PETROLOGICAL SIGNIFICANCE OF SUB-SOLIDUS PHASE TRANSITIONS IN MIXED CRYSTALS

BY

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With 15 figures in the text.

Abstract. The phase transitions of mixed crystals at sub-solidus conditions are discussed from a theoretical physico-chemical point of view.

Two different types of sub-solidus transitions are found to exist in rock-forming solid solutions. (1). The eutectic type in which only the one component of a mixed crystal series changes into another modification, decomposes, or reacts with other minerals. Under these conditions the transformation or reaction point (or rather—line) in the P,T-diagram varies with varying composition of the solid solution in an analogous manner as the melting or saturation point in eutectic melts or liquid solutions. And (2.) the isodimorphic type by which both end members of a two component mixed crystal change to other modifications, decompose, or react with other minerals. In that case the sub-solidus transition equilibrium is analogous to the melting equilibrium of mixed crystals.

12 examples from rock-forming silicates are discussed broadly. These examples show that the transformations in mixed crystal series can be used as suitable continuous geological P,T-registrators. They further show that there exists gradual rather than discontinuous transitions between the several critical or typomorphic parageneses of the different mineral facies of rocks.

According to papers dealing with metamorphism the chemical composition of some mixed crystals among the common minerals varies with varying degree of metamorphism.

In this connection we may ask if the varying composition of the mixed crystals is due only to differences in the chemical composition of the rocks under consideration, or if there also exists a law of relation between the metamorphic grade and the composition of the mixed crystals. If the latter be the case, the petrologist has very suitable geological temperature and pressure indicators in this inter-relation between the composition of the mixed crystals and the P, T-conditions. The great advantages of such P,T-indicators is the possibility of a continuous registration of temperature and pressure during the metamorphism.
In fact, the petrographic experience suggests a regular relation between the metamorphic grade and the composition of some mixed crystals among rock-forming minerals. It may be well-known, for instance, how the composition of the garnet group varies from Fe-rich almandine in low grade schists to Mg-rich pyrope in high grade eclogites and granulites. Additional examples are the variations in the composition of hornblende and plagioclase with varying degree of metamorphism. The hornblende usually grows richer in Al and Fe$^{++}$ as the P,T-conditions increase. The plagioclase is enriched in the anorthite-molecule with increasing metamorphic grade. The varying Fe$^{++}$/Mg ratio in biotite is often interpreted as a result of variations in the metamorphic conditions whereunder the biotites are formed. But, since Fe$^{++}$-rich biotites sometimes are found in low grade rocks, sometimes in high grade rocks, we cannot unconditionally take a regular relation between the Fe$^{++}$/Mg ratio in biotite and the P,T-conditions for granted. This variation in the biotite is probably more governed by the chemical environment than by the physical conditions.

To be able to employ the important possibilities which here seem to stand at the disposal of the geologist in determining the P,T-conditions during the reactions in the earth's crust, we have to investigate accurately the physico-chemical laws of the mixed crystals. We have to find the relation between the average chemical composition of the mineral assemblage under consideration, the composition of the mixed crystals in the assemblage, and the P,T-conditions.

Before discussing the physico-chemistry of the mixed crystals, we shall refresh our memory concerning the elementary theory of the chemical stability of the compounds.

Independent on the way of reaction, the thermodynamically stable parageneses are determined by the average chemical composition of the system under consideration, and the gas tension of the different compounds which may be formed under the given P,T-conditions. The stable association consists of the minerals giving minimum partial and also total gas tension.

Since the gas tension of the minerals varies with temperature and pressure, different parageneses may give minimal partial gas tension by varying P and T, and constant average composition.

Different assemblages may accordingly be stable at different temperature and pressure, but identical average chemical composition. On this fundamental physico-chemical law the facies classification of metamorphic rocks is based.¹

According to the said connection between the gas tension and the stability of compounds, the just discussed relation between the composition of mixed crystals and the P,T-conditions whereunder they are formed, indicates a dependence between composition and partial gas tension of mixed crystals. Because of the lack of experiments we have no empirical evidence of the variation of the partial gas tension or of the solubility (which depends on the gas tension itself) with the composition in rock-forming solid solutions. Indirectly some of the melting diagrams of the minerals give important information on the stability and gas tension in the sub-solidus phase. But the most important knowledge of gas tension, stability, and, accordingly, the reaction of solid solutions in common silicates, is due to the analogy conclusion we can draw from the theoretical and experimental metallography.²

The relation between partial gas tension and the composition of mixed crystals is fundamental for the understanding of their reactions and stability. Mixed crystals, which also have been called solid solutions, are in many ways similar to liquid solutions. The well-known osmotic laws are applicable both in the liquid solutions and in the solid solutions of the mixed crystals.

For convenience we shall only discuss two-component systems. Then we have: The partial gas tension of one component in a mixed crystal increases gradually with increasing molecular concentration of the same component in the solid solution.

In real crystals there seldom or never exists a direct proportionality between the partial gas tension and the molecular concentration in the solid phase. But in so-called ideal mixed crystals the partial gas tension is directly proportional to the concentration, and the partial gas tension may be expressed by the well known Raoult's equation:

\[ P_{Am} = P_A \cdot \frac{m}{m+n} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \]  

¹ P. Eskola: Norsk geol. tidsskr. Bd. 6, 1921.
Fig. 1. The partial gas tension of a solution AB in the case of complete miscibility. On ideal osmotic solubility the partial gas tensions follow the solid lines $A-P_B$ and $B-P_A$ respectively. With real solutions the gas tensions lie above or beneath these two lines.

where $P_A$ is the gas tension of the pure component $A$; $P_{Am}$ is the partial gas tension of the composition $A_m \cdot B_n$; $m =$ mol. of $A$, and $n =$ mol. of $B$ in the solution. (Fig. 1.)

In such an ideal solid solution the chemical affinity between two unequal molecules is identical with the affinity between to equal molecules. Coincidently there must be no distortion in the lattice during the mixing. (This ideal case may perhaps occur in “mixed crystals” containing isotopes: NaCl$^{85}$. NaCl$^{87}$.)

