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THE RÔLE OF TEMPERATURE IN MINERALOGY*

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ABSTRACT

Temperature endows a mineral with energy beyond that of its static crystal structure. This excess energy is the cause of many well-known mineralogical relationships, which can be comprehended as transformations.

Three different structural changes may occur in the transformation of one crystalline phase to another (polymorphism). High-low transformations may be called *displacive* from a structural viewpoint since they correspond with slight displacements of the atoms. Forms connected by displacive transformations always have related symmetries, the high-temperature form having the higher symmetry. Sluggish transformations may be called *reconstructive* since they correspond structurally to destruction of one structure and construction of a new structure from the same units. Changes of coordination number are brought about by a *semi-reconstructive* transformation. Gradual transitions correspond structurally with disordering of the atoms in the structure. Forms connected by gradual transition also have related symmetries.

Disorder is the cause of solid solution. Falling temperature requires ordering. If the crystal which must become ordered is a solid solution, it is necessary for one phase to trans-

* Address of the retiring President of The Mineralogical Society, delivered at the twenty-eighth annual meeting of the Society, Ottawa, Ontario, December 29, 1947.

form into two; in other words, the ordering causes unmixing. Many common minerals, such as the feldspars, have hitherto unrecognized high-temperature forms due to a disorder transition.

Another kind of transformation develops when an energy increase can disrupt *part* of the structural unit. When the character of the structure permits this, a reaction series results. Thus Bowen's reaction series is merely a series of increasingly fragmented silicate units.

Disorder is an important factor in metamorphism. Whenever the temperature is high enough to cause crystal growth (grain growth), it is also high enough to support a sufficient amount of diffusion to render the structure a blotter for certain foreign atoms. The diffusion of these atoms causes a wave of replacement. In a crude way, replacement amounts to a diffusion of the smaller atoms through the interstices of the larger ones. Since the volume of a mineral is dominated by the volume contribution of its larger atoms, replacement tends to occur on an approximately volume-by-volume basis, a characteristic of the process which was empirically discovered by Lindgren many years ago. In metasomatism studies, the oxygen (or other large atom) should be regarded as constant rather than some oxide, such as silica or alumina.

Among the thermo-structural relations which invite further investigation is the entire feldspar problem. The alkali feldspar relations are briefly discussed. It is also pointed out that the natural plagioclases do not constitute a simple solid solution series, but that the low-temperature part of the plagioclase phase diagram must have as end-members, low albite and low anorthite, and that intermediate members are not solid solutions of these end members, but mixtures of them.

INTRODUCTION

The mineralogist is accustomed to think of certain minerals as high temperature minerals and of others as low temperature minerals. He often fixes the general temperature range of deposition of a mineralogical suite with the aid of mineral thermometers. In a similar way, the petrologist knows that certain igneous rock types are of comparatively high temperature origin while others arise at lower temperatures. He also deduces that certain metamorphic events occurred at high temperatures, others at comparatively low temperatures.

Temperature is evidently an important parameter to the geologist. Minerals are the ultimate geological units, and it is obviously desirable that the geologist have an intelligent understanding of the rôle of temperature in the relationships between these units. It is the purpose of this address to bring together some of the more important temperature relationships between minerals, and particularly to show that these relationships can be understood in terms of the structures of the minerals involved. Naturally, in the short time available, the subject cannot be treated exhaustively, so attention will be directed to certain cases which recommend themselves either because of simplicity or geological interest.

Temperature relationships between minerals may be generically regarded as kinds of transformations. This term may be used to cover not

only polymorphism, but also such relations as solid solution, unmixing, reaction pairs in a reaction series, and even some of the relations of metamorphism.

POLYMORPHISM

Thermodynamic Background—The simplest kind of transformation is one involving the change of one crystalline modification into another, namely the polymorphic transition. The general thermodynamic account of the polymorphic transition is well known. Under a given set of conditions, each of the several polymorphic forms of a compound is characterized by an important potential, its free energy. Thermodynamically, a reaction tends to occur which causes a decrease in the free energy of the system. Thus all possible polymorphic forms tend to transform into the one characterized by the minimum free energy. This form is said to be the stable form under the given conditions.

The free energy, A , is the difference between two quantities:

$$A = E - TS, \quad (1)$$

where E is the internal energy, T is the absolute temperature, and S is the entropy. This last quantity is a kind of logarithmic measure of the

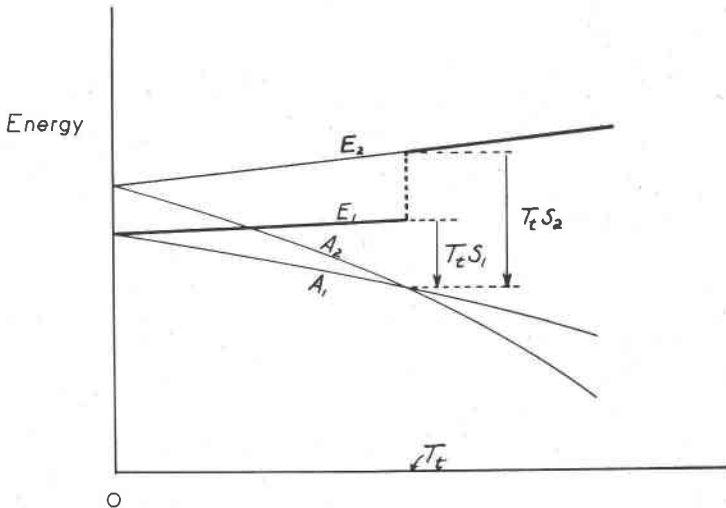


FIG. 1

amount of departure of the crystal from perfect order. Such disorder can be caused not only by departure of an atom from its equilibrium position due to heat motion, but also due to a kind of solid solution.

