

# The Phase Rule and One- and Two-Component Systems

## Questions to be Considered in this Chapter:

1. How do crystallization and melting of chemically complex natural systems differ from simple systems such as water–ice?
2. How might we simplify natural systems in laboratory studies sufficiently to understand the complexities?
3. How can we formally analyze the behavior of systems in phase diagrams in order to make the dynamics most clear and to understand the effects of changing intensive variables?
4. Why do minerals crystallize (or melt) in repeatable sequences, and what controls the sequence?
5. How do liquids and associated mineral solids vary in composition during crystallization or melting?

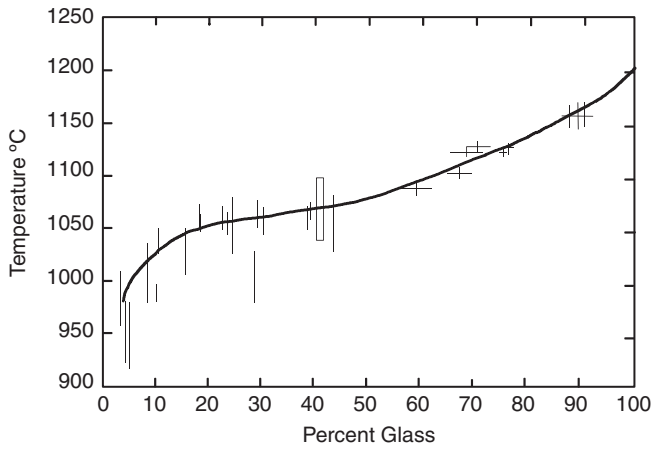
## 1 INTRODUCTION: CRYSTALLIZATION BEHAVIOR OF NATURAL MAGMAS

In this chapter, we address the behavior of simple chemical systems as analogues of more complex natural ones. To see why it is advantageous to do so, let's begin by observing what happens when a natural melt crystallizes. In a work that combined natural samples of a cooling magma with laboratory analysis, Wright and Okamura (1977) studied the crystallization behavior of the Makaopuhi lava lake in Hawaii. They drilled through the thin crust of the lava lake and sampled the magma beneath, using stainless steel and ceramic probes. Because the upper portion of the ponded basaltic magma cools from the surface downward, by inserting the probe deeper into the liquid, just beneath the crust, one can sample progressively hotter portions of the magma. Thermocouples were also inserted into the drilled holes to determine the temperature gradient in the magma, in order to estimate the temperature at which each sample was collected. The result is a series of samples of uniform basaltic composition collected at a range of known cooling temperatures.

Once extracted, the small samples cool quickly and solidify. Fortunately, this process is so rapid that the solidification of the liquid portion of the sample has no time to form crystals. Rather, it rapidly solidifies (“quenches”) to a glass (a solid phase with no ordered arrangement of the atoms). If any crystals were present in the original liquid at depth, they remain embedded in the newly formed glass because they, too, have no time to grow or react with the melt during quenching. Wright and Okamura took these types of quenched samples to the laboratory for chemical and microscopic analysis.

The results of the Makaopuhi study are summarized in Figures 1 to 3. Figure 1 shows that the amount of glass (representing liquid magma at the time of sample acquisition) decreases continuously from 100% at ~1200°C to 0% at ~950°C. Liquid is progressively replaced by crystals over this temperature range. Contrast this to some familiar simple substance, such as H<sub>2</sub>O. At atmospheric pressure, water solidifies to ice at a constant 0°C. The Makaopuhi lava, on the other hand, began to crystallize at 1205°C and only became completely solid when it got 250° cooler.

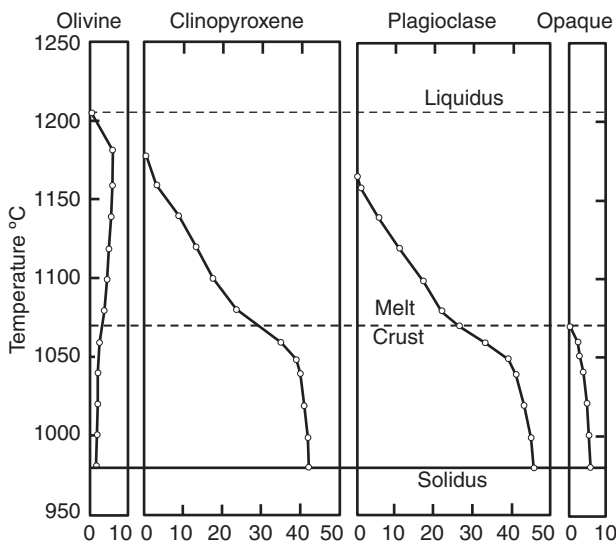
Figure 2 shows that a specific sequence of solids formed as the magma cooled. Olivine began to crystallize first, followed by pyroxene, then plagioclase, and finally opaque iron–titanium oxide minerals (ilmenite and titanomagnetite).



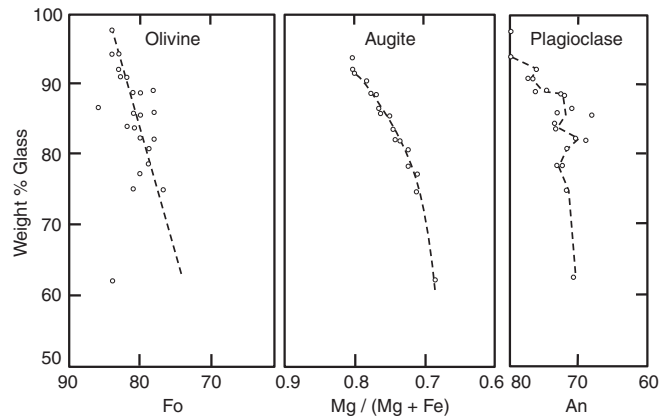
**FIGURE 1** Percent melt (glass) as a function of temperature in samples extracted from the cooling of basalt of the Makaopuhi lava lake, Hawaii. Lines represent ranges observed. After Wright and Okamura (1977).

If you remember Bowen's Reaction Series from previous classes, it might help a bit as you consider basaltic melt crystallization. The formation of olivine, followed by pyroxene, is exactly what Bowen's Series predicts. Plagioclase crystallization at Makaopuhi, however, begins to form after pyroxene and not along with olivine, as Bowen's Series indicates. Another unusual feature in Figure 2 is that the amount of olivine increases as crystallization of the magma proceeds from 1205 to 1180°C, and then *decreases* as the melt cools and crystallizes further. Microscopically, the early-forming olivines first grew and then began to appear embayed and corroded below 1180°C, indicating that the olivine began to be resorbed (consumed by reacting with the melt) as cooling progressed.

Figure 3 shows that the composition of the minerals also varies with temperature. The mafic phases get more Fe



**FIGURE 2** Weight percent minerals in Makaopuhi lava lake samples as a function of temperature. From Wright and Okamura (1977).



**FIGURE 3** Model composition of minerals in Makaopuhi lava lake samples. From Wright and Okamura (1977).

rich, whereas the plagioclase, although somewhat irregular, gets less calcic and more sodic (in agreement with Bowen's Series). Although not shown in Figure 3, the composition of the glass also changed progressively during crystallization, with the remaining glass becoming preferentially depleted in Mg, Fe, and Ca.

Instances in which we can observe the crystallization behavior of natural melts are rare. We can study crystallization indirectly, however, by using sequential textures or by creating melts in the laboratory. From such textural and experimental criteria, we have confirmed that melts do indeed crystallize over a temperature range, a sequence of minerals forms over that range, and the composition of most minerals varies across the range as well. But there are many variations on this theme. Clearly, the minerals that form in a granite are not the same as those that form in a basalt, nor, we have discovered, is the temperature range over which that crystallization takes place the same. More silicic melts crystallize at lower temperatures than basalts, and the mineral sequence in silicic magmas may begin with biotite or amphibole and end with alkali feldspar or quartz. The actual sequence of minerals that crystallizes varies with composition and pressure. Parts of the sequence may even be reversed from one rock type to another.

From the accumulated textural and experimental data, we can make the following general observations about the complex crystallization behavior of natural melts (following Best, 1982):

1. Cooling melts crystallize from a liquid to a solid over a range of temperature.
2. Several mineral phases crystallize over this temperature range, and the number of minerals tends to increase as temperature decreases.
3. Minerals usually crystallize sequentially, generally with considerable overlap.
4. Minerals that involve solid solution change composition as cooling progresses.
5. The melt composition also changes during crystallization.