If the unit cells of the two components are more or less different, and the affinity between two unequal molecules is not greater than between two equal molecules, then there is no longer ideal osmotic miscibility between the components, and the curves of partial gas tension lie above the straight lines of fig. 1. If, on the contrary, the affinity between two unequal molecules is greater than the affinity between two equal molecules, and the deformation of the lattice during the mixing is negligible, then the partial gas tension curves may lie beneath the straight lines of fig. 1.

Complete miscibility between two compounds depends on the conditions that the lattice distortion and the repulsion between two unequal molecules do not exceed a given maximum critical value. At these maximum deformation and repulsion values the partial gas tension of a component in a solid solution of definite composition equals the gas tension of the same pure component, or of a solution with a greater concentration of the considered component. On transgressing the mentioned maximum deformations of the lattice, an exsolution of the mixed crystals must take place since the partial gas tension of a component in the solution exceeds the gas tension of the same pure component or of a solution with greater concentration of the same component. (Fig. 2.)
Fig. 2. The partial gas tensions of a mixed crystal, AB, in the case of incomplete miscibility. The B-richest end member of the solution (Am Bn) has a B-gas tension which equals the gas tension of the pure B-end member.

Fig. 3. The partial Mg- and Fe-gas tensions of a completely miscible Fe—Mg silicate. (X equals a part of the compounds which is the same for both end members.)

The two-component mixed crystals of metallic alloys usually are of the composition: Am Bn where A and B are metallic elements. Here it is natural to speak about the partial gas tensions of the components A and B since they are pure elements. In the rock-forming minerals on the other hand, the components which build up the mixed crystals are commonly complicated chemical compounds. Here it is more expedient to consider the partial gas tensions of the substitutable isomorphous elements. (The partial gas tensions of Na and Ca in plagioclase, and of Mg and Fe in hornblende, for instance.)

We know little or nothing about the composition and tension of the gas phase of silicates. Probably the silicate molecules in the gas are more or less dissociated; elementary atoms also must be present. We may for instance speak about the partial oxygen tension of a oxyde.

According to the preceding discussion it is obvious that also the partial gas tension of an isomorphous element in a silicate increases with increasing molecular concentration in the crystal of the component containing the considered element. In a perfectly miscible Mg—Fe

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silicate for instance, the partial gas tensions of Mg and of Fe principally vary with the composition as seen in fig. 3.

After this discussion we shall consider some of the reactions in mixed crystals which are of petrological importance.

I. EUTECTIC TYPE

Eutectic type with modification changes.

The one component, AX, in a mixed crystal (A,B) X¹ exists in two different modifications: AX¹ and AX². Only AX¹ is isomorphously miscible with BX¹. The component BX exists only in the modification BX¹ which is stable all over the stability field of both AX¹ and AX². (X be the part of the compounds which is equal in both the pure components.)

It is important to keep in mind that never the whole amount of the component AX of the mixed crystal (A,B) X¹ is able to separate as the P,T-conditions cross the border-line from modification AX¹ into AX².

If the modification AX² is the stable one, then the gas tension of AX² is lower than that of AX¹. But according to the previously discussed theory of mixed crystals the partial gas tension of A in (A,B) X¹ increases with increasing concentration of the AX-component from zero to a value which maximally equals the A-gas tension of pure AX¹. Consequently, in spite of the gas tension of AX¹ being higher than that of AX², there must always exist a definite mixture, (AₓBₘ) X¹, the partial A-tension of which equals the partial A-tension of the pure modification AX². It is obvious that a mixed crystal of exactly the mentioned composition must exist in stable equilibrium with the pure modification AX².

The gas tension of both AX¹ and AX² varies with the P,T-conditions. The composition of the mixed crystal the A-tension of which equals the A-tension of the modification AX² must therefore vary with varying temperature and pressure.

If AX¹ is the high temperature modification, then AX² is in stable equilibrium with gradually A-poorer solid solutions as the temperature decreases below the transformation point: AX¹ ⇋ AX². With AX² as the high temperature modification the same takes place at rising temperatures above the transformation point.
Fig. 4. Eutectic sub-solidus equilibrium diagram. The mixed crystal \((A, B)X^1\) is the high temperature or pressure modification.

Fig. 5. Eutectic sub-solidus equilibrium diagram. The mixed crystal is the low temperature or pressure modification.

At constant temperature similar conditions exist under varying pressure according as \(AX^1\) is the high or low pressure modification.

The transformation temperature and heat being given, the following equation exists between temperature and composition of the mixed crystal which is in stable equilibrium with the pure \(AX^2\) modification:

\[ u \left( 1 - \frac{T}{T_u} \right) + K_2 \alpha_2^2 + RT \ln \left( 1 - \alpha_2 \right) = 0 \ldots \ldots \ldots \]  

\( u \) = molar heat of transition  
\( T_u \) = temperature of transition  
\( \alpha_2 \) = mol. percent of AX in \((A, B)X^1\)  
\( K_2 \) = characteristic constant for the crystal.

The principal equilibrium equation of such phase transition may be stated:

\[ (A_mB_n)X^{1}_{(m+n)} \rightleftharpoons (A_{m-s}B_n)X^{1}_{(m-s+n)} + aAX^2 \ldots \ldots \ldots \ldots \]  

\(^1\) U. Dehlinger, loc. cit. p. 24.
In the preceding pages it was assumed that the compound \( BX^1 \) was stable over the whole stability field of both \( AX^1 \) and \( AX^2 \). More commonly \( BX \) also occurs in two or more modifications, say \( BX^1 \) and \( BX^8 \). If \( BX^8 \) is not miscible with \( AX^2 \), then \( BX^8 \) exists in equilibrium with \( (A, B) X^1 \) in a similar manner as does \( AX^2 \).

These conditions of stability in solid solutions are accordingly analogous to the equilibrium conditions in eutectic melts and liquid solutions. The mixed crystal represents the melt, and the immiscible crystals \( AX^2 \) and \( BX^8 \) represent the solid precipitates of the eutectic melt or liquid solution. Fig. 4 and fig. 5 are the sub-solidus equilibrium diagrams of eutectic types. In fig. 4 the mixed crystal is the high temperature (pressure) modification, in fig. 5 the immiscible modifications are the high temperature (pressure) phases.