At absolute zero, the TS term vanishes, and the free energy becomes equal to the internal energy of the crystal, E . Thus, at very low temperatures, the internal energy dominates the free energy, and the polymorphic form with the least internal energy tends to be the stable one. But with increasing temperature the TS term becomes increasingly important, and it may happen (Fig. 1) that, due to the possibility of larger entropy in a second structural arrangement, its TS term so reduces its free energy that, in spite of greater E , the difference between these two terms is greater than that for the first polymorphic form. If this occurs before the first form disintegrates by melting, then the second form becomes the stable one, and the first form tends to transform into it. The temperature at which the free energies become just equal is the transition temperature.

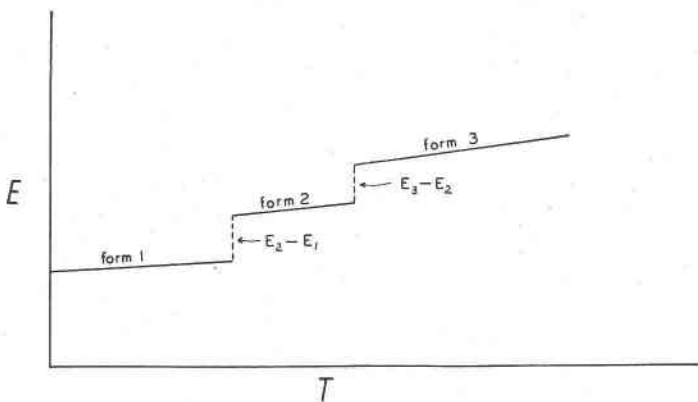


FIG. 2

Note that the second form has a higher internal energy, E , than the first form, and that the difference between the E of the second form and the E of the first form must be supplied to the latter to make the transition occur. This difference is the latent heat of the transition, and, from what has been said, it must be positive for the first transformations. More generally, it can be shown on thermodynamic grounds that it must always be positive in the direction of increasing temperature. For this reason, if one plots the internal energies of a series of polymorphic forms, there results a series of sloping steps, Fig. 2. The significance of this is that a series of polymorphic forms stable at increasing temperatures must have increasing internal energies.¹

¹ Buerger, M. J., and Bloom, M. C., Crystal polymorphism: *Zeits. Krist. (A)*, **96**, 194 (1937).

Conversely, the entropies of a series of polymorphic forms increase for the forms stable at increasing temperatures. Since the entropy involves the volume over which the atoms may be disordered, there is a tendency for the forms of higher entropy to have greater open spaces available for thermal motion. While this does not necessarily involve openness of the entire structure, it often does, so high temperature forms tend to be less dense than low-temperature forms. It should be observed that temperature and pressure tend to impose opposite conditions, for, while high temperature tends to require an open structure, high pressure tends to require a compact one.

Structural Control of Polymorphic Transformations—Polymorphic transitions differ radically in the speed of the transformation. Of course, this depends on the type of barrier opposing the transition. From a structural point of view, the speed of the transformation should depend on the characteristics of the two structures it connects, and on the path of the structure during the transformation. The barrier opposing the transformation and regulating its speed should be represented by the structural bonds which it is necessary to disturb during the transformation.

When the structural barriers are taken into consideration, polymorphic transitions fall into the following classification:

CLASSICAL TRANSFORMATIONS

Reconstructive
Semi-reconstructive
Displacive

DISORDERING TRANSFORMATIONS

Domain disordering
Rotational disordering
Substitutional disordering

The Classical Transformation—A polymorphic transformation classically involves a change from one ordered structure to a different one. (Here, "ordered" disregards the vibrational disorder of thermal motion.) It is characterized by sharp discontinuities in physical properties.

It has been long recognized that two distinct and radically different types of transformation may be involved between the several polymorphic forms and one and the same substance. Sosman has called these² sluggish and high-low transformations. The first is an exceedingly slow transformation while the second is extremely rapid. These very different transformation speeds can be understood by recognizing two different transformation mechanisms:

² Sosman, Robert B., *The Properties of Silica* (The Chemical Catalog Co.), New York, 1927.

There exist polymorphic pairs whose structures are so different that the only way a transformation can be effected is by disintegrating one structure into small units and constructing a new edifice from these units. Such a transformation is appropriately called a *reconstructive transformation*. Examples are the transformation between senarmontite and valentinite, and the transformations between any of the pairs of the set, quartz-tridymite-cristobalite.

A reconstructive transformation requires the breaking of all the first coordination bonds of some small unit (probably the SbO_3 triangle in Sb_2O_3 , and the SiO_4 tetrahedron in SiO_2). The barrier is approximately the heat of vaporization of such a unit. If the vapor pressure of the substance is low, as it is for most minerals at the transformation point, such a transformation may not go on at an appreciable rate unless the mineral is in the presence of a solvent which permits the unit to exchange its bonds in the structure for bonds in the solvent, which then transports the unit to the new structure. This structural transformation obviously corresponds with the phenomenological sluggish transformation.