6. The minerals that crystallize, as well as the sequence in which they form, depend on the temperature and composition of the melt.
7. Pressure can affect the temperature range at which a melt crystallizes. It may also affect the minerals that crystallize.
8. The nature and pressure of any volatile components (such as  $\text{H}_2\text{O}$  or  $\text{CO}_2$ ) can also affect the temperature range of crystallization and the mineral sequence.

At this point, it may seem that magmas are simply too complex to understand. The chemical complexity of natural melts makes it difficult to focus on the various factors that control the behaviors described above. A basaltic melt doesn't behave the same as a granitic one, but why? Which of the many chemical variables is responsible for what aspect of the difference? A successful approach is to simplify the systems we study. By doing so, we reduce the complexity and make it possible to assess the effects of individual chemical constituents and minerals during crystallization and melting.

Of course, there is a price for this benefit, and that price is that the simplified systems are not really the natural ones that interest us. We may understand the simple "model" systems better, but the results may not apply directly to the more complex natural phenomena. Nonetheless, we shall see that this approach has been of great benefit to petrologists. With a bit of theory and some experimental results from simplified systems, we can understand the basis for the behaviors listed above. Application of model systems to real rocks is indeed possible, and we shall do so effectively.

## 2 PHASE EQUILIBRIUM AND THE PHASE RULE

If we are to understand the simplified systems that follow, we need a bit of theoretical preparation. We want to be able to analyze systems in a way that allows us to grasp the dynamics of each and to account for the contribution of each chemical constituent to the variations in those dynamics. If we understand how the introduction of additional constituents affects a system, we can not only understand each new system better, but we become prepared to apply the systems we study to the more complex systems in nature. The phase rule is a simple, yet rigorous and elegant, theoretical treatment for this approach. To develop the phase rule, we must first define a few terms.

A system is some portion of the universe that you want to study. In the lab, we get to choose the system, but in the field, the system may be forced upon us. The surroundings can be considered the bit of the universe just outside the system. A system may be open (if it can transfer energy and matter to and from the surroundings), closed (only energy, such as heat, may be exchanged with the surroundings), or isolated (neither energy nor matter may be transferred).

Although we commonly refer to the state of a system as simply whether it is a liquid, solid, or gas, physical chemists have a far more specific definition of the term. To them, to specify the state of a system is to provide a complete description of the macroscopic properties of that system. For example, consider a system composed of pure water. It may be contained in a glass, but we can define the system as only the water and consider the glass a part of the surroundings. We can measure the temperature ( $T$ ), pressure ( $P$ ), volume ( $V$ ), mass ( $m$ ), density ( $\rho$ ), composition ( $X$ ), or any of a number of other possible parameters of the water and thereby determine each. All these variables must be known if the state of the system is to be completely described. However, once a critical number of these variables is known, the others become fixed as a result because many of the properties are interdependent. For example, if we know the mass and the volume of our water, we know its density. But just how many of these variables must we specify before the others are determined? The phase rule was formulated to address this question.

A phase is defined as a type of physically distinct material in a system that is mechanically separable from the rest. A phase may be a mineral, a liquid, a gas, or an amorphous solid such as glass. A piece of ice is a single phase, whereas ice water consists of two phases (the ice and the water are separable). Two pieces of ice are mechanically separable, but because they are equivalent, they are considered different pieces of the same phase, not two phases. A phase can be complex chemically (such as a tequila sunrise), but as long as you cannot separate it further by mechanical means, it is a single phase.

A component is a chemical constituent, such as Si,  $\text{H}_2\text{O}$ ,  $\text{O}_2$ ,  $\text{SiO}_2$ , or  $\text{NaAlSi}_3\text{O}_8$ . We can define individual components as we please, but, for purposes of the phase rule treatment, we shall define the number of components as the minimum number of chemical species required to completely define the system and all of its phases. For example, ice water, although two phases, has but one component ( $\text{H}_2\text{O}$ ). We could define it as H and O, but because  $\text{H}_2\text{O}$  describes both ice and water as a single component, not two, it is preferred for phase rule purposes. A pure mineral, such as albite, has a single component ( $\text{NaAlSi}_3\text{O}_8$ ). Minerals that exhibit solid solution, however, are commonly treated as multicomponent systems. Plagioclase is commonly a single phase that comprises two components:  $\text{NaAlSi}_3\text{O}_8$  and  $\text{CaAl}_2\text{Si}_2\text{O}_8$ . Why? Because we need to vary the proportions of these two components to determine the state of plagioclases of varying composition.

The proper choice of the number of components for the application of the phase rule is not always easy. The choice commonly depends on the behavior of the system and the range of conditions over which it is studied. For example, calcite may be considered a single-component system ( $\text{CaCO}_3$ ). Although this is true at relatively low temperatures if we heat it to the point that it decomposes to

solid CaO and gaseous CO<sub>2</sub>, it would be a two-component system because we would have to use both CaO and CO<sub>2</sub> to describe the composition of the solid and gaseous phases. Compare this to our ice water: a single component suffices to describe the chemical composition of each phase. But for calcite, lime (CaO), and CO<sub>2</sub>, we require two components, separately or in combination, to describe them all. This concept will become clearer with practice.

The variables that must be determined to completely define the state of a system can be either extensive or intensive in nature. Extensive variables depend on the quantity of material (the extent) in the system. Mass, volume, number of moles, etc. are all extensive variables. Such variables are not intrinsic properties of the substances in the system. In other words, it is possible to have 10 g of water, or 100 g. Either way, it's still the same water. Although it is nice, perhaps, to have more of some things (money, influence . . .) and less of others (debts, nose hairs . . .), such extensive variables are of little concern to us now, as they do not affect the macroscopic properties (the state) of matter in a system.

Intensive variables, on the other hand, don't depend upon the size of the system and are properties of the substances that compose a system. Intensive variables include pressure, temperature, density, etc. If we divide any extensive variable by another one, the extent cancels, and the ratio is an intensive variable. For example, the volume of a phase divided by the number of moles is the molar volume, an intensive variable. Density (mass divided by volume) is another example. These latter two intensive variables are certainly properties that can change for substances in a closed system, and therefore must be specified if we are to determine the state of that system. The molar volume and density of water is different at 10°C than at 50°C, and it is also different than the corresponding values for CO<sub>2</sub> at the same temperature. Because materials expand with increasing heat and contract with increasing pressure, the pressure and temperature must also be specified when describing the state of a system. Another important intensive variable is the composition of the phases present. Although the number of moles of Fe and Mg in olivine are extensive variables, the ratio of Fe/Mg is intensive and affects such properties as molar volume, density, etc.

There are a large number of possible intensive variables, and we've seen that many are interdependent. We now return to the question stated above: How many must we specify before the others are fully constrained and the state of the system is known? The phase rule of Gibbs (1928) is designed to do this. If we define  $F$ , the number of degrees of freedom (or the variance) of a system, as the minimum number of intensive variables that need to be specified to completely define the state of the system at equilibrium, the phase rule can be expressed as:

$$F = C - \phi + 2 \quad (\text{the Gibbs phase rule}) \quad (1)$$

Where  $\phi$  is the number of phases in the system, and  $C$  is the number of components. A rigorous derivation of the

phase rule (Gibbs, 1928) is based upon the number of variables (one for each component, plus  $P$  and  $T$ ) minus the number of equations relating those variables [one for each phase]. Hence,  $F = C + 2 - \phi$ . The mathematics of Equation (1) is simple enough and tells us that for each component we add to a system, we must specify one additional intensive variable to completely constrain the state of the system. For each additional phase, there is one fewer variable that needs to be specified. Once we have specified this critical number of independent intensive variables, all other intensive variables are fully constrained (invariable).

The phase rule applies only to systems in chemical equilibrium. One cannot count disequilibrium assemblages, such as incomplete replacement of biotite by chlorite in a cooled granitic rock, as separate phases for most phase rule applications. The reaction of biotite to chlorite is typically arrested because the rock cooled too quickly for the reaction to run to completion. As a more extreme example, consider the great number of mineral phases that can coexist in a clastic sediment such as a graywacke. These minerals are collected together and deposited by clastic processes, but they are not in chemical equilibrium at low, near-surface temperatures, and to apply the phase rule to such a system would be useless.

### 3 APPLICATION OF THE PHASE RULE TO THE H<sub>2</sub>O SYSTEM

Let's see how the phase rule works by applying it to a very simple system: the heating of ice on a hot plate. The system is defined by a single component, H<sub>2</sub>O, so  $C = 1$ . If we begin with ice at equilibrium at some temperature below 0°C (we left the window open in January), then our system is completely solid, and  $\phi = 1$  as well. The phase rule [Equation (1)] at this point would tell us:

$$F = 1 - 1 + 2 = 2$$

meaning that we must specify only two intensive variables to define the system completely. In the natural world, pressure and temperature are the most common independent variables, so if we were to specify  $P$  and  $T$ , the state of the system would be completely defined. If we were to specify -5°C and 0.1 MPa (atmospheric) pressure, all the other intensive parameters of the ice would necessarily also be fixed (density, molar volume, heat capacity . . . everything). By fixed, I mean that they are measurable parameters that are constant properties of ice under the conditions specified.