Examples 1 and 2 (p. 52, 53) are of this eutectic type with modifications changes.

**Eutectic type with decomposition.**

The previously discussed eutectic equilibria must also exist if the component \( AX \) in the solid solution \( (A, B) X^1 \) does not occur in two modifications, but decomposes into two or more minerals, none of which is able to substitute \( B \) for \( A \) in their lattices.

In this case we have the following equilibrium equation:

\[
(A_m B_n) X^1_{(m+n)} \rightleftharpoons (A_{m-a} B_n) X^1_{(m-a+n)} + b A Y + c A Z \ldots \ldots \ldots (4)
\]

where: \( b + c = a \); and \( B \) is not isomorphous with \( A \) in \( A.Y \) and \( A.Z \). Example 3 (p. 54) is of this type.

**Eutectic type with reaction products.**

As a third possibility of the eutectic equilibria the component \( AX \) of the mixture \( (A, B) X^1 \) is assumed to react with a second mineral forming a third mineral. The thus formed reaction-mineral be unable to accept \( B \) for \( A \) in its lattice. In that case also the \( P,T \) conditions effect the equilibrium between a mixed crystals of definite composition and the reaction product. The equilibrium can bee stated as follows:

\[
(A_m B_n) X^1_{(m+n)} + a \cdot CY \rightleftharpoons (A_{m-a} B_n) X^1_{(m-a+n)} + a A \cdot C \cdot XY \ldots \ldots (5)
\]

where \( B \) cannot be substituted for \( A \) in the compound \( A.C.X.Y \).

Example 5 (p. 58) represents this type of eutectic equilibrium.
II. ISODIMORPHIC TYPE

Isodimorphic type with modification changes.

In the previously discussed eutectic types of sub-solidus equilibria the modification AX\(_2\) which was in stable equilibrium with the mixed crystal (A B) X\(^1\) was unable to accommodate any B-ions in its lattice.

In the general case, however, A and B are mutually exchangeable in all crystal phases.

The simplest case of this equilibrium type is an ideal isodimorphic series i.e. two isodimorphic series (A, B) X\(^1\) and (A, B) X\(^2\) the pure components of which are dimorphous modifications of the compounds AX and BX.

Usually the transition points: AX\(^1\) \(\leftrightarrow\) AX\(^2\) and BX\(^1\) \(\leftrightarrow\) BX\(^2\) do not coincide, and the transition point for intermediate compositions must therefore vary with varying composition. By considering the partial gas tensions of the solid solutions (A, B) X\(^1\) and (A, B) X\(^2\) in a similar manner as was done for the eutectic type p. 47, we arrive at an equilibrium diagram as shown in fig. 6.

At every temperature between the transition temperatures of the pure end components, the two mixed crystals (A, B) X\(^1\) and (A, B) X\(^2\) which occur in stable equilibrium, are of different composition. We shall not go through the whole development of the diagram by means of the partial gas tension of the two mixed crystals, we shall only keep in mind that for the two crystals which are in equilibrium, the partial A-tensions of both crystals must be equal at the same time as the partial B-tensions of both crystals are equal.

Since the relation between partial gas tensions and composition are analogous for mixed crystals and mixed liquids, the equilibrium diagram: mixed crystal\(^1\) \(\leftrightarrow\) mixed crystal\(^2\) equals the melting diagram of mixed crystals.

For the isodimorphic transition we can use the equation:

\[(A_m B_n) X_{(m+n)}^{1} \leftrightarrow (A_{m-a} B_{n-b}) X_{(m+n-a-b)}^{1} + (A_{a} B_{b}) X_{(a+b)}^{2} \ldots \ldots \]  

which indicates that a mixture \((A_m B_n) X_{m+n}^{1}\) splits up into two phases of different A/B relations.
Fig. 6. The principal equilibrium diagram of the sub-solidus transition between isodimorphic series.

**Isodimorphic type with decomposition or reaction.**

The isodimorphic transition is only a phase transition between two different *modifications* of the end members. Analogous equilibrium must also exist if both the end compounds split up into two or more minerals, or react with other minerals. In these cases the reactions of the end members are:

\[
\begin{align*}
AX^1 & \Leftrightarrow AY + Z \\
BX^1 & \Leftrightarrow BY + Z
\end{align*}
\]

or

\[
\begin{align*}
AX^1 + Y & \Leftrightarrow AZ + Q \\
BX^1 + Y & \Leftrightarrow BZ + Q
\end{align*}
\]

where A and B are substitutable in \((A, B) X^1\) and \((A, B) Y\) or \((A, B) Z\) respectively.

Examples 6—12 (p. 60—70) are of these different varities of the isodimorphic types.

**III. EXAMPLES**

**Example 1. The epidote—plagioclase equilibrium.**

The equilibrium which exists between plagioclase and epidote (or better zoisite) in low and medium grade rocks is approximately of the discussed eutectic type (p. 47). Epidote or zoisite may be looked

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1 T. Strand: Norges geol. unders. Nr. 159 p. 43—47. 1943.
2. Ramberg: Norsk geologisk tidsskr. 23, p. 120—135. 1944.
upon as the low temperature modification of the anorthite-compound. Consequently there must exist an equilibrium between epidote and a plagioclase mixed crystal of gradually anorthite-poorer composition as the temperature decreases below the transition point: anorthite $\leftrightarrow$ zoisite. (Fig. 7.) The molar volumes of anorthite and zoisite indicate that the latter is the high pressure modification of the two minerals, hence the plagioclase which is in stable equilibrium with zoisite must grow gradually richer in albite as the pressure increases above the transition pressure: anorthite $\leftrightarrow$ zoisite by constant temperature. Temperature and pressure act against each other on the zoisite—plagioclase equilibrium. Under regional metamorphic conditions the influence of the temperature upon the equilibrium exceeds the influence of the pressure, and accordingly the plagioclase successively must grow richer in anorthite by increasing metamorphic grade. The equation can be given as:

\[
\text{High T.} \quad \text{Low T.} \\
\text{An}_{m} \cdot \text{Ab}_{n} \leftrightarrow \text{An}_{(m-x)} \cdot \text{Ab}_{n} + y \text{ zoisite} \quad . . . . . \quad (9)
\]

But because of the small difference in the chemical composition of anorthite and zoisite the equilibrium: plagioclase $\leftrightarrow$ zoisite is not only dependent on the P,T-conditions. The average composition of the paragenesis plays a role. In supersilified and H$_2$O-saturated rocks only the ratio Ca/Al effects the equilibrium at constant P and T. Since the Ca/Al ratio is greater in zoisite than in anorthite, Ca-rich environments in the pore liquid will displace the equilibrium towards zoisite and albitic plagioclase. Al-rich environments, on the other hand, will displace it towards anorthtitic plagioclase.

