The Interpretation of Geological Phase Diagrams

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W. H. FREEMAN AND COMPANY
San Francisco

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Printed in the United States of America

Library of Congress Catalog Card Number: 75–182129

International Standard Book Number: 0–7167–0254–1

1 2 3 4 5 6 7 8 9

Preface

Most textbooks currently used in geology courses include rather sketchy presentations of phase equilibria, and the student is often expected to memorize a few phase diagrams without gaining any real understanding of the nature of the various mineralogical reactions that such diagrams record. There is also a large gap between the conventional petrology text and the phase equilibrium data in the literature. This gap has widened in recent years with the proliferation of information on high-pressure, hydrothermal, and various gas-containing systems.

This book is intended for supplementary use in graduate and undergraduate courses in petrology and for reference use. Emphasis is on the interpretation and understanding of simple and moderately complex phase diagrams; the treatment of the subject is not intended to be exhaustive. Most of the examples chosen for discussion are of pertinent geological systems: others, some of which are hypothetical, are included to demonstrate particular types of diagrams or reactions. Much attention is given to systems that are under either fluid pressure or confining pressure. Bibliographic references are given at the back of the book to enable the reader to consult original works for more extensive descriptions of experimental techniques or for information on the geological ramifications of laboratory studies.

The approach used here is essentially the traditional method of the petrologist – the description of the continuous changes that take place in the kind and number of phases along paths of equilibrium crystallization or melting, as heat and/or pressure is applied or withdrawn from the system. The thermodynamics and crystal chemistry behind the phase relations presented are not discussed. References to these topics do, however, appear in the bibliography.

I wish to thank the staff and students of the Department of Mineralogy of The Ohio State University and of the Vening Meinesz Laboratory of The University of Utrecht, Netherlands, for their many discussions and helpful assistance. In particular, I wish to thank Dr. Charles Shultz for his critical reading of the manuscript, Mrs. Kathleen Wuichner for her assistance in typing, and my wife, Diane, for her patience and encouragement.

January 1972 *Ernest G. Ehlers*

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1

Pertinent Definitions and the Phase Rule

In order to read the geological literature on phase equilibria and understand the implications of the Phase Rule (the basis of the classification of equilibrium relationships), one must be familiar with some of the standard terminology. The few terms defined here will be used throughout the book, and should be understood before the reader proceeds further.

System

A system is any part of the universe that has been isolated for the purpose of considering changes that take place within it in response to differing conditions. A system may be a liquid within a beaker, a magma chamber, or even an entire planet. Usually we shall regard a system as a particular chemical substance or group of substances that exists independent of quantity or location.* Thus one may consider as a system any mixture of the three oxides CaO, Al_2O_3, and SiO_2. The oxides may exist together on the moon or in a submarine in the depths of the Sea of Okhotsk. Systems may be further subdivided into closed or open. A *closed system* is one that changes only by receiving energy from the external environment or by yielding energy to it; an *open system* may exchange both matter and energy with the external environment.

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*Normally such variables as gravity or magnetism are not taken into consideration.

Equilibrium

A system may be either at equilibrium or nonequilibrium. A system at equilibrium is in its lowest energy state consistent with the imposed conditions; it has no tendency to change spontaneously. A nonequilibrium system is one that is either changing or has a tendency to change. Similarly, a system may be defined as stable, metastable, or unstable. A *stable system* is one that is at equilibrium, whereas a *metastable system* is one that may appear to be at equilibrium but in fact is not at its lowest energy state (Fig. 1). Many of the denser minerals, such as diamond, kyanite, jadeite, or coesite, are truly stable only under pressures higher than one atmosphere; they persist metastably because reaction rates at low pressures and temperatures are extremely slow. Similarly, many minerals formed at high temperature, such as sanidine or cristobalite, are metastable at room temperature. An *unstable* mineral or mineral assemblage is one that is either in the process of changing to a more stable arrangement or just on the verge of doing so.

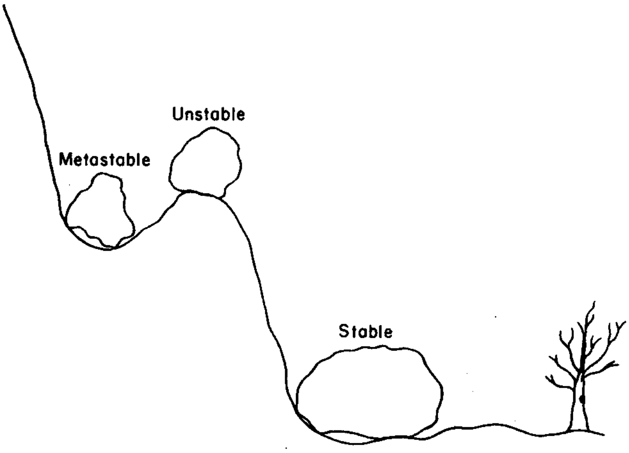

FIGURE 1
The various states of equilibrium, assuming ground level to represent the most stable state.

