

## Theory of nucleation in silicate melts

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### Abstract

This paper presents a kinetic theory of nucleation in silicate melts which assumes that the activation energy for molecular attachment is the dominant factor controlling the time constant for nucleation, that the rate controlling step is the addition of individual tetrahedra or parts of tetrahedra, that the activation energy is proportional to the number of T-cation–oxygen bonds broken during the attachment of tetrahedral groups, and that the average number of T-cation–oxygen bonds broken increases as the melt and crystal structures become more polymerized. The theory predicts that nucleation should typically be faster for less polymerized melt and for less polymerized crystals and that if two crystalline phases are stable relative to the melt the less polymerized crystal should nucleate fastest. As shown by the data for the alkali disilicates, however, details of the melt structure can be important and should be considered if known.

### Introduction

Recent experimental and petrographic work has shown that nucleation of metastable phases and suppression of nucleation to undercoolings of many tens of degrees are common phenomena in programmed cooling and isothermal experiments with silicate melts and in volcanic igneous rocks (Walker *et al.*, 1976; Grove and Bence, 1977, 1979; Kirkpatrick, 1978; Naney and Swanson, 1980; Kirkpatrick *et al.*, 1980, 1981, and manuscript). The purpose of this paper is to develop a simple mechanistic model for nucleation of silicate crystals from silicate melts using classical nucleation theory and recent advances in our understanding of the structure of silicate melts.

### Observations

The experimental and petrographic observations of metastability and nucleation suppression indicate that crystalline silicate phases with less polymerized structures often nucleate metastably instead of stable phases with more polymerized structures and that nucleation of phases with less polymerized structures is often suppressed less than the nucleation of phases with more polymerized structures. Walker *et al.* (1976) found that in programmed cooling experiments with the lunar picritic basalt 12002 the nucleation of olivine, which has a structure composed of isolated silica tetrahedra, is sup-

pressed less than the nucleation of pyroxene, which has a chain structure, and that the nucleation of pyroxene is suppressed less than the nucleation of plagioclase feldspar, which has a framework structure. Kirkpatrick *et al.* (1981) found that in programmed cooling experiments with diopside composition melt olivine nucleates before clinopyroxene, even though diopside clinopyroxene is the equilibrium phase. Metastable nucleation of olivine also occurs in programmed cooling experiments with compositions along the MgO–SiO<sub>2</sub> join which have an enstatite polymorph or cristobalite on the liquidus (Kirkpatrick *et al.*, manuscript).

Metastable olivine occurs instead of stable low-calcium pyroxene in igneous rocks also. In rapidly cooled mid-ocean ridge pillow basalts groundmass olivine is ubiquitous, whereas pigeonite, the equilibrium phase, is almost universally absent (Bryan, 1972; Kirkpatrick, 1978). Metastable groundmass olivine is also common in place of stable low-calcium pyroxene in subaerially erupted basalts from the Hawaiian–Emperor seamount chain (Kirkpatrick *et al.*, 1980).

Crystalline phases other than olivine also nucleate metastably. Naney and Swanson (1981), for instance, found that in isothermal experiments at 8 kbar with iron- and magnesium-bearing granite and granodiorite compositions phases with chain and sheet structures (pyroxenes, amphiboles, and mi-

cas) nucleate much more easily than plagioclase and alkali feldspar.

These observations were the initial inspiration for the development of the theory presented in this paper and are, for the most part, consistent with its predictions and our present understanding of the structure of silicate melts.

### Classical nucleation theory

The classical theory of nucleation was developed by Volmer and Weber (1926), Becker and Doring (1935), Zeldovitch (1943), Frenkel (1946), Turnbull and Fisher (1949), and Kaschiev (1969), among others. The theory has recently been reviewed by Zettlemoyer (1969) and Kirkpatrick (1981). This section briefly summarizes the ideas to be used here.

The traditional microscopic picture of nucleation is that in any phase there are small scale, constantly varying fluctuations in composition and structure. If the product phase is thermodynamically stable with respect to the parent phase, a cluster of atoms with the structure and composition of the product phase can grow by a fortuitous sequence of attachments of atoms or molecules. The reason that it takes a fortuitous sequence of atomic or molecular attachments for the nucleus to form is that the total free energy of a small cluster is larger than the free energy of the same atoms in the parent phase, even if the product phase is stable relative to the parent phase. In the classical theory this extra energy is associated with the surface energy of the cluster. Calculations by Hoare and Pal (1972) have shown that it is better to consider the extra energy to be distributed throughout the cluster, at least for small clusters. Nonetheless, there is still an energy barrier which must be overcome. The cluster with the maximum energy is termed the critical cluster.

In addition to this thermodynamic barrier to nucleation, there is also an activation energy barrier,  $\Delta G_a$ , that every atom or molecule which attaches to a cluster must overcome. In transition state theory (Glasstone *et al.*, 1941) the rate of addition,  $Z$ , of atoms or molecules to a cluster is given by

$$Z = nv \exp(-\Delta G_a/RT) \quad (1)$$

where  $R$  is the gas constant,  $T$  is absolute temperature,  $v$  is the frequency of successful attempts, and  $n$  is the number of atoms or molecules in the reactant phase next to the cluster.