On the other hand, there exist polymorphic pairs which are structurally so similar that a very slight displacement of the relative parts of one structure serve to transform it into the other without the disruption of any of the first-coordination bonds of the atoms. Mathematically speaking, such polymorphic pairs are topologically equivalent. This kind of transformation may be called a *displacive* transformation. Examples are the high-to-low quartz, and high-to-low cristobalite transitions.

Phenomenologically, the displacive transformation is the high-low transformation. It has some remarkable characteristics. It occurs instantaneously and cannot be delayed because the barrier to transformation is low compared with level of the available thermal energy. It, therefore, occurs spontaneously, and is transmitted as a wave along with the transmission of heat in the crystal. For this reason, it is impossible to preserve the high form by mere quenching. Furthermore, a symmetry relation exists between the high and low forms. The low form always contains some of the symmetry elements of the high form.³ It is because of this that the transformation from the high to the low form frequently gives rise to inversion twins.⁴

The symmetry relationship between polymorphic pairs connected by a displacive transformation is often a useful tool in mineralogical investigation.⁵ One sometimes sees reference to a general rule to the effect that

³ Buerger, M. J., Derivative crystal structures: *Jour. Chem. Phys.*, **15**, 1-16 (1947).

⁴ Buerger, M. J., The genesis of twin crystals: *Am. Mineral.*, **30**, 469-482 (1945).

⁵ Buerger, M. J., and Buerger, Newton W., Low-chalcocite and high-chalcocite: *Am. Mineral.*, **29**, 55-65 (1944).

any high temperature form has a higher symmetry than the corresponding low temperature form. This is not true. The symmetry relation only holds if the pair of polymorphs is separated by a displacive transformation or by an ordering transformation (see beyond).

There is still another type of transformation which occupies a position which is somewhat intermediate between the displacive transformation and the reconstructive transformation. This is here designated the *semi-reconstructive transformation*. With some structural pairs, it is possible to discover a transformation scheme whereby one form may be imagined to be transformed into the other sheet by sheet. Each sheet changes in shape and is sheared relative to neighboring sheets.⁶ The importance of this possible type of transformation appears to depend on whether the structural change in polymorphism involves a change in coordination number or not. When it does, this transformation may be rapid. Where it does not, it appears to be sluggish, and then it is merely a specific mechanism for effecting a reconstructive transformation. This is because the process always requires a change in bonds in the first coordination sphere, and therefore resembles a reconstructive transformation. If a semi-reconstruction transformation is imagined to occur between structures of the same coordination, this scheme requires a change of coordination which implies a disruption of first coordination bonds. This imposes a barrier equivalent to that found in a reconstructive transformation to such changes, and the transformation is accordingly very slow except in metals, where the first coordination actually occurs between an atom and its surrounding electron gas. On the other hand, where the relation between the polymorphs requires a change of coordination anyway, and where this scheme specifically supplies the required change, there is no intermediate barrier, and the transformation may be quite rapid. This is presumably the kind of rather rapid transformation which takes place in iron, cesium chloride and ammonium chloride.

In semi-reconstructive transformations, there is no necessary symmetry relation between the high and low forms. The coordination number, however, changes so that it is ordinarily higher for the low form and lower for the high form. For example, with increase in temperature, there is a change in coordination number from 8 to 6 in the transformation of cesium chloride and similar compounds, from 4 to 2 in tin, and from 12 to 8 in the highest transformation of iron. This coordination change is consistent with low energy, low entropy for the low form, and high energy, high entropy for the high form, as will be pointed out later. The rule is

⁶ Shôji, Hikoroku, Geometrische Beziehungen unter den Strukturen der Modifikationen einer Substanz: *Zeits. Krist. (A)*, **77**, 381-410 (1931).

violated apparently only by the lower structural transformation of iron, which may be complicated by a residue of magnetic features.

Disordering Transformations—Increase in temperature favors increase in entropy and this may involve disorder of all kinds. There are several types of transitions due to disorder other than vibrational disorder, which are connected with such phenomena as ferromagnetism and ferroelectricity. For the most part such transitions are not of direct interest in mineralogy. Rotation is another type of disorder which occurs at elevated temperatures. If a crystal contains tight groups of atoms, thermal agitation can sometimes set such groups into rotation and consequently throw that part of the crystal into rotational disorder. It seems likely that the transformation of calcite at 970° C. observed by Boecke⁷ is of this character, and corresponds with the onset of rotation of the CO₃ group.

While the types of disorder just mentioned are not of much interest mineralogically, there is another type of disorder which is of paramount interest to mineralogists. This is the transformation due to substitutional disorder. This was first suggested for crystals by Tamman,⁸ on the basis of the increase of electrical resistance in Cu₃Au with rising temperature. The matter was confirmed in an *x*-ray investigation by Johansson and Linde,⁹ but the concept was not generally accepted by physicists until it was popularized by Bragg and Williams.¹⁰ Since then there have been numerous theoretical and experimental contributions to the subject. It should be pointed out, however, that the disorder transformation had already been deduced by mineralogists,¹¹ for such a transformation is required to explain some of the well-known mineralogical cases of solid solution and of unmixing. On the other hand, mineralogists have made comparatively little subsequent use of this transformation in explaining certain features of crystals which are probably more prominent in mineralogy than in any other field.

If a crystal contains two (or more) chemically-different kinds of atoms which play similar rôles in the crystal structure, then, under appropriate thermal conditions, disorder may occur between these atoms, provided that the thermal agitation required does not first decompose the crystal

⁷ Boecke, H. E., Die Schmelzerscheinungen und die umkehrbare Umwandlung des Calciumcarbonats: *Neues. Jahrb. f. Min., etc.*, 1912, I, 91–121, esp. 113–118.