Petrographic experience seems to prove that the difference in the Ca/Al ratios of the common minerals: garnet, hornblende, biotite and diopsidic pyroxene has no important effect on the equilibrium plagioclase $\leftrightarrow$ zoisite. That is to say that the composition of the plagioclase which is in stable equilibrium with zoisite in common rocks is principally determined by the P,T conditions.

But in rocks carrying calcite the equilibrium is displaced towards almost pure albite and zoisite also at high temperature$^1$ (reaction skarn rocks) because of the high CaO-concentration in the pore liquid. Whether or not the Al-rich environments in cyanite-carrying rocks move the equilibrium towards basic plagioclase, I have not been able to find out.

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Fig. 7. Sub-solidus equilibrium diagram of plagioclase and epidote. The ratio \((\text{Ca}, \text{Na}_2)/\text{Al}\) of the paragenesis which the diagram represents lies between \(\frac{1}{2}\) and \(\frac{2}{3}\). Quartz and water can be present without influencing the transition line: epidote \(\leftrightarrow\) plagioclase. I, II, III and IV represent the green schist facies, the epidote amphibolite facies, the amphibolite facies and the granulite facies respectively. At point \(x\) epidote (zoisite) exists together with a plagioclase of the composition \(y\). As the metamorphic grade increases from \(x\) to \(z\) the composition of the plagioclase follows the line \(yz\), and at point \(z\) epidote disappears. Concerning the borderlines between the different facies see p. 70—73.

**Example 2. The talc—anthophyllite equilibrium.**

Another illustration of the equilibrium of the eutectic type between minerals, exists in the association: talc-anthophyllite (the name anthophyllite in this connection means the total mixed series between Fe·· and Mg-silicates).

In anthophyllite, Fe·· and Mg ions are mutually substitutable to a high degree. In the lattice of talc only about 2 percent of the MgO may be substituted for by FeO. As all petrographic experiences show, the anthophyllite is stable at higher temperatures than talc. Talc may be looked upon as the low temperature modification of pure Mg-anthophyllite. Accordingly there exists an equilibrium between talc and anthophyllite of successively Fe-richer composition as the temperature decreases below the transition-point: talc \(\leftrightarrow\) Mg-anthophyllite:

\[
\text{Mg-rich anthophyllite} + \text{quartz} + \text{H}_2\text{O} \leftrightarrow \text{Mg-poor anthophyllite} + \text{talc} \quad \text{(10)}
\]

\[
\text{high T} \quad \text{low T}
\]
Fig. 8. Equilibrium diagram of the Fe-Mg silicates at sub-solid state. (Quartz and water may exist besides the other minerals in the figure.) The lowest part of the diagram shows the talc→anthophyllite equilibrium of eutectic type. The upper part represents the isodimorphic type of equilibrium between orthopyroxene and cummingtonite or anthophyllite. I, II, III, and IV represent the green schist, the epidote amphibolite, the amphibolite and the granulite facies respectively. At point X, talc exists together with an anthophyllite of composition (Fe/Mg ratio) Y. By increasing metamorphic grade the Fe/Mg-ratio of the anthophyllite which is in equilibrium with talc, follows the line YZ. By passing the point Z the talc disappears, and only anthophyllite exists up to the point a where hypersthene of composition b appears. First above point c the anthophyllite disappears.

Because of the difference in the Mg/Si and Mg/H_2O ratios in talc and Mg-anthophyllite, the above equilibrium is only valid for supersilified and H_2O-saturated rocks. (Fig. 8.)

The association: talc-anthophyllite is not very common, and the equilibrium between the two minerals is thus of no great importance as a geological P,T indicator. In the study of metamorphic facies in provinces consisting of greatly diversified rocks it is, on the other hand, also important to include critical parageneses of rare rocks.

Example 3. The talc, calcite—actinolite equilibrium.

The paragenesis: actinolite, calcite, and talc is a good example of the eutectic sub-solidus transition with decomposition. (Actinolite means the total mixed crystal series between Fe and Mg-silicate.)

The pure Mg-component of the mixed crystal actinolite — the tremolite — decomposes at a relatively low temperature into talc and calcite according to the equation:
Fig. 9. Equilibrium diagram of the (Fe,Mg)-
lime silicates in sub-solidus state. The miner-
als in the diagram are saturated in silica,
water and lime so that quartz, water and
calcite may be present besides the other
minerals without displacing the equilibrium.
The ratio Ca/(Fe, Mg) of the parageneses
which the diagram represents is equal to,
or greater than unity. At point X talc and
calcite are in equilibrium with an actinolite
of composition Y. (The talc may have the
Fe/Mg-ratio Z.) At point q talc disappears
and the actinolite has grown richer in Mg.
At point a a diopside of composition b (and
calcite) occurs. I, II, III and IV represent
approximately the green schist, the epidote
amphibolite, the amphibolite, and the granu-
lite facies respectively (see also p. 66.)

\[
\begin{align*}
7 \text{H}_2\text{O} + 6 \text{Mg}_6\text{Ca}_3\text{Si}_8\text{O}_{22} (\text{OH})_2 & \rightarrow 5 \text{Mg}_6\text{Si}_8\text{O}_{20} (\text{OH})_4 \\
& + 12 \text{CaCO}_3 + 8 \text{SiO}_2
\end{align*}
\]

(11)

Because of the inability of talc to accept Fe for Mg in its lattice,
the Fe⁺⁺-component of the actinolite series cannot react in the same way.