When a reactant phase, such as a melt, is brought

from its stability field into the stability field of a product phase, such as crystals, it takes some period of time before any clusters reach the critical size and can grow to macroscopic size. This is because in the stability field of the reactant phase clusters of the product phase are very small, and after the conditions change it takes some time for a fortuitous sequence of attachments to bring the cluster to critical size. After the first crystal nucleates, the rate of nucleation is low but increases until it reaches a steady state value. The average time it takes for the first nucleation event to occur and the time to reach steady state are both related to a time constant,  $\tau$ , given by the relationship (Kaschiev, 1969)

$$\tau = \frac{8kT}{\pi^2 \gamma^* Z \alpha^*}$$

where  $k$  is Boltzmann's constant,  $\gamma^*$  is the surface area of the critical nucleus,  $\alpha^* = -(\partial^2 \Delta G_{tot} / \partial i^2)_{i=i^*}$ ,  $i^*$  the number of atoms in the critical nucleus, and  $Z$  is the rate of addition of atoms or molecules given by equation (1). The most important parameters affecting the time constant, then, are the activation energy for atomic or molecular attachment, and the shape of the  $\Delta G_{tot}$  versus cluster radius curve near the critical radius. This later depends on the extra energy of the cluster (surface energy in the classical formulation) and the thermodynamic driving force. Because the activation energy is in the exponent, variations in its value are likely to have the greatest effect on variations in the time constant.

The requirements for nucleation of a metastable crystalline phase from a melt and no nucleation of the stable crystalline phase are that they both be thermodynamically stable relative to the melt and that the time constant for the nucleation of the metastable phase be much shorter than that for the stable phase. The amount that nucleation of a phase is suppressed in a programmed cooling experiment is also proportional to its time constant. Both crystalline phases are stable relative to the melt if the temperature is below the metastable extension of the liquidus surface of the metastable phase (Fig. 1). For the time constant of the metastable phase to be shorter requires some combination of lower surface energy, higher thermodynamic driving force, and lower activation energy of attachment. In most cases a higher thermodynamic driving force for the metastable phase seems unlikely because the undercooling with respect to the metastable liquidus must always be less than the undercooling with

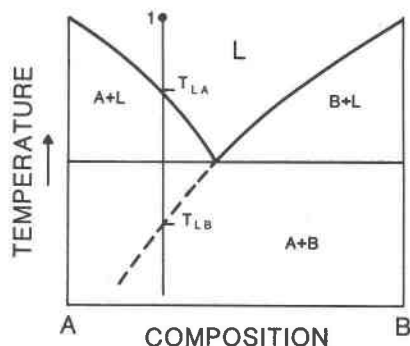


Fig. 1. Generalized phase diagram of a simple eutectic system showing the metastable extension (dashed line) of the liquidus surface of phase B. For composition 1 metastable crystallization of phase B before phase A is possible only below  $T_{LB}$ .  $T_{LA}$  is the stable liquidus temperature of phase A.

respect to the stable liquidus. Little is known about crystal-liquid surface energies for geologically important phases, so that it is difficult to say much about the effects of surface energy at the present time. As noted above, however, because the activation energy is in the exponent in equations (1) and (2), this parameter must play a dominant role in controlling the time constant for nucleation. The rest of this paper will concentrate on examining how the activation energy varies with melt structure and the structure of the nucleating phases.

### Melt structure

The physical picture of the structure of silicate melts that has been developed in recent years and that will be adopted here can be called a quasi-crystalline model. In this picture the nearest neighbor interactions between atoms in the melt are considered to be similar to those in a crystal, although the melt does not possess the long range order of a crystal. Because it is the nearest neighbor interactions that most greatly affect chemical reactions, this picture seems likely to be a good first order approximation for examining nucleation.

It is generally assumed that tetrahedral groups form the basis for the structure of silicate melts. In large part this is because atoms in four-fold coordination generally form strong bonds (Table 1). In particular, the silicon-oxygen bond is the strongest bond of any importance in silicate materials. This idea is consistent with the X-ray radial distribution function data in silicate glasses (Wright, 1974; Taylor and Brown, 1979) and forms the basis of all recent structural interpretation of these glasses.

In this quasi-crystalline model, the melt is considered to consist of polymers of tetrahedral groups

Table 1. Bond strengths and coordination number of oxides of important cations in igneous melts. After Kingery *et al.* (1976).

CATION	VALENCE	COORDINATION NUMBER	SINGLE-BOND STRENGTH (KJ/GRAM ATOM)
Si	4	4	443
Al	3	4	330-422
P	5	4	368-464
Ti	4	6	305
Al	3	6	222-280
Mg	2	6	155
Ca	2	8	134
Na	1	6	84
K	1	9	54

held together by larger cations (called modifier cations) which are in somewhat distorted sites between the oxygen atoms of the tetrahedra. The silica polymers are viewed as ranging from monomers (isolated tetrahedra) through dimers, chains, and sheets, to three-dimensional units (frameworks).

Recent Raman spectroscopy of a wide variety of silicate melts has added some additional information to this picture. A number of workers (Brawer and White, 1975, 1977; Mysen *et al.*, 1980a,b; Mysen *et al.*, 1981a,b) have interpreted their Raman data to indicate that, unlike most crystals, a melt of a given composition contains more than one polymer type. Mysen and his coworkers recognize five types of anionic structural units (polymers): monomers, dimers, unbranched single chains, sheets, and three-dimensional units (frameworks). Different composition ranges have different polymer types present. Table 2 reproduces the interpretation of Mysen *et al.* (1980a) for the polymer types present in melts of various compositions.

In general, as the percentage of tetrahedrally coordinated cations (silicon, aluminum, ferric iron) increases the melt becomes more polymerized. This

Table 2. Summary of polymeric units and melt sites present in silicate melts for different ranges of nonbridging oxygen atoms, NBO, per tetrahedrally coordinated cation, T, (after Mysen *et al.*, 1981b). T-cations include Si, Al,  $Fe^{+3}$ , and P.

$\frac{NBO}{T}$	POLYMER TYPES PRESENT	TYPES OF MELT SITES PRESENT
4.0-2.1	Monomer, Dimer, Chain	$Q_0, Q_1$
2.1-1.0	Monomer, Chain, Sheet	$Q_0, Q_1, Q_2, Q_3$
1.0-0.05	Chain, Sheet, Framework	$Q_1, Q_2, Q_3$

agrees with the thermodynamic calculations of Hess (1980) and many others. Curve-fitting procedures allow the percentages of different polymer types to be calculated from the Raman data (Seifert *et al.*, 1981).

