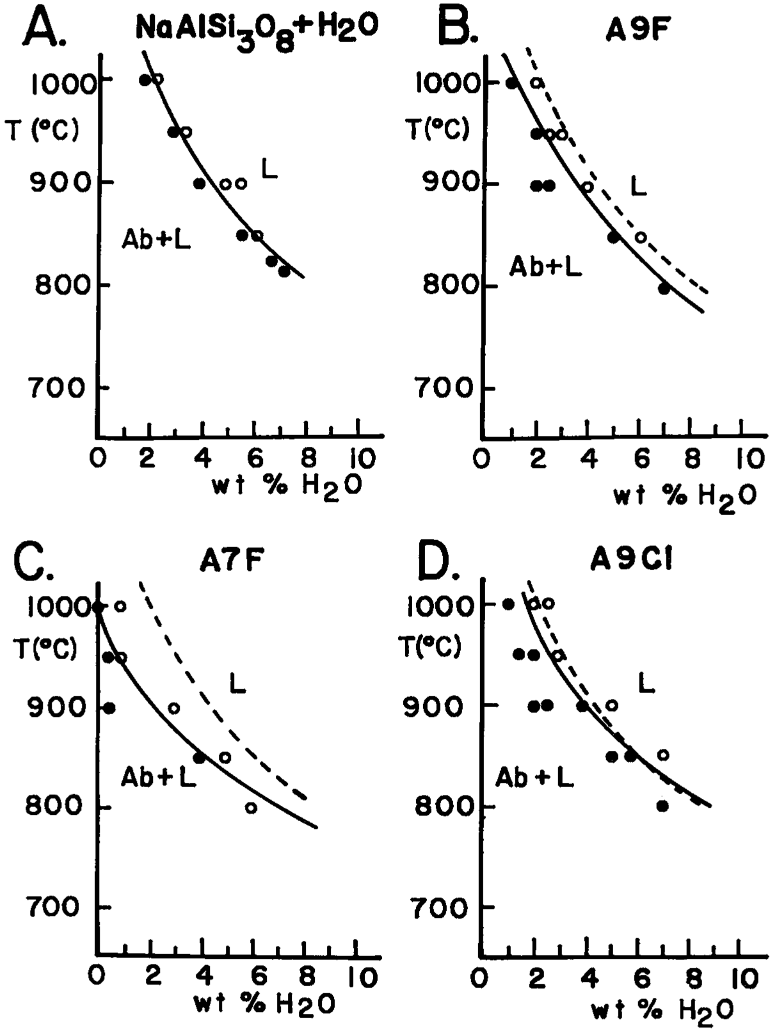

FIG. 1. Vapor-undersaturated liquidus curves at 2500 bars for: A) $NaAlSi_3O_8 + H_2O$, B) $NaAlSi_3O_8$ + 0.73 wt.% F (A9F), C) $NaAlSi_3O_8$ + 2.20 wt.% F (A7F), and D) $NaAlSi_3O_8$ + 1.35 wt.% Cl (A9Cl). Solid dots represent Ab+L, and open circles, L. Dashed curve in B, C, and D is the hydrous liquidus from A.

experiments. On the other hand, there is a regular decrease in liquidus temperature with increasing F content (A9F–A7F, Fig. 1). These experiments confirm the results of earlier studies that report a lowering of liquidus temperatures with increasing F content (Wyllie & Tuttle 1961, 1964, Koster van Groos & Wyllie 1968, 1969, Wyllie 1979, Manning 1981). Reconnaissance experiments have been made in the subliquidus region of these systems, but without systematic effort to determine subliquidus phase relations. The liquidus relations shown in Figure 1 were not reversed, but we believe that these results show a close approach to equilibrium, as judged by the consistent results from one isotherm to another. Liquidus temperatures show a regular decrease with increasing amounts of water. Selection of appropriate water contents [A9F + 2.0 wt.% H_2O (A9F+2), A9F + 2.5 wt.% H_2O (A9F+2.5), A7F + 0.5 wt.% H_2O (A7F+0.5), A9Cl + 2.0 wt.% H_2O (A9Cl+2)] results in the range of liquidus temperatures of 940° to 990°C (Fig. 1) for crystal-growth experiments. The degree of undercooling in the crystal-growth experiments is approximately constant (ΔT A9F+2: 60°C, ΔT A9F+2.5: 40°C, ΔT A7F+0.5: 70°C, ΔT A9Cl+2: 90°C; all at 900°C) at a given isotherm. Determination of liquidus relations assures generation of a homogeneous liquid from which to nucleate and grow crystals.