Phase

A phase is any part of a system that is physically distinct and mechanically separable from other parts of the system. There exists a boundary surface between different phases. Phases may exist in the solid, the liquid, or the gaseous state. Gases are completely miscible with each other, regardless of composition; consequently there can be only a single gas phase in a system at equilibrium. Although many liquids can be mixed in any proportion to form a single phase, some are partially or completely immiscible (such as oil and water); such liquids remain as separate phases with a distinct boundary surface between them. Some solids have very strict compositional limits (like quartz, which can exist only as relatively pure SiO_2); others show a wide variation in chemical composition: the plagioclase feldspars may have compositions ranging from $NaAlSi_3O_8$ to $CaAl_2Si_2O_8$. Because of the compositional limits of many solid phases, there is commonly more than one solid phase in a system.

Phase Diagram

A phase diagram is a graphic representation of the assemblage of phases that exist in a system as a function of the imposed conditions. The conditions that describe the system are usually taken as pressure, temperature, and composition, although other variables may be used. The phase assemblages indicated on the diagram are normally equilibrium (minimum energy) assemblages, but occasionally the diagrams are used to show nonequilibrium relationships.

Phase Rule

A postulate of basic importance in the classification and use of phase diagrams is the Phase Rule, derived by J. Willard Gibbs in the 1870's (see Gibbs, 1961) and later explored in more detail by many others. The thermodynamic basis of this rule is discussed in most standard textbooks on physical chemistry. The usual statement of the Phase Rule is:

$$P + F = C + 2$$

where P = the number of phases, F = degrees of freedom, and C = minimum number of components. The term C, *component*, refers to the minimum number of chemical constituents that are necessary and sufficient to describe the composition of all phases within the system. This immediately allows any system to be classified according to the number of chemical constituents present. A system that, under various conditions, may consist of water, ice, or steam, or various combinations of these, must be classified as a one-component system, since all of the phases consist of the same composition, H_2O.

Consider a system that, under various conditions, contains quartz (SiO_2), tridymite (SiO_2), cristobalite (SiO_2), and the pyroxene enstatite ($MgSiO_3$). There are two different phase compositions represented, and the system would be considered a two-component system. The choice of components in this example would normally be SiO_2 and $MgSiO_3$. If an additional phase, such as the olivine forsterite (Mg_2SiO_4) were possible in this system, the system must

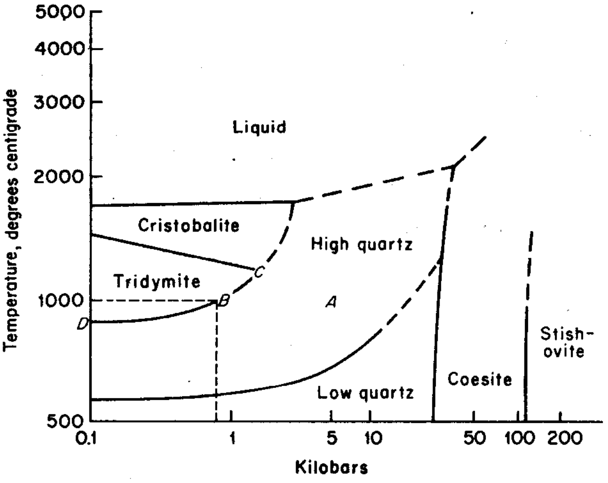

FIGURE 2
The one-component system SiO_2. [After Ostrovsky (1966); the coesite-stishovite boundary line has been revised in accordance with new data (personal communication from Ostrovsky).]

still be regarded as two-component, because all possible phases could be made up of SiO_2, Mg_2SiO_4, or a mixture of these (e.g., $SiO_2 + Mg_2SiO_4 = 2MgSiO_3$). The addition of the mineral periclase (MgO) to the system would not change the number of components, as all phases would be regarded as consisting of SiO_2, MgO, or a mixture of these.

If one were considering a system in which calcite ($CaCO_3$) undergoes a thermal decomposition to portlandite (CaO) and CO_2, it would be incorrect to regard this as a three-component system (Ca-C-O), as all of the phases can be represented in composition by two components, CaO, CO_2, or a mixture of these. The Phase Rule does not stipulate the nature of the particular components chosen, but merely the minimum necessary number. For convenience in graphical representation certain obvious combinations are chosen over others.