The assemblage: talc, calcite, and quartz together must be regarded
as the low temperature "modification" of tremolite. Talc, calcite, and
quartz must accordingly exist in stable equilibrium with gradually
Fe⁺⁺-richer actinolite as the temperature decreases below the reaction
point of equation 11. The equation of this equilibrium is:

\[
\text{Mg-rich actinolite} + \text{H}_2\text{O} \rightarrow \text{talc} + \text{Fe-rich actinolite} + \text{calcite} + \text{quartz}
\]

(12)

It is obvious that the equilibrium between a variable actinolite
and the other above-mentioned minerals is only dependent on the
P,T-conditions if all the minerals: talc, calcite, and quartz are present
in the paragenesis.
In rocks carrying all the mentioned minerals the composition of the actinolite may represent a suitable geological thermometer and barometer in the lowest part of the epidote amphibolite facies. Fig. 9 shows the sub-solidus equilibrium diagram of this association.

**Example 4. The equilibria of the Al-carrying hornblende and of augite.**

When Al replaces Si or (Mg,Fe) in the actinolite-tremolite molecules, the so-called common hornblende appears.

In accordance with the view of different investigators, the lattice of hornblende is able to take up more Al the higher the P,T-conditions. Now we can consider the variation of Al in hornblende from the same view-point as is used in the preceding examples of mixed crystals.

The common hornblende may be looked upon as a solid solution of the pure Al-free actinolite-tremolite molecules and the most Al-saturated "actinolite-tremolite" molecules. For convenience the Fe and Na-contents are disregarded.

As the Al-rich end component of the series mentioned the common hornblende with the greatest known Al-content must be chosen. The Al-richest varieties of the common metamorphic hornblende lie approximately on the line between (Fe,Mg)-garnet and epidote or anorthite in the ACF-diagram. These Al-end members of the hornblende series will therefore be formed by reaction between garnet and epidote (or anorthite). The Al-richest end components are only produced at the highest P,T-conditions within which hornblende is stable. At lower metamorphic grade the Al-richest hornblende component is unstable and splits up into epidote (anorthite), and almandine-pyrope garnet in accordance with the following equation:

\[
3\text{Ca}_2\text{Al}_8\text{Si}_8\text{O}_{12}\text{OH} + 5(\text{Fe,Mg})_8\text{Al}_2\text{Si}_8\text{O}_{12} \xrightarrow{\text{epidote}} (\text{Fe,Mg})_5(\text{Al}_6,\text{Si}_1,\gamma)\text{O}_{22}(\text{OH})_2 \xrightarrow{\text{hornblende}} \text{H}_2\text{O}.
\] (13)

It is obvious that the other end components of the hornblende series, the pure actinolite-tremolite molecules, cannot react in the same manner. Hence there must exist an eutectic sub-solidus equilibrium.

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Fig. 10. Sub-solidus equilibrium diagram of the common hornblende and augite. It is the isomorphism between Si and Al in the hornblendes and pyroxenes which is of importance for this diagram. The effects of the Mg/Fe-ratios are only slightly indicated by the stipled curves. The solid line from E₃ up to the left is the boundary line between the common hornblende-field and the garnet, epidote-hornblende-field at intermediate Fe/Mg-ratio. The two stipled lines from E₁ and E₂ up to the left are the boundary lines between the mentioned stability fields at Fe/Mg-ratios equal to ∞ and 0, respectively. By great Mg/Fe-ratio there exists an eutectic point at E₁ because of the fact that pure tremolite splits up into calcite and talc, and that talc is not able to accommodate Al in the lattice. The eutectic point gradually moves towards the right and disappears by great Fe/Mg-ratios of the paragenesis. At point x an actinolitic hornblende of composition y exists in association with epidote and garnet by intermediate Fe/Mg-ratios. (By Mg-rich environment only garnet and epidote without hornblende exist at point x, by Fe-rich environment garnet and epidote exist together with common hornblende of composition u). By increasing metamorphic grade, the Al-content of the hornblende which is in equilibrium with epidote and garnet (or chlorite) increases; the composition of the hornblende follows the curve YZ. At point Z the hornblende is able to accommodate the whole Al-content of the considered assemblage, and epidote and garnet disappear. Between point Z and c the composition of the hornblende is independent of the physical conditions. At point c the stability field of augite is reached and the hornblende splits up in an augite of composition d and hypersthene or cummingtonite. The points a and b are equivalent to Z at pure Fe- or Mg-parageneses respectively. I, II, III and IV represent the same mineral facies as described in figs. 8 and 9. (See also p. 70—73.)

These conditions are schematically shown in fig. 10. The Fe/Mg-ratio
of the paragenesis has been disregarded in spite of its great importance to the mentioned equilibrium. Mg-rich environments may probably raise the reaction point of equation 13, great Fe-amounts, on the contrary, will lower it (the stipled lines on the fig. 10).

The upper part of the diagram 10 shows the equilibrium conditions of the augite-diopside series. It demands an explanation. In an earlier paper I have been able to prove that the upper P,T-border of the stability field of pure actinolite-tremolite lies lower than the upper P,T-borderline of Al-richer hornblende. Tremolite and actinolite split up into diopside and cummingtonite at the same metamorphic grade at which an Al-rich common hornblende is stable. But if the metamorphism is high enough, even the Al-rich hornblende is unstable and reacts forming augite and hypersthene. The equilibrium between common hornblende and augite is accordingly of the isomorphomorphic type broadly discussed on p. 50.

Example 5. The biotite—feldspar, garnet equilibrium.

The common paragenesis in granitic gneisses and in granite pegmatites: potash feldspar, garnet and biotite (muscovite) is an illustration of the sub-solidus eutectic transition with reaction products.