### Molecular processes during nucleation

Because the time constant for nucleation depends exponentially on the activation energy for atomic or molecular attachment, differences in this activation energy have a very significant effect on how long it takes crystals of a particular phase to nucleate and on whether or not a metastable phase will nucleate before the stable phase. It is usually difficult to make any estimate of the activation energy for a chemical reaction without actually measuring the temperature dependence of the reaction rate. In the case of nucleation from silicate melts, however, it is possible to estimate at least how the activation energy varies with melt composition and crystal structure.

To do this it is necessary to make a number of assumptions. The most important of these concerns the physical picture of how atoms or molecules move from the liquid state to the crystalline state at the surface of the nucleus. The nature of this reaction in a silicate melt must be fundamentally different from that in a gas or dilute solution. In a gas or dilute solution atoms or molecules move through the reactant phase, impinge on the surface, and either stick to it or leave it. For nucleation in a melt, the components of the nucleus surround it and are in fact bonded to it. All that must occur for an atom or molecule to attach to the nucleus surface is for it to break or stretch its bonds with atoms in the melt, make the right bonds with atoms in the surface of the nucleus, and take on the correct orientation to be part of the crystal. The activation energy for this process is the difference in free energy between the atom or molecule in the melt next to the nucleus and the activated state during the reaction. As is discussed below, the exact configuration of the activated complex is not of importance in the present analysis of the problem. Jackson *et al.* (1967) have shown that for liquid to crystal phase transformations there is no transition region between the melt and crystal in which atoms exist in states intermediate between the melt state and the crystalline state. This implies that for nucleation we need not consider activation energies of reactions to intermediate states.

Another important assumption is that the activa-

tion energy is related to the number and strength of the bonds being broken and made during the addition of atoms or molecules to the nucleus surface. Table 1 lists the strengths of some important metal-oxygen bonds. Because the bonds between oxygen and tetrahedrally-coordinated cations (T-cations) are so strong and because tetrahedral groups appear to retain their integrity in the melt, it seems likely that they also retain their integrity during the attachment process. If this is true, it also seems likely that the addition of the tetrahedral groups to the surface is the rate controlling step in the reaction. Because the T-cation-oxygen bonds are so strong, the tetrahedral cations surround themselves with oxygen, and the vast majority of oxygen atoms attach in conjunction with T-cations. There are likely to be few vacant oxygen sites in the melt or on the surface of the nucleus. Because many more bonds are broken in the attachment of a tetrahedral group than in the attachment of a modifier cation, and because the T-cation-oxygen bonds that must usually be broken for this to occur are stronger than the modifier-oxygen bonds, the model to be developed here emphasizes the number of T-cation-oxygen bonds that are broken during the attachment process. In fact, as the number of T-cation-oxygen bonds broken in an attachment increases, the number of modifier-oxygen bonds broken decreases.

It will also be assumed that all tetrahedra attach individually, not as groups. This is because this will usually be the process with the lowest activation energy. To break a multi-tetrahedron group out of a polymeric unit usually requires the breaking of more than one T-cation-oxygen bond (unless the unit is dangling by one tetrahedron) and more modifier-cation-oxygen bonds than for a single tetrahedron. The addition of an entire polymeric unit requires the breaking of some large number of modifier-cation-oxygen bonds. In addition, the attachment of a large polymeric unit, whether an entire unit or a fragment, requires that a large number of bonds be broken simultaneously, that the unit move onto the surface in some coordinated way, and that the unit reorganize internally to take on the crystal structure. These requirements must be related to the frequency of successful attachment, but at the present are difficult to qualify.

The one process that may compete with monomer attachment is the attachment of entire dimer units. In this case no T-cation-oxygen bonds and a relatively small number of modifier-cation-oxygen

bonds are broken. This could lead to an activation energy similar to that for the addition of a monomer. This process is not considered here, however, and all tetrahedra are assumed to attach individually.

The nature and number of bonds broken during the attachment of a tetrahedral group to the surface of a nucleus depends on both the structure of the site that the group is leaving and the structure of the site at which it is attaching. To make discussion easier a simple notation, adopted in part from DeJong *et al.* (1981), will be followed. In this notation the letter Q denotes a site in the melt from which a tetrahedral group is leaving, and the letter A a site on the nucleus surface to which a tetrahedral group is attaching. The numerical subscript (0 to 4) denotes the number of T-cation–oxygen bonds that must be broken for the group to leave from or attach to the site.

To illustrate the relationship between the bonds broken and the melt and crystal structures, first consider the attachment of a monomer unit (a  $Q_0$  tetrahedron) in the melt to the surface of small crystal-like clusters with different structures. For a monomer unit to break loose from the melt requires breaking of only modifier–oxygen bonds. No T-cation–oxygen bonds are involved. The activation energy for this should, then, be relatively low. This is true no matter what the structure of the surface site.

To make bonds with the nucleus surface requires in most cases the breaking of T-cation–oxygen bonds at the reaction site. The only case where this is not true is for  $A_0$  sites, which occur in structures containing isolated tetrahedra, and for the addition of the first tetrahedron of a new polymeric unit in a crystal, such as the first tetrahedron of a new chain on the surface of a pyroxene. Although the latter case may be important at very large undercoolings where the critical radius is very small, it will not usually have a significant affect on the activation energy because only a small fraction of tetrahedra will start new polymeric units. Kuo and Kirkpatrick (1982) have shown that the critical radius for nucleation in diopside glass at undercoolings of  $10^\circ$  to  $20^\circ\text{C}$  is of the order of 600 to  $700\text{\AA}$ , a size much larger than a unit cell.