The term *F*, degrees of freedom (variance), can best be discussed with reference to a phase diagram. Figure 2 shows the one-component system SiO_2. Temperature in degrees centigrade is shown increasing logarithmically on the vertical axis, and pressure in kilobars is shown increasing to the right logarithmically on the horizontal axis. *One kilobar* is equal to 1000 bars, and *1 bar* is equal to 0.9869 *atmosphere*. Every point within the diagram represents a particular pressure and temperature. Furthermore, the interior of the diagram is subdivided to indicate the stability regions of the various SiO_2 phases. Thus the diagram can be used to determine the phase or phases that exist at equilibrium for any pressure and temperature. In addition to being able to exist as gas or liquid, solid SiO_2 is able to exist in six different structural modifications (polymorphs). At point *A* (1000°C and 5 kb.), high quartz is the stable

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phase; at point *B*, high quartz and tridymite exist together; and at *C*, high quartz, tridymite, and cristobalite exist together.

The term *F*, *degrees of freedom*, can be defined as the minimum number of variables that must be fixed in order to define perfectly a particular condition of the system. To do this it is sometimes sufficient to indicate the number of phases present, but often the temperature and pressure must also be stated. If one stipulates that the conditions are such as to allow the three phases cristobalite, tridymite, and high-quartz to exist together, the phase diagram shows that there is only one point, *C*, at which this is possible. The coexistence of these three phases is possible only at a particular pressure and temperature. The pressure and temperature are found from the coordinates of the diagram. As it is not necessary to state *PT* values to define the condition of the system, the number of degrees of freedom is zero. The condition of the system is perfectly defined by the statement that the three phases coexist. This may be derived from the Phase Rule by substituting the proper numbers:

$$P + F = C + 2$$

$$3 + F = 1 + 2$$

$$F = 0$$

Three phases coexisting in a one-component system lead to a condition where $F = 0$, a condition of invariance. The point *C* is an invariant point. Neither *P* nor *T* may vary (no freedom) without causing one or two of the phases to be eliminated.

Conversely, although both tridymite and high-quartz coexist at the point *B*, the coexistence of these two phases does not uniquely define the *P* and *T* of the assemblage, as there is a variety of combinations of *P* and *T* (along the line *CBD*) at which these two phases coexist. To define the condition of the system perfectly, one must be able to determine the pressure and temperature of the phase assemblage. This can be achieved by stipulating either the pressure or temperature of the two-phase assemblage. If tridymite and high-quartz coexist stably at 1000°C, it can be deduced from the diagram that the pressure on the system is somewhat less than 1 kb. There is one independent and one dependent variable. One independent variable is another way of stating that this condition has one degree of freedom or one degree of variance. For this reason, such transition lines are referred to as univariant curves. This condition is easily derived from the Phase Rule by substituting the proper values for the terms:

$$P + F = C + 2$$

$$2 + F = 1 + 2$$

$$F = 1$$

The various transition curves throughout the diagram are all univariant curves, and each possesses one degree of freedom.

To state merely that the condition of the system is such that high quartz exists alone (such as at point A) is not sufficient to define the condition of the system completely. High quartz can exist in a wide variety of P and T combinations. Pressure and temperature can be varied independently without changing the phase assemblage. The phase field of high quartz, as well as those of the other single phases, is a divariant region. Use of the Phase Rule indicates two degrees of freedom.

The Phase Rule not only allows classification of systems, but is a great aid in interpreting the diagram of the system. In the diagram for the SiO_2 system (Fig. 2), it can be noted that there is no region or point at which more than three phases can stably coexist. If a four-phase assemblage were postulated for this system, the Phase Rule would indicate that this was an impossible condition for a stable assemblage, since negative degrees of freedom are indicated:

$$P + F = C + 2$$

$$4 + F = 1 + 2$$

$$F = -1$$

Because the term F gives the minimum number of variables that must be fixed to define the condition of the system, the number must be either positive or zero. The maximum number of stable coexistent phases in a system will be present when $F = 0$. This argument can be applied to multicomponent systems; for example, it can be immediately deduced that the maximum number of stably coexisting phases in a 20-component system is 22. If additional phases are present, the system is not in equilibrium. This criterion has been used in metamorphic petrology to determine whether a particular mineral assemblage is in equilibrium (see Turner, p. 55, 1968). If the number of phases present exceeds that stipulated by the Phase Rule, nonequilibrium is proven, but the converse is not necessarily true. Although the number of phases present may be consistent with equilibrium conditions, some phases may be unstable under the set conditions. Applying the Phase Rule to metamorphic assemblages is often difficult because of lack of precise knowledge of the number of components present.