Experiments (both phase equilibria and crystal growth) with A9F and A7F did not produce any evidence of a hydrous or halogen-rich vapor phase, but experiments with A9Cl did contain apparently Cl-rich bubbles in the glass, indicating the presence of a Cl-rich vapor phase. All of the starting materials were loaded in air at 1 bar. Thus all of the experiments contained air. Upon quenching, some very small bubbles of vapor were found to be present in the A9F and A7F glasses, presumably representing air that was exsolved from the melt upon quenching (Swanson 1979). These bubbles are all single phase (no fluid or crystals). The H_2O and F were apparently dissolved in the A9F and A7F glasses. Bubbles in the A9Cl glass were considerably larger than the air bubbles and contained fluid + vapor + NaCl crystals. Strictly speaking, all of the experiments did contain a vapor (air or a Cl-rich vapor). In this paper, the terms vapor-saturated and vapor-undersaturated will be used to refer to the solubility of a halogen-bearing hydrous vapor phase in the melt, in accord with accepted terminology (*e.g.*, Whitney 1975).

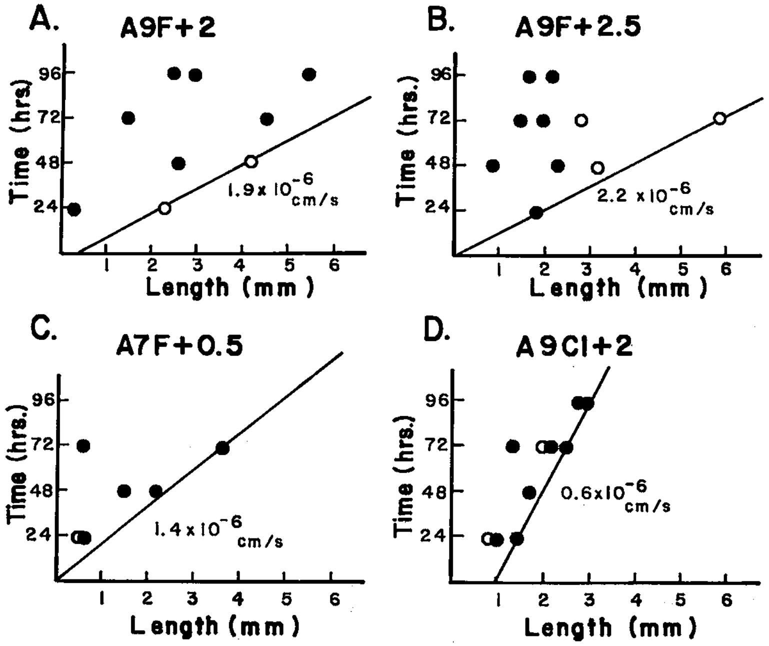

FIG. 2. Growth curves for compositions used in this study at 900°C and 2500 bars. A) A9F+2, ΔT 60°C, B) A9F+2.5, ΔT 40°C, C) A7F+0.5, ΔT 70°C, D) A9Cl+2, ΔT 90°C. Growth rates are based on maximum amount of crystal growth from either heterogeneously nucleated crystals (open circles) or internally nucleated crystals (solid dots).

Crystal growth

Results of crystal-growth experiments at 900° and 850°C at 2500 bars are shown on Figures 2 and 3. The largest amount of both internal and heterogeneous crystal-growth in each experiment is plotted on Figures 2 and 3. Two experiments were made for each bulk composition at 24, 48, and 72 hours. Each growth isotherm on Figures 2 and 3 thus could have a maximum of four data points (assuming each of the two experiments had sites for both internal and heterogeneous nucleation). Obviously, from the paucity of data on Figures 2 and 3, not all of the experiments led to the nucleation of crystals. Additional experiments were made at 850°C for 6 and 12 hours and at 900°C for 96 hours in an attempt to overcome the problems of the probabilistic nature of nucleus formation (Kirkpatrick 1975, Fenn 1977, Swanson 1977).