We can think of  $F$  as the number of variables that we must specify, or we can think of it as the number of variables that we are free to change independently. The fact that  $F$  variables can vary independently explains why we need to specify each. In the present case, we are free to change two intensive variables as long as the value of the other parameters in the phase rule ( $C$  and  $\phi$ ) remain the same. With our ice, we have  $F = 2$  and have chosen  $P$  and  $T$  as the ones that

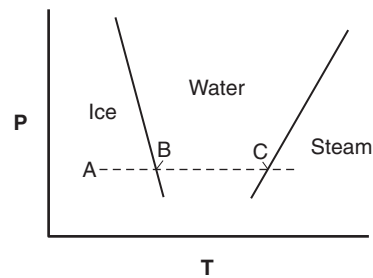
we shall specify. Alternatively, we could say that we can change  $P$  and  $T$  independently in our pan of ice (either or both), and still have only ice.

Let's heat the system at constant pressure (turn on the hot plate beneath our pan of ice). We can heat it initially with no change in the parameters of the phase rule (i.e.,  $F$  remains equal to 2 as long as  $\phi$  and  $C$  are both equal to 1). At each new temperature we can specify  $T$ , and the other intensive parameters also have new values (e.g., the ice expands, so the density changes). The phase rule still holds, however, telling us we need to specify two intensive variables if we want to fix the others.

Eventually we heat the ice until a new phase appears: the ice begins to melt, and ice and water coexist stably at equilibrium in the pan. Now  $\phi = 2$  and  $F = 1 - 2 + 2 = 1$ . We need to specify only *one* intensive variable to completely define the state of the system. Which variable do we choose? Pressure or temperature? *The phase rule cannot make this choice for us.* It tells us about the variance, but it cannot choose the variables for us. In other words, the phase rule is a tool for the analysis of chemical systems; it does not attempt to tell a system how it should behave. The responsibility is ours to apply the phase rule appropriately and interpret the results.

If we look at a pressure–temperature **phase diagram** for the  $\text{H}_2\text{O}$  system in Figure 4, we can interpret the phase rule more clearly. We began at point A in the field labeled “Ice” and moved along the dashed path to the melting point (point B on the ice–water boundary). Initially in the ice field we could vary pressure and temperature independently and still have only one phase. Thus we had to specify both variables to define the state of the phase. When we heated the ice to point B, we encountered the line separating the ice and water fields, meaning that both phases can coexist at equilibrium (“ice water”) under  $P$ - $T$  conditions anywhere along this line. Because  $\phi = 2$ , then  $F = 1$ , meaning that we must specify only *one* variable now (pressure *or* temperature), and all the other intensive variables for *both* phases are then determined. This may seem counterintuitive at first because we now have twice as many phases, each with its own density, molar volume, etc. to be determined, but the phase rule tells us that for each new phase, the number of *independent* variables is actually decreased. For example, if we specify that ice and water are at equilibrium at a pressure of 0.1 MPa (atmospheric pressure, represented by our dashed line in Figure 4), then the temperature *must be*  $0^\circ\text{C}$  (point B). We thus know both  $T$  and  $P$ , and the density, molar volume, etc. of each phase are therefore fixed.

Alternatively,  $F = 1$  means that we cannot vary pressure *and* temperature independently anymore without changing the parameters of the phase rule (i.e., losing a phase). Consider point B in Figure 4 again. If we were to vary pressure independently vertically upward, we would leave the water–ice equilibrium boundary curve and enter the water field, losing ice and changing the phase rule parameter  $\phi$  to one. If we were to raise the pressure and still maintain  $\phi = 2$ , we would have to change temperature in a sympathetic fashion so as to remain on the ice–water equilibrium line. So if  $\phi = 2$ ,  $P$  and  $T$  are not independent. More generally, we can



**FIGURE 4** Schematic pressure-temperature phase diagram of a portion of the  $\text{H}_2\text{O}$  system.

say that, at equilibrium in a one-component, two-phase system (such as ice water), *there must be a relationship between pressure and temperature.* This relationship is expressed as the *slope* of the equilibrium curve that separates the ice and water fields on the pressure–temperature diagram (Figure 4). If we change either variable, we would also have to change the other along the curve to maintain two coexisting phases.

As mentioned above, the phase rule tells us the variance but can't choose which variable(s) are determinative. If we run our experiment in a lab on a hot plate at atmospheric pressure, the phase rule is not aware that pressure is not a possible variable. We can simply remember that one of our variables is fixed, or we can modify the phase rule to account for such restricted operating conditions. If all of our experimentation is conducted at constant pressure, we have forced the removal of a degree of freedom from our analysis. Under these conditions, the phase rule (Equation 1) would be reduced to:

$$F = C - \phi + 1 \quad (\text{isobaric}) \quad (2)$$

We could use a similarly reduced phase rule for any system with one fixed variable (e.g., constant temperature, constant volume).

In our constant 0.1 MPa pressure system, having ice water at equilibrium on our hot plate in the lab, Equation (2) tells us that  $F = 1 - 2 + 1 = 0$ . Such a system is completely fixed. The temperature must be  $0^\circ\text{C}$ , and every intensive variable of both phases is determined. At a constant pressure, we cannot change the temperature of our ice water as long as we have two phases. *We can add heat, but this won't change the temperature!* The hot plate is hot, pumping heat into the system, but the phase rule tells us that the temperature must remain constant as long as ice and water are both in the pan. Here we see an example of the difference between *heat* and *temperature*. In thermodynamics, heat has the symbol  $q$ . Heat is supplied to the ice water and has the effect of melting the ice *at a constant temperature* until the ice is consumed. **This heat, which drives the transition from the solid to the liquid form, is called the latent heat of fusion.**

Once we have melted all the ice, we again have one phase (water). Returning to our general system with variable pressure, Equation (1) tells us that  $F = 1 - 1 + 2 = 2$ , and

we must specify temperature and pressure independently, just as we did for the single-phase ice case. This is true until we get to the boiling point; then  $\phi$  becomes 2 again, and  $F$  returns to 1, and we get a situation similar to that of water + ice discussed previously. Because  $F = 1$ , there is a relationship between pressure and temperature, expressed by the slope of the water–steam boundary curve in Figure 4. There is no reason, however, that this slope has to be the same as that of water–ice. The slope of each is determined not by the phase rule but by the molar volume and entropy of the coexisting phases, as expressed by the Clapeyron equation.

If the pressure is fixed, as in our lab, the modified phase rule [Equation (2)] for  $\phi = 2$  reduces  $F$  to 0, meaning we can only have boiling water (coexisting water and steam at equilibrium) at a single specific temperature (100°C at 0.1 MPa). **The heat supplied at this constant temperature converts the water to steam and is now called the latent heat of vaporization.**

Some cooks think that briskly boiling water is hotter than slowly boiling water. This is clearly impossible as long as liquid water and water vapor coexist (a prerequisite for boiling). The added (wasted) energy used for brisk boiling simply supplies the latent heat to make more steam. If your cooking goal is to reduce the quantity of liquid, go ahead and boil away briskly. If you're only trying to cook some pasta, however, boil it as slowly as you can and save some money.

Smart cooks know how to get boiling water hotter than 100°C. They use a pressure cooker, which frees them from the 1 atmosphere restriction. Because water and steam coexist in the pressure cooker, the temperature and pressure must change along the water–steam boundary curve in Figure 4. Because heat is added, the pressure must increase because the boundary has a positive slope. This situation could get dangerous because the pressure could explosively overcome the strength of the container. That's why a valve with a weight is placed on the top of a pressure cooker. Once the pressure reaches a specific value, the vapor lifts the weight, and steam is released. Thus pressure cookers operate at a constant, though elevated, pressure (and therefore constant elevated temperature). Incidentally, the steam released by the valve instantly drops to atmospheric pressure while cooling only slightly in the one-phase steam field of Figure 4. Released steam is thus *very* hot and can cause severe burns. Most cooks know of another way to elevate the temperature of boiling water a little: They add salt. But this violates our premise of a single-component system (constant composition) and will be dealt with later.