⁸ Tamman, G., Die chemischen und galvanischen Eigenschaften von Mischkristallreihen und ihre Atomverteilung: *Zeit. Anorg. Chem.*, **107**, 1–239 (1919).

⁹ Johansson, C. H., and Linde, J. O., Röntgenographische Bestimmung der Atomanordnung in Mischkristallreihen Au-Cu und Pd-Cu: *Ann. Physik*, **78**, 439–459 (1925).

¹⁰ Bragg, W. L., and Williams, E. J., The effect of thermal agitation on atomic arrangement in alloys: *Proc. Roy. Soc., A*, **145**, 699–730 (1934).

¹¹ Buerger, M. J., The temperature-composition-structure behavior of certain crystals: *Proc. Nat. Acad. Sci.*, **20**, 444–453 (1934).

by melting it. This phenomenon may be discussed in elementary and general terms as follows:

Suppose a crystal contains, among its many atoms, two, designated **A** and **B**, which occupy similar structural positions in the structure. For example **A** and **B** may be Cu and Fe in tetrahedral coordination in a sulfide, or they may be Al and Si in tetrahedral coordination in a silicate, or they may be Fe and Ti in octohedral coordination in an oxide. Suppose all other atoms in the structure are symbolically represented by **C**. The composition of the crystal is now symbolically represented by **ABC**.

Now the temperature energy of the crystal has an average value of kT , where k is Boltzmann's constant, and T is the absolute temperature. The atoms **A** and **B** are held to their positions by bonds also having definite energy values. If the temperature is high enough to make the thermal energy, kT , comparable with the bond energy, then the thermal energy may occasionally detach an atom from one or more of its bonds and partially free it from its place in the structure. If the structure contains any opening, atoms **A** and **B** may temporarily be ejected into them. This is particularly probable in open structures such as those of some of the tetrahedrally linked sulfides. If neighboring **A** and **B** atoms are simultane-

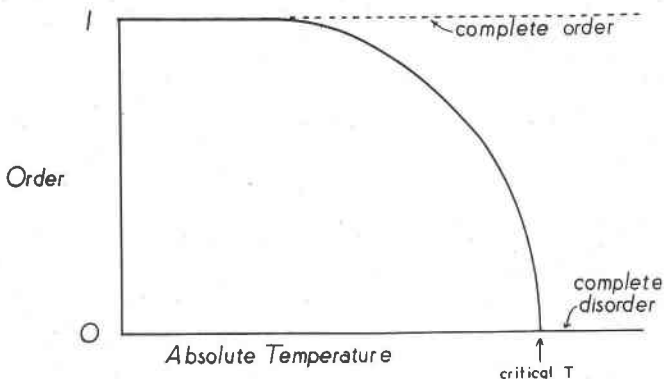


FIG. 3

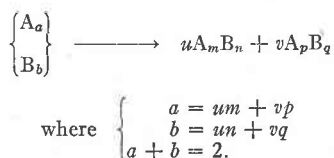
ously ejected from their positions in the structure, they may either return to their original positions, or they may interchange positions provided their motions are correctly directed. If the latter occurs, then this pair of **A** and **B** atoms is in disorder. This increases the energy of the crystal by an amount which will be designated V . (If there were not this energy difference favoring the original structure, it would not have crystallized as an ordered structure.) Two tendencies now oppose one another. The interchange energy, V , tends to favor the return of dis-

DISORDER AND UNMIXING

A mineral capable of disorder can be expected to exist in quite different compositions depending on whether it was deposited above or below the critical temperature of disorder. If the temperature of formation is below the disordering temperature, the structure must reject an excess of **A** or **B** atoms and accept only formulary amounts of **A** and **B**. On the other hand, if the temperature of formation is above the disordering temperature, nothing prevents an excess of **A** or **B** from entering the structure, for the structure does not distinguish between **A** and **B** atoms. With an excess of **A** atoms the composition of the crystal can be represented by

$$\left\{ \begin{array}{l} A_{1+x} \\ B_{1-x} \end{array} \right\} C, \quad \text{or} \quad \left\{ \begin{array}{l} A_a \\ B_b \end{array} \right\} C, \quad \text{where } a + b = 2.$$

Consider what happens when this disordered crystal of irrational composition is cooled below its disordering temperature. The structure cannot transform into an ordered structure because this requires the ratio of a to b to be a simple fraction. The atoms can attain order, however, if the disordered crystal decomposes into two ordered crystals. This can occur as follows, in so far as the ordering of **A** and **B** are concerned:



Here a and b are not integers but m and n , also p and q , are integers. Thus the irrational ratio of a to b is transformed into the irrational amounts u and v of the two new ordered crystals. This process, of course, is unmixing, specifically complete unmixing from complete solid solution.

For simplicity, unmixing has been discussed as the extreme case of splitting a completely disordered crystal into two completely ordered ones. This corresponds to having the disordered crystal above the critical temperature and the ordered crystals at absolute zero. Actually, the ordering process covers a range of temperatures, partly because the transformation temperature depends on composition, partly because there is a permissible small amount of disorder at any non-zero temperature.