Data on Figures 2 and 3 do not define a simple linear pattern of growth rates. Some of the scatter obviously is related to the limited space available for crystal growth in the capsules (2 mm O.D., 18 mm pre-crimp length), but much of the scatter probably is related to the probabilistic character of nucleation (*e.g.*, Kirkpatrick 1975). Growth rates shown on Figures 2 and 3 are drawn to give maximum values. For one bulk composition at one isotherm (A7F+0.5, Fig. 2), the resulting growth-rate uses the maximum amount of crystal growth in one experiment, and the growth rate is through the origin. In the other bulk compositions, two experiments define the growth rate, and the negative intercept on the time axis is a measure of the lag time for nucleation in the system (Fenn 1977). This method is justified by considering the limitations on determination of the time of crystal growth (Fenn 1977, Swanson 1977). All that is known about the length of time of crystal growth is the amount of time the experiment was held at the growth isotherm. This amount of time certainly must represent a maximum value for the time of crystal growth. Experiments in similar silicate systems (Lofgren 1974, Fenn 1977, Swanson 1977) indicate that feldspar does not nucleate instantaneously from an undercooled silicate melt, as a result of the so-called nucleation lag effect (Swanson 1977). This result is also found in the present study; in experiments of less than 48 hours at low ΔT, there is generally a failure once per experiment to nucleate crystals. Because of this

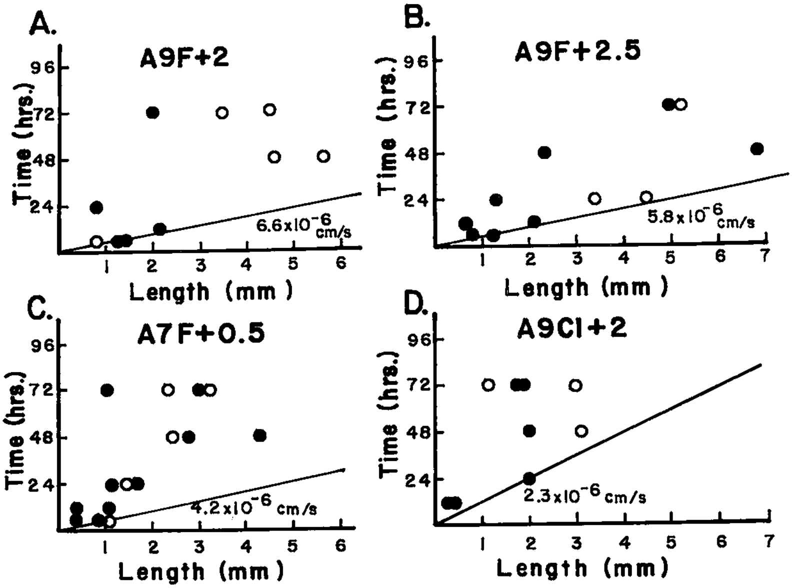

FIG. 3. Growth curves for compositions at 850°C. A) A9F+2, ΔT 110°C, B) A9F+2.5, ΔT 90°C, C) A7F+0.5, ΔT 120°C, D) A9Cl+2, ΔT 140°C. See Figure 2 for technique and symbols.

TABLE 1. SUMMARY OF RATES OF ALBITE GROWTH*

Composition	Growth Isotherm °C	ΔT °C	Growth Rate 10^{-6} cm/s	Nucl. Lag hrs
A9F + 2	900	60	1.9	10
A9F + 2.5	900	40	2.2	0
A7F + 0.5	900	70	1.4	0
A9Cl + 2	900	90	0.6	38
A9F + 2	850	110	6.3	4
A9F + 2.5	850	90	5.0	2
A7F + 0.5	850	120	2.1	9
A9Cl + 2	850	140	1.2	20

* derived from Figures 2 and 3. Nucl.: nucleation.

nucleation problem, growth times used in Figures 2 and 3 must be maximum values, and calculated rates of crystal growth must be minimum values. Results from other experiments in this study typically approach the growth-rate line based on the largest crystal (Figs. 2, 3), which suggests that the technique does provide a valid measure of growth rates in these systems.