Let's now apply the phase rule to some simple model systems of geological significance. The phase diagrams we shall use have been derived empirically (by experiments on simple mineral systems). As you are, I hope, beginning to recognize, the phase rule is a theoretical treatment that helps us understand the dynamics of the systems represented by these diagrams. Remember that the phase rule is  $F = C - \phi + 2$  for the general case (not artificially fixing pressure or tem-

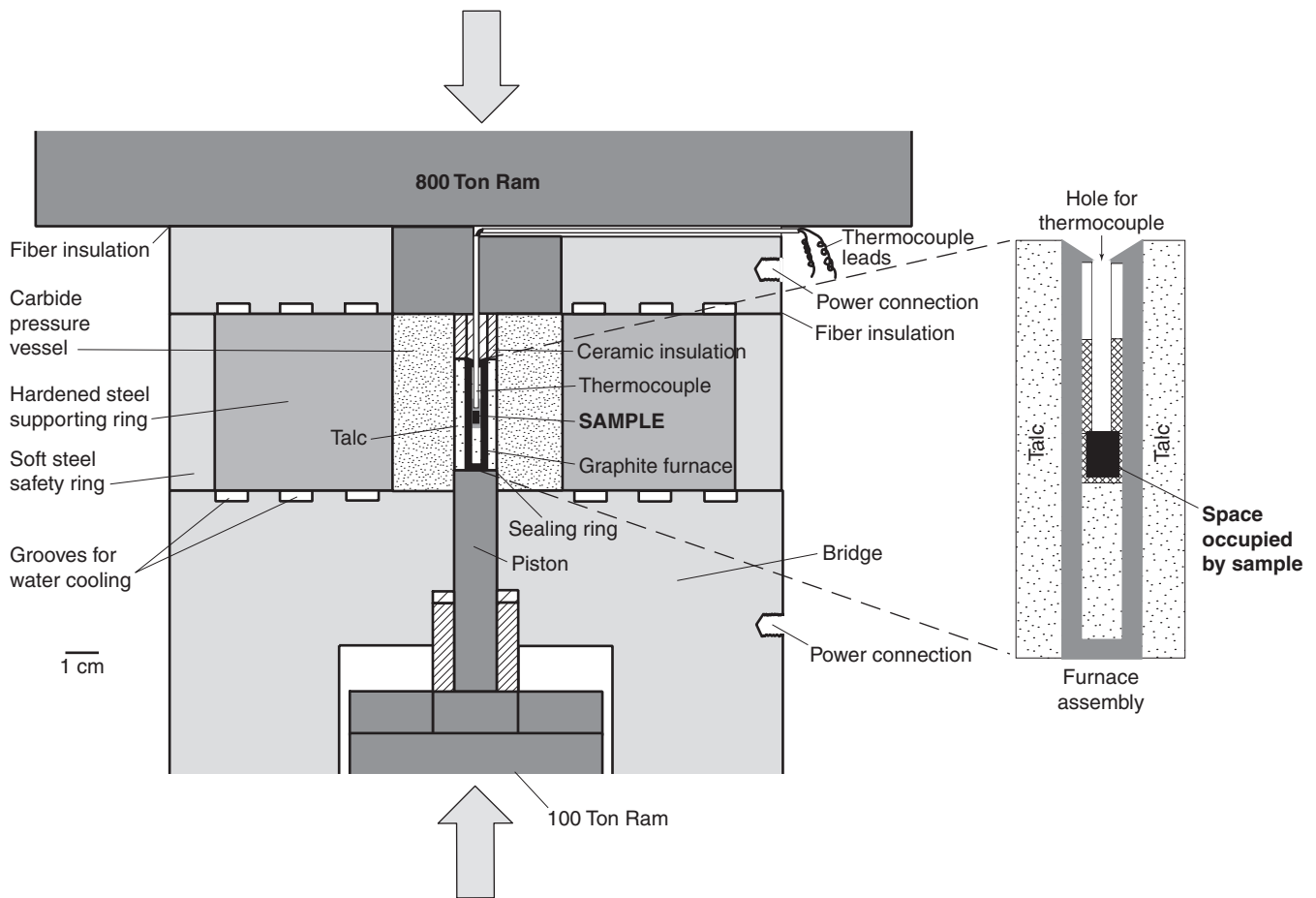
perature) and that the final term is decreased by 1 for each variable that we fix externally. We shall look at a number of synthetic and natural rock systems.

Experiments on silicate systems require furnaces capable of melting rocks (or chemically simplified rock analogs) at high pressure. **Figure 5 is a schematic cross section through a typical high-pressure furnace. Note that the size of the cylindrical sample in Figure 5 is less than 1 cm in diameter. In furnaces that are combined with high-pressure hydraulic rams, small samples can be heated to temperatures sufficient for complete melting at pressures equivalent to those attained in the upper mantle. The sample is prepared and inserted into the furnace, and the furnace is then closed and gradually heated as the pressure is increased by the ram. The pressure is loaded vertically in Figure 5, but the furnace is confined radially, so that the horizontal pressure quickly approaches that of the vertical load. A thermocouple inserted just above the sample records the temperature attained and permits external temperature control. The result is that we can expose a sample to a variety of temperatures and pressures. In the ensuing discussion, we shall begin with the simplest one-component experimental systems and gradually explore the effects of added chemical complexity.**

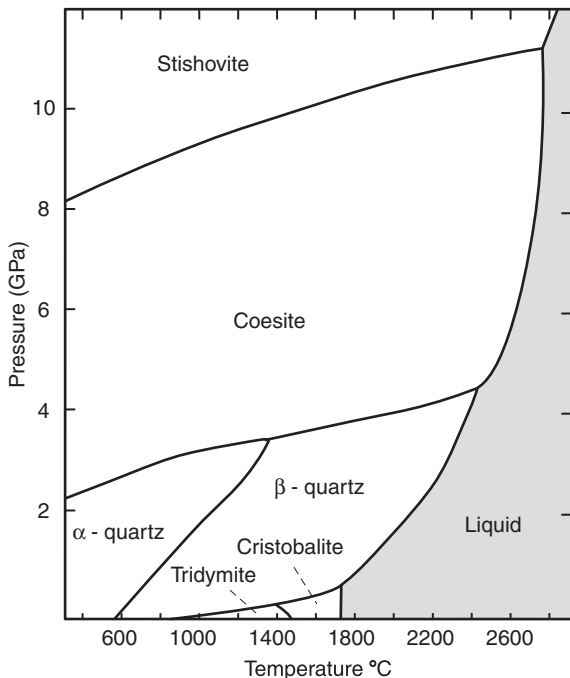
#### 4 ONE-COMPONENT SYSTEMS

**Figure 6 is the pressure–temperature phase diagram for the SiO<sub>2</sub> system. The upper limits of 10 GPa and 1900°C reflect generous limits of pressure and temperature to which a pure SiO<sub>2</sub> phase would typically be subjected in nature (remember, 1 GPa represents the approximate pressure at the base of 35 km of continental crust, and SiO<sub>2</sub> minerals are not common in the mantle or core). There are a number of solid silica polymorphs, and there is a liquid phase, each with a stability field shown on the diagram.**

For conditions that fall within any one field in Figure 6, only one phase is stable, hence  $\phi = 1$  and  $F = 1 - 1 + 2 = 2$ . **These areas are called divariant fields because the variance in them is two.** Both pressure and temperature are variable for these single-phase situations, and both must be specified to determine the state of any one-phase system. Curves separating the fields represent conditions under which two phases coexist at equilibrium. Because  $\phi = 2$  and  $F = 1 - 2 + 2 = 1$ , the curves are called **univariant curves**. Along these curves, because two phases coexist, one need only specify pressure *or* temperature. Specifying one of these permits us to determine the other from the location on the curve, and thus the state of the whole system (both phases) is defined. This is true for any two phases in stable equilibrium, such as water and ice in Figure 4, cristobalite and liquid in Figure 6, or any two coexisting silica polymorphs. For example, if I were to ask at what temperature  $\alpha$ - and  $\beta$ -quartz coexist at 1 GPa, we could look along the curve separating the fields of low quartz and high quartz at the pressure specified and determine the temperature: approximately 810°C. Note the positive slope for any solid/liquid equilibrium curve.



**FIGURE 5** Cross section through a typical furnace for the experimental study of natural and synthetic rocks and minerals at pressures equivalent to depths as great as 150 km. Diagonally hatched areas are steel, and stippled areas are typically ceramic. After Boyd and England (1960). Copyright © AGU with permission.



**FIGURE 6** Pressure-temperature phase diagram for  $\text{SiO}_2$ . After Swamy et al. (1994). Copyright © AGU with permission.