Since biotite is stable in this paragenesis it is not easy to see why potash feldspar and garnet do not react forming biotite according to the equation:

\[
\text{garnet: } (Fe, Mg)_3 Al_2 Si_3 O_{12} + 2 \text{KAlSi}_8 O_{16} + 2H_2 O \rightarrow \text{feldspar: garnet feldspar}
\]

\[
\text{K: } (Fe, Mg)_3 AlSi_5 O_{10} (OH)_2 + \text{KAl}_8 Si_5 O_{10} (OH)_2 + 3 Si O_2 \rightarrow \text{biotite muscovite}
\]

But since the garnet in pegmatites and granites according to general experience are spessartine — almandine varieties, the paragenesis: garnet, potash feldspar, biotite does not indicate any incomplete equilibrium.

In common biotites from granites and pegmatites, Mn cannot replace Fe or Mg to any considerable extent. Because of this fact, pure Mn-garnet cannot react with potash feldspar forming biotite.

1 H. Ramberg loc. cit. p. 105.
The garnets of granites and pegmatites are thus approximately two-component mixed crystals: spessartine—almandine, of which only the almandine component can react with feldspar, giving biotite.

It seems to be empirically proved that the biotite is stable at lower temperature and pressure than the combination: almandine—potash feldspar, i.e. that the right side of equation 14 is stable at low, and the left side at high temperature and pressure. Accordingly there must exist a varying equilibrium between biotite, potash feldspar, and Fe\textsuperscript{3+}, Mn garnet. In this equilibrium the garnet must gradually grow richer in spessartine as the temperature decreases below the reaction point of equation 14.

Only when potash feldspar occurs in the presence of quartz and water the equilibrium between biotite and garnet is determined by the P,T-conditions regardless of the chemical environment. In the absence of potash feldspar (which is the visible proof of potassium-excess) even the Mn-free garnet may occur together with biotite at low temperatures, the amount of potassium in the paragenesis being insufficient to form biotite from the almandine. Disregarding Mg the equilibrium equation may be written:

\[
\begin{align*}
\text{high T.} & & \text{low T.} \\
\text{Mn-poor (Fe, Mn)-garnet} + \text{K-feldspar} + \text{H}_2\text{O} & \rightleftharpoons \text{Mn-rich garnet} + \\
+ \text{biotite} + \text{muscovite} + \text{quartz} & \ldots \ldots \ldots \\
\end{align*}
\]

(15)

(Commonly biotite is so rich in Al that muscovite does not appear in equations 14 and 15.)

In the granulite facies even pure Fe, Mg-garnet may exist in contact with potash feldspar without forming biotite. At that high temperature and pressure biotite is probably unstable. The transition point of equation 14 consequently coincides with the lowest borderline of the P,T-field represented by the granulite facies. The Mn/(Fe, Mg) ratio of the garnet which occurs in equilibrium with biotite and potash feldspar thus represents a geological P,T-indicator valid in the interval between granulite facies and the stability field of low grade pegmatites and gneisses, (epidote amphibolite facies). According to the literature\textsuperscript{1} the petrographic experience supports this theoretical explanation. The garnets which are found in the low temperature clelandite-quartz pegmatites are often approximately pure spessartines. The granulite garnets, on the contrary, are usually very low in Mn. In

\textsuperscript{1} W. I. Wright: Am. min. 23 p. 436. 1938.
Fig. 11. The equilibrium diagram of biotite, potash feldspar, and spessartine-almandine garnet. The relation between the different elements in the parageneses which the diagram represents is seen from the fig. SiO₂ (as quartz), Al₂O₃ (as muscovite) can be present in excess. H₂O must be present, and CaO may also occur in plagioclase without displacing the equilibrium. It is the Mn/(Mg, Fe) ratio which is of importance for the diagram. At point X exists a garnet of the Mn/(Fe, Mg) ratio Y in equilibrium with potash feldspar and biotite. By increasing metamorphism the Mn/(Fe, Mg) ratio of the garnet follows the curve YZ: the garnet grows richer in Fe and/or Mg, concomitantly the amount of biotite decreases. At point Z all the biotite is split up to garnet and feldspar.

I, II, III and IV represent the same facies of gneisses carrying potash feldspar, and in granites, the spessartine component in the garnet varies from low to high, these rocks being formed at different P,T-conditions.

Fig. 11 is an equilibrium diagram showing the stability conditions of the garnet paragenesis. For convenience the effect of the Fe/Mg ratio on the equilibrium is disregarded.

Example 6. The orthohypersthene—clinohypersthene equilibrium.

The series: orthorhombic hypersthene — clinohypersthene is a typical isodimorphic series. The monoclinic series consists of the high temperature modifications.

For the pure Mg-component, the enstatite, the transition temperature is about 1140°; and for the Fe-richest hypersthene investigated, the transition temperature is about 995° according to Bowen and Schairer.¹

It is of great interest that Bowen and Schairer have been able to show experimentally the transformation in sub-solidus phase between monoclinic and orthorhombic hypersthene. According to their experiments and equilibrium diagram a very small two phase interval seems to exist between the monoclinic and rhombic members. But there is some indication that the perfect sub-solidus equilibrium of the pyroxenes of intermediate composition was not developed during Bowen and Schairer's experiment. For the pure Mg-enstatite and the Fe-richest hypersthene the transition is very sharp at 1445° and 995° respectively. For the intermediate bronzite members, however, the transition is unprecise; the orthorhombic bronzites could be superheated by 300° above their transition temperature. But by using NaF as a catalyst the transition of the bronzites became distinct. "In working with added NaF it was found that some monoclinic crystals would form from orthorhombic even at low temperature where we had every reason to believe that the orthorhombic was the stable form." Above 1120° an orthorhombic bronzite of definite composition recrystallized to clinobronzite only. "But below 1120° newly formed crystals of bronzite appear together with the clino-bronzite, which proves the stability of the orthorhombic bronzite at temperatures below 1120° and places the transformation temperature at 1120°."

Bowen and Schairer assumed that the clinobronzite which appears together with the orthorhombic bronzite was unstable; it was formed below its stability temperature. Because of this assumption Bowen and Schairer thought the immiscibility field between orthorhombic and clino-hypersthenes to be very small.

It seems natural to me, however, that the fact that both orthorhombic and monoclinic bronzites were formed together at temperatures below 1120° indicates that there exists a larger transformational field between the two pyroxenes than assumed by Bowen and Schairer.