The activation energy for the attachment of a monomer to an  $A_0$  site is the lowest possible, because only modifier–oxygen bonds must be broken. The addition of a monomer to  $A_1$  sites, which occur on the surfaces of nuclei with double-chain,

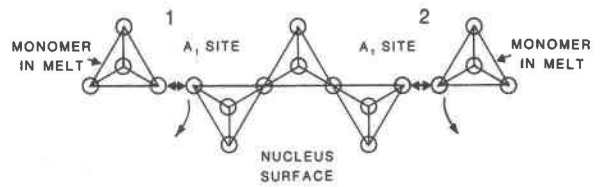


Fig. 2. Diagram showing attachment of monomer units ( $Q_0$  sites) from the melt to the  $A_1$  ends of a single chain on a nucleus surface. In this case one T-cation–oxygen bond must be broken for attachment to occur and one oxygen atom must be removed from the reaction site. On end 1 the atom removed comes from the attaching site; on end 2 the removed atom comes from the attaching monomer.

sheet, and framework crystal structures and are essentially all that occur in single chain structures, requires the breaking of one T-cation–oxygen bond. This process is illustrated schematically in Figures 2 and 3. For the monomer and the  $A_1$  site to link up, one oxygen, from either the monomer or the surface site must be removed from the reaction site and be rejected to the melt, depolymerizing it. The activation energy for this process should be larger than for the addition of a monomer to an  $A_0$  site.

The addition of monomers to  $A_2$  sites, which occurs on the surfaces of nuclei with double chain, sheet, and framework structures, requires the breaking of two T-cation–oxygen bonds. This process is illustrated schematically in Figure 3. For a monomer to link up with an  $A_2$  site two oxygens, from either the monomer or the nucleus surface, must be removed from the reaction site. The activation energy for this reaction should be larger than for the addition of a monomer to an  $A_1$  site.

The addition of a monomer to an  $A_3$  site, which

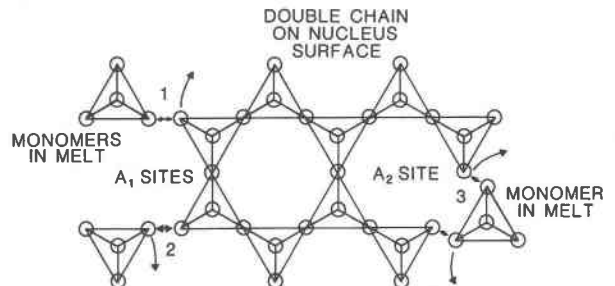


Fig. 3. Diagram showing attachment of monomer units in the melt to the different sites on the surface of a nucleus with a double chain structure. At sites 1 and 2 the monomers are attaching at  $A_1$  sites and at site 3 at an  $A_2$  site. At  $A_2$  sites two T-cation–oxygen bonds must be broken and two oxygen atoms removed from the reaction site. Note that once one six-member ring is formed only four tetrahedra are needed to complete the next ring. Three of these attach at  $A_1$  sites, one at an  $A_2$  site.

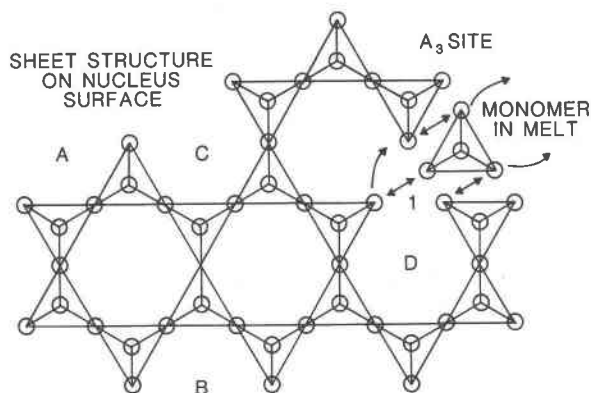


Fig. 4. Diagram showing the possible kinds of uncompleted rings on the surface of a nucleus with a sheet structure and the attachment of a monomer unit in the melt at an  $A_3$  site (reaction site 1). Ring A needs four tetrahedra to be completed. Three of these attach at  $A_1$  sites, one at an  $A_2$  site. Ring B needs three tetrahedra to be complete. Two of these attach at  $A_1$  sites, one at an  $A_2$  site. Ring C needs two tetrahedra to be complete. One of these attaches at an  $A_1$  site, one at an  $A_2$  site. Ring D needs one tetrahedron to be complete, it attaches at an  $A_3$  site. Note that the attachment of a monomer at an  $A_3$  site requires that three T-cation-oxygen bonds be broken, and that three oxygen atoms be removed from the reaction site.

occurs on the surface of nuclei with sheet and framework structures, requires the breaking of three T-cation-oxygen bonds. This process is illustrated for a sheet structure in Figure 4. This type of site on a framework is best viewed on a 3-dimensional ball and spoke model. During this reaction three oxygen atoms must be removed from the reaction site. The activation energy of this reaction should be larger than for the addition of a monomer to an  $A_2$  site.

In Figures 2, 3, and 4 the removal of oxygen atoms and the formation of bonds between tetrahedra are shown as separate steps. This need not be true. Both could occur simultaneously. It is possible in Figure 2, for instance, for the activated complex to consist of a silicon atom surrounded by five oxygens, four from its own tetrahedron and one from the surface site. Decay of the activated complex would, then, consist of simultaneous removal of one of the oxygen atoms and collapse of the tetrahedron onto the surface.

Regardless of whether the various parts of the attachment reactions occur sequentially or simultaneously, the number of oxygen atoms that must be removed from the reaction site is the same for a given type of attachment. Because the analysis presented here assumes that the activation energy is proportional to the number of T-cation-oxygen

bonds broken, it is not affected by the exact configuration of the activated complex.

