# *Chapter* 4

# CRYSTALLIZATION OF MAGMAS

The magmatic origin of basalt and rhyolite was first recognized in the late 1700s in Italy and France through observation of active volcanoes and correlation of their known products with similar looking ancient rocks. As obvious as this interpretation now seems, one alternative eighteenth-century theory of the origin of basalt held that it was precipitated from a primeval ocean, much as evaporites and some limestones are now known to form. Observation of volcanoes in Italy and France greatly impressed James Hutton (a Scotsman) with the importance of underground heat. He had observed a baked coal seam in Scotland that was adjacent to basaltic dikes, and he had also noted an example of forceful injection of basalt into overlying sediments. In the nineteenth-century spirit of empiricism, and to obtain further information on the nature and origin of basalt, James Hall (an Englishman) heated basalt samples in crucibles in his laboratory and found that they melted between 800° and 1200°C. Rapid cooling of the melt produced a glass, whereas slower cooling produced a fine-grained crystalline aggregate similar to basalt. Subsequent studies of igneous rocks revealed that most are composed of silicate minerals whose individual melting points are well over 1000°, some as high as 1800°C. Investigations into the formation of basaltic melts have shown that complete melting is typically achieved at 1100°–1200°C, whereas granitic melts form at a lower temperature range of 650° – 800°C.

Much vital information about igneous rocks comes from field, hand specimen, and thin section investigations, as already discussed. Petrologists determine the identity and proportions of the minerals in igneous rocks and note special textures and structures that give clues to the processes that formed them. An understanding of an igneous rock is formed mainly from observations in the field, especially those regarding areal variation in mineralogy or texture; from laboratory studies of thin sections, which establish mineral content; and from analyses of chemical composition. However, the processes of formation of all plutonic rocks and of many volcanic rocks cannot be observed directly. A petrologist is thus forced to rely on laboratory experiments and the application of crystallization and melting theory to infer the actual processes and the physical conditions of magma formation and crystallization. The *phase diagram* is the fundamental tool used by petrologists, materials scientists, and metallurgists (in fact, any scientist who deals with molten materials) to illustrate crystallization and melting. This type of diagram is nothing more than a graphical portrayal of the stability ranges of minerals and melts as functions of bulk composition, temperature, and pressure. In this chapter and the next two, we present the fundamentals of construction and interpretation of igneous phase diagrams, the principal technique for understanding the origin, crystallization, and evolution of magmas.

## LABORATORY EXPERIMENTS ON MAGMAS

The experiments performed in 1792 by James Hall are one of the earliest examples of experimental igneous petrology. Hall's studies were necessarily restricted to the melting of existing rocks because he was unable to synthesize rock compositions from chemical reagents. However, modern chemical knowledge and equipment allow such syntheses to be carried out and the results to be analyzed with great precision. In experimental laboratories it is possible to reproduce the entire range of compositions, temperatures, and pressures that might exist in nature during the formation and crystallization of magmas. The phase diagrams that petrologists use are constructed and calibrated on the basis of the results of these experiments.

In principle, the experimental method in petrology seems simple and analogous to preparing a meal (perhaps inspiring the phrase "cook and look" for reconnaissance experiments)—mixing the ingredients, heating them up, and enjoying the result. In fact, the procedures are more complicated and the experimental plan very carefully thought out. The desired initial starting compositions are made from either pure reagents or analyzed minerals, carefully weighed, mixed, and homogenized by grinding. For high-temperature experiments (called *runs*), the starting materials are commonly fused (melted), cooled to form a glass, and then ground to a uniform fine grain size to ensure compositional homogeneity. Experiments at low temperatures commonly use reactive chemical gels to increase ordinarily slow reaction rates. Crystalline seeds can be added to provide favorable nucleation sites for minerals that are slow to nucleate. Because processes studied in the laboratory must necessarily be made to proceed at rates higher than those in nature, the experimentalist must skillfully exploit rate-enhancing shortcuts and technical tricks that do not compromise the applicability of the results to natural rocks. Heating equipment used in experimental petrology is quite varied, ranging from one-atmosphere furnaces wound with platinum wire (much like megatoasters) to internally heated hydraulic presses capable of reproducing the pressure and temperature conditions of the earth's mantle. Other equipment includes hydrothermal reactors, which can maintain samples at moderate temperatures and pressures in the presence of selected fluid species (generally either water or carbon dioxide).

After the sample has been subjected to the desired pressure-temperature conditions for a sufficient time (typically hours to weeks), the pressure and temperature are suddenly reduced to quench or "freeze in" the mineral-melt assemblage that equilibrated during the run. Supercooled melts commonly solidify without crystallization to form glasses. Examination of the glass and embedded crystals with a petrographic microscope and X-ray diffraction tells the experimental petrologist what minerals coexisted with melt at the run conditions and the relative proportions of crystals and melt. More detailed examination involves single-crystal X-ray or electron microprobe techniques. All the resultant data on the mineral-melt assemblages for each selected bulk composition at various pressures and temperatures are the input data for construction of phase diagrams. Thousands of such diagrams have been produced for geologic and industrial purposes; many have been collected and published in a multivolume collection by the American Ceramic Society (*Phase Diagrams for Ceramists*). Because phase diagrams are in essence the technical language of igneous petrogenesis, a number of them are examined here as we develop the straightforward principles used in their interpretation by the geologist.

## EQUILIBRIUM AND THE PHASE RULE

One of the most important late nineteenth and early twentieth century advances in petrology was the appreciation that rocks and magmas typically behave rather rigorously according to the laws of physics and chemistry, with the proviso that enough time is available for the processes that "enforce" these laws. In particular, the laws of thermodynamics have been found to have great applicability to petrologic processes. The word *thermodynamics* tends to intimidate many students; and, in fact, there is a substantial body of complicated theory that has been developed by scientists and engineers over the last 150 years or so. However, thermodynamics is simply the codification of a number of fairly obvious principles, such as the flow of heat from a hot body to a cool body and conservation of energy and mass. At least the more basic concepts of thermodynamics cannot be avoided in explaining how magmas form and crystallize. The key to appreciating thermodynamic concepts is to focus on applications, and we firmly believe these concepts, as applied to rocks and igneous processes, are perfectly accessible and understandable to the typical student.

### *Equilibrium*

The first important concept is **equilibrium,** which simply means that a geologic system (rock or magma) is in a state where there is no driving force for change; that is, the temperature, pressure, and proportions of minerals and melt (if present) remain fixed. If the physical conditions of the system are changed, for example, by altering either the temperature or pressure (or both), the system is no longer in equilibrium and must typically shift the type or proportions of the minerals (or amount and composition of melt) by reaction to achieve a new state of equilibrium. As with all physical and chemical processes, the spontaneous attainment of equilibrium in petrology is a process of energy minimization. If the system is not in its energy-minimum state, something generally happens (crystallization or melting in igneous systems) until the system achieves a new energy minimum. For example, if a magma cools through the temperature where the first crystals appear and then remains at constant temperature, the proportions of melt and crystals will remain unchanged once equilibrium is established. But if the magma is then allowed to cool a bit more, additional crystallization will occur and the proportion of minerals relative to melt will increase. In most petrologic cases, perturbation of equilibrium is caused by changes in temperature or pressure and only rarely by bulk compositional changes.

It is convenient to consider the concepts of open and closed systems and of mass balance in the context of equilibrium. A **closed system** is one in which thermal and mechanical energy can be exchanged with the surroundings, but mass cannot be exchanged. Therefore, an igneous rock or magma that is regarded as a closed system can undergo variation in temperature and pressure, but the content of chemical constituents remains fixed. Conversely, an **open system** can exchange both energy and mass with the surroundings. The process of mass transfer is commonly referred to as metasomatism, although this is more common in metamorphic than igneous systems. Petrologists generally regard water, carbon dioxide, and other volatile constituents such as fluorine and chlorine as mobile constituents and do not typically include them in a discussion of open versus closed system behavior. **Mass balance** is the concept of preservation of a constant bulk composition during operation of chemical or physical processes in rocks. Thus the shift of chemical constituents from one physical state to another (as in crystallization of melts) or from one mineral to another must be balanced around maintenance of constant overall composition (excluding volatiles). Mass balance is the chemical principle that lies behind the algebraic technique of reaction balancing, and its application to interpretation of crystallization sequences by using phase diagrams is discussed in this and the following two chapters.

## *Phases*

The equilibrium relationships of minerals and melts can be described most easily by using phase diagrams. A *phase* is usually defined as a physically distinct part of a system (for example, a melt or a particular species of mineral) that is mechanically separable from other phases in the system, at least theoretically. Chemically, phases can have either a fixed composition (for example, quartz, $SiO_2$), or a variable composition (for example, melts or solid solution phases such as plagioclase). More than one phase can have the same composition (for example, polymorphs such as quartz, tridymite, and cristobalite, or sillimanite and andalusite) as long as each phase has distinctive physical properties (for example, different crystal structures, densities, or viscosities). A magmatic system can contain a melt phase (or, rarely, more than one), a gas or supercritical fluid phase, and one or more crystalline phases such as olivine, augite, or plagioclase. A phase diagram is a graphical means of showing the pressure-temperature-composition stability regions of different phases or groups of phases (Figure 4-1). Because only two variables can be shown in the two dimensions on a piece of paper, a petrologist must choose which two of these three variables to portray.

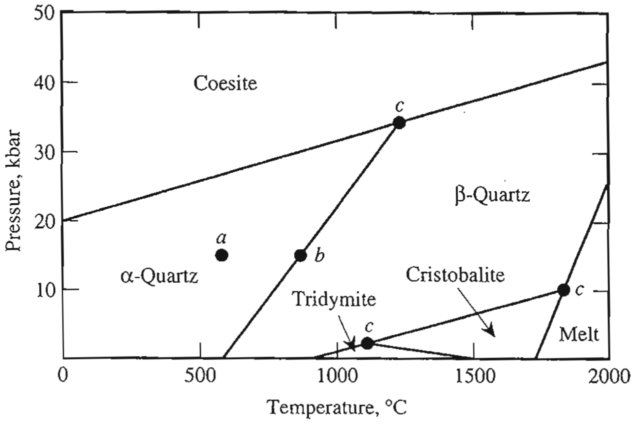


**FIGURE 4-1**

*P-T* diagram for the one-component system $SiO_2$, showing the divariant, single-phase stability fields for α- and β-quartz, tridymite, cristobalite, coesite, and molten $SiO_2$. Labeled points are discussed in the text. [After D. T. Griffin, 1992, *Silicate Crystal Chemistry* (New York: Oxford University Press), Fig. 1-1.]