But it is reasonable to think that the perfect chemical equilibrium was not developed at the transformation of the bronzite members. In the pure end component the transition between the rhombic and monoclinic modification may be explained as a distortion of the lattice analogous to the transition: \( \alpha \)-quartz \( \rightarrow \beta \)-quartz. No chemical diffusion between the two different phases is necessary. In the

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1 Bowen and Schairer, loc. cit.
bronzitic crystals, however, the compositional difference of the two phases which are in stable equilibrium demands a chemical diffusion between the two phases. Mg and Fe must migrate from one crystal to another. Without NaF as a catalyst this chemical reaction was not able to take place in the solid phase. But it is of course not evident that the added NaF in the experiment of Bowen and Schairer was able to develop the complete equilibrium in the solid phase.

Similar isodimorphic transitions are found by other equilibrium experiments also. Greig and Barth have for instance proved the existence of a two phase field between carnegieite and nephelite.

In nature clinohypersthene (pigeonite) only occurs in basic lavas and meteorites. According to the rapid cooling of lavas a perfect development of the equilibrium is not probable. The miscibility between clinohypersthene and diopside in pigeonites surely also influences the equilibrium between clinohypersthene and hypersthene. (p. 68.) The mentioned sub-solidus equilibrium can therefore probably not be used as any suitable P,T-indicator.

In regional metamorphic rocks, in migmatites and perhaps in some plutonic igneous rocks the equilibria between the minerals are well on the way to complete attainment. Isodimorphic series among metamorphic minerals may therefore give usable geological thermometers and barometers. Ideal isodimorphic series, however, are not common among metamorphic minerals. But in the case where the fields of stability of two isomorphic series: \((A, B)_X\) and \((A, B)_Y\) where \(X\) and \(Y\) differ more or less, border against each other, the equilibria conditions are analogous to the conditions in isodimorphic series, (see p. 52 equations 7 and 8).

**Example 7. The orthohypersthene—anthophyllite equilibrium.**

Bronzite: \((Mg, Fe)_2 Si_2 O_6\), and anthophyllite: \((Mg, Fe)_7 Si_8 O_{22} (OH)_2\) are two isomorphic series of the above mentioned type. The difference in composition of the two minerals is made up by the \(H_2 O\)-content and the greater \(Si/(Mg, Fe)\) ratio of the hornblende. But since both minerals are saturated in silica, and the pyroxene may probably be stable in the presence of \(H_2 O\), we may consider the system with excess of quartz and water. Then the transformation: pyroxene \(\rightarrow\) anthophyllite is in principle analogous to the transformation between ideal isodimorphic series.

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There is every reason to believe that the transformation temperature of the pure Fe-members is lower than that of the pure Mg-members, in analogy with most other Fe-Mg silicates. Accordingly the sub-solidus equilibrium diagram is schematically shown in fig. 8 (p. 54).

Orthorhombic pyroxene is a critical mineral for the granulite facies in regional metamorphic rocks. Antophyllite is supposed to be unstable at P,T-conditions higher than those of the amphibolite facies. From fig. 8 we see that the transformation temperature: hypersthene \( \rightarrow \) antophyllite varies with varying Fe/Mg ratio. Fig. 8 further indicates that both pyroxene and hornblende may exist side by side in stable equilibrium (in excess of quartz and water), by definite correlations between P,T and Fe/Mg ratios. In accordance with this consideration the P,T-borderline between granulite and amphibolite facies will be very indistinct if based on the transformation: orthorhombic pyroxene \( \rightarrow \) antophyllite.

The equilibrium conditions become complicated by the occurrence of monoclinic cummingtonite at temperatures below the stability field of bronzite.¹

Bowen and Schairer's synthesis of fluorine cummingtonites is in good accordance with the explanations above.²

Orthorhombic pyroxenes of different compositions were mixed with NaF and heated. The products were fluorine cummingtonites of different compositions. In harmony with the theoretical, diagram fig. 8, the newly formed hornblendes always had greater Mg/Fe ratios than the pyroxenes (tab. I). In spite of the possibility that the complete equilibrium was not attained, such differences in the Mg/Fe ratio of pyroxenes and hornblendes at least indicate a higher transformation temperature for Mg-members than for Fe-members, and the existence of a transformation field between the two phases.

<table>
<thead>
<tr>
<th>Pyroxene</th>
<th>Hornblende</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mol% Mg-silicate</td>
<td>Mol% Mg-silicate</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>84</td>
<td>87</td>
</tr>
<tr>
<td>68</td>
<td>73</td>
</tr>
<tr>
<td>47</td>
<td>62</td>
</tr>
<tr>
<td>26</td>
<td>48</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

¹ A. N. Winchell: Am. min. 20, p. 329; 1935.
² Am. min. 20, p. 543, 1935.
Fig. 12. Equilibrium diagram of the chlorite-garnet association.

Fig. 13. Equilibrium diagram of the (Mg, Fe)-alumosilicates in sub-solidus state. The ratio \((\text{Fe, Mg})/\text{Al}\) is \(\frac{1}{2}\). All the minerals are saturated in silica so that quartz can occur all over the diagram without any distortion effect. \(\text{H}_2\text{O}\) must be present.

I, II, III and IV represent the same facies as in fig. 7—8, (see also p. 70—73).

**Example 8. The chlorite—garnet equilibrium.**

In low grade schists the paragenesis: chlorite—almandine is often encountered. The ratio \((\text{Mg, Fe})/\text{Al}\) is approximately equal in both minerals. But the relative contents of Si of the two mineral series differs, and in contradistinction to garnet chlorite contains \(\text{H}_2\text{O}\).

In the presence of quartz and water the association chlorite and almandine must either be explained by chemical unstability or by the effect of the Mg/Fe ratios of the parageneses.