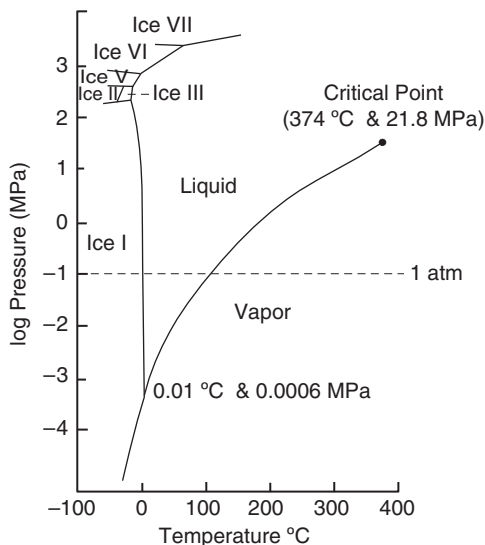
Note that there are also points where univariant lines intersect. At these points, *three* phases coexist. When  $\phi = 3$ ,  $F = 1 - 3 + 2 = 0$ . Whenever three phases coexist at equilibrium in a one-component system, the system is completely determined, and these points are called **invariant** points. Such points are obviously possible only at specific temperatures and pressures. Try this yourself. Under what conditions are low quartz, high quartz, and coesite stable together? What about high quartz, cristobalite, and liquid?

The phase rule and phase diagrams are very closely related. You have probably noticed that the variance of a system corresponds directly to the dimensions of the appropriate assemblage in the diagram. Divariant assemblages ( $F = 2$ ) exist as two-dimensional fields (areas) on the phase diagram. Univariant assemblages ( $F = 1$ ) are represented by the one-dimensional curves that act as boundaries between the divariant fields, and invariant assemblages are represented by the zero-dimensional points where three fields meet.

Figure 6 is a fairly representative one-component  $P$ - $T$  phase diagram for minerals, showing a high- $T$  liquid field and a solid field that may be subdivided into fields for various polymorphs. For substances with lower melting points and higher vapor pressures (natural liquids, gases, and some minerals), there may also be a vapor phase field. The phase

diagram for H<sub>2</sub>O shown in Figure 4 is only figurative, simplified to illustrate our discussion of heating ice in a lab. The experimentally determined phase diagram is shown in Figure 7. As with silica, there are several solid polymorphs of ice, each with its own stability range. The negative slope of the ice I/liquid curve is very rare. Ice I has a greater volume than the liquid. This irregularity, however, does not extend to the other ice polymorphs. Note the vapor field and the boundary for the transition from ice to steam at very low pressure. **The process whereby a solid passes directly to a vapor is called sublimation.** The phase rule treatment for sublimation is the same as for any one-component, two-phase situation.

There are several invariant points in the H<sub>2</sub>O system—for example, where ice I, water, and steam all coexist. Note also that the liquid/vapor curve ends in a **critical point** at 374°C and 21.8 MPa. You can see from the diagram that it is possible to begin with liquid water at 0.1 MPa, increase the pressure above the critical pressure, heat it above the critical temperature, and then decrease the pressure again to produce steam. The effect is to create steam from water, but at no point in the process do two phases, water and steam, coexist. When increasing pressure is applied to coexisting water and vapor along the equilibrium curve in Figure 7, the vapor compresses more than the liquid, and their properties (density, etc.) gradually converge. At the critical point, they become identical. **At pressures and temperatures above the critical point (called the supercritical region), there is no distinction between the liquid and vapor phases.** The conditions required to create a supercritical fluid in aqueous systems are readily attainable in igneous and metamorphic processes. **The terms liquid and vapor lose their meaning under these conditions, and we call such phases supercritical fluids, or simply fluids.**



**FIGURE 7** Pressure–temperature phase diagram for H<sub>2</sub>O (after Bridgman, 1911, 1935–1937). Ice IV was created using D<sub>2</sub>O and is not stable for H<sub>2</sub>O.

## 5 TWO-COMPONENT (BINARY) SYSTEMS

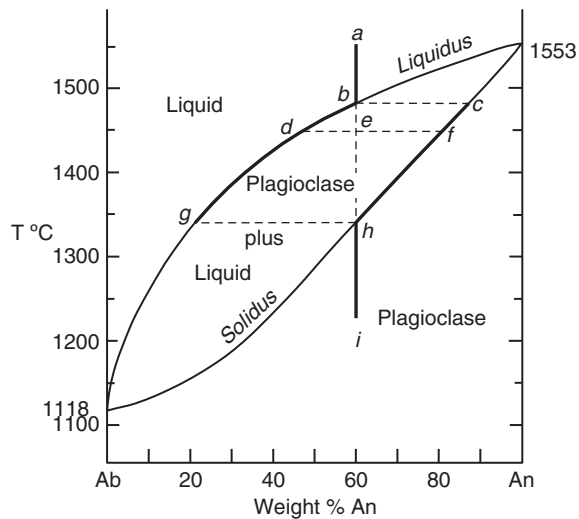
When a second component is added to a system, it can interact with the first in a number of different and interesting ways. We shall investigate four common types of geological binary systems. Because  $C = 2$ , the variance can be as high as 3 in one-phase systems, requiring three-dimensional diagrams to illustrate properly. Rather than attempt this, we simplify most two-component igneous systems and illustrate their cooling and melting behavior on phase diagrams by fixing pressure and discussing the interactions of temperature and the compositional variables. If we restrict pressure, the phase rule becomes  $F = C - \phi + 1$  [Equation (2)] in the discussions that follow. Because temperature–composition ( $T$ - $X$ ) diagrams depreciate the importance of pressure in natural systems, we will occasionally discuss pressure effects on the systems in question in this chapter.

### 5.1 Binary Systems with Complete Solid Solution

First, we shall look at a system exhibiting **complete solid solution**, in which both components mix completely with each other. The plagioclase system, composed of the two components NaAlSi<sub>3</sub>O<sub>8</sub> and CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>, is a common example. Note that the two components given are equivalent to the phases albite and anorthite, respectively. There might be a tendency to confuse components and phases here. Remember that  $C$  (the number of components in the phase rule) is the *minimum* number of chemical constituents required to constitute the system and all of its phases. It is most convenient to treat this system as the *two* components CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>-NaAlSi<sub>3</sub>O<sub>8</sub>, corresponding to the composition of the two phases. This is not a coincidence because this choice of  $C$  is the easiest one we can make to represent the phases in the system. Using the simple oxides, CaO-Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> may seem like a more logical choice for chemical components, but it results in a larger number of components than is necessary (thus violating the definition of  $C$ ). For the remainder of this chapter, I shall often use the mineral abbreviation to indicate components and the mineral name proper to refer to the phases in a system. Thus the abbreviation Ab will be used to indicate the component NaAlSi<sub>3</sub>O<sub>8</sub>, and An will indicate CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>. From your mineralogy course, you may remember that the solid solution for this system involves the *coupled substitution* of (Na<sup>1+</sup> + Si<sup>4+</sup>) for (Ca<sup>2+</sup> + Al<sup>3+</sup>) in a constant AlSi<sub>2</sub>O<sub>8</sub> reference frame. Figure 8 is an isobaric temperature–composition ( $T$ - $X$ ) phase diagram at 0.1 MPa pressure. Before we proceed to analyze the behavior of the system, I must stress that all the phase diagrams we shall cover are *empirically* determined by melting real mineral samples and analyzing the results.

At each end of the horizontal axis in Figure 8, we have a one-component system, representing each pure





**FIGURE 8** Isobaric  $T$ - $X$  phase diagram for the albite–anorthite system at 0.1 MPa (atmospheric) pressure. After Bowen (1913). Reprinted by permission of the *American Journal of Science*.

“end-member” of the solid-solution series, pure albite on the left and pure anorthite on the right. Each of these pure systems behaves like a typical isobaric one-component system, in that the solids melt at a single fixed temperature, at which solid and liquid coexist in equilibrium ( $\phi = 2$ ), just as in our ice–water example. Applying the isobaric phase rule [Equation (2)] with  $C = 1$  and  $\phi = 2$  yields  $F = 1 - 2 + 1 = 0$ . Albite melts at 1118°C, and anorthite melts at 1553°C.

Now we proceed to the effects of an added component on either pure system. First, the addition of the Ab component to pure anorthite lowers the melting point (just as adding salt lowers the melting point of ice on a frozen sidewalk). Adding An to pure albite raises its melting point. But this is not the only effect. Crystallization of multicomponent melts becomes much more interesting than pure one-component melts.