## *Components*

With the one-component system shown in Figure 4-1, the choice is easy: There are zero compositional variables (the system is always fixed as pure $SiO_2$), and pressure and temperature are the only variables. **Components** are defined as the minimum number of chemical constituents that are required to describe the compositions of all phases in the system. Note that a component is *not* a mineral, although components can have the same compositions as mineral phases. Components are principally used for bookkeeping in describing the composition of the system. The one fundamental rule for defining components is, *There can never be more components than phases in a system.* If a rock consists of three minerals, then only three components are required to be defined. These commonly can be the actual compositions of the minerals, but other choices may be more appropriate. If a fluid or a silicate melt is present, it is also considered to be a phase.

When components are defined in the most traditional way as the simple major-element oxides that make up a chemical analysis, most igneous rocks end up with 10 or 12 components. This number of components probably exceeds the number of solid minerals (plus melt) and is incorrect if it does so. The correct alternative is to recombine simple oxides into larger mineral building blocks. Examples include two molar units of MgO plus one molar unit of $SiO_2$ to form one molar unit of $Mg_2SiO_4$ (forsterite) or one unit of CaO plus one unit of MgO plus two units of $SiO_2$ to form one unit of $CaMgSi_2O_6$ (diopside). This subdivision of a system into mineral components makes no implications about the actual minerals present and is thus independent of the actual physical conditions that dictate the actual minerals. The most commonly used units for relative amounts of components are *moles*, the standard chemical unit, and *mole percents* (abbreviated mol%) or *mole fractions* (abbreviated $X$) for ratios of components. For example, in the two-component system forsterite-diopside, the compositional midpoint is designated as 50 mol% diopside (or forsterite). The application of these units will be apparent in the following discussion of phase diagrams.

## *The Phase Rule*

In the $SiO_2$ system, there are seven known phases (six solids and one melt, all with the composition $SiO_2$) whose stability fields can be shown within the pressure-temperature ($P$-$T$) limits of a $P$-$T$ diagram (Figure 4-1). The six solids ($\alpha$-quartz, $\beta$-quartz, tridymite, cristobalite, coesite, and stishovite) are all polymorphs of $SiO_2$, and each, along with the melt, occupies a unique stability area on the diagram that reflects the $P$-$T$ range over which it is thermodynamically stable (the ultrahigh-pressure phase stishovite has not been shown in Figure 4-1, because it only occurs above about 80 kbar). The stability areas are called *divariant areas,* because both pressure and temperature can be independently changed a small amount and the same phase remains stable. Divariant areas are separated by lines that are called phase boundaries or *univariant lines.* Two phases can coexist only along one of these special lines that indicate a specially restricted range of $P$-$T$ conditions. These lines are univariant because only one variable can be independently changed while maintaining the system at two phases. Three phases can coexist only at points where three lines and areas come together (labeled $c$ in Figure 4-1). Because no change in pressure or temperature is possible while three phases coexist, these are called *invariant points.*

Point $a$ on the diagram, at a pressure of 15 kilobars (abbreviated as kbar; 1 kbar ≈ 1000 atmospheres) and a temperature of 500°C, falls within the area labeled $\alpha$-quartz. If equilibrium is maintained (that is, if pressure and temperature remain constant), then the component $SiO_2$ should exist only as the $\alpha$-quartz form. It is possible that chemical components can crystallize as a phase not described by the equilibrium phase diagram at the pressure and temperature of formation. In this case, the system is in a state of disequilibrium, and the phase is *unstable* if it is in the process of changing into a more stable phase. A *metastable* phase has higher energy than the stable equilibrium phase but persists for an extended time without changing, as a result of very slow reaction rates. (In fact, igneous and metamorphic rocks exposed at the earth's surface consist mostly of metastable minerals that have $P$-$T$ stability fields appropriate to their formation deep in the earth.)

Returning to Figure 4-1, consider what happens when stable $\alpha$-quartz at the $P$-$T$ point $a$ is heated while pressure remains constant at 15 kbar. The $\alpha$-quartz remains stable until the $\alpha$-quartz–$\beta$-quartz phase boundary at $b$ is encountered. Here $\alpha$-quartz begins the polymorphic phase transformation to $\beta$-quartz. If the temperature were held constant at $b$, both phases would coexist in a "steady state," with $\beta$-quartz transforming to $\alpha$-quartz at exactly the same rate that $\alpha$-quartz transforms to $\beta$-quartz. This point is made to emphasize that equilibrium is actually a dynamic process. The same atoms do not remain in one phase or the other for unlimited periods; the key to the concept of equilibrium is that the *proportions* of phases do not shift. Instead, the rates of transformation in both directions are equal. At 15 kbar and temperatures above $b$, all $\alpha$-quartz would spontaneously and irreversibly transform to $\beta$-quartz, whereas below $b$, all $\beta$-quartz would similarly become $\alpha$-quartz.

To reiterate: If there is only one phase in this one-component system, then both pressure and temperature can be varied independently without altering the phase assemblage. This behavior is called *divariance* because the values of two variables can be modified. If two phases exist in equilibrium with each other, then only one *environmental variable,* as pressure and temperature are called, can be varied independently, a constraint resulting in *univariance.* If three phases coexist, then the system has no variability in pressure and temperature and is *invariant.* There is no limit to the *total* number of phases that can exist within a particular chemical system over all pressures and temperatures, and therefore no limit to the number of divariant regions, univariant lines, or invariant points. But as discussed, there are very definite limits to how many phases can *coexist in a stable fashion* at a single pressure and temperature. At equilibrium, the $P$-$T$ point labeled $a$ in Figure 4-1 has one stable phase; point $b$ has two stable phases; and the points $c$ have three coexisting phases.

### *Derivation of the Phase Rule*

The general relationships among phases, components, and the environmental variables pressure and temperature were described in the 1870s by J. W. Gibbs as the *phase rule*. The phase rule provides a means of classifying systems. It also describes the maximum number of phases that can coexist in a system of any complexity, thus providing a means to test whether the minerals in a rock are coexisting in a stable equilibrium. Derivation of the phase rule can be made in terms of the variance of a system or the number of degrees of freedom ($F$); or, in other words, how many variables can be independently varied without changing the phase assemblage. The variable $F$ is equal to the number of unknown relationships minus the number of known (dependent) relationships. The unknown relationships include the number of phases and their compositions. Assume that there are $p$ phases, and each phase contains some of each of the components $c$ that describe the system. Just as the composition of each phase can be given in terms of atomic or mole fractions or weight percentages of each of the components, the number of unknowns in the composition of each phase is $c - 1$; that is, if all the concentrations but one are known, the last is known by difference. Because $p$ phases are present, the total number of compositional unknowns is $p(c - 1)$. In addition to compositional variables, the system is subject to a particular (but unknown) pressure and temperature that are the same for all phases in the system. The number of unknown variables in the system is therefore $p(c - 1) + 2$.

With regard to the known or dependent variables or restrictions, thermodynamics has established that the tendency of each component to react (known as the chemical potential) is the same in all coexisting phases. If it were not, there would be a lower energy configuration for the system, which would thus not be in equilibrium, and reaction would occur. If the chemical potential for a component were to be determined for one phase, it would therefore be known for all phases. Hence for each component there are $p - 1$ dependent relationships, and the total for the system is $c(p - 1)$.

Subtracting the known or dependent relationships from the unknown ones gives the phase rule, a statement of the variance of a system:

$$F = p(c - 1) + 2 - c(p - 1)$$
$$F = c - p + 2$$

If the system is restricted by fixing an environmental variable such as pressure (known as an *isobaric* condition) or temperature (known as an *isothermal* condition), the number of unknown relationships is reduced by 1, and the phase rule becomes $F = c - p + 1$. This discussion assumes the system to be closed, that is, no material enters or leaves. If the system is open to movement of mobile components (commonly fluid components such as water or carbon dioxide), the number of dependent variables is increased by the number of mobile components $m$. Thus

$$F = p(c - 1) + 2 - [c(p - 1) + m] = c - m - p + 2$$

Let us apply the phase rule to the one-component system already discussed (see Figure 4-1). If it is stated that three phases coexist within the system (as at points $c$), the phase rule indicates that the assemblage is invariant:

$$F = c - p + 2$$
$$F = 1 - 3 + 2$$
$$F = 0$$

Without reference to the diagram, it is obvious that a three-phase assemblage has no degrees of freedom and therefore can exist only at one specific temperature and pressure; this is, of course, true for all three-phase assemblages. Because there cannot be negative degrees of freedom, stable coexistence of more than three phases in a one-component system is impossible.

A two-phase assemblage (as at point $b$) can be shown to be univariant:

$$F = c - p + 2$$
$$F = 1 - 2 + 2$$
$$F = 1$$

The assemblage is maintained with change in one variable (either pressure or temperature) if a dependent change is made in temperature or pressure, respectively, so as to stay on the univariant line (as at $b$).

Divariant equilibrium is present in the one-phase regions of the diagram (such as point $a$), because

$$F = c - p + 2$$
$$F = 1 - 1 + 2$$
$$F = 2$$

Both pressure and temperature can be changed independently and the same one-phase assemblage is maintained.

## TWO-COMPONENT SYSTEMS

### *Geometric-Topologic Properties*

The basic two-component or *binary* system with congruently melting phases is of significant interest to petrologists. **Congruent melting** means that the pure solid phase melts completely at the melting temperature to produce a liquid of the same composition as the solid. The simplest binary systems of this type are bounded at the ends by two pure solids and their behavior can be portrayed in a two-dimensional diagram that plots either temperature as a function of composition (isobaric diagram) or pressure as a function of composition (isothermal diagram), with the other environmental variable held constant. The exact arrangement of divariant areas, univariant lines, and invariant points is referred to as the *topology* of the diagram.

Igneous petrologists typically use the isobaric temperature-composition diagram (commonly referred to as an *isobaric T-X diagram,* where $X$ refers to mole fraction, the compositional variable) because many magmas crystallize under constant pressure. Figure 4-2 shows the 1-bar isobaric phase relations in the binary system $CaMgSi_2O_6-CaAl_2Si_2O_8$ (diopside-anorthite), which is a useful analog for a simple basalt. Temperature increases upward on the ordinate, and composition is shown horizontally. Any point within the diagram represents a particular ratio ($X$) of diopside *component* to anorthite *component* at a particular temperature ($T$). The ratios of components are given as mole percentages in this diagram, but a weight percent scale can also be used. In Figure 4-2, $X_{an}$ is the mole percentage of anorthite component, and therefore $X_{an} = n\ CaAl_2Si_2O_8/(n\ CaAl_2Si_2O_8 + n\ CaMgSi_2O_6)$, where $n$ is the number of moles. On this scale, the mineral diopside has $X_{an} = 0$, and the mineral anorthite has $X_{an} = 1.0$.