The unmixed crystal pairs grow in such a relation to one another as to minimize the energy of the new surface of separation. Now, two structures can have a low energy interface if they have a common structural plane. If they have only one common structural plane, the boundary between unmixed structures tends to be planar. For this reason sheet-like

unmixing structures are common. Cubanite in chalcopyrite provides an example. If the two crystals are nearly or exactly isostructural, they have many structural planes in common and the exolved crystal tends to have a bleb-shaped form. Chalcopyrite in sphalerite is an example of such an unmixed form.

Whenever unmixing occurs from a crystal having the compositional form of a double salt, it is an indication that a considerable amount of disorder is tolerated among the metals of the double salt. This suggests a possible disordering transformation in the host mineral involved. Possible examples of the disorder transformation can be inferred from the following examples of unmixing from double salts:

silver	from dyscrasite
cubanite	from chalcopyrite
chalcopyrite	from bornite
pyrrhotite	from pentlandite
chalcopyrite	from stannite
hematite	from ilmenite
albite and anorthite	from labradorite (see beyond)

DIFFUSION, DISORDER AND LIMITED SOLID SOLUTION

The process of ordinary self-diffusion in crystals resembles that of substitutional disorder. It occurs when the thermal energy is sufficient to detach atoms from the bonds to their nearest neighbors. Thus partly freed, the atoms may return to their own places or they may interchange places with their neighbors. The latter instances contribute to diffusion. As is the case of disorder, this type of diffusion may be expected to take place most readily in the more open structures, such as the tetrahedral structures.

In self-diffusion, there is no interchange energy, V , as in the case of disorder, because the diffusing atoms are alike. However, any given level of the thermal energy is capable of supporting a certain amount of disorder. Thus, if impurity atoms are available at the time of the formation of the crystal, they can be tolerated up to the allowed disorder level and are accordingly accepted up to this level by the structure. When the temperature falls, however, this amount of disorder can no longer be thermally maintained, and unmixing ensues provided an appropriate guest structure of low energy exists.

Examples of unmixing from solid solutions which were maintained by thermal diffusion are:

chalcopyrite	from sphalerite
bornite	from chalcocite
millerite	from lineaite

ilmenite	from hematite
ilmenite	from magnetite
albite	from orthoclase

METAMORPHISM AND GEOCHEMISTRY

I have endeavored to focus your attention more and more sharply on the disordering tendency of temperature. We have seen that the disorder supported by temperature occurs not only as simple vibrational disorder, but also as domain disorder, rotational disorder, and finally substitutional disorder. This last is nothing more than a generalized type of diffusion. This very feature provides the essential mechanism of metamorphism, and more generally, it is the agent of geochemistry.

Metamorphism involves many factors which we cannot consider in any detail. Specifically, it often involves pressure, a discussion of which is outside the range of this discourse. I do wish, however, to point out that the really essential factor in metamorphism is temperature, and that without an adequate temperature level there is no metamorphism.

Consider one of the simplest instances of metamorphism, the matter of the recrystallization and grain growth of a monomineralic rock, such as a limestone. To drive recrystallization, some kind of energy difference is required. This is ordinarily supplied in the form of strain energy consequent upon plastic deformation.¹² The energetics are then somewhat analogous to those involved in a polymorphic transformation. The strained material is, in effect, a metastable polymorph, and the energy difference between the strained and unstrained mineral is the potential which drives the transformation. It is opposed by a structural barrier which prevents the transformation unless temperature provides the required activation energy. During the recrystallization, the crystalline matter at points of greatest strain transforms into small strain-free nuclei. The process probably takes place by essentially a semi-reconstructive transformation. The temperature of recrystallization is known to be lowered with increasing strain energy,¹² but it would not occur at all if it were not for the existence of temperature, for the energy associated with the temperature is required to supply the activation energy necessary for the transformation. Nor would the subsequent growth of crystal dimensions occur in metamorphism unless thermal energy supplied the activation energy necessary to remove atoms from one crystal and implant them on the growing crystal. Thus, no limestone would ever recrystallize at absolute zero, nor would it recrystallize in geologically

¹² Buerger, M. J., and Washken, Edward, Metamorphism of minerals: *Am. Mineral.*, 32, 296-308 (1947).

available time unless the temperature is above a certain level characteristic of the mineral and its strain. Of course, this is why unmetamorphosed limestones exist in very old rocks.

It is known that the activation energy of grain growth in metals is about twice the activation energy required to make the metal atoms diffuse through their own solid structure.¹³ The reason for this, evidently, is that more bonds must be broken to transport an atom across a crystal boundary than to merely pass it along in the same structure. *There is an important geological significance to this relation, for it implies that whenever the temperature is sufficiently high to cause spontaneous growth of the crystals, it is already maintaining a very high level of diffusion.* In this condition, the smaller atoms, at least, may be expected to be rather freely migrating through the remainder of the structure of the crystal. Thus, whenever the rock is in a condition to recrystallize, it is also something of a blotter for available atoms, thanks to temperature. It is, therefore, evident that wholesale diffusion must play an important rôle in the transfer of chemical material in metamorphism.

Not only must diffusion play an important rôle in metamorphism, but it appears that sulfide replacement in ore deposits is on a similar footing, for such features as unmixing bespeak free diffusion. The process occurs at lower temperatures in sulfides than in the rock minerals because the tetrahedral coordination of sulfur imposes a rather open structure on its minerals. Thus, at moderate temperatures a sulfide can hardly avoid blotting up the atoms supplied to it by the surrounding solutions. As the atoms are passed along, a wave of replacement ensues.