Values of growth rates are shown on Figures 2 and 3 and range from 0.6 to 2.2 X 10^{-6} cm/s at 900°C and from 1.2 to 6.3 X 10^{-6} cm/s at 850°C (Table 1). Growth rates at 850°C are uniformly higher than growth rates at 900°C (Table 1). Nucleation is expected to occur more quickly at higher ΔT (Kirkpatrick 1975), but faster nucleation is not the only reason for the increase in growth rates with increasing ΔT. Two bulk compositions (A9F+2.5 and A7F+0.5) have growth rates that pass through the origin at both 900° and 850°C (Figs. 2, 3), and both compositions have higher rates of growth at 850°C. The higher rates of growth at 850°C are thus at least partially related to the initial increase in growth rates with increasing ΔT observed in silicate systems (Kirkpatrick 1975, Fenn 1977, Swanson 1977). The greater range in observed growth-rates at 850°C is due to the higher growth-rates resulting from the F-bearing systems (Fig. 3). The highest rates of growth are in the A9F systems at both 900° and 850°C, where both compositions (A9F+2, A9F+2.5) have similar growth-rates. The A9Cl+2 system has the lowest growth-rate at both isotherms, whereas rates of growth in the A7F+0.5 composition are intermediate between those for the A9F and A9Cl+2 compositions.

The shape of the crystals in the Cl- and F-bearing systems are very similar. Figure 4 illustrates typical textural relations of crystals grown at 900°C. A semiradial arrangement of faceted crystals surrounded by quenched silicate liquid (now glass) typifies the results of successful experiments in these systems. The facets developed on these crystals and the semiradial texture are typical of silicate crystals grown at values of ΔT of 50–100°C (Lofgren 1974, Fenn 1977, Swanson 1977). Textures observed in crystal-growth experiments carried out at both isotherms are similar, but the modal proportion of crystals is larger in the 850°C experiments, as predicted from phase relations. Comparison of these albite crystals with crystals of

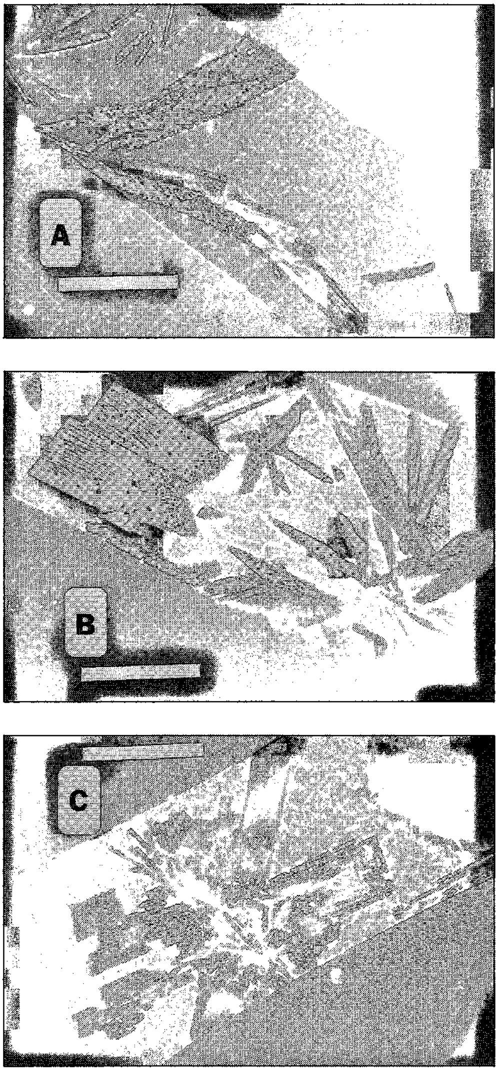

FIG. 4. Photomicrographs of albite crystals grown at 900°C. White bar in each photo is 1 mm. A) A9F+2, 72 hours at growth isotherm, B) A7F+0.5, 72 hours at growth isotherm, C) A9Cl+2, 96 hours at growth isotherm.

alkali feldspar grown by Fenn (1977) from hydrous melts (no F or Cl) shows similar morphologies at equivalent ΔT.