There are three phases on this diagram: diopside (pure $CaMgSi_2O_6$) on the left side, anorthite (pure $CaAl_2Si_2O_8$) on the right side, and melt (variable ratio of the two components) in the middle. It is exceptionally important to keep in mind that $CaMgSi_2O_6$ and $CaAl_2Si_2O_8$ can exist *either* as mineral phases or as "molecular" chemical components mixed together in a melt. It must be specified whether minerals (phases) or components are meant when either the chemical compositions or the names diopside and anorthite are used. The crystal structures of the minerals control their compositions and determine that the *mineral* diopside is $CaMgSi_2O_6$ and the *mineral* anorthite is $CaAl_2Si_2O_8$. There is no such compositional restriction of the relatively structureless melt. Pressure is not shown on this isobaric diagram but could be represented by an extra coordinate at right angles to $T$ and $X$; graphically, this could be shown in a more complicated three-dimensional perspective drawing.

The phase assemblages in the different areas of the diagram are labeled in Figure 4-2 for different combinations of $T$ and $X$. The fields for diopside and anorthite solids are represented by the vertical lines at either end of the diagram, and the liquid field is bounded at lower temperatures by the two curved lines. The bulk composition shown at $a$ (80% $CaAl_2Si_2O_8$ and 20% $CaMgSi_2O_6$) consists entirely of homogeneous liquid at 1600°C. At 1370°C, this same composition ($b$) is composed of liquid (at $e$) plus crystals of anorthite (at $d$); and at 1200°C ($c$), it contains no liquid but is a mixture of crystals of diopside (at $f$) and anorthite (at $g$). The determination of the phase assemblage on a binary phase diagram is simply a question of finding the proper $T$-$X$ point on the diagram and reading off the phases that occur at either end of a horizontal line going to the nearest phase boundaries.

If this process is carried one step further, percentages and compositions of each of the phases present at points $a$, $b$, and $c$ can be determined quantitatively. Point $a$ at 1600°C is located in the one-phase field of liquid. Because the entire system consists of liquid, it is obvious that the liquid composition must equal the bulk composition, that is, 80% anorthite and 20% diopside. Point $b$ at 1370°C represents a two-phase assemblage: liquid plus

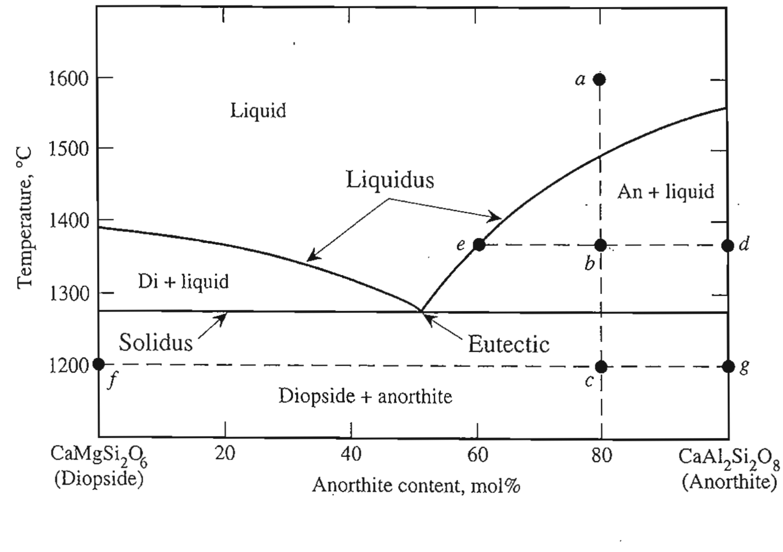


**FIGURE 4-2**

The simplified two-component system $CaMgSi_2O_6$–$CaAl_2Si_2O_8$ (diopside-anorthite) at 1 bar pressure. The melting point of diopside is at 1392°C, that of anorthite is at 1553°C, and the eutectic point is at 1274°C. Liquidus and solidus curves and eutectic point are indicated. Labeled points are described in the text.

anorthite. The horizontal line (commonly called a *tie line*) through *b* connects the phase boundaries of liquid at *e* and anorthite at *d*. Remember that liquid can have any composition within the liquid field, whereas diopside and anorthite are constrained to be pure phases at the ends of the horizontal coordinate. The percentages of liquid and anorthite crystals can be determined from this horizontal line, keeping in mind two of the most fundamental properties of equilibrium phase diagrams. First, all phases in equilibrium must be at the same temperature and pressure and thus must lie on a horizontal line at a specific temperature. Second, *mass balance* in a closed system demands that the compositions of all the phases added together must equal the original unique bulk composition (Baldy's law: Some of it plus the rest of it equals all of it). Qualitatively, if point *b* were slightly to the right, the system would contain more anorthite crystals at 1370°C; if it were slightly to the left, there would be a greater proportion of liquid.

Exact percentages of liquid and crystals can be obtained by using the so-called *lever rule*, a geometric property of any tie line with fixed end points that represents a mass balance around an intermediate compositional point. The intermediate point represents the bulk composition (analogous to a fulcrum in physics) and either falls closer to one end than the other or is in the exact middle. The length of the tie line segment from the intermediate point to one end of the line is proportional to the amount of the phase on the *other* end. This principle is illustrated in Figure 4-2: The tie line segment from *b* to *d* divided by the total tie line length (*de*) represents the proportion of liquid, and the segment from *b* to *e* divided by length *de* represents the proportion of anorthite. The lengths of the tie line segments are perfect analogs of the compositional units used on the horizontal axis. In this case, the bulk composition is given by *b* (80 mol% $CaAl_2Si_2O_8$, 20 mol% $CaMgSi_2O_6$), the liquid composition by *e* (62 mol% $CaAl_2Si_2O_8$, 38 mol% $CaMgSi_2O_6$), and the anorthite composition by *d* (100 mol% $CaAl_2Si_2O_8$). The weight percentages of liquid *e* and anorthite *d* are given by where *b* falls on the line between them:

mol% anorthite (at *d*) = (length *be*/length *de*) × 100
mol% liquid (at *e*) = (length *bd*/length *de*) × 100

If we use actual measurements from Figure 4-2 (given as arbitrary length units, *l.u.*), then the result is

mol% anorthite = (1.6 *l.u.*/3.6 *l.u.*) × 100 = 44.4 mol%
mol% liquid = (2.0 *l.u.*/3.6 *l.u.*) × 100 = 55.6 mol%

(The reader is encouraged to double-check this by measuring the figure with a millimeter scale and converting arbitrary length units to millimeters.)

The lower limit of the divariant area representing the field of liquid alone is indicated in Figure 4-2 by the two curved lines that are known as the *liquidus lines.* They represent the lowest temperatures at which liquid of any composition can exist without beginning to crystallize. The single horizontal line that forms the upper boundary of the region in which only solids exist is called the *solidus.* Note that the solidus temperature is equal to the temperature at which the lowest temperature liquid can exist in the system. The single point where the two liquidus lines meet the solidus line is called the **eutectic point** and represents both the temperature and composition of the lowest temperature melt. To either side of the eutectic, the areas between liquidus and solidus lines are regions where liquid and one solid coexist in equilibrium if a *T-X* point falls within them.

## *Equilibrium Crystallization*

The temperature at which crystallization begins in various compositions is indicated by the liquidus lines. The end points of these lines are the congruent melting points (or, alternatively, freezing points) of the pure phases that bound the system. The liquidus lines themselves represent the freezing point depression caused by adding a second component to a pure compound. A well-known example is the effect of adding salt to water. A little salt added to water causes the freezing point to be depressed slightly below 0°C; more salt lowers the freezing point even more. This freezing point lowering occurs on both sides of the system, of course, and the two liquidus curves are generated. The point where they cross, the eutectic point, represents the lowest temperature at which liquid (at the eutectic composition) can exist. This point is fixed in *T-X* space on an isobaric diagram and is therefore an invariant point. Why is it invariant? Recall that the phase rule for an isobaric binary system is

$$F = c - p + 1$$

In this situation, there are two components (a binary system) and three phases (anorthite, diopside, and melt). Therefore

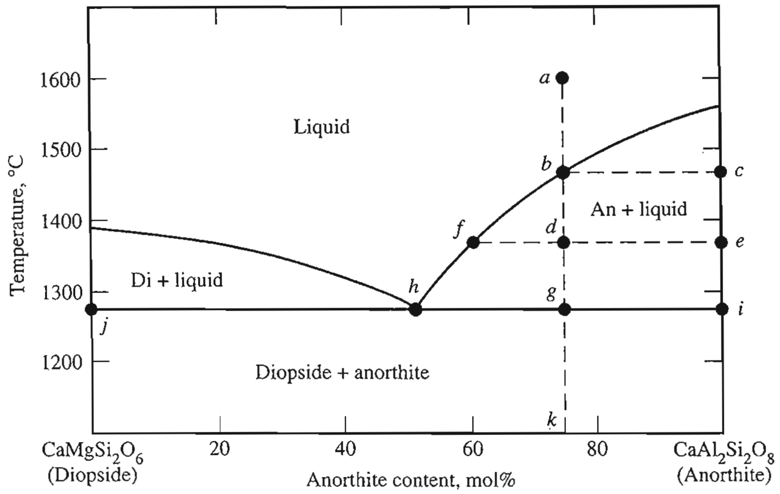
$$F = 2 - 3 + 1$$
$$F = 0$$

The decrease in freezing temperatures due to admixture of a second component can be best understood in terms of the dynamics of crystal formation and dissociation on an atomic scale.

**Equilibrium crystallization** is the crystallization process that will be analyzed geometrically for various

**FIGURE 4-3**

Equilibrium crystallization within the simplified binary system $CaMgSi_2O_6$–$CaAl_2Si_2O_8$ (diopside-anorthite) at 1 bar pressure. Labeled points are described in the text.



binary systems in this chapter. This must not be confused with the basic thermodynamic concept of equilibrium. Instead, it refers to maintenance of a mass balance in a closed system; that is, the crystals that have formed remain in contact with melt and continually equilibrate with it. Crystallization paths on *T-X* diagrams are therefore constrained by the bulk composition, especially the end points where liquid is all used up and crystallization ceases. In the first example, the binary system of two congruently melting minerals, any liquid within the system must end up at the eutectic before it finishes crystallizing, but we show later in more complicated systems that this is not always the case. In Chapter 6 we examine another more complicated process called **fractional crystallization** in which crystals are physically separated from the liquid, thus causing the system to become *open,* that is, to have a changing bulk composition.