Lindgren long ago pointed out¹⁴ that replacement occurs on approximately a volume-by-volume basis. While the field evidence for this has been obvious, the mechanism for accomplishing it has been obscure. Diffusion suggests the mechanism. There is a tendency on the part of crystals to have their volumes determined by their largest atoms. Thus, the volumes of the rock minerals are dominated by their oxygen atoms and the volumes of the sulfides are dominated by the packing of the sulfur atoms. Replacement is, therefore, substantially a matter of the diffusion of new metals into the volumes dominated by oxygen or sulfur atoms. Thus diffusion supplies a mechanism for approximately maintaining volume during replacement.

In studying metamorphism, it is customary to consider that some oxide, such as silica or alumina, has remained constant while other oxides

¹³ Beck, Paul A., Kremer, Joseph C., and Demer, L., Grain growth in high purity aluminum: *Phys. Rev.*, **71**, 555 (1947).

¹⁴ Lindgren, Waldemar, Mineral Deposits, 3rd edition (McGraw-Hill, New York), p. 798 (1928).

have varied in the process. Evidently a closer approximation would be that the *oxygen* content has remained nearly constant while the wandering interstitial metals themselves have varied with the change.

GENERAL STRUCTURAL CHARACTERISTICS AND TEMPERATURES

Polymorphism is essentially a matter of the variation of structures in a one-component system with temperature (or other conditions). In the discussion of polymorphism, it was seen that certain generalizations could be made in understanding the variation of structure with temperature. Some of these features are of such generality that they can be carried over into a discussion of phase changes in multicomponent systems.

Coordination Number and Temperatures—In discussing the semi-reconstructive transformation in polymorphism, it was pointed out that the higher temperature polymorph tends to have lower coordination. This feature is not peculiar to polymorphism, although it is more obvious in that relation than in more general relationships merely because the variable of chemical composition is held constant. More generally, if an atom can assume several possible coordinations, there is a general tendency for it to display the lower coordination in crystals formed at elevated temperature. In mineralogy, aluminum is well-known to assume coordinations with oxygen of either four or six, perhaps even five, and there is some evidence that different coordinations can also be displayed by iron, boron, and possibly magnesium. In typically high temperature crystals, there is a tendency for aluminum to assume a coordination of four, and in this rôle it often substitutes for silicon. In typical lower temperature minerals, it tends to assume six coordination. The four and six coordination tendencies of aluminum are illustrated in feldspar and the clay minerals, respectively, which are characteristically high and low temperature minerals. Minerals of intermediate temperature affiliations may have both four and six coordinated aluminum, as in the case of the micas.

The general tendency for lower coordinations at higher temperatures appears to be a matter of high entropy coupled with lower internal energy. Atoms in lower coordination are freer to wander over larger volumes, and thus have larger entropies. At the same time, if the bond is electrostatic, and the atom can assume either high or low coordination, the low coordination is the one of high energy. In this way, the free energy

$$A = E - TS$$

is minimized by high coordination at low temperature and low coordination at high temperature.

It might be pointed out that this situation, which has been discussed for the first coordination of an atom, holds for the second coordination

as well, and in an even more obvious form. Thus, in the displacive transformation, the first coordinations of all atoms are constant, but in their higher coordinations, particularly the second coordinations, all atoms move away from one another as the temperature is increased through the transformation point. This provides greater space for thermal motion, thus increasing the entropies of the atoms at the expense of energies of their second coordinations and the energy of bond distortion.

Melting and Reaction Relations—There is an interesting relation between the arrangement of minerals in Bowen's discontinuous reaction series and the order of increased sharing of oxygen atoms by silicon atoms in the silicates. In all silicates, the silicon atom is surrounded by four oxy-

Number of oxygen atoms shared per silicon tetrahedron	Type	Example	Bowen's discontinuous reaction series
0	orthosilicates	olivine	olivine
1	pyrosilicates	melilite	
2	metasilicates	pyroxene	{ Mg pyroxenes
half 2, half 3	double chain silicates	amphiboles	{ Mg, Ca pyroxenes amphiboles
3	sheet silicates	micas	{ biotite
4	network silicates	quartz	{ muscovite quartz

gen atoms in tetrahedral coordination. Each oxygen atom may belong to one silicon atom only or it may be shared between two neighboring silicon atoms. If it is shared, then the oxygen:silicon ratio is reduced, and the formula of the silicate departs from the formula of the pure tetrahedron, namely SiO_4 . Since each silicon tetrahedron may share any number up to four oxygen atoms with its neighbors, several silicate formulae are possible which depart the more from SiO_4 the greater the number of the four possible oxygen atoms shared. The general sharing schemes which have been found by crystal structure studies of the silicates are shown in comparison with Bowen's reaction series, in the accompanying table. The comparison between Bowen's reaction series and the number of shared oxygens in the silicon tetrahedron is striking. What is its significance?

Two factors appear to be involved. In the first place, it must be evident that thermal agitation sufficient to disintegrate a structure of linked tetrahedra must leave fragments of simpler linking. Thus a mica sheet

could conceivably be disintegrated into amphibole double chains, pyroxene single chains, melilite pairs, or single unshared tetrahedra, all plus a residue. In a similar manner any of the linked structures higher in the series can be disintegrated into fragments of structures having less sharing. Thus with increasing temperature the breakdown sequence is networks, multiple chains, single chains, tetrahedron pairs, and single tetrahedra, all plus a residue which appears as a glass. This corresponds very well with Bowen's up-temperature sequence, except for the presence in the theoretical sequence of the pyrosilicates which are absent in Bowen's series.