To understand this, let’s use the phase rule to analyze the behavior of a melt of intermediate composition. Consider cooling a melt of composition  $a$  in Figure 8. We refer to **the composition of the system as the bulk composition** ( $X_{\text{bulk}}$ ). The composition in question is 60% anorthite and 40% albite, by weight. This composition may be referred to as  $\text{An}_{60}$ . Note:  $\text{An}_{60}$  is usually a reference to *mole % An*. The notation doesn’t preclude its use for *weight % (wt. %)*, and because Figure 8 has been created for *weight %*, we will use it this way. At point  $a$  in Figure 8, at about 1600°C, we have a single liquid of composition  $\text{An}_{60}$ . In this case, the liquid composition is equal to the bulk composition because the system is entirely liquid. Because  $C = 2$  and  $\phi = 1$ , Equation (2) yields  $F = 2 - 1 + 1 = 2$ . There are thus 2 degrees of freedom for a single two-component liquid at constant pressure. What are they? Once again, any two intensive variables will do, but they should be geologically realistic. Because the diagram is a temperature–composition diagram, it might seem appropriate to choose these two. What are the possible compositional variables? They must be intensive,

so the choices are the weight (or mole) *fraction* of any component in any phase. We can define the weight fraction of the An component in the liquid phase:

$$X_{\text{An}}^{\text{liq}} = n_{\text{An}} / (n_{\text{An}} + n_{\text{Ab}}) \text{ in the liquid} \quad (3)$$

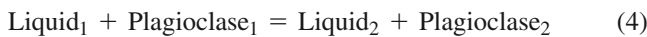
where:  $n$  = number of grams of any component

If the system weighs 100 g, and  $n_{\text{An}} = 60$  g, then  $X_{\text{An}}^{\text{liq}} = 60 / (60 + 40)$ , or 0.60. The phase rule thus tells us that, if we have a liquid in the Ab–An system *at fixed pressure*, we must specify  $T$  and a single compositional variable to completely determine the system. If we choose to specify  $T$  as 1600°C, and  $X_{\text{An}}^{\text{liq}} = 0.60$ , *all* the other variables, such as density and the other compositional variables, are fixed. Under the present circumstances, the only remaining intensive compositional variable is  $X_{\text{Ab}}^{\text{liq}}$ . Because the system is binary, it follows that  $X_{\text{Ab}}^{\text{liq}} = 1 - X_{\text{An}}^{\text{liq}} = 0.40$ .

If we cool the system to point  $b$  in Figure 8, at about 1475°C, plagioclase begins to crystallize from the melt. *However, the plagioclase that first forms has a composition at  $c$  ( $\text{An}_{87}$ ), a different composition than that of the melt.* How does the phase rule help us understand what’s going on at this point? Because  $C = 2$  and  $\phi = 2$ ,  $F = 2 - 2 + 1 = 1$ . Now we must specify only *one* intensive variable to completely determine the system. If we specify any one of  $T$ ,  $X_{\text{An}}^{\text{liq}}$ ,  $X_{\text{Ab}}^{\text{liq}}$ ,  $X_{\text{An}}^{\text{plag}}$ , or  $X_{\text{Ab}}^{\text{plag}}$ , the others must be fixed. From Figure 8 we can see that this is true. Whereas the one-component system has a single curve separating the liquid and solid fields, there are now **two curves that specify a relationship between the composition of both the liquid and the solid with respect to the temperature. The upper curve is called the liquidus. It specifies the composition of any liquid that coexists with a solid at a particular temperature. The lower curve is the solidus, which specifies the composition of any solid that coexists with a liquid phase at some particular temperature.** Remember that these diagrams are determined *empirically*. There is no way to theoretically predict the actual compositions, and the phase rule merely tells us about the variables, not what values they should have. We can thus specify one variable, such as  $T = 1475^\circ\text{C}$ . If plagioclase and liquid coexist,  $\phi = 2$ , then we specify a horizontal line at 1475°C that intersects the liquidus at point  $b$  and the solidus at point  $c$ . Points  $b$  and  $c$  represent the composition of the liquid and solid, respectively, which we could determine from the abscissa. The system is therefore fully determined. **The dashed line connecting  $b$  and  $c$  is called a tie-line, and it connects the composition of coexisting phases, by definition at a particular temperature.** Try choosing another temperature and determine the composition of the phases that coexist at that  $T$ . Next, choose any other variable from the list above. If your choice of temperature meets the requirement that  $\phi = 2$  on Figure 8, you can determine all the remaining variables. If  $\phi = 2$  for this system at fixed pressure, we need only specify one intensive variable to determine the full state of the system. In a practical sense, temperature behaves as a determining variable most commonly in nature.

What the phase rule then says for this situation is: **For a two-component–two-phase system at a fixed pressure, the composition of both phases (in this case the liquid and the solid) depend only upon temperature.** This follows directly from the liquidus and solidus curves on Figure 8. The phase diagram, which is determined by experiment, is a manifestation of the relationships predicted by the phase rule. Picture this situation in a magma chamber at some particular depth (pressure) in the crust. The composition of the plagioclase that crystallizes from a melt is a function of the temperature of that melt and thus changes as temperature changes.

As we continue to cool our original bulk mixture of 60% An below 1475°C (point *b* in Figure 8), the compositions of both coexisting phases (liquid and solid) vary. The liquid composition changes along the liquidus from *b* toward *g*, whereas the plagioclase changes from *c* toward *h*. This process is one in which the solid *reacts with* the liquid, enabling the exchange of components between them, resulting in a compositional change in the phases. Such reactions that have at least 1 degree of freedom, and thus occur by exchange over a range of temperatures (and/or pressures), are called **continuous reactions**. In this case, the generalized reaction may be represented by:



By cooling, new Liquid<sub>2</sub> becomes incrementally more Na rich than old Liquid<sub>1</sub>, and new Plagioclase<sub>2</sub> becomes more Na rich than old Plagioclase<sub>1</sub>.

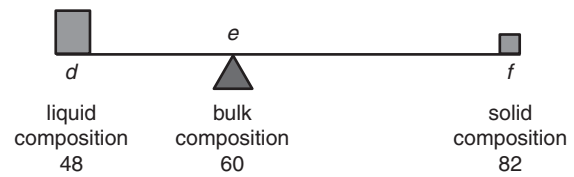
We can use the length of the tie-lines at any specified temperature to calculate the *relative* amounts of the phases. At 1445°C and a bulk composition of An<sub>60</sub>, for example, we have the tie-line *d-f* connecting the liquid and solid phases in Figure 8. The bulk composition = *e*, whereas the composition of the liquid = *d* (An<sub>49</sub>), and plagioclase has composition *f* (An<sub>82</sub>). The relative amount of liquid versus solid is calculated geometrically by reference to Figure 9, in which the quantities of each phase must balance on the bulk composition fulcrum point.

Using the lengths of the tie-line segments:

$$\frac{\text{amt}_{\text{liq}}}{\text{amt}_{\text{plag}}} = \frac{\overline{ef}}{\overline{de}} \quad (5)$$

where:  $\overline{ef}$  = length of the line segment *e-f*  
 $\overline{de}$  = length of the line segment *d-e* in Figures 8 and 9

This approach is called the **lever principle**, and it works like a fulcrum, with the amounts of the phases balanced at the fulcrum point represented by the bulk composition in Figure 9. According to Equation (4), the amount of a given phase is proportional to the length of the segment on the *opposite* side of the fulcrum. The closer a phase is to the fulcrum point (bulk composition), the more predominant it is. At 1445°C  $\overline{ef} = \text{An}_{82} - \text{An}_{60} = 22$  and  $\overline{de} = \text{An}_{60} - \text{An}_{48} = 12$ . Thus the proportion of liquid/solid is 22/12, or 1.83, or 65% liquid



**FIGURE 9** Use of the lever principle to determine the relative quantities of two phases coexisting along an isothermal tie-line with a known bulk composition.

by weight. At 1475°C, the liquid composition was essentially equal to the bulk composition, corresponding to the first appearance of a few crystals of plagioclase of composition *c*. As we continue to cool the system, with a constant bulk composition,  $\overline{ef}$  gets progressively larger, whereas  $\overline{de}$  gets smaller, corresponding with a decreasing ratio of liquid to solid, just as we would expect to occur upon cooling. Note that as cooling of the two-phase system in Figure 8 continues, *the composition of both the solid and liquid becomes richer in the Ab (low melting point) component*. As the temperature approaches 1340°C, the composition of the plagioclase reaches *h*, which is equal to the bulk composition (An<sub>60</sub>). Obviously, there can be only a tiny amount of liquid present at this point. This last liquid has composition *g* (An<sub>22</sub>) in Figure 8. Continued cooling consumes this immediately. We then lose a phase and gain a degree of freedom. We have only a single solid phase below 1340°C (plagioclase of composition An<sub>60</sub>) that cools along the line *h-i*. With a single phase,  $F = 2 - 1 + 1 = 2$ , so we must specify both *T* and a compositional variable of the plagioclase to specify the system completely.