The easiest approach to demonstrating an equilibrium crystallization path in this simplest binary system is to draw a vertical line down from a selected bulk composition (Figure 4-3); this line of constant composition and variable temperature (*ak*) is called an *isopleth.* The isopleth goes through the various phase fields of the diagram, and the sequence of assemblages that must occur during the crystallization of the magma can be read progressively downward. At any temperature in a two-phase field, the percentages of the phases present can be determined by using tie line calculations. The progressive assemblages encountered along the *ak* isopleth are liquid, anorthite + liquid, diopside + anorthite + liquid (at the eutectic temperature), and finally diopside + anorthite below the solidus.

The liquid *a* is cooled to the liquidus at *b,* where the first crystals of anorthite appear at *c.* With further cooling, the liquid composition moves down along the liquidus curve toward the eutectic, all the time crystallizing anorthite. The movement of the liquid composition toward the eutectic can be appreciated by understanding that the removal of $CaAl_2Si_2O_8$ component from the liquid as anorthite crystals must drive the composition of remaining liquid toward enrichment in $CaMgSi_2O_6$. Note carefully that this effect is due solely to decrease in the amount of liquid and removal of $CaAl_2Si_2O_8$, *not* to any addition of $CaMgSi_2O_6$. The proportions of liquid and anorthite could be continuously monitored (for example, when the isopleth is at *d*) by examining the relative lengths of tie line segments from the isopleth to anorthite (*de,* amount of liquid) and from the isopleth to the liquidus (*df,* amount of anorthite). As cooling reaches the eutectic temperature at *g,* the anorthite crystals at *i* are in equilibrium with liquid at *h,* the eutectic composition. Diopside now begins to precipitate from the liquid as anorthite continues to crystallize. The proportions of anorthite and diopside crystallizing at the eutectic are given by the relative lengths of *jh* (anorthite) and *ih* (diopside), that is, the same as the eutectic liquid composition. These compositions must be the same because the liquid does not and cannot change its composition as crystals are precipitated at the eutectic. Crystallization continues without any further temperature change (because both pressure and temperature are fixed at an invariant point) until the liquid is completely consumed at 1280°C. The solid assemblage diopside + anorthite then cools from *g* to *k,* and ultimately to room temperature. The ratio of diopside to anorthite in the final rock is given by Di/An = *gi/gj.*

Some pedagogic concepts that substantially help in understanding the evolution of liquids and solids in phase diagrams have been developed by S. A. Morse (1980). These concepts are liquid composition (LC), total solid composition (TSC), and instantaneous solid composition (ISC). Figure 4-4 shows how a crystallization

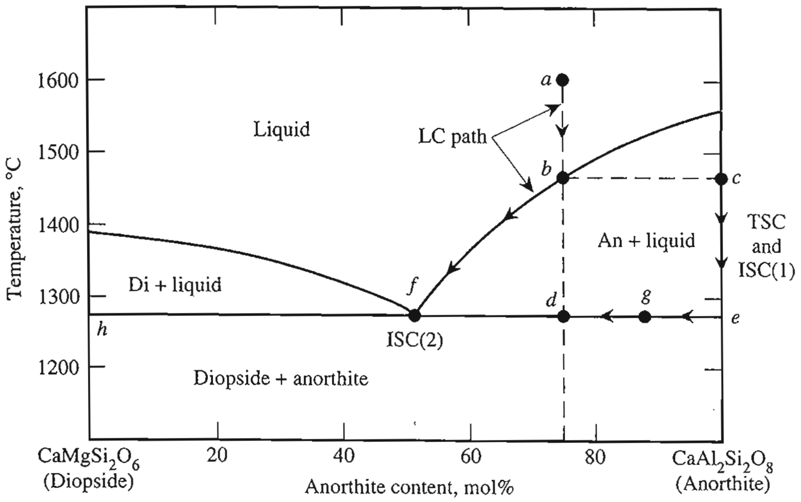


**FIGURE 4-4**

Equilibrium crystallization sequence within the simplified binary system $CaMgSi_2O_6-CaAl_2Si_2O_8$ (diopside-anorthite) portrayed with the LC-TSC-ISC terminology (Morse 1980). The labeled points and paths are described in the text.

path like that already examined can be interpreted by using these new concepts. A magma at *a* cools until crystallization of anorthite begins at *b*, when the liquidus is reached. The LC follows the isopleth until point *b* and then proceeds along the liquidus with further cooling. When the liquid is at *b*, the ISC(1) is at *c* because only anorthite is crystallizing. For the entire cooling interval through the anorthite + liquid field, tie lines connect the LC with both ISC(1) and TSC, which are coincident between *c* and *e*. When the liquid (LC) reaches the eutectic, the ISC and TSC diverge, as ISC(2) is now at the eutectic composition and TSC is still at *e*. As eutectic crystallization proceeds, LC does not change but TSC moves horizontally across the solidus as diopside joins anorthite in the solid assemblage. The limit on TSC during equilibrium crystallization is point *d*, because the total solid assemblage obviously cannot become more diopside-rich than the isopleth. When TSC reaches *d*, the liquid is exhausted and crystallization is complete.

The TSC can be used to determine proportions of liquid, diopside, and anorthite during eutectic crystallization. For example, consider that TSC has reached point *g*. There are two pairs of tie lines that can be used. The position of the isopleth (*d*) relative to the TSC (*g*) and the eutectic liquid composition (*f*) provides information on proportions of liquid (tie line *gd*) and total solids (*df*)—in this case, roughly 50% of each. The relative proportions of diopside and anorthite within the total solids can be calculated from the position of the TSC (*g*) on the tie line from diopside to anorthite (*he*). The resultant tie line segments yield approximately 84% anorthite and 16% diopside in the 50% of the system that is solid. The total system composition is therefore 50% liquid, 42% anorthite, and 8% diopside.

## TWO-COMPONENT SYSTEMS WITH AN INCONGRUENTLY MELTING PHASE

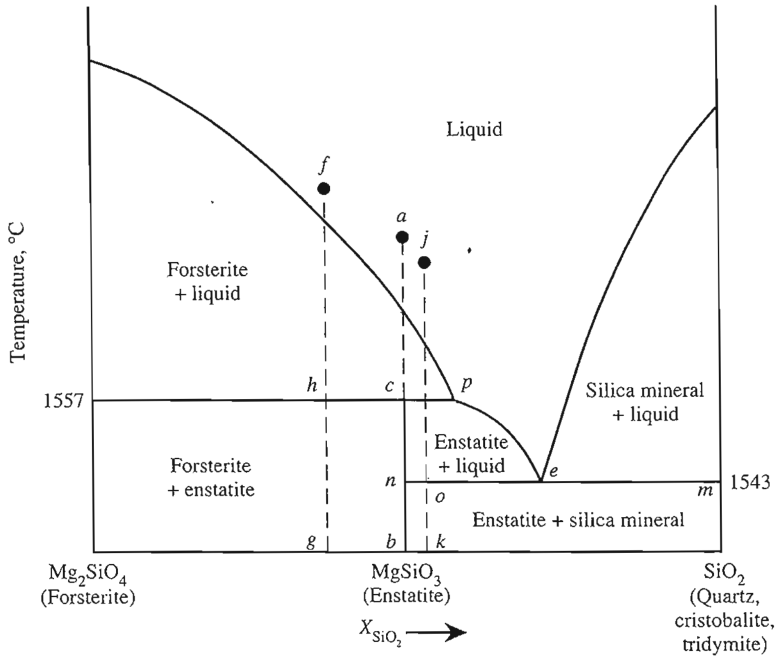
### Geometric-Topologic Properties

**Incongruent melting** occurs when a solid phase does not simply melt but breaks down to form both a liquid and another solid phase, neither having the same composition as the original phase. The compositions of the melt and new solid must, of course, add up to that of the melting phase to maintain mass balance. There are several binary systems of considerable petrologic interest in which an intermediate compound melts incongruently. The bounding solid phases are congruent in these systems, as was also the case in the basic binary system diopside-anorthite. In this section, we discuss the crystallization behavior of melts in binary systems that contain an incongruent solid.

The system forsterite-quartz ($Mg_2SiO_4-SiO_2$) is shown in Figure 4-5. The congruent bounding solid phases are forsterite and one of the $SiO_2$ polymorphs, cristobalite, tridymite, or quartz, depending on temperature. Enstatite ($MgSiO_3$) is the intermediate compound that melts incongruently. The composition and temperature limits of this phase are shown as the vertical solid line *bc*. Going from left to right across the diagram, the possible solid phase assemblages are forsterite alone, forsterite + enstatite, enstatite alone, enstatite + tridymite (or quartz), and tridymite (or quartz) alone. Notice that there is no stable divariant field for forsterite + tridymite (or quartz). These phases, when mixed, will react to form enstatite plus whichever of them is in excess.

**FIGURE 4-5**

Schematic, simplified *T-X* diagram for the binary system $Mg_2SiO_4-SiO_2$ (forsterite-quartz, cristobalite, tridymite). Note the incongruent melting behavior of enstatite and thus the generation of a peritectic, or reaction, point at *p*. Labeled points are described in the text.



The topologic significance of divariant regions, univariant lines, and invariant points is the same as in previous figures. However, now there are two invariant points involving liquid: the eutectic (*e*) (1543°C) between enstatite and tridymite, and another point (*p*) at 1557°C. This new point (*p*) is called a **peritectic point.** It is quite different from the eutectic, because liquid can leave as cooling proceeds, moving down the liquidus to the eutectic point, which is always the lowest temperature liquid composition in the system. This peritectic liquid composition at (*p*) is the special composition produced by the incongruent melting of enstatite to liquid plus forsterite crystals. Alternatively, if crystallization is considered, it is possible to describe the process at the peritectic point as the reaction of liquid (*p*) with forsterite crystals to form enstatite crystals. The presence of a peritectic point therefore has considerable significance for the crystallization sequence.

## *Equilibrium Crystallization*

Before crystallization paths in this type of system are discussed, it is important to stress one critical principle that applies to equilibrium crystallization in all the more complicated binary and ternary systems. In any of these systems with peritectic points, the final liquid composition will be at an invariant point but will *not necessarily* be at a eutectic. The final liquid must be the one that can coexist with the final crystalline assemblage, according to the rules for equilibrium crystallization. Therefore, the first thing to be done in interpreting crystallization in a liquidus phase diagram is to examine what the isopleth indicates about the final assemblage.