Different crystal structures present different numbers of the various surface sites to the melt. Because of this the average activation energy for the attachment of a monomer to a crystal also depends on the crystal structure.

For the addition of monomers to olivine and other phases that contain only isolated silica tetrahedra the activation energy should be relatively low, because no T-cation-oxygen bonds need be broken. Given the assumptions discussed above, this is the lowest possible activation energy for the addition of a tetrahedral group.

The activation energy for the attachment of monomers to single-chain structures (primarily pyroxenes) should be significantly larger than for attachment to orthosilicates. This is because the surface sites on single chain structures are, except for the first tetrahedron of each chain, all  $A_1$  sites (Fig. 2). In this case one T-cation-oxygen bond must be broken per tetrahedron.

The activation energy for the addition of a monomer to an epidote-like structure, which is made of equal numbers of isolated tetrahedra and dimers, should be between the activation energy for monomer attachment to an orthosilicate and a single chain structure. This is because two thirds of the tetrahedra can attach without breaking any T-cation-oxygen bonds, whereas one third must break one.

The activation energy for the attachment of a monomer to a crystal structure with dimers only, such as melilite, should be larger than that for epidotes but less than that for single chain structures. For a melilite-like structure, one half of the tetrahedra can attach without breaking any T-cation-oxygen bonds, whereas the other half must break one.

The average activation energy for the attachment of a monomer to the surface of a nucleus with a six-member ring structure, such as beryl or tourmaline, should be about the same as for a single chain structure. This is because the first tetrahedron of a ring attaches at an  $A_0$  site, the next four attach at  $A_1$  sites, and the last attaches at an  $A_2$  site. This gives an average of one T-cation-oxygen bond broken per tetrahedron.

The attachment of a monomer to a nucleus with a double chain (amphibole) structure is similar to that of a ring structure, except that the only tetrahedron which attaches at an  $A_0$  site is the first in the chain.

Figure 3 illustrates the addition of monomers to a double chain. Once the first ring forms, each additional ring forms by the addition of four tetrahedra, three of which attach at  $A_1$  sites and one of which attaches at an  $A_2$  site. Thus, on the average one and one quarter T-cation–oxygen bonds are broken per tetrahedron. The activation energy for the addition of monomers should be slightly higher than for a single chain structure.

The addition of a monomer to the surface of a sheet structure requires on the average slightly more T-cation–oxygen bonds to be broken per tetrahedron than for a double chain, and the activation energy should be correspondingly higher. The arrangement of tetrahedra in a sheet can be thought of as a two-dimensional array of six-member rings. Once a few rings form, additional rings can be completed by the addition of one, two, three, or four tetrahedra. Figure 4 illustrates part of a sheet with these three types of open rings. To complete a ring that needs two additional tetrahedra requires one to attach at an  $A_1$  site and the other to attach at an  $A_2$  site. To complete a ring that needs three tetrahedra requires two to attach at  $A_1$  site. To complete a ring that needs three tetrahedra requires two to attach at  $A_1$  sites and one to attach at an  $A_2$  site. To complete a ring that needs four tetrahedra requires three to attach at  $A_1$  sites and one to attach at an  $A_2$  site. The average number of silicon–oxygen bonds broken in attaching a monomer to a sheet structure depends on the direction in the plane of the sheet in which the nucleus is growing most rapidly. For relatively equidimensional sheets the number is about 1.3 to 1.4, slightly higher than for a double chain. There may also be a few  $A_3$  sites in the middle of a sheet. These are equivalent to surface T-vacancies and are likely to be numerically insignificant.

For the attachment of a monomer to the surface of a framework structure the average number of T-cation–oxygen bonds broken is even larger, about two, and the activation energy is proportionally higher. This is because there are some  $A_3$  sites on the surface of a framework, many  $A_2$  sites, and some  $A_1$  sites. Because of the difficulty of representing a framework on a two-dimensional figure, the reader can most easily visualize these sites on a three-dimensional ball and spoke model of a framework structure. Attachment of tetrahedra at sites which require breaking of four T-cation–oxygen bonds is not a surface process because sites like this are internal T-vacancies.

In all the cases just discussed which require the breaking of T-cation–oxygen bonds oxygen atoms must be rejected to the melt at the reaction site. There is no way at present to determine whether it is more likely that this rejected oxygen is from the attaching tetrahedron or the nucleus surface. In either case its effect is to depolymerize the melt.

Unlike the attachment of a monomer unit to a nucleus surface, the attachment of a T-cation and its associated oxygen atoms from a more polymerized unit requires the breaking of T-cation–oxygen bonds in the melt. If, for instance, a group detaches from a  $Q_1$  site, which can occur in dimers, at the ends of chains, and on the edges of sheets and 3-dimensional units, it must break one T-cation–oxygen bond. There seems to be no reason why the detaching unit cannot leave as an  $\text{SiO}_4^{-4}$  group or an  $\text{SiO}_3^{-2}$  group (or the appropriately changed groups for other T-cations). In the first case the shared oxygen leaves with the detaching group, in the second it remains in the melt. If the detaching unit is an  $\text{SiO}_4^{-4}$  group, it is ready made to fit onto an  $A_0$  site, just like a monomer. The activation energy for this attachment is larger than that for the attachment of a monomer at the same site, however, because one T-cation–oxygen bond has been broken. Thus, the frequency of this process would be less.