Crystallization of any liquid of a composition intermediate between pure Ab and pure An will behave in an analogous fashion.

Equilibrium **melting** is simply the opposite process. The divariant one-phase solid system of composition *i* in Figure 8 heats up until melting begins. The partially melted system is univariant, and the first liquid formed has composition *g*. The first liquid to form is not the same as the solid that melts. As heating continues, the compositions of the solid and liquid are constrained to follow the solidus and liquidus, respectively (via a continuous reaction). The liquid moves to composition *b* as the plagioclase shifts to composition *c* (the composition of the last plagioclase to melt). Whether the process is crystallization or melting, the solid is always richer in An components (Ca and Al) than the coexisting liquid. Ca is thus more **refractory** than Na, meaning that it concentrates in the residual solids during melting.

Notice how the addition of a second component affects the crystallization relationships of simple one-component systems:

1. There is now a **range of temperatures over which a liquid crystallizes (or a solid melts) at a given pressure.**
2. Over this temperature range, the compositions of both the liquid melt and the solid mineral phases change.

Compare these to the list of eight observations on the crystallization behavior of natural melts in Section 1. Even though we have studied only a simple model system, the processes responsible for observations 1, 4, and 5 should be getting clear.

The above discussion considers only **equilibrium crystallization and equilibrium melting**, in which the plagioclase that crystallizes or melts remains in chemical equilibrium with the melt. It is also possible to have *fractional crystallization or melting*. **Purely fractional crystallization involves the physical separation of the solid from the melt as soon as it forms. If we remove the plagioclase crystals as they form (perhaps by having them sink or float), the melt can no longer react with the crystals.** The melt composition continues to vary along the liquidus as new plagioclase crystallizes along the solidus. Because the crystals are removed from the system, however, *the melt composition continuously becomes the new bulk composition*, thus shifting inexorably toward albite. As a result, the composition of both the final liquid and the solids that form from it will be more albitic than for equilibrium crystallization and will approach pure albite in efficiently fractionating systems. Fractional crystallization implies that a range of magma types could be created from a single parental type by removing varying amounts of crystals that have formed in a magma chamber.

**Fractional melting is another important geologic process. Purely fractional melting refers to the nearly continuous extraction of melt increments as they are formed. If we begin to melt a plagioclase of  $An_{60}$  composition in Figure 8, the first melt has composition  $g$  ( $An_{20}$ ).** If we remove the melt, the residual solids become progressively enriched in the high-melting-temperature component and continuously become the new bulk composition of the remaining solid system. The final solid, and the liquid that may be derived from it, shift toward anorthite.

**Most natural magmas, once created, are extracted from the melted source rock at some point before melting is completed. This is called **partial melting**, which may be fractional melting or may involve equilibrium melting until sufficient liquid accumulates to become mobile.** For example, suppose we begin with  $An_{60}$  in Figure 8 and melt it at equilibrium to 1445°C, at which point there is 65% melt (according to the lever principle) with a composition  $d$  ( $An_{49}$ ). If melt  $d$  rises to a shallow magma chamber and cools, the bulk composition in the chamber is now  $An_{49}$ , as is the final plagioclase to crystallize from this melt (assuming equilibrium crystallization). *Partial melting, then, increases the concentration of the low-melting-point component in the resulting melt system* ( $An_{49}$  rather than  $An_{60}$ ). Likewise, it increases the concentration of the high-melting-point component in the residual solids (point  $f$ ,  $An_{82}$ , at the time of melt extraction).

Partial melting processes have some important implications for the source of melts. Suppose we partially melt the mantle to produce a basaltic liquid. If only small quantities of melt are produced, the remaining solid mantle must be more refractory (enriched in high-temperature

components) than the melt produced. The mantle source will also be progressively depleted in the low-melting-point components and gradually become more refractory as partial melting continues over time, requiring successively higher temperatures in order to melt. Unless the melted source rocks are replenished by mixing with unmelted mantle, they may become sufficiently refractory that further melting is inhibited.

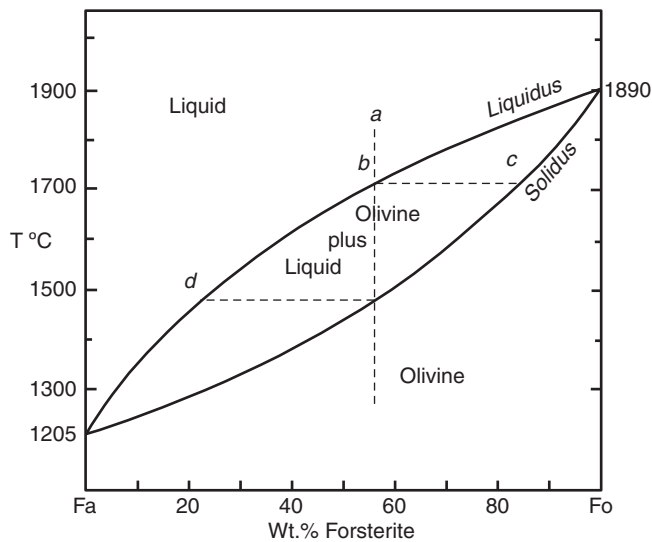
As soon as a system permits the solid and liquid portions to have different compositions, separating these phases can have a profound effect on the composition of the derivative systems. The ability to change the composition of magmas and the resulting rocks by fractional processes of melting and crystallization are thus prime methods for the production of the range of compositions of igneous rocks found at the surface of the Earth. Indeed these fractional processes are probably more common in nature than their equilibrium counterparts. We shall encounter numerous examples of these phenomena, both experimental and natural, as we proceed in our study of igneous processes.

**Compositional zoning is another disequilibrium process that can occur in solid-solution systems. Rather than react with the melt and re-equilibrate, a mineral may simply add a rim with a composition equal to the solidus composition.** Plagioclase, for example, may add a rim of new growth rather than react to maintain a single composition throughout. This results in a more calcic core and a progressively more sodic rim. Plagioclase is noted for this characteristic because the re-equilibration exchange is not simply Na for Ca but requires Al for Si as well, and this involves breaking the strong Si-O and Al-O bonds, which inhibits re-equilibration. Figure 8 implies that uniform cooling would produce successive rims of progressively more albitic composition (“normal” zoning).

Solid solutions are common in natural minerals. The most common substitution in the mafic minerals is that between Fe and Mg. This occurs in all mafic minerals and has an effect on the melting relationships similar to that in plagioclase. The olivine system,  $Mg_2SiO_4$  (Fo, forsterite) –  $Fe_2SiO_4$  (Fa, fayalite), is illustrated in Figure 10. Mg and Fe have the same valence and similar size. Mg is slightly smaller and thus forms a stronger bond in the mineral phase. As a result, the Mg-rich end-member typically has a higher melting point in olivine and other mafic minerals, and Mg is thus enriched in the solid as compared to the liquid at intermediate compositions. A melt of composition  $a$  ( $Fo_{56}$ ), for example, will first produce a solid at  $c$  ( $Fo_{84}$ ) at about 1700°C, and it will completely crystallize at 1480°C, when the final liquid (point  $d$ ,  $Fo_{23}$ ) is consumed. The behavior of the olivine system is entirely analogous to that of plagioclase.

## 5.2 Binary Eutectic Systems

Adding a second component certainly has a profound effect on a one-component system, but the effects are not limited to solid-solution behavior. In a great number of



**FIGURE 10** Isobaric  $T$ - $X$  phase diagram of the olivine system at atmospheric pressure. After Bowen and Schairer (1932). Reprinted by permission of the *American Journal of Science*.

binary systems, the additional component does not enter into a solid solution but changes the melting relationships nonetheless. As an example of a binary system with no solid solution, let's turn to a system with considerable natural applicability. The system  $\text{CaMgSi}_2\text{O}_6$  (Di, diopside)– $\text{CaAl}_2\text{Si}_2\text{O}_8$  (An, anorthite) is interesting in that it provides a simplified analog of basalt: clinopyroxene and plagioclase. The system is illustrated in Figure 11 as another isobaric (atmospheric pressure)  $T$ - $X$  phase diagram. In this type of system, there is a low point on the liquidus, point  $d$ , called the **eutectic point**. Such systems are thus called **binary eutectic systems**. Because there is no solid solution, there is no solidus (although some petrologists refer to the line  $g$ - $h$  as a type of solidus).