For example, in Figure 4-5 there are three isopleths indicated: *ab*, *fg*, and *jk*. The ultimate solid phase assemblage for each can be predicted by examining each isopleth below its appropriate solidus. For isopleth *ab*, the solidus is at the temperature of the peritectic point, and the ultimate solid assemblage is enstatite alone. For *fg*, the solidus is the same, and the solid assemblage is forsterite + enstatite. The last liquid for each of these isopleths must be at the peritectic point, *p*. If any liquid were to become more silica-rich than *p*, it would have to move down the enstatite liquidus (curve *pe*) and ultimately crystallize some tridymite at the eutectic, and there can be no tridymite along either of these first two isopleths. The third isopleth, *jk*, has a solidus at the eutectic temperature, and the solid phase assemblage predicted is enstatite + tridymite. This liquid will pass through the peritectic point as it cools, but it must leave the peritectic and move down to the eutectic to crystallize tridymite before the liquid is exhausted. Interpretation of crystallization paths is straightforward if this basic principle of using the isopleth to predict the final solid assemblage, and thus the final liquid composition, is kept in mind.

Now consider the actual equilibrium crystallization sequence for each of the isopleths in Figure 4-5. For *ab*, the liquid will cool until it intersects the liquidus curve for forsterite and crystals begin to form. As cooling proceeds and forsterite crystals precipitate, the liquid composition shifts continuously down the liquidus until it finally reaches the peritectic point *p*. Peritectic points are commonly referred to as "reaction points" because that is exactly what now occurs. The liquid at *p* has become so relatively rich in silica that it cannot coexist with forsterite, and it therefore reacts with all the existing forsterite crystals, dissolving them and forming new crystals of enstatite. Because the isopleth has exactly the right proportions of $Mg_2SiO_4$ and $SiO_2$ to make a rock composed of 100% enstatite, the liquid must remain at *p* until it is used up at exactly the same instant that the last bit of forsterite is converted into enstatite.

The early crystallization sequence for isopleth *fg* is much the same as for *ab*, except that crystallization begins at a slightly higher temperature. The same reaction begins when the liquid reaches the peritectic point. However, this isopleth indicates that there must be some forsterite in the final "rock." Therefore the reaction does not proceed to completion as before, but the liquid is used up well before all the forsterite is consumed, and the final solid assemblage is approximately 25% forsterite and 75% enstatite.

For the third isopleth, *jk*, crystallization of forsterite begins at a lower temperature and continues until the peritectic is reached. Again, reaction begins and forsterite is converted to enstatite. But this isopleth shows that the final assemblage has no forsterite; instead it is enstatite + tridymite. The peritectic reaction must therefore go to completion, at which point the remaining liquid coexists only with enstatite. The liquid composition leaves the peritectic point and shifts down the enstatite liquidus toward the eutectic. At the eutectic, tridymite joins enstatite in crystallizing until the liquid is consumed and the final solid assemblage is about 87% enstatite and 13% tridymite. This estimate is derived from the position of the *jk* isopleth relative to the compositions of enstatite and silica. The proportion of enstatite is thus represented by the length of line *om* divided by the length of *nm*; the proportion of tridymite is represented by *on* divided by *nm*.

The ISC, TSC, and LC concepts of Morse also can be used to describe these sequences. The use of these concepts for simple equilibrium crystallization may seem redundant, but the value will become apparent when more complex systems and melting behavior are encountered. For all three isopleths, ISC and TSC move down along the forsterite composition line while the three liquids are crystallizing only forsterite. Again, for all three isopleths, the ISC jumps to the enstatite composition when the LC reaches the peritectic because that is the instantaneous composition of crystalline material being produced. Adding this new ISC to the TSC at *d* pulls the TSC to the right along the *de* line until it reaches either the isopleth or the enstatite composition. For isopleth *fg*, the liquid is used up when the TSC reaches *h*; and for isopleth *ab*, liquid is totally consumed when TSC reaches *c*. For the third isopleth, *jk*, there is still liquid left when the TSC reaches *c*. As the liquid moves down the enstatite liquidus, the TSC and ISC move down-temperature along the line *cb*, because the only solid coexisting with liquid is enstatite. When the liquid reaches the eutectic, the ISC now jumps to the eutectic composition because both enstatite and tridymite are crystallizing. The addition of this new ISC to the TSC at *n* shifts the TSC to the right along the *nm* line until it intersects the isopleth at *o*, and the final liquid is consumed.

## TWO-COMPONENT SYSTEMS WITH COMPLETE SOLID SOLUTION

The systems discussed so far contained no solid solution between the various mineral phases, but most natural minerals show at least partial and even complete solid solution behavior. The plagioclase system $NaAlSi_3O_8-CaAl_2Si_2O_8$ shows essentially complete mixing of the end members, at least at high temperatures. A bulk composition chosen between the end members will crystallize as a single phase. As noted earlier in the book, such intermediate compositions are indicated as molecular percentages of the end members, as in $Ab_{10}An_{90}$, or more simply $An_{90}$. The crystallization behavior of liquids within this chemical system is shown in Figure 4-6. There are two regions containing only one phase—a liquid field at high temperature and a plagioclase field at low temperature—separated by a two-phase crystal-liquid "solid solution" loop. A melt of composition *a* is a single-phase liquid of composition $An_{65}$; a crystal at point *b* is a single-phase plagioclase of composition $An_{65}$. Point *c* along this isopleth consists of about 40% liquid of composition *d* and 60% plagioclase of composition *e*. The upper boundary of the two-phase region is the liquidus and the lower one is the solidus; they represent the lower and upper temperature limits, respectively, for a single phase of any composition.

Equilibrium crystallization within this system is straightforward. For the isopleth shown, liquid *a* will cool until it intersects the liquidus at *f*. The plagioclase composition in equilibrium with this liquid is *g*, as indicated by the intersection of a tie line from the liquidus to the solidus. Removal of this more calcic plagioclase from liquid at *f* will drive the liquid toward enrichment in $NaAlSi_3O_8$ as it cools along the liquidus. As liquid compositions progressively move down the liquidus, the coexisting plagioclase must become more sodic as well, as its composition moves along the solidus. Proportions of liquid and crystals can be determined by the relative tie line segment lengths. When the plagioclase composition

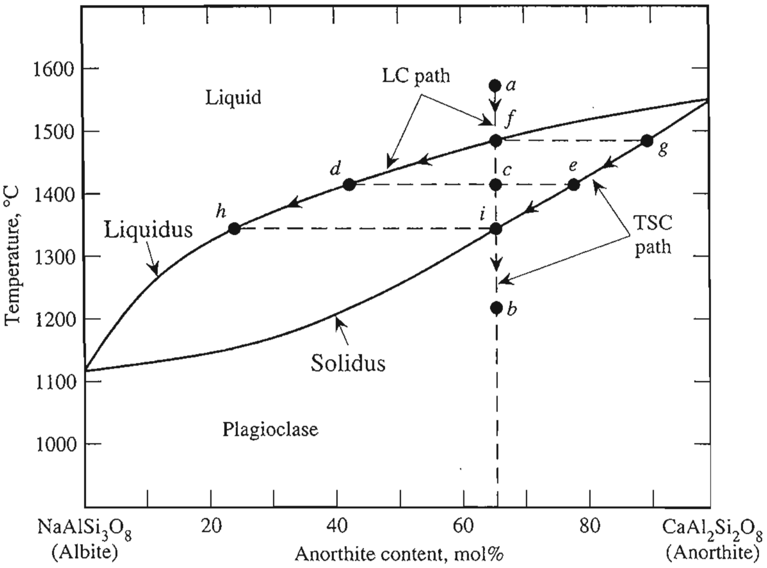


**FIGURE 4-6**

The binary system $NaAlSi_3O_8$–$CaAl_2Si_2O_8$ (albite-anorthite) at 1 bar pressure. Liquidus and solidus curves are labeled. Albite melts at 1118°C and anorthite at 1553°C. Labeled points and LC and TSC paths are explained in the text. [Based on experiments reported by N. L. Bowen, 1913, *Am. J. Sci.*, *4*, 35, Fig. 1.]

reaches the isopleth at *i*, the last bit of liquid is consumed at composition *h*. Using the alternative way of describing the crystallization path, we say that the LC follows the isopleth from *a* to *f*, then proceeds along the liquidus to *d* and *h*. The TSC starts at *g*, then moves down along the solidus to *e* and finally *i*. The interpretation of an ISC in this type of diagram is tricky, but it could be considered to be infinitesimally further along the solidus than the TSC, and thus "pulls" the TSC along toward the isopleth.

Ideal equilibrium crystallization in this type of diagram assumes a constant shift in the composition of plagioclase from the first calcic seeds to the more sodic final composition and implies compositionally homogeneous plagioclase crystals during the whole process. Such reequilibration of the interior plagioclase compositions in larger crystals would require diffusion of the plagioclase components through the crystal structures in the solid state. This diffusion process is very slow in plagioclase, and thus ideal or perfect equilibrium crystallization behavior may actually be unachievable except under conditions of unrealistically slow cooling rates, although some plutonic rocks have nearly homogeneous plagioclase. However, many natural plagioclases, and particularly those in volcanic or hypabyssal rocks such as andesites, show chemical zoning that is due to the inability of the diffusion process to homogenize the crystals (Figure 4-7). Only the outermost portion of the crystal

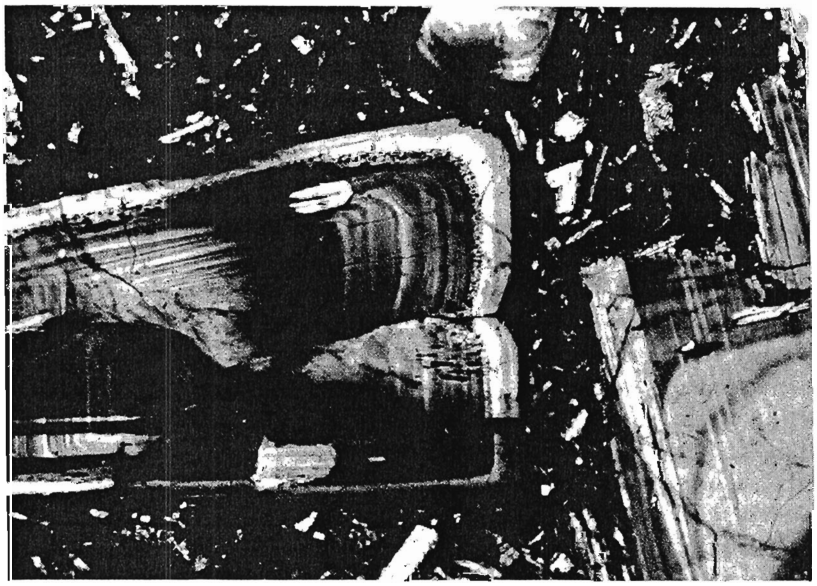


**FIGURE 4-7**

Oscillatory zoning of plagioclase phenocrysts in andesite. Compositional zoning as revealed by differences in extinction angles shows changes in external grain shape during growth. Polysynthetic twin bands parallel the longer grain edges. Sample from Washoe, Nevada; width of field of view is about 0.3 mm.

is truly in equilibrium with the liquid at any point during crystallization, and a more calcic core remains. This zoning in plagioclase from a calcic core to sodic rim is referred to as normal zoning. Reversed zoning can also occur; in this case, rims are more calcic than cores. Oscillatory zoning occurs when plagioclase crystals show bands of alternating Ca:Na ratio (see Figure 4-7). Interpretations of reversed and oscillatory zoning generally involve models of injections of new batches of more calcic magma into a magma chamber.