The attachment of an  $\text{SiO}_4^{-4}$  unit that has detached from a  $Q_1$  site onto an  $A_1$  site requires a total of two silicon–oxygen bonds to be broken, one in the melt and one at the attachment site. An  $\text{SiO}_3^{-2}$  unit, is, on the other hand, ready made to fit onto an  $A_1$  site without breaking any additional silicon–oxygen bonds. Thus, the activation energy for the attachment of a  $\text{TO}_3^{-n}$  unit would be much less than that for the attachment of a  $\text{TO}_4^{-n}$ , and most attachments from  $Q_1$  sites to  $A_1$  sites occur by the attachment of  $\text{TO}_3^{-m}$  groups. If  $\text{TO}_3^{-n}$  groups attach to  $A_2$  or  $A_3$  sites, one or two additional T-cation–oxygen bonds must be broken, and one or two oxygens must be removed from the reaction site. In these cases, within the assumptions of the model presented here, the activation energy would be the same as if a monomer were attaching. This is because in both cases a total of two or three T-cation–oxygen bonds must be broken.

Similarly, if a T-cation–oxygen group detaches from a  $Q_2$  site, which can occur in the middle of chains and at some sites on the edges of sheet or 3-dimensional units, it can leave (assuming the T-cation is Si) as an  $\text{SiO}_4^{-4}$  group, an  $\text{SiO}_3^{-2}$  group, or



an  $\text{SiO}_2^0$  group. The four oxygen group is ready made to attach at an  $A_0$  site, and behaves like a monomer except that the activation energy for its attachment is much larger because it has already broken two T-cation–oxygen bonds in the melt. The three oxygen group behaves like the three oxygen group that has left a  $Q_1$  site in the melt, except that its activation energy for attachment is larger because it has broken two T-cation–oxygen bonds in the melt instead of only one. The two oxygen group is ready made to fit onto an  $A_2$  site. The activation energy for this attachment is about the same as for the attachment of a monomer at an  $A_2$  site because the same number of T-cation–oxygen bonds are broken. To attach at an  $A_0$  or  $A_1$  site, the two-oxygen group must gain two or one oxygens, respectively, and the activation energy for these attachments is higher than that for the attachment of a monomer at the same sites. To attach at an  $A_3$  site, it must lose one oxygen, and the activation energy is proportional to the breaking of three T-cation–oxygen bonds.

If a T-cation–oxygen group leaves a  $Q_3$  site, which can occur in the middle of a sheet or on the surface of a framework polymer unit, it must break three T-cation–oxygen bonds. By taking different numbers of oxygen atoms from the melt with it, it may leave as, say, an  $\text{SiO}_4^{-4}$  group, an  $\text{SiO}_3^{-2}$  group, an  $\text{SiO}_2^0$  group, or an  $\text{SiO}^{+2}$  group. The behavior of the first three types is similar to the behavior of the same types of groups leaving other melt sites, except that their activation energies of attachment are larger because they will have broken three T-cation–oxygen bonds in leaving the melt instead of zero, one or two. The  $\text{SiO}^{+2}$  group is ready-made to fit onto an  $A_3$  site. Because only three silicon–oxygen bonds are broken during the attachment, the activation energy would be about the same as for the attachment of a monomer unit.

Table 3 lists various aspects of each of the possible combinations of melt and surface sites that can occur. The minimum activation energy (most frequent) attachment configurations are underlined in this table.

#### Effects of tetrahedrally-coordinated cations other than silicon

Recent Raman spectra interpretations by Mysen and his coworkers (Mysen *et al.*, 1980a,b, 1981a,b) as well as other work which they reference indicates that cations other than Si, including Al, Ti, P, and sometimes  $\text{Fe}^{+3}$ , are in four-fold coordination

in silicate melts, but that they do not generally mix randomly with the silicon atoms. If the activation energy of nucleation is related to the number and strength of the bonds broken in attaching the tetrahedrally-coordinated cations and their associated oxygens, the presence of cations other than silicon in tetrahedral coordination in the melt should reduce the activation energy because the bond strengths of the other cations with oxygen are weaker than that of silicon. Because of the different ways the other cations enter the melt, however, the effects are likely not to be this straightforward.

Aluminum apparently enters the more polymerized units in the melt in preference to less polymerized units (Mysen *et al.*, 1981b). Thus, the activation energy of nucleation of the more polymerized phases should be reduced by the presence of alumi-

Table 3. Summary of T-cation–oxygen bonds broken and formed during attachment of the various molecular groups at the various surface sites on silicate nuclei.\*

MELT SITE (T-CATION- OXYGEN BONDS BROKEN IN LEAVING MELT SITE)	O ATOMS PER T-CATION IN ATTACHING GROUP	SURFACE SITE	O ATOMS REJECTED AT ATTACH- MENT SITE	TOTAL T- CATION OXYGEN BONDS BROKEN DURING REACTION
$Q_0(0)$	4	$A_0$	0	<u>0</u>
		$A_1$	1	<u>1</u>
		$A_2$	2	<u>2</u>
		$A_3$	3	<u>3</u>
$Q_1(1)$	4	$A_0$	0	1
		$A_1$	1	<u>2</u>
		$A_2$	2	<u>3</u>
		$A_3$	3	4
	3	$A_1$	0	<u>1</u>
		$A_2$	1	<u>2</u>
		$A_3$	2	<u>3</u>
$Q_2(2)$	4	$A_0$	0	2
		$A_1$	1	3
		$A_2$	2	4
		$A_3$	3	5
	3	$A_1$	0	2
		$A_2$	1	3
		$A_3$	2	4
	2	$A_2$	0	<u>2</u>
		$A_3$	1	<u>3</u>
$Q_3(3)$	4	$A_0$	0	3
		$A_1$	1	4
		$A_2$	2	5
		$A_3$	3	6
	3	$A_1$	0	3
		$A_2$	1	4
		$A_3$	2	5
	2	$A_2$	0	3
		$A_3$	1	4
	1	$A_3$	0	<u>3</u>

\* The underlined cases have the minimum number of T-cation–oxygen atoms broken for each type of surface site, have the minimum activation energy, and are the most likely to occur if the proper melt sites are present. Reactions involving the addition of oxygen atoms to attaching T-cation–oxygen groups have not been included because they always require more T-cation–oxygen bonds to be broken than the reactions listed.



num in place of some silicon. This is because attachment from the  $Q_2$  and  $Q_3$  sites of sheets and frameworks in the melt onto the  $A_2$  and  $A_3$  sites on sheet and framework crystals breaks no more T-cation–oxygen bonds than attachment from  $Q_0$  and  $Q_1$  sites, which are abundant in less polymerized units. In fact, many of the more polymerized crystalline phases, including feldspars, feldspathoids, and micas, require aluminum as well as silicon, so that their activation energy of nucleation may well be lower than would be predicted without consideration of the strength of the aluminum–oxygen bonds. The effects of aluminum may even be enough to reduce the activation energy of nucleation of micas to less than that of amphiboles.