In summary then, it is possible to classify systems in terms of components. From the Phase Rule, and the number of phases present, the degrees of freedom of any phase assemblage can be determined. A divariant phase assemblage (such as the high-quartz field, Fig. 2) may be subject to change in two variables—pressure and temperature (or concentration, in systems of more than one component); these changes may take place independently. A univariant phase assemblage (curve CBD, Fig. 2) may be maintained if a change of one variable is accompanied by a dependent change in a second variable. An invariant phase assemblage (point C, Fig. 2) can be maintained only if pressure, temperature, composition, or any other dependent variables are not allowed to vary. It is the task of the experimental investigator to specify the conditions of invariancy and univariancy.

The reader should be cautioned that although many experimentally determined reactions satisfy requirements of the Phase Rule, they may not represent true equilibrium relations. The mere fact that an investigator has repeatedly synthesized a phase under particular conditions of pressure and temperature does not necessarily mean that that phase is the most stable phase under those conditions. It may merely indicate that the phase is more stable than the original starting materials. Given sufficient time (perhaps years rather than days), the mineral may convert to a still more stable form. The question of metastable reactions is particularly important in relatively low-temperature hydrothermal reactions. In an excellent discussion on the determination of equilibrium in experimental systems, Fyfe (1960, p. 565) concludes with the following statement: "Where, as has commonly happened, experimental results conflict with inferences based on geological observations, the experimentalist has a special responsibility to scrutinize and state clearly the limitations of his laboratory procedures." Similarly, the man in the field should remind himself of these limitations when applying experimental data to field problems.

2

Binary Systems

Because one-component (unary) systems are usually described in terms of variation in both temperature and pressure, they will not be discussed here; instead, they are taken up in Chapter 6, "Systems Under Confining Pressure." We therefore begin with the study of two-component (binary) systems at atmospheric pressure. For systems under atmospheric pressure, the Phase Rule (normally written $P + F = C + 2$) must be altered to $P + F = C + 1$, as pressure is not a variable. In this form it is called the Condensed Phase Rule, since any gas phase may be regarded as condensed to a liquid or as present in negligible quantities.

The simplest type of equilibrium relationship is exemplified by the behavior of the two-component system $CaAl_2Si_2O_8$ (anorthite) and $CaSiTiO_5$ (sphene), shown in Figure 3. The abscissa indicates composition, with pure $CaSiTiO_5$ at the left and pure $CaAl_2Si_2O_8$ at the right. The percentage of the component $CaAl_2Si_2O_8$ increases from left to right, as indicated by the numbered scale. The percentage of the other component increases from right to left, and is not indicated by a numbered scale. In most phase diagrams the percentages of components are given in weight percent; in some they are given in mole percent. The ordinate indicates temperature, which in most diagrams is stated in degrees Centigrade; diagrams prepared for use in ceramics, however, may state the temperature in degrees Fahrenheit.

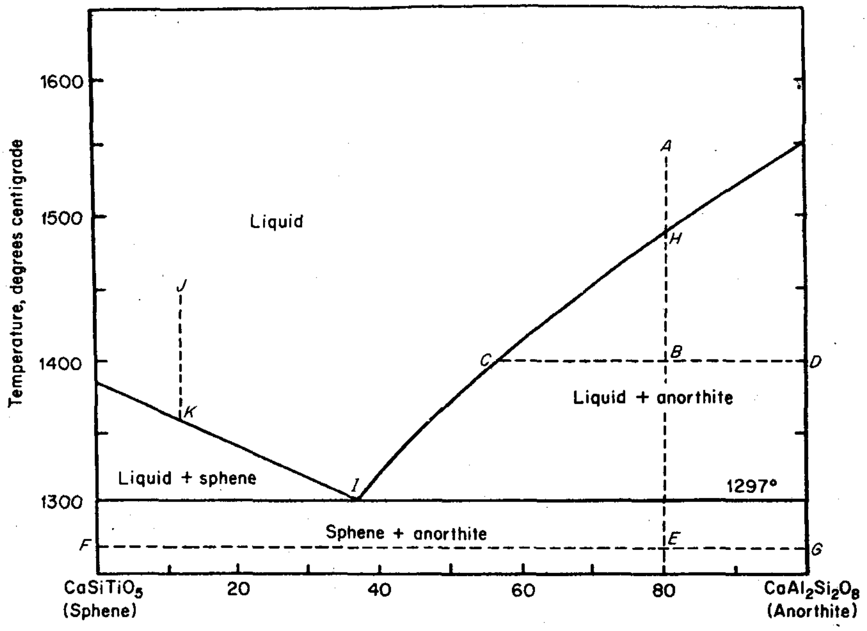

FIGURE 3
The binary system $CaSiTiO_5$—$CaAl_2Si_2O_8$.
[After Prince (1943).]