## TERNARY SYSTEMS

### *Simple Ternary Systems*

Ternary systems present a special problem in graphical representation because an extra dimension is needed to represent the extra compositional variable. Compositions of the three components in ternary systems are typically represented at the corners of an equilateral triangle (Figure 4-8). Each corner represents 100% of that com-

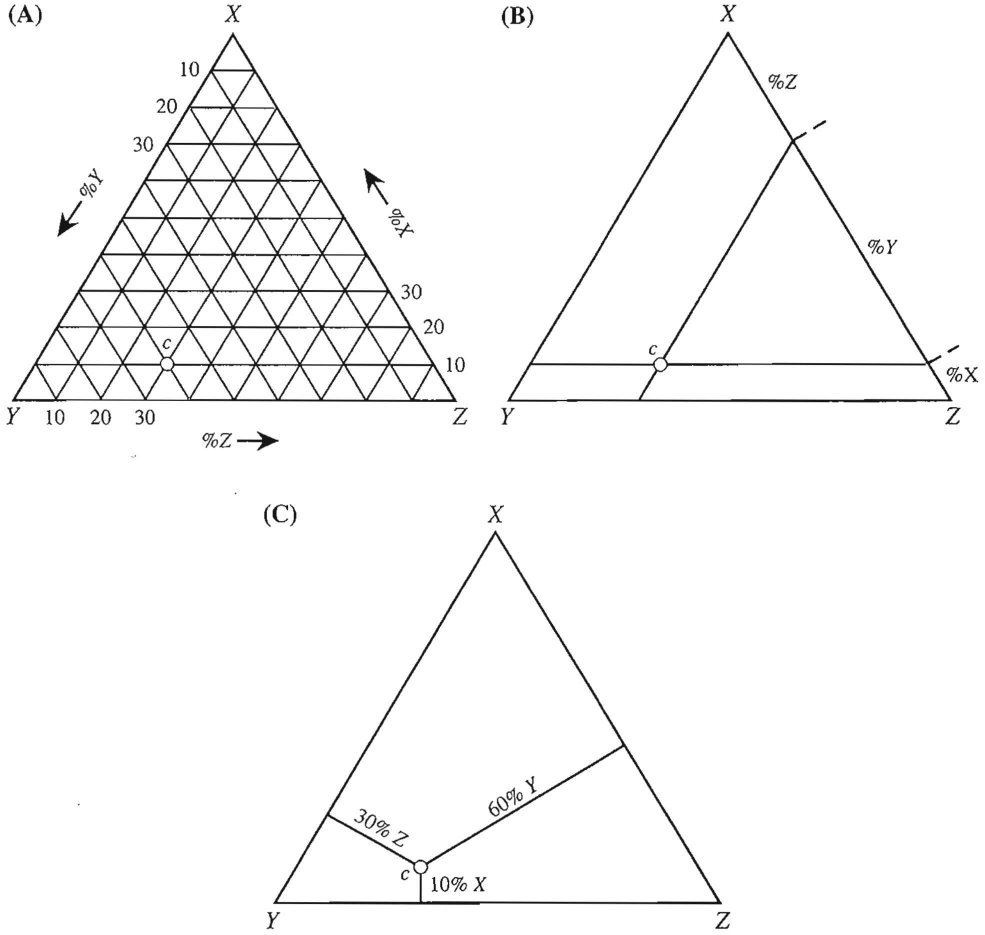


**FIGURE 4-8**

Methods for plotting the position of a point *c* in a triangular diagram. **(A)** Plotted on triangular graph paper. Percentages of components *X*, *Y*, and *Z* are read directly from the labeled coordinate axes. **(B)** Determination of *c* by the two-line method. Two lines are drawn through *c* parallel to any two of the sides of the triangle (here *XY* and *YZ*). The intersection of these two lines with the third side (*XZ*) divides that side into three parts whose lengths are proportional to the relative amounts of components *X*, *Y*, and *Z*. **(C)** Determination of point *c* by construction of perpendicular lines through *c* to each of the sides of the triangle. The relative lengths of these three perpendicular lines yield the percentages of components *X*, *Y*, and *Z*.

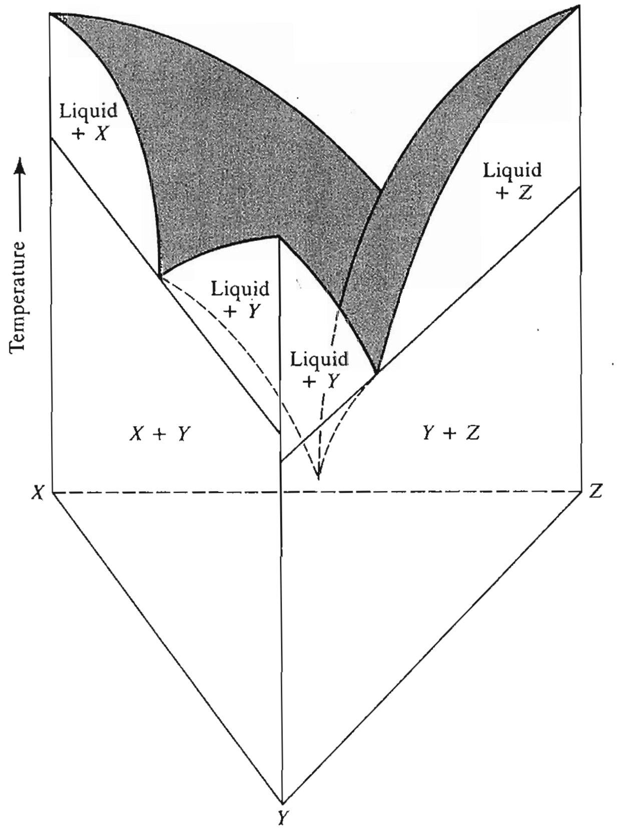


**FIGURE 4-9**

Temperature-composition model of the general ternary system *XYZ*. Each of the three vertical sides is a binary *T-X* system. The shaded top shows the ternary liquidus surfaces. Dashed lines are the three cotectics that lead downward to the ternary eutectic.

ponent; points along the edges consist of mixtures of the two components at the ends of the line; points within the triangle indicate mixtures of all three components. Ternary systems can be viewed as three individual binary systems joined together, for example, the systems *XY*, *XZ*, and *YZ* in Figure 4-9.

If both dimensions on paper are used for compositional representation in a triangle, a temperature coordinate can be erected perpendicular to the composition triangle. A perspective view of this is shown in Figure 4-9, with the liquidus for each mineral now expressed as a *surface* rather than as a curved line because of the extra compositional dimension. The liquidus and solidus lines for *XY* and *YZ* are shown on their respective sides of the triangle. The liquidus lines of the binaries are connected in the third dimension to form the liquidus *surfaces* that are shown as the shaded upper portion of Figure 4-9.

Accurate representation of phase relations in such perspective drawings would be very difficult, so ternary liquidus systems are shown with the liquidus surfaces contoured with lines of equal temperature (isotherms) in the same manner that a topographic map is contoured for elevation. The representation is as if the observer is looking down at a three-dimensional object. Figure 4-9 shows this for the simplest ternary system, which is composed of three simple binary eutectic systems, in this case *XY*, *XZ*, and *YZ*.

When the liquidus surfaces are contoured for temperature, one obtains the standard ternary representation that is usually used in the petrologic literature. Such a system is shown in Figure 4-10, the system $CaMgSi_2O_6-Mg_2SiO_4-CaAl_2Si_2O_8$ (diopside-forsterite-anorthite) at 1 bar, which represents an idealized olivine basalt. The simplified ternary phase diagram in Figure 4-10 shows the three liquidus surfaces of diopside, forsterite, and anorthite separated by heavy lines where the liquidus surfaces intersect. These lines are called *boundary curves* or **cotectic lines.** Their high-temperature ends are the individual binary eutectics in the three bounding binary systems. (Using the topographic metaphor for the contoured liquidus surfaces, we can consider these lines as analogs for stream valleys.) The boundary curves separate the primary crystallization fields of the three solid phases, which are labeled to indicate which solid phase crystallizes first for any liquid composition falling within the field. When cooled, a liquid of composition *a* will intersect the liquidus surface for forsterite at 1700°C and begin to crystallize forsterite. Liquid *b* will begin crystallization of anorthite at 1400°C. A liquid that coincidentally lies exactly on one of the boundary curves will simultaneously begin crystallizing both phases — in this case, diopside and forsterite. A liquid at *e*, the intersection of all three primary phase fields, will simultaneously begin to crystallize all three phases. This minimum-temperature point is called the *ternary eutectic.* Note that the isotherm intersections on the boundary curves point upward (thermally) in the same way that topographic contours "V" upstream on a map. Arrows are typically added to the boundary curves to indicate the direction of decreasing temperature.