Titanium apparently enters silicate melts in three dimensional Al + Ti rich regions and in discrete Ti-rich units, whereas phosphorus apparently enters in Al + P rich regions and in discrete P-rich units (Mysen *et al.*, 1980b, 1981a). Whether these components affect the activation energy of nucleation is not known. Titanium certainly reduces the incubation time for nucleation (Kuo and Kirkpatrick, 1982). Because they enter Al-rich units, simple considerations would seem to indicate that Ti and P might affect the activation energy of attachment of an aluminum oxygen group (and presumably a Ti or P unit), but not a Si unit. Their effect on nucleation may also be in totally different ways, perhaps by their acting as substrates on which heterogeneous nucleation can occur.

#### Comparison with experimental and observational results

As noted in the introduction, the predictions of the theory presented here are, with a few exceptions, in good agreement with the available experimental and observational evidence.

The experimental observation of forsterite nucleation before clinopyroxene in programmed cooling experiments with diopside composition melt (Kirkpatrick *et al.*, 1981) and of forsterite nucleation before orthopyroxene and cristobalite in compositions along the MgO–SiO<sub>2</sub> join (Kirkpatrick *et al.*, manuscript) are all as predicted by the theory. Mysen *et al.* (1980a) indicate that the melt structures of these compositions consist of either monomers, dimers, and chains, or monomers, chains, and sheets. In either case, the presence of monomers ( $Q_0$  sites) allows addition of silica tetrahedra to olivine nuclei (with only  $A_0$  surface sites) without the breaking of any silicon–oxygen bonds. This is

likely to occur most readily in transient volumes that consist primarily of monomers. The attachment of silicon–oxygen groups to the surfaces of pyroxene nuclei, even in transient monomer-rich volumes, requires the breaking of at least one silicon–oxygen bond because the pyroxene surface consists mostly of  $A_1$  sites. Attachment on cristobalite nuclei surfaces requires on the average about two silicon–oxygen bonds to be broken, and thus nucleation of cristobalite should be slow.

Nucleation of pyroxenes, amphiboles, and micas instead of the stable feldspar phases in isothermal experiments with melts of granitic and granodioritic composition (Naney and Swanson, 1980) are also consistent with the theory presented here. Mysen *et al.* (1980a) indicate that the melt structures of these compositions consist of three-dimensional units, sheets, and chains, although water was present in the runs, and the melts could be less polymerized. Attachment of T-cation–oxygen groups on the surfaces of pyroxene nuclei with  $A_1$  sites on the surface, and amphiboles and mica nuclei, with  $A_1$  and  $A_2$  sites on the surface, can occur relatively easily in transient volumes that consist primarily of chains and perhaps sheets (*i.e.*, mostly  $Q_1$  and  $Q_2$  sites). These phases can accept T-cation–oxygen groups onto the  $A_1$  surface sites from  $Q_1$  sites with the breaking of only one T-cation–oxygen bond, and onto the  $A_2$  sites from  $Q_1$  and  $Q_2$  sites with the breaking of two T-cation–oxygen bonds. The feldspars, on the other hand, require an average of two T-cation–oxygen bonds to be broken to attach a tetrahedral group. As noted above, the presence of aluminum in the tetrahedral sites in micas may reduce the activation energy enough that nucleation of mica is faster than nucleation of amphibole.

The main discrepancy between the theory discussed here, the experimental and observational evidence, and the melt structure interpretations of Mysen and his coworkers is the apparently metastable nucleation of olivine instead of pyroxene in basalts. The observational evidence is that olivine often occurs in the groundmass of tholeiitic basalts (both mid-ocean ridge and ocean island) instead of the presumably stable orthopyroxene or pigeonite, and that olivine nucleation is delayed less than pyroxene nucleation in programmed cooling experiments with basaltic compositions (Walker *et al.*, 1976; Kirkpatrick, 1978; Grove and Bence, 1977, 1979; Lofgren *et al.*, 1979; Kirkpatrick *et al.*, 1981). Mysen *et al.* (1980a) interpret the Raman data to indicate that the structure of melts of basaltic

composition consists of chains, sheets, and three-dimensional units. If this is true, there would seem to be no great activation energy advantage for the nucleation of olivine relative to pyroxene. This is because for the lowest activation energy both of these phases would have to receive silicon-oxygen groups from  $Q_1$  sites with the activation energy proportional to the breaking of one silicon-oxygen bond.

These nucleation phenomena in natural basalt flows could well be due to effects other than the effect of melt structure on the activation energy. Most of the tholeiites that have groundmass olivine also have olivine phenocrysts or microphenocrysts, which implies that the crystallization of the groundmass began from within the olivine stability field. Lofgren (1978) has shown, using programmed cooling methods, that nucleation occurs very rapidly in melts never heated above the liquidus and cooled from just below the liquidus. This is presumably due to the presence of abundant clusters of barely sub-critical size that can grow to super-critical size quickly. The pyroxene may not nucleate because cooling begins above its appearance temperature.