Let's discuss equilibrium cooling and crystallization of a liquid with a bulk composition of 70 wt. % An from point  $a$  in Figure 11. This  $T$ - $X$  phase diagram is also isobaric, so Equation (2) with a single liquid yields  $F = 2 - 1 + 1 = 2$ . We can thus specify  $T$  and  $X_{\text{An}}^{\text{liq}}$  or  $X_{\text{Di}}^{\text{liq}}$  to completely determine the system. Cooling to 1450°C (point  $b$ ) results in the initial crystallization of a solid that is *pure* An (point  $c$ ).  $F = 2 - 2 + 1 = 1$ , just as with the plagioclase system. If we fix only one variable, such as  $T$ , all the other properties of the system are fixed (the solid composition is pure anorthite, and the liquid composition can be determined from the position of the liquidus at the temperature specified).

As we continue to cool the system, the liquid composition changes along the liquidus from  $b$  toward  $d$  as the composition of the solid produced remains pure anorthite. Naturally, *if anorthite crystallizes from the melt, the composition of the remaining melt must move directly away from An* (on the left in Figure 11) as it loses matter of that composition. The crystallization of anorthite from a cooling liquid is another **continuous reaction**, taking place

over a range of temperature. The reaction may be represented by:



We can still apply the lever principle [Equation (5)] at any temperature to determine the relative amounts of solid and liquid, with the fulcrum at 70% An. If we do so at a number of temperatures, we would see that the ratio of solid to liquid increases with cooling, as we would expect.

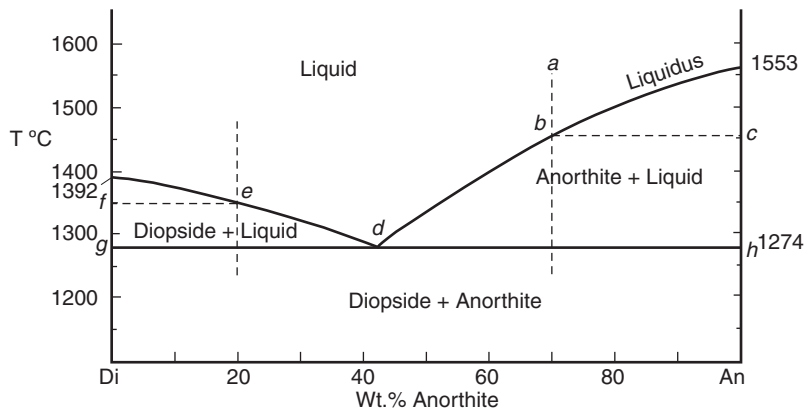
At 1274°C, we have a new situation: diopside begins to crystallize along with anorthite. Now we have *three* coexisting phases, two solids and a liquid, at equilibrium. Our horizontal (isothermal) tie-line connects pure diopside at  $g$ , with pure anorthite at  $h$ , and a liquid at  $d$ , the eutectic point minimum on the liquidus.  $\phi = 3$ , so  $F = 2 - 3 + 1 = 0$ . This is a new type of invariant situation, not represented by any specific invariant point on the phase diagram. Because it is invariant,  $T$  and the compositional variables for all three phases are fixed (points  $g$ ,  $d$ , and  $h$ ). The system is completely determined and remains at this temperature as heat is lost and crystallization proceeds (just as with our ice water and boiling water, as discussed above). The amount of liquid decreases, and both diopside and anorthite are produced. Because the *amounts* (extensive variables) of all three phases change at a constant temperature, it is impossible to determine the relative amounts of them geometrically using the lever principle. The lever principle can be applied, however, to determine the ratio of diopside to anorthite that is being crystallized at any instant from the eutectic liquid. If the liquid composition is the fulcrum (about 42% An), and the solids are pure (0% An and 100% An), the ratio of diopside to anorthite crystallizing at any moment must be 58/42. Removing this ratio keeps the liquid composition from changing from the eutectic as crystallization proceeds.

The fact that the compositions of diopside, anorthite, and liquid are collinear is an example of an important relationship that we encounter often in petrology. It is one type of geometric relationship that implies a possible reaction. When three points are collinear, the central one can be created by combining the two outer compositions (in the proportion determined by the lever principle). In the present case the reaction must be:



because liquid is in the middle. This type of reaction is a **discontinuous reaction** because it takes place at a *fixed* temperature until one phase is consumed. When crystallization is complete, the loss of a phase (liquid, in this case) results in an increase in  $F$  from 0 to 1, and thus temperature can once again be lowered, with the two phases diopside and anorthite coexisting at lower temperatures. Because the composition of the two solids is fixed, we have a unique opportunity to determine exactly which of our intensive variables is free to vary; temperature is the only variable left.

A discontinuous reaction involves one more phase than a corresponding continuous reaction in the same system, and



**FIGURE 11** Isobaric (0.1 MPa)  $T$ - $X$  phase diagram of the diopside–anorthite system. After Bowen (1915b). Reprinted by permission of the *American Journal of Science*.

because this decreases the variance, the compositions of the reacting phases do not vary as the reaction progresses. Only the proportion of the phases changes (usually until one phase is consumed). Such reactions are discontinuous in the sense that the phase assemblage changes at a single temperature due to the reaction. In this case, diopside + liquid gives way to diopside + anorthite as the system is cooled through the reaction temperature (1274°C).

Let's see what happens on the left side of the eutectic point. Cooling a liquid with a composition of 20 wt. % An results in the crystallization of pure diopside first, at 1392°C as the liquidus is encountered at point *e* in Figure 11. Diopside continues to crystallize as the liquid composition proceeds directly away from diopside toward point *d*. At point *d* (1274°C again), anorthite joins diopside and the eutectic liquid in the same invariant situation as above. The system remains at 1274°C as the discontinuous reaction, liquid = Di + An, runs to completion, and the liquid is consumed.

In these eutectic systems note that, for any binary bulk composition (not a pure end-member), *the final liquid to crystallize must always be at the eutectic composition and temperature*. The final cooled product of a binary liquid with no solid solution must contain both anorthite and diopside. To get there, we must have them both coexisting with a melt at some point, and that melt has to be at the eutectic point. Remember that solid-solution systems do not behave this way. In them, crystallization is complete when the composition of the solid becomes equal to the bulk composition, so the final liquid, and the temperature, depends on the bulk composition.

**Equilibrium melting** is the opposite of equilibrium crystallization. Any mixture of diopside and anorthite begins to melt at 1274°C, and the composition of the first melt is always equal to the eutectic composition *d*. Once melting begins, the system is invariant and will remain at 1274°C until one of the two melting solids is consumed. Which solid is consumed first depends on the bulk composition. If  $X_{\text{bulk}}$  is between Di and *d*, anorthite is consumed first, and the liquid composition will follow the liquidus with increasing temperature toward Di until the liquid composition reaches  $X_{\text{bulk}}$ , at which point the last of the remaining diopside crystals will melt. If  $X_{\text{bulk}}$  is between An and *d*, diopside is consumed first, and the liquid will progress up the liquidus toward An.

Note the discontinuities between either one-component end-member and the binary mixture. For example, pure anorthite melts at a single temperature of 1553°C. If we add just a tiny amount of Di to this, the first melt occurs at 1274°C and has a composition equal to *d*. Of course, there won't be much of this melt. (Use the lever principle if you don't see why.) As temperature increases in this An<sub>99</sub> mixture, the amount of melt increases gradually and becomes rapidly more anorthitic. Melting is extensive and complete just below 1553°C.

**Fractional crystallization** has no effect on the path followed by the liquid in eutectic systems without solid solution. Unlike in the plagioclase or olivine systems, removing a solid of constant composition does not affect the composition of either of the two final minerals or of the last liquid. The compositions of the minerals are fixed, and the liquid must reach the eutectic composition whether or not the solids are removed. Only the composition of the final rock is affected. Following equilibrium crystallization, the final rock composition is the same as the bulk composition. If fractional crystallization is efficient, the final rock composition is equal to the eutectic because earlier crystals are lost and the last liquid is always the eutectic liquid.

**Partial melting**, however, does affect the path that the liquid follows. Perfect fractional melting (removal of any melt increment as soon as it forms) should not occur in nature. As we shall see later, a critical amount of melt (perhaps 1 to 10%) must form before it can be physically removed from the solid. A smaller amount will merely wet the mineral grain boundaries and remain adsorbed to the crystal surfaces. Nonetheless, if a few percent partial melt were almost continuously removed from an initially solid sample of diopside + anorthite, and the first melts were (necessarily) of the eutectic composition *d*, the melt increments being removed would continue to be of composition *d*, until one of the solid phases was finally consumed by melting. Then the remaining solid would be a one-component system. Therefore, no melting would occur between 1274°C and the melting point of the remaining pure phase, so the composition and the temperature of the melt being extracted would *jump discontinuously* from *d* at 1274°C to either pure diopside at 1392°C or pure anorthite at 1553°C, depending on the initial bulk composition and which phase is consumed first. Thus a