Consider the cooling and equilibrium crystallization of a ternary melt such as *a*. It remains completely liquid until it has cooled to 1700°C; the melt intersects the forsterite liquidus surface and crystals of forsterite begin to form. The liquid is depleted in forsterite component and thus moves directly away from the forsterite corner toward the diopside-forsterite boundary curve along line *ah*. This *liquid descent line* is drawn by extending a line from the forsterite corner through the original melt composition and on to the boundary curve. When the evolving melt composition reaches the boundary curve of the diopside field at *h*, diopside joins forsterite in crys-

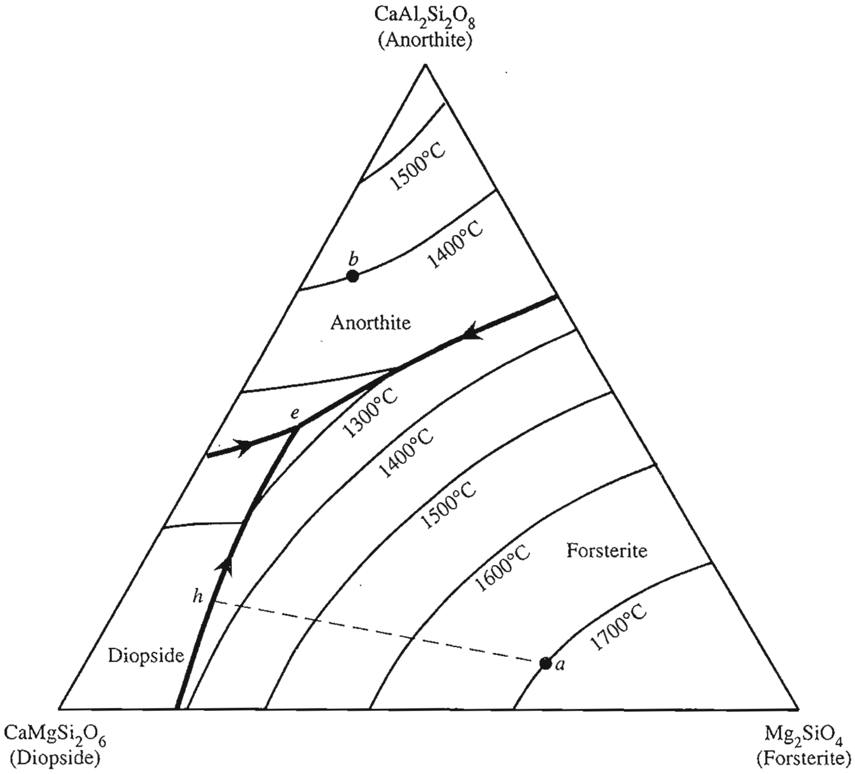


**FIGURE 4-10**

Simplified ternary diagram for the system $CaMgSi_2O_6-Mg_2SiO_4-CaAl_2Si_2O_8$ (diopside-forsterite-anorthite) at 1 bar pressure, eliminating the pseudoternary field of spinel. Labeled points are described in the text. The eutectic point at *e* is at 1270°C. [Adapted from E. F. Osborn and D. B. Tait, 1952, *Am. J. Sci.*, Bowen Volume, Fig. 4.]

tallizing. The melt now moves "down" (toward a lower temperature) the boundary curve and directly away from a point on the diopside-forsterite binary that represents the proportions of these two phases that are coprecipitating. The degree of curvature of a boundary curve reflects the changing proportions of **coprecipitating** phases; at any instant, the tangent line to the curve at the melt composition projects back to the instantaneous solid composition. The liquid further evolves by cooling and moving toward the ternary eutectic, which it eventually reaches. At this point, all three solid phases coprecipitate, and their proportions are exactly those of the eutectic composition. The system remains at eutectic temperature until all the liquid is consumed, and the proportions of solid phases in the crystallized material are those of the initial magma composition *a* — in this case, roughly 60% forsterite, 35% diopside, and 5% anorthite.

In the alternative view of crystallization, the LC is at *a* until the melt cools to 1700°C. When crystallization of forsterite begins, both the ISC and the TSC are at the forsterite corner of the ternary (Figure 4-11) and remain there until the liquid intersects the boundary curve at *h*. When diopside begins crystallizing, the ISC jumps to the point on the diopside-forsterite edge where the tangent to the boundary curve at *h* intersects. Addition of this ISC to the TSC draws the TSC from the forsterite corner toward diopside. As liquid (LC) moves down the boundary curve, the ISC will shift slightly and progressively toward the diopside corner as a result of the slight curvature in the curve. While LC moves toward the eutectic, TSC moves further along the diopside-forsterite edge. The limit on its movement is the line from the eutectic through *a* to its intersection with the diopside-forsterite edge, because the tie line that connects the TSC with the LC must equal the bulk composition and therefore must always pass through point *a* (see the two tie lines in Figure 4-11). Once the liquid reaches the eutectic, the ISC now jumps to the eutectic composition and begins to "pull" the TSC along the tie line toward *a*. Of course, when the TSC reaches *a*, there is no remaining eutectic liquid and the system is entirely crystallized.

## *Complex Ternary Systems*

Ternary systems are commonly more complex than the relatively simple one just illustrated. Some of these complexities arise from the presence of compounds of intermediate composition (either binary or ternary), incongruent melting, and the effects of solid solution. A reader interested in the details of advanced ternary systems is referred to Morse (1980). A useful introduction to the characteristics of more complicated diagrams can be obtained from consideration of the ternary system $CaMgSi_2O_6-NaAlSi_3O_8-CaAl_2Si_2O_8$ (diopside-albite-anorthite) (Figures 4-12A and B). This system is a

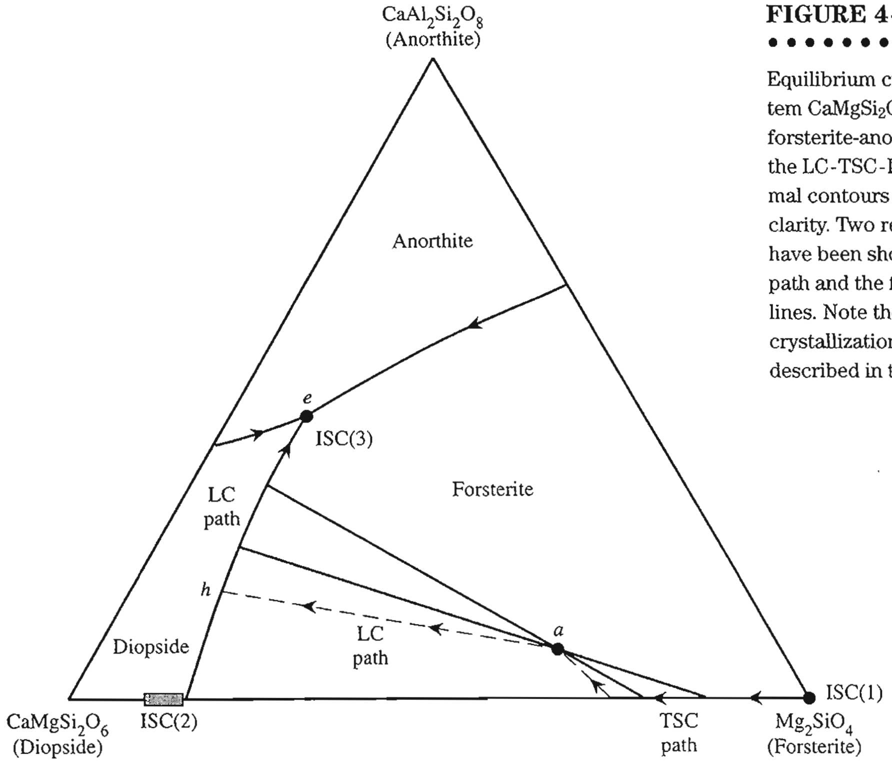


**FIGURE 4-11**

Equilibrium crystallization in the simplified ternary system $CaMgSi_2O_6$–$Mg_2SiO_4$–$CaAl_2Si_2O_8$ (diopside-forsterite-anorthite) (as in Figure 4-10), portrayed with the LC-TSC-ISC terminology (Morse 1980). The isothermal contours from Figure 4-10 have been removed for clarity. Two representative intermediate LC-TSC tie lines have been shown as solid lines. The initial stage of LC path and the final stage of TSC path are shown by dashed lines. Note the jumps of ISC from (1) to (2) to (3) during crystallization. The labeled points and paths are described in the text.

good approximation of simple basaltic magmas, from which the minerals diopside and plagioclase crystallize in the *P-T* range characteristic of the earth's crust.

In the three bounding binary systems (Di-An, Di-Ab, and An-Ab), there is complete solid solution between albite and anorthite end members, but none between diopside and plagioclase of any composition. Therefore, any melt bulk composition within the ternary should cool and crystallize to two solid phases, diopside plus plagioclase of appropriate Ca:Na ratio. The final proportions of diopside and plagioclase are calculated (as in binary diagrams) by the relative lengths of the tie lines from the original liquid composition to composition points of the two phases crystallized. For example, liquid *e* in Figure 4-12A will crystallize to a final solid assemblage of about 80% plagioclase ($An_{50}$) and 20% diopside.

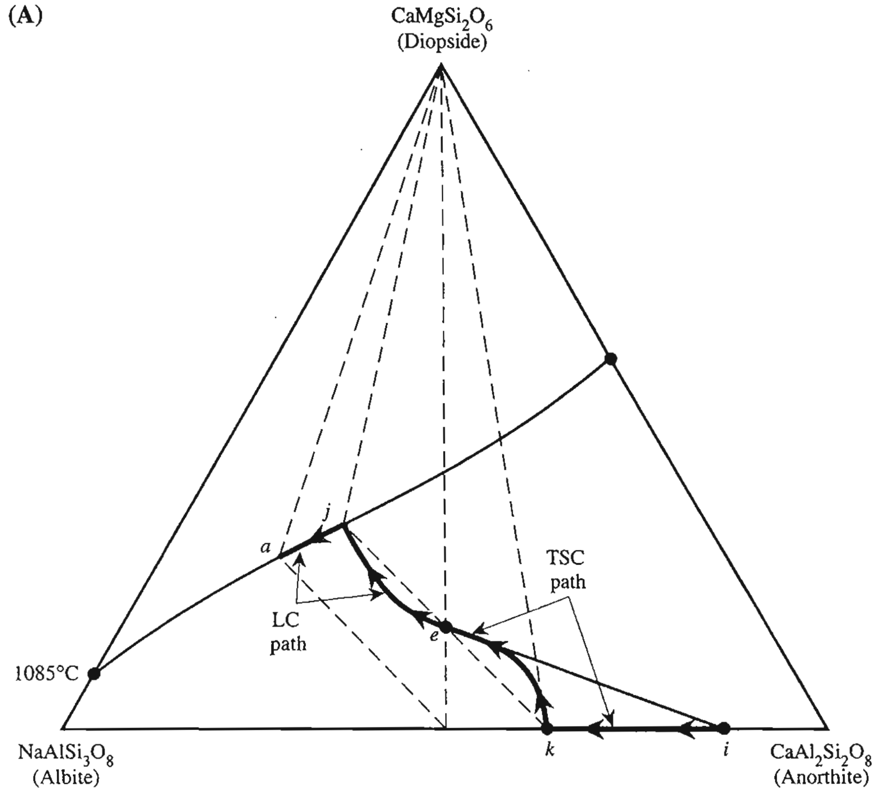
Note that there is only one boundary curve in the ternary diagram, which has this geometry because there can be only one two-phase boundary when there are only two solid phases possible within the system. In other words, with a maximum of three coexisting phases possible (diopside + plagioclase + melt), the lowest phase rule variance is one. The phase rule for an isobaric system is defined as

$$F = c - p + 1$$

There are three components ($CaMgSi_2O_6$, $NaAlSi_3O_8$, and $CaAl_2Si_2O_8$) and three phases (diopside, plagioclase, melt), so

$$F = 3 - 3 + 1 = 1$$

There cannot be any invariant points such as eutectics or peritectics in the interior of this type of system. Keep in mind, however, that the lowest temperature point on the boundary curve (labeled as 1085°C) could be considered invariant because a liquid there is fixed in both composition and temperature. The trick to the phase rule analysis of this point is that the 1085°C point is actually the *binary* eutectic on the albite-diopside join, and therefore $F = 2 - 3 + 1 = 0$. Because this system is isobaric, any liquid composition on the boundary curve can only coexist with a single plagioclase composition (plus diopside); thus liquid *a* coexists with plagioclase *b* and diopside (Figure 4-12B). The actual compositions of plagioclase coexisting with liquids on the plagioclase liquidus or on the boundary curve (as shown by the dashed lines in Figure 4-12) can only be determined by experiment; they cannot be predicted geometrically from the diagram. If liquid *a* is the liquid in stable coexistence with plagioclase *b*, then initial melts such as *e* or *f* must have their final liquid composition at *a*, as discussed below.