Most programmed cooling experiments, however, cannot be explained in this way. They were cooled from about 10°C above the liquidus, which presumably reduced the radii of the sub-critical clusters to values well below the critical radius at small undercoolings. In some of these experiments (Walker *et al.*, 1976; Grove and Bence, 1977, 1979) the container material was high-purity iron. In these cases nucleation apparently occurred on the capsule walls. In other experiments Pt and Fe wire loops were used (Lofgren *et al.*, 1979), and there was less surface area on which heterogeneous nucleation could occur. Pt and Fe wire loops in fact seem to enhance the difference between olivine and pyroxene nucleation.

One additional discrepancy is the apparent difficulty with which garnet nucleates in high-pressure phase equilibrium experiments (Mysen, personal communication, 1982). This may be due to a difference in Al coordination, tetrahedral in the melt, octahedral in the crystals.

There are several possible explanations for these discrepancies between observation and prediction. At the present time it is difficult to choose among these possibilities. It may be that the basic theory has neglected some factor that allows olivine nucleation to occur more rapidly than pyroxene nucleation, even if  $Q_0$  sites are not present in the melt.

This could be the surface energy or thermodynamic driving force terms which have been specifically neglected or some totally unconsidered factor. It could also be that the interpretation of the Raman spectra are wrong or that there is actually a low concentration of  $Q_0$  sites in melts in this composition range that is too small to be detected by Raman methods, but which is large enough to allow easy olivine nucleation.

### Discussion

The theory presented here is based on classical nucleation theory and a simple picture of how the attachment of molecular groups onto the surface of silicate nuclei takes place. Although it explains qualitatively a variety of nucleation phenomena in igneous rocks and experiments with silicate melts, it is limited in that it deals only with the activation energy part of the nucleation rate equation. It neglects both the thermodynamic driving force and the excess energy of the clusters (surface energy of the classical formulation). Neither does it deal explicitly with the effects of heterogeneities, thermal history, or different modifier cations. Like all theories based on transition state theory, it is also difficult to quantify.

What it does do is provide a way of rationalizing and predicting nucleation behavior in silicate systems. Its application depends on our presently imperfect knowledge of the structural units in the melt phase. The Raman spectroscopy data have given a general picture of how melt structure varies with composition, but more detail is needed to treat specific problems.

An example of a more detailed study in which the modifier cations have a large effect is the  $SiK\beta$  emission work on alkali and alkaline earth silicate glasses by DeJong *et al.* (1981). These authors infer on both experimental and theoretical grounds that in silicate melts lithium atoms preferentially attach to oxygen atoms that are part of silica tetrahedra which already have other neighboring lithium atoms, whereas the heavier alkalis (Na, K, Cs) prefer to be as far from each other as possible. In lithium disilicate melt this leads to a bimodal distribution of sites, with an abundance of monomers ( $Q_0$  sites) and  $Q_1$  sites on the one hand the  $Q_4$  sites on the other. The  $Q_4$  sites must be in three dimensional units which have few Li atoms within them and mostly  $Q_2$  and  $Q_3$  sites on their surfaces. The abundance of the latter sites is small. In melts of the heavier alkali disilicates the uniform distribution of

metals leads to an abundance of  $Q_3$  sites. DeJong *et al.* state that the presence of  $Q_0$  and  $Q_1$  sites in Li-disilicate explains the long standing question of why Li-disilicate melt nucleates internally and Na- and K- disilicate melts do not. This idea is fully consistent with the ideas represented here. The alkali-disilicates have a sheet structure, which must have mostly  $A_1$  and  $A_2$  sites on the nucleus surface. Silicon-oxygen groups in  $Q_0$  or  $Q_1$  sites, which are abundant in Li-disilicate, can attach to  $A_1$  and  $A_2$  sites by breaking one or two silicon-oxygen bonds. Thus, nucleation of Li-disilicate can occur relatively easily in melt volume fluctuations rich in  $Q_0$  and  $Q_1$  sites. Attachment from the  $Q_3$  sites, which dominate in the Na- and K- disilicate compositions, is more difficult because three silicon-oxygen bonds must be broken to add a silicon-oxygen group to an  $A_1$  or  $A_2$  site.

Another factor that has been neglected by the theory presented here is the energy barrier presented by any structural rearrangement needed in the melt when a molecular group in the melt moves to the nucleus surface. An example of this may occur in feldspar composition melts. Using X-ray radial distribution function data Taylor and Brown (1979) have proposed that the structures of Na- and K-feldspar glasses are based on six-member rings of tetrahedral groups similar to the tridymite structure, whereas the structure of anorthite composition melt, like the crystal structure of all feldspars, is based on 4-member rings of tetrahedral groups. They argue that for alkali feldspars the local changes in melt structure that occur as the 6-member rings in the melt change to 4-member rings in the nuclei are the reason that anhydrous alkali feldspar melts crystallize so slowly. How to deal with this energy barrier in a systematic way is not clear. The absolute rates of nucleation and crystal growth are unknown for anhydrous alkali feldspars, and the differences may be due to the effect of the modifier cations alone. K-feldspar melt, for instance, is far more viscous than Na-feldspar melt, and this difference, due apparently only to the different cations, may extend to crystallization phenomena.

A final comment about the application of the ideas discussed here to other problems is probably in order. Although these ideas were developed to understand nucleation, similar attachment processes must occur at the interface between melt and crystal during crystal growth. As for nucleation the rate of the interface process during crystal growth

can be described by an expression that involves an activation energy term. This activation energy seems likely to be closely related to the activation energy of attachment on the surface of a nucleus and may well be interpretable in terms of the theory developed in this paper.

### Acknowledgments

I wish to thank Dr. D. M. Henderson, Rick Oestrike, Dave Bieler, Lung-Chuan Kuo, and Brian Reck for their comments about the ideas in this paper. This work was supported by NSF Grant EAR79-03923.

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*Manuscript received, January 26, 1982;  
accepted for publication, August 20, 1982.*