This is a purely geometrical picture. A bond picture is also involved. As an obvious consequence of Pauling's rules, the number of atoms which bond together the silicate units depends on the number of *unshared* oxygen atoms. Thus, the greater the sharing, the fewer the bonding atoms, the looser the binding of silicate units to one another, per silicon atom, and the lower the temperature of disintegration of the structure.

Consider, now, the effect of aluminum. If the aluminum proxies for silicon in certain tetrahedra, the saturation of the oxygens of those tetrahedra is reduced and they are capable of contributing to stronger bonding between silicate units than without the aluminum. In this way, the presence of aluminum proxying for silicon in a silicate increases its disintegration temperature and consequently raises its position in the reaction series. This is true for both discontinuous and continuous reaction series. The effect of aluminum in a discontinuous reaction pair can be seen in the higher position of leucite (Al:Si=1:2) with respect to orthoclase (Al:Si=1:3). The effect of aluminum in a continuous reaction series is illustrated by the higher position of anorthite (Al:Si=1:1) with respect to albite (Al:Si=1:3).

SOME THERMO-STRUCTURAL PROBLEMS OF MINERALOGY

I conclude my remarks by pointing out the nature of some of the outstanding, yet simple, problems which concern the mineralogist interested in structure. The purely geometrical aspects of the structures of many mineral groups are now fairly well established. The forefront of structural interest has, therefore, moved to the elucidation of some of the more general problems of mineralogy. Chief of these is the clarification and explanation of phase relationships. The relationships between the feldspars may be taken as a typical case. Something is known of these relationships, but much remains to be done before they are truly cleared up.

The Alkali Feldspars—It has been recognized for some time that the alkali feldspars display polymorphism. Thus microcline is triclinic while

the orthoclases, adularia and sanidine, are monoclinic. It is known that prolonged heating transforms adularia slowly into sanidine,¹⁵ but that it has proven more difficult¹⁶ to experimentally transform microcline into sanidine. Barth¹⁷ suggested an explanation for the microcline-sanidine relationship. Expressed in present day language, he postulated that one aluminum and three silicon atoms, which occupy similar structural rôles in the alkali feldspars, are in disorder in sanidine but are ordered in microcline. Since disorder gives rise to statistical high symmetry while order requires reduced symmetry, this accounts for the monoclinic-triclinic feature of the polymorphism. (Incidentally, the Scotch-plaid twinning of microcline is reminiscent of order twinning.)

Barth is less certain about the adularia-sanidine relationship, but he suggests that some aluminum-silicon rearrangement is responsible for this also. If order and disorder among the aluminum and silicon atoms accounts for the microcline-sanidine relationship, as I believe it does, it is easy to understand that the thermal energy required to interchange the silicon and aluminum over the barrier of their oxygen coordination may be too high to allow appreciable experimental conversion of microcline to sanidine. But if this is so, it ought also to prevent the conversion of adularia to sanidine, which is not in accord with the data. An alternative explanation of the change from adularia to sanidine is that it might be concerned with the diffusion of potassium through the somewhat open structure. It is possible that the diffusing potassium atoms might occupy unequivalent voids in sanidine, while they occupy equivalent voids in adularia. This amounts to saying that the adularia-sanidine relationship is concerned with disorder of the alkali, while the microcline-orthoclase relationship is concerned with disorder in the aluminum-silicon content of the feldspar. At the present time, the whole situation is in an unsatisfactory state for lack of data and only further structural studies will clear it up.

The Plagioclase Feldspars—The same state of near-knowledge pervades our understanding of the plagioclase relationships. The plagioclases are usually cited as the classical example of perfect solid solutions. Yet mineralogists have had information for eight odd years indicating that this is not the truth. A mere reconnaissance structural investigation of the plagioclases by Chao and Taylor¹⁸ showed that the relationship is

¹⁵ Barth, Tom. F. W., Permanent changes in the optical orientation of feldspars exposed to heat: *Norsk. Geol. Tidssk.* 12, 57-72 (1931).

¹⁶ Spencer, Edmondson, The potash-soda feldspars. I. Thermal stability: *Mineral. Mag.*, 24, 453-494, esp. 480-481 (1937).

¹⁷ Barth, Tom. F. W., Polymorphic phenomena and crystal structure: *Am. Jour. Sci.* (5), 27, 273-286 (1934).

¹⁸ Chao, S. H., and Taylor, W. H., Isomorphous replacement and superlattice structures in the plagioclase feldspars: *Proc. Roy. Soc. (A)*, 176, 76-87 (1940).

much more complicated. They found that, while albite has a cell comparable with the sanidine cell, anorthite has a cell twice as high. More astounding, labradorite is not a solid solution of albite and anorthite, but a composite mixture of albite and anorthite.