Any point within a phase diagram specifies both a composition and a temperature. The solid lines within the diagram outline regions, or fields, of temperature and composition, and the phase assemblages that exist in equilibrium within these fields are indicated by labels. As we are here considering only condensed systems, these regions are limited to assemblages of four kinds —liquid, liquid and solids, solids, and, rarely, liquid and liquid. Depending on the complexity of the system, a phase diagram may contain more than one of each kind of region. Phase diagrams are prepared from data obtained by heating samples of various mixtures of minerals, chemicals, or glasses to particular temperatures and then determining the phase assemblages that exist at those temperatures. For silicate systems this is usually accomplished by rapidly chilling (quenching) heated samples, thus preserving the high-temperature phase assemblages metastably at lower temperatures.

Observe first that in Figure 3 the various regions of the diagram are labeled as consisting of either one or two phases—liquid, liquid and sphene, liquid and anorthite, and sphene and anorthite. Any point in a one-phase field consists of a single phase with a composition indicated directly below, on the abscissa. A sample corresponding to point *A* within the diagram is a liquid phase with a composition of 80 weight percent $CaAl_2Si_2O_8$ and 20 weight percent $CaSiTiO_5$. A sample of the same bulk composition, but at a lower temperature (point *B*), lies within a two-phase region; the compositions of the two phases in that region are found by drawing a horizontal line through the point in question to the extremes of the region – in this example, the points C and D. Such a line is referred to as a *tie line,* or less commonly as a *conode.* This line indicates the compositions of the two phases that are in equilibrium with each other. The composition of the liquid phase, indicated at C, is found by reference to the abscissa to be about 57 weight percent $CaAl_2Si_2O_8$ and 43 weight percent $CaSiTiO_5$. The composition of the solid phase, indicated at point D, is that of pure anorthite, $CaAl_2Si_2O_8$. If this same bulk composition were cooled to point E within the two-phase field sphene and anorthite, it would consist of these two crystalline phases, whose compositions are read at the extreme left and right of the diagram, at points F and G; these points are connected by a tie line through E.

The tie line not only indicates the individual compositions of coexisting phases at any point within two-phase fields, but also indicates the relative *amounts* of each that exist under equilibrium conditions. Consider again the tie-line that joins liquid C with coexisting anorthite at D. It can be seen that if the bulk composition of the sample (indicated by B) is closer to the composition of one of the two phase, then the one to which it is closest must be present in the largest amount. If the bulk composition falls exactly at the midpoint between the compositions of the two phases, the phases are present in equal amounts. It is possible, therefore, to measure the distances along the tie line from the bulk composition point to each of the phase composition points and determine the relative amount of each phase present. In this example, the length CB is a measure of the relative amount of anorthite present, BD the amount of the liquid phase, and CD the total. Putting this another way we can say that

$$\frac{BC}{CD}(100) = \frac{2.25\text{ cm}}{4.15\text{ cm}}(100) = 54.2 \approx 54\%\text{ anorthite}$$

$$\frac{BD}{CD}(100) = \frac{1.90\text{ cm}}{4.15\text{ cm}}(100) = 45.8 \approx 46\%\text{ liquid}$$

This simple but extremely useful relationship has been graced with the name *Lever Rule.*

Figure 3 indicates that the mineral sphene melts at 1382°C and anorthite at 1550°C. Melts of pure sphene or anorthite will completely freeze or melt at these temperatures. Liquids formed by melting mixtures of these two minerals are completely miscible, as is shown by the single continuous liquid region in the diagram. Melts of intermediate composition have a complex freezing or melting behavior. The melt labeled A in Figure 3 consists of 80 percent of the $CaAl_2Si_2O_8$ component and 20 percent of the $CaSiTiO_5$ component. Although this melt consists mainly of $CaAl_2Si_2O_8$, it will not freeze at 1550°C, as does pure $CaAl_2Si_2O_8$. The effect of admixing $CaSiTiO_5$ is to depress the freezing point of the melt below that of pure $CaAl_2Si_2O_8$. The liquid can be cooled to a temperature of about 1490°C before freezing begins (point H). At temperatures

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