There is some suggestion within these experiments that albite nucleation is enhanced in the F-bearing system relative to the A9Cl system. Estimates of lag time given for nucleation in Table 1 are higher in the A9Cl + 2 composition (20 to 38 hours) than in the F-bearing systems (0–10 hours). Lag times in the F-bearing compositions are comparable to the lag times in the hydrous system devoid of F and Cl (Table 2).

TABLE 2. RATES OF ALBITE GROWTH* IN THE SYSTEM $NaAlSi_3O_8 + H_2O$ AT 2500 BARS

Wt.% H_2O	Growth Isotherm °C	ΔT °C	Growth Rate 10^{-6} cm/s	Nucl. Lag hrs
3.9	900	22	0.81	1.5
3.5	900	42	1.42	9.5
3.0	900	75	3.24	24
3.0	850	125	71.1	0

* P.M. Fenn, unpublished data. Nucl.: nucleation.

DISCUSSION

The dissolution of F in silicate melts lowers melting temperatures in silicate systems (Wyllie & Tuttle 1961, Koster van Groos & Wyllie 1968, Wyllie 1979, Manning 1981), whereas the relatively low solubility of Cl in silicate melts (Wyllie & Tuttle 1964, Kilinc & Burnham 1972) explains the little effect it has on phase equilibria. The addition of F to H_2O-undersaturated melts of albite composition in this study lowered the liquidus temperature approximately 25°C for the A9F composition (0.73 wt.% F) and about 50°C for the A7F system (2.20 wt.% F). In contrast, the addition of Cl did not produce any measurable change in the liquidus temperatures.

Crystallization kinetics also reflect the contrasting behavior of F and Cl in the silicate melts. Growth rates for albite are higher in the presence of F than in the Cl-bearing systems (Table 1). The apparent differences are larger at 850°C than at 900°C, but the system with Cl invariably has the lowest growth-rate. The amount of Cl in A9Cl + 2 (1.35 wt.% Cl) exceeds the solubility of Cl in the silicate melt, and a Cl-rich vapor phase is present in the A9Cl crystal-growth experiments. Previous studies of growth of feldspar and quartz in the presence of a hydrous vapor phase have shown that the growth rates are lower relative to growth rates measured in vapor-undersaturated melts (Fenn 1977, Swanson 1977). Perhaps the presence of the vapor phase accounts for the lower growth-rates in the A9Cl composition.

Despite the higher concentration of F, growth rates in the A7F composition are lower than in the A9F compositions (Table 1). In order to minimize the difference in degree of undercooling, H_2O contents of the A7F composition used for crystal-growth studies was low (0.5 wt.%) compared to the A9F compositions (2 and 2.5 wt.%). This difference in H_2O contents may explain the differences in growth rates between A9F and A7F compositions. Fenn (1977) found that *maximum* growth-rates were not affected by the H_2O content of the melt (as long as the system was vapor-undersaturated), but subtle differences in growth rates were found at low values of ΔT as a function of H_2O content. The results reported by Fenn (1977) do not show any consistent pattern of lower growth-rates with either higher or lower H_2O contents.

Rates of growth of albite are not enhanced by the presence of F or Cl relative to growth rates in halogen-free hydrous melts at equivalent values of ΔT (Tables 1, 2). Results at 900°C do not show appreciable differences between growth rates in A9F and A7F (1.4 to 2.2 X 10^{-6} cm/s, Table 1) and growth rates in the system $NaAlSi_3O_8$–H_2O (1.4 to 3.2 X 10^{-6} cm/s, Table 2) at values of ΔT of 42° or 75°C. Growth rates in the F-bearing systems at 850°C (2.1 to 6.3 X 10^{-6} cm/s, Table 1) are actually an order of magnitude *lower* than the measured growth-rate in the hydrous system (71 X 10^{-6} cm/s, Table 2). Growth rates of albite in the Cl-bearing system are uniformly lower than those in the F-bearing or hydrous systems (Tables 1, 2).