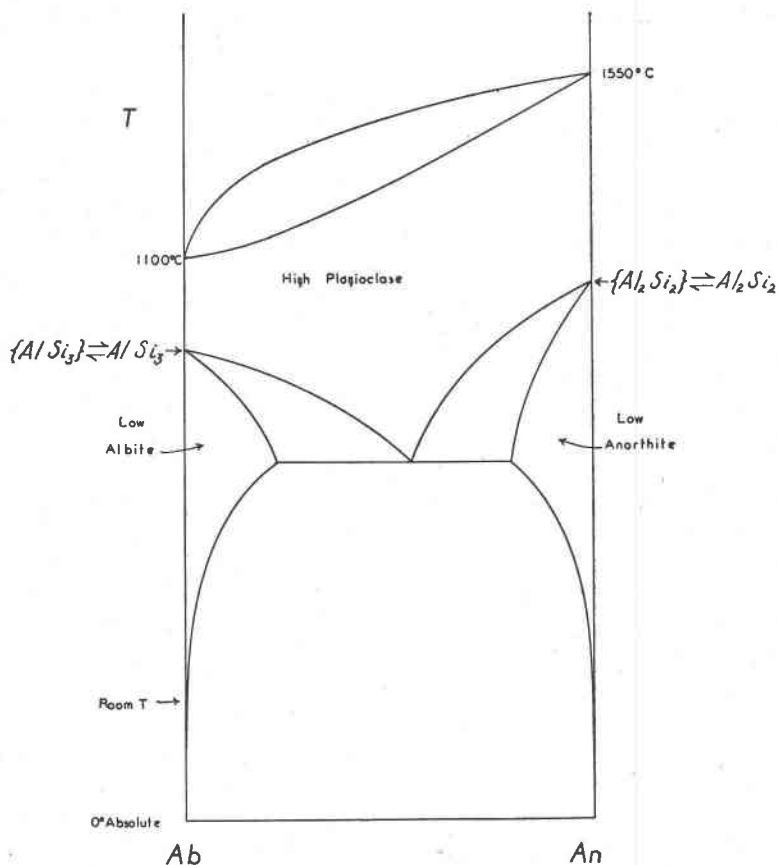


FIG. 4

Chao and Taylor presented mere data, without attempting to explain what they had found. I do not believe that their findings in any way vitiate the early phase diagram work^{19,20} on the precipitation of albite-anorthite solid solutions crystals from high-temperature melts. In my opinion their findings merely give experimental proof for what is quite

¹⁹ Day, A. L., and Allen, E. T., The isomorphism and thermal properties of the feldspars: *Carnegie Inst. Pub.* 31 (1905).

²⁰ Bowen, N. L., Melting phenomena of the plagioclase feldspars: *Am. Jour. Sci.* (4), 35, 577-599 (1913).

obvious from an order-disorder point of view, namely, that complete solid solutions are stable and to be expected at high temperatures, but they are most unnatural and unstable at low temperatures, where order is required. When the natural feldspars are found below their ordering temperature, one cannot expect them to be in the form of solid solution crystals. This view, though radical, follows directly from the general theory I proposed some fifteen years ago for such situations.¹¹

To give specific form to my view of the plagioclase relationships, Fig. 4 is presented. On this diagram nothing is quantitative except the well-known melting relations of the crystals. The other aspects of the diagram are arrived at by realizing that the $\{\text{AlSi}_3\}$ of albite and the $\{\text{Al}_2\text{Si}_2\}$ of anorthite certainly require ordering at lower temperatures. The purely geometrical conditions for ordering a pair of atom species in the ratio 1:3 are different than required for the ordering of a pair of atom species in the ratio 1:1. Albite must, therefore, order as a different phase from anorthite and at a different temperature than anorthite, probably at a lower temperature. Furthermore, at reduced temperatures, it is impossible for irrational amounts of Al and Si, such as called for in intermediate feldspars, to become ordered without the splitting of the crystal into two phases. Thus, ordering the disordered pair $\{\text{Al}_a\text{Si}_b\}$ requires unmixing. Since albite and anorthite are both capable of becoming ordered, their structures are available for this purpose, and one would expect the disordered pair of atoms to become ordered by establishing these two specific ordered crystal forms as follows:



Here, conservation of atoms requires

$$\begin{cases} a = x + 2y \\ b = 3x + 2y \\ a + b = 4 \end{cases}$$

This, of course, is merely a specific example of the theory which was discussed more abstractly under *Disorder and Unmixing*.

This theory postulates three plagioclase phases. Both albite and anorthite have a common high temperature, disordered form, but distinct low temperature, ordered forms. (The high temperature form may well be monoclinic, and both albite and pericline twinning may be concerned with the inversion.) It also requires that the stable low temperature state of the intermediate plagioclases is that of a mixture of end members, not solid solutions. If the intermediate plagioclase was formed above the ordering temperature, then the room temperature form of the stable mixture is an unmixed aggregate. If the plagioclase was deposited below the ordering temperature, then the form of the stable mixture is

that of an overgrowth or intergrowth of end members. All of this may be complicated by a second inversion concerned with the ordering of the alkali atoms. It should be noticed that conditions of deposition are not always conducive to the achievement of equilibrium. Slow deposition from nonviscous media favor equilibrium.

The plagioclase situation should be a warning not to accept solid solutions as necessarily stable at room temperatures. Chances are good that any solid solution mineral formed at the comparatively high temperatures ordinarily assumed for the formation of igneous and some metamorphic rocks is not a stable solid solution at the temperature of observation, because considerable more order is required at this low temperature. The presence of play of colors, such as so frequently seen in labradorite, or of schiller, or opalescence, may provide a clue that the crystal is possibly not, indeed, a solid solution.

I hope that in this sketchy account I have been able to convince you that it is important for a mineralogist to have a background of dynamic structural crystallography, and that such a background provides a rational frame for understanding and filing away his knowledge of the temperature relations of minerals.