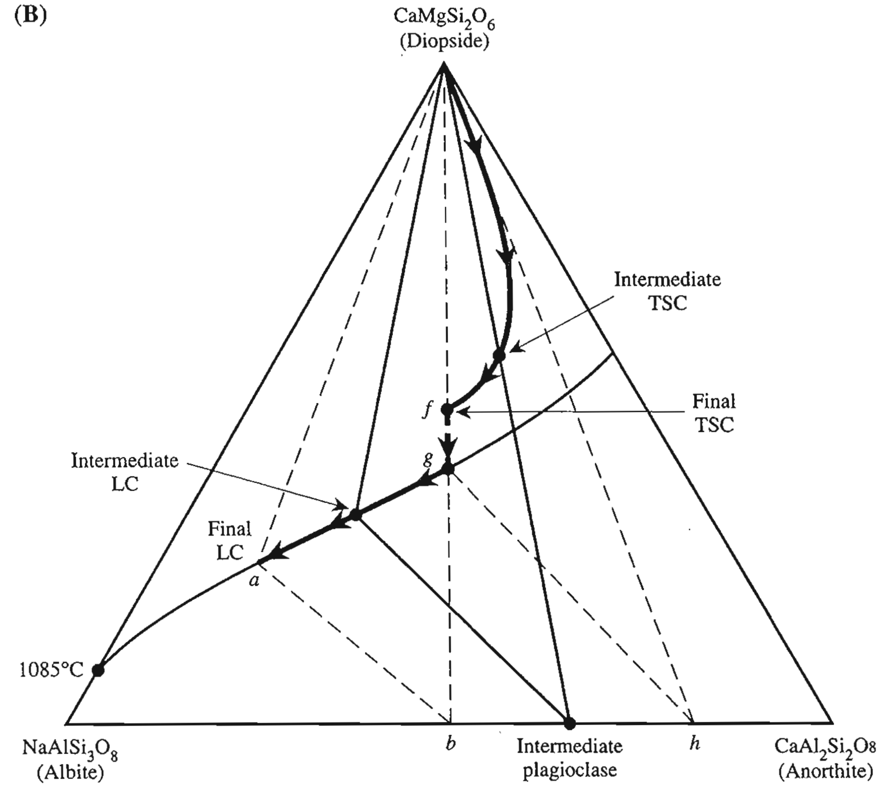


**FIGURE 4-12**

**(A)** Equilibrium crystallization in the complex ternary system $CaMgSi_2O_6$–$CaAl_2Si_2O_8$–$NaAlSi_3O_8$ (diopside-anorthite-albite), portrayed with the LC-TSC method (Morse 1980) for a melt of composition *e* initially saturated with plagioclase. LC path is from *e* to *j* to *a*; TSC path is from *i* to *k* to *e*. Solid line shows tie line from melt to initial plagioclase (*i*), and the two dashed triangles show the initial (right) and final (left) three-phase triangles. **(B)** Equilibrium crystallization of a melt composition (*f*) saturated with diopside. LC path is from *f* to *g* to *a*; TSC path is from diopside to *f*. Dashed triangles are the initial (right) and final (left) three-phase triangles. The solid triangle shows one intermediate three-phase triangle, along with the LC, TSC, and plagioclase composition for this stage in crystallization.

The crystallization of a liquid at *e* in Figure 4-12A is somewhat complicated because of plagioclase solid solution effects during primary crystallization on the plagioclase liquidus surface. Cooling of liquid *e* results in intersection with the plagioclase liquidus and the beginning of crystallization of a very calcic plagioclase at *i* (determinable only by experiment). As this plagioclase is removed, the liquid moves directly away from it down the liquidus surface (labeled LC path). The liquid descent path must be curved, because, as the liquid cools and becomes more sodic, the plagioclase composition is also constantly shifting to the left toward *k* (labeled TSC path). The convex-downward curved LC path shown in Figure 4-12A is thus composed of a very large number (approaching infinity) of infinitely short, straight increments that progressively become more nearly vertical as the boundary curve (cotectic) is approached. The LC path must intersect the boundary curve at *j* because liquid of this composition and plagioclase at *k* constitute a tie line passing through the initial liquid composition *e*. When the liquid reaches *j*, diopside (in addition to plagioclase) begins to crystallize and the LC path now follows the cotectic from *j* toward *a*. As diopside joins plagioclase in the solids, the TSC path leaves the plagioclase join at *k* and shifts toward *e*. The TSC path is curved as shown because it constantly trends toward the ISC, which is approximately at the midpoint of the plagioclase-diopside tie line. The end of the TSC path must be at *e*, because this is the bulk composition of the initial magma; when TSC arrives at *e*, the LC is at *a* and crystallization is complete.

Now consider the equilibrium crystallization of liquid *f* (Figure 4-12B). Cooling to the liquidus surface, this melt begins to crystallize diopside. As diopside component is removed, the liquid composition shifts directly away from the diopside corner in a straight line and down-temperature to the cotectic at *g*. When LC arrives at *g*, plagioclase joins diopside in crystallizing. Experimentally determined tie lines from cotectic liquids to plagioclase indicate that plagioclase at *h* coexists with liquid at *g*. The triangle Di*hg* is the initial three-phase triangle for cotectic crystallization. The ISC now being removed from the liquid lies about midway along a line from plagioclase *h* to the diopside corner. As melt becomes depleted in this ISC, LC moves directly away down the cotectic toward *a*, as shown by the arrows; an intermediate LC is labeled. As the liquid cools and becomes more sodic, the crystallizing plagioclase becomes more sodic as well, as indicated by the dashed tie lines in Figure 4-12B. When the liquid reaches *a*, the tie line from plagioclase *b* to diopside passes through the bulk composition, indicating that the proportion of liquid has dropped to zero and that the system consists entirely of diopside + plagioclase of composition *b*. The TSC path begins at diopside and only leaves this composition when the LC reaches *g* and plagioclase crystallizes. The addition of this new solid mix to the already crystallized diopside draws the TSC down toward *h*. The TSC remains on the diopside-plagioclase tie line as LC evolves down the cotectic, but as this tie line sweeps to the left, so must the TSC. This progressive shift causes the TSC to move in a curved path (Figure 4-12B) until it intersects point *f* at the same instant that liquid is at *a* and plagioclase at *b*. When TSC equals the initial liquid composition, the liquid is all used up.

To recapitulate: When the liquid at *f* has evolved down to the boundary curve, the system consists of three phases (liquid + plagioclase of composition *h* + diopside) that constitute the corners of a subtriangle within the overall triangular system. At the instant that the LC reaches the boundary curve and plagioclase first begins to crystallize, the original liquid composition (and bulk composition) *f* lies almost exactly on one edge of the triangle — that from diopside to liquid. As liquid and plagioclase compositions both become more sodic during cooling, the triangle sweeps toward the left, pivoting on the diopside corner of the ternary, and both plagioclase and diopside increase at the expense of liquid. During this whole evolution, the original liquid composition lies within the triangle, this position indicating that all three phases are present (their exact proportions can in fact be calculated by using principles from Figure 4-8). When the liquid reaches *a* and the plagioclase reaches *b*, the plagioclase-diopside leg of the triangle now intersects the bulk composition, thus indicating that liquid is totally exhausted.

In both of the above examples, continuous reaction-equilibration between liquids and plagioclase has been assumed. With incomplete reaction (due to rapid cooling, removal of early-formed crystals, and so on), a variety of plagioclase compositions will result (for example, preserved calcic cores in zoned crystals). The liquid in such a nonequilibrium case will be enriched in sodium and may evolve further along the boundary curve than its predicted composition under equilibrium crystallization. This scenario is examined in Chapter 6.

## SUMMARY

Experimentally determined phase diagrams of binary, ternary, and more complex systems support critical models for magma crystallization processes that cannot be directly observed in nature. They show the sequences of minerals that precipitate from melts of various compositions, information that is quite useful in interpreting the meaning of many igneous textures. The phase rule is a basic tool in describing the behavior of phases within a chemical system. The phase assemblages in one- and two-component systems are determined by the particular combination of temperature and pressure to which the system is subjected. Within systems of two or more components, melting can be congruent or incongruent. Crystallization behavior is strongly influenced by the amount of solid solution between solid phases and by the formation of compounds of intermediate composition.

## STUDY EXERCISES

**1.** Explain the concept of equilibrium as it applies to igneous processes and igneous rocks.

**2.** In binary temperature (*T*)-composition (*X*) diagrams such as Figure 4-2, why are compositions of solid minerals represented by vertical lines, whereas melts can have compositions across the width of the diagram? Why are the two variables *T* and *X* chosen for this and most igneous diagrams?

**3.** In Figure 4-3 or 4-4, pick a composition that lies above the diopside-liquidus curve and work out the equilibrium crystallization of this melt using both the traditional and the LC-ISC-TSC approaches.

**4.** In Figure 4-6, for bulk composition at the temperature (≈1420°C) where LC is at *d* and TSC is at *e*, what are the relative proportions of melt and plagioclase crystals? (Use a measuring scale for this lever-rule calculation.)

**5.** What are the relative proportions of the components diopside, forsterite, and anorthite in composition *b* shown in Figure 4-10? (*Hint:* Use Figure 4-8B or 4-8C and measure using a scale.)

**6.** There are three cotectic lines in the diopside-forsterite-anorthite ternary system (Figure 4-10) but only one in the ternary system albite-anorthite-diopside (Figure 4-12). Why? How many ternary eutectic points are there in each system?

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