Lag times for nucleation appear to be shorter in the hydrous and F-bearing systems than in the Cl-bearing systems. At 900°C, lag times in the F-bearing systems are either zero or 10 hours, whereas the lag times in the hydrous system are 10 or 24 hours at equivalent values of ΔT. These lag times are considerably shorter than the 38 hours measured in the Cl-bearing system (Table 1). Results at 850°C show the same pattern; short lag times for nucleation in the F-bearing (2–9 hours) and hydrous (0 hours) systems, and longer times for the Cl-bearing system (20 hours). The presence of the small vapor bubbles in A9Cl + 2 may somehow delay the nucleation of albite in this, the only vapor-saturated composition. Previous results (Fenn 1977, Swanson 1977, 1979) on feldspar nucleation from a vapor-saturated silicate melt did not show any heterogeneous nucleation of feldspar on vapor bubbles. Instead, the results here suggest the vapor actually inhibits nucleation. Fluorine in anhydrous silicate melts enhances nucleation (Mukherjee & Rogers 1967), but the effect does not appear to be additive beyond the effect of H_2O.

CONCLUSIONS

Addition of F in hydrous silicate systems dramatically lowers liquidus temperatures, but produces relatively little change in crystallization kinetics. The temperature of the vapor-undersaturated liquidus was lowered 25 to 50°C in this study relative to results in the F-free system. Similar results have been reported by other investigators for both liquidus and solidus temperatures (*e.g.*, Wyllie 1979, Manning 1981). In contrast, rates of crystal growth of albite are not increased by the addition of F. In fact, growth rates were *lower* in the F-bearing systems at 850°C than in the F-free systems.

Viscosity of silicate melts also is lowered by the dissolution of F. This factor, together with the lowered solidus temperatures, are at least partially responsible for the coarse-grained minerals in pegmatite. Lower solidus temperatures permit a longer time for crystallization in pegmatite systems; the lowered viscosity should reflect higher mobility for crystal-forming components within the crystallizing magma.

If the mere presence of F in a granitic system were sufficient to produce really large crystals, why then are the really large crystals confined to pegmatites? Why do tin-enriched granites, with their high concentrations of F, not produce giant crystals? The lowered solidus temperatures in these F-enriched granites do seem to promote a longer history of fractionation in these magmas (*e.g.*, Swanson *et al.* 1988, 1990), but large crystals (pegmatitic texture) appear only at the vapor-saturated stage of crystallization. Perhaps the development of large crystals requires the presence of a vapor phase.

The Cl-rich vapor phase present in the A9Cl system in this study promoted a somewhat lower rate of albite growth and delayed nucleation, relative to either the hydrous or the F-bearing hydrous systems. Perhaps the large *range* of crystal sizes that defines the pegmatitic texture reflects a range (short to long lag times) of nucleation events in a vapor-saturated magma. A vapor phase is an integral part of most models of pegmatite crystallization (*e.g.*, Jahns & Burnham 1969). In some cases, such as the "pockets" in some pegmatites (Foord 1977, Stern *et al.* 1986), growth of large crystals clearly has been associated with this vapor phase. Any of the growth rates measured in this study could produce a 10-m crystal of albite in a few tens of years. The size of the "giant" crystals (Jahns 1953) in pegmatite may be the result not of rapid rates of growth, but instead of fortuitous nucleation events, whereas the small crystals reflect delayed nucleation.

Little is known, at least in the published literature, about grain-size distributions in pegmatites. A study of grain-size distributions within various zones of granitic pegmatites, together with a study of phase geochemistry, should provide a test for the proposed nucleation-controlled development of granitic texture. For example, Shearer *et al.* (1985) have used the trace-element content of K-feldspar to model fractionation in pegmatitic systems in the Black Hills of South Dakota. The model proposed here for pegmatite crystallization predicts that feldspar grains of different sizes within the same zone of a Black Hills pegmatite should show increased degrees of fractionation from larger (early nucleated) to smaller (later nucleated) crystals. Such a test will have to await a future study.

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