It is of great significance that the garnets in low grade rocks always are Mg-poor almandine while the chlorites in the same rocks are relatively richer in Mg. Exactly this difference in the Mg/Fe ratios of chlorite and almandine will appear if Mg-chlorite transforms to
pure pyrope at higher temperatures than Fe-chlorite transforms to pure almandine. Fig. 12 shows the conditions at the phase transition: chlorite $\leftrightarrow$ (Fe,Mg)-garnet. The equilibrium diagram is probably not valid at the Mg-end. Pyrope is stable only at high P,T-conditions, and it does not seem probable that chlorite is the mineral which occurs immediately beneath pyrope in the P,T scheme (page 64 fig. 13).

Before leaving the garnet—chlorite association, we shall look at the extreme low temperature parageneses containing spessartine-rich garnets.

In some regional metamorphic provinces garnet appears before the biotite isograde. Empirically these low temperature garnets are richer in spessartine than the usual almandines occurring in and above the biotite isograde.¹

Physico-chemically the paragenesis may be explained by the fact that the presence of Mn suppresses the partial gas tension of Fe and Mg above the garnet. The (Fe, Mg) gas tension of the garnet may thus be lower than the (Mg, Fe) gas tension of chlorite even at low temperature. In this way manganese will stabilize garnet at temperatures lower than usual. In other words: there exists a eutectic equilibrium between chlorite and (Mn, Fe, Mg)-garnet. The chlorite is the low temperature modification of the (Fe, Mg)-garnet; but the Mn-garnet has no low temperature modification which is miscible with chlorite.

**Example 9. The garnet—cordierite equilibrium.**

The association: cordierite—(Fe, Mg)-garnet occurs in some gneisses and granulites. The chemical compositions of cordierite and garnet allow the two minerals to exist in stable equilibrium at certain (Fe, Mg)/Al-ratios in the paragenesis regardless of the Fe/Mg-ratio. But cordierite and garnet also occur together in rocks in which the (Fe, Mg)/Al-ratio is different from the above mentioned permissible values. Such parageneses are to be explained by the Fe/Mg-ratios.

In Fe-rich rocks almandine occurs, in Mg-rich rocks cordierite.²

The association garnet, cordierite and anthophyllite is common. Anthophyllite is the pure (Fe, Mg)-silicate which is stable at the same P,T-conditions as cordierite and garnet. The pyrope-component of

---

² P. Eskola, in Barth, Correns, Eskola, loc. cit. p. 354.
the garnet may be assumed to form from pure Mg-cordierite and Mg-anthophyllite as shown by the equation:

\[
21 \text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18} + 12 \text{Mg}_7\text{Si}_8\text{O}_{22} (\text{OH})_2 \xrightleftharpoons{} 42 \text{Mg}_8\text{Al}_2\text{Si}_3\text{O}_{12} + 12 \text{H}_2\text{O} \tag{16}
\]

cordierite anthophyllite pyrope

Pure Fe-cordierite is probably unstable, but cordierite containing about 60 mol. per cent Fe-silicate is known. Pure almandine may theoretically be formed from Fe-anthophyllite and a hypothetical Fe-cordierite:

\[
21 \text{Fe}_2\text{Al}_4\text{Si}_5\text{O}_{18} + 12 \text{Fe}_7\text{Si}_8\text{O}_{22} (\text{OH})_2 \xrightleftharpoons{} 42 \text{Fe}_8\text{Al}_2\text{Si}_3\text{O}_{12} + 12 \text{H}_2\text{O} \tag{17}
\]

Fe-cordierite Fe-anthophyllite almandine

The garnet-side of the equations is probably realized at high pressure; the cordierite side, on the contrary, is the high temperature side. (Under ordinary pressure cordierite melts directly without forming pyrope.)

Under the P,T-conditions of regional metamorphism it seems as if the effect of pressure exceeds the effect of temperature. Accordingly the right hand sides of equations 16 and 17 are stable at high grade and the left hand sides at lower grade of metamorphism. Further we suppose a higher transformation point of equation 16 than of 17.

In nature these schematic conditions are complicated by the above discussed equilibria between garnet and chlorite, and between chlorite and cordierite. Taking these facts into account we obtain a diagram as shown in fig. 13. Fig. 13 explains the equilibrium condition between (Fe, Mg, Al)-silicates during regional metamorphism approximately.

**Example 10. The actinolite—diopside equilibrium.**

In the two series: actinolite and diopside, similar equilibrium conditions must exist at definite (Fe, Mg)/Ca-ratios. There is a considerable difference in the (Fe, Mg)/Ca-ratios in the actinolite and the diopside series. In quartzous rocks saturated with H₂O the two minerals may therefore occur together in stable equilibrium within a relatively great (Fe, Mg)/Ca-interval, regardless of the Fe/Mg-ratio. But actinolite and diopside are also found together at an average

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1 A. Brammall and B. Rama Rao, Min. Mag. XXIV p. 257, 1936.
2 P. Eskola: The Mineral facies of rocks. Norsk geologisk tidsskrift 6, 1921
chemical composition different from the permissible ones. In some marbles, for instance, actinolite and diopside occur in contact with calcite. But in that case the actinolite is often richer in Fe than the diopside.¹

For the transformation: actinolite $\rightarrow$ diopside we may put forth the equations:

For low $T$:

$$\text{SiO}_2 + \text{CaFe}_5\text{Si}_8\text{O}_{22}(\text{OH})_2 + 3\text{CaCO}_3 \rightarrow 5\text{CaFeSi}_2\text{O}_6 + \text{H}_2\text{O} + \text{CO}_2$$  \hspace{1cm} (18)

acting as actinolite and hedenbergite as diopside.

For high $T$:

$$\text{SiO}_2 + \text{CaMg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2 + 3\text{CaCO}_3 \rightarrow 5\text{CaMgSi}_2\text{O}_6 + \text{H}_2\text{O} + \text{CO}_2$$  \hspace{1cm} (19)

acting as tremolite and diopside as diopside.

where the transformation point for eq. 19 lies higher than for eq. 18. The upper part of diagram 9 results from the explained condition, and from the petrographic experience that the pyroxene side of the equations is stable at higher metamorphic grade than the actinolite side.

Example II. The phlogopite—calcite, microcline equilibrium.

The characteristic mica of the metamorphic limestones is phlogopite. The mineral occurs in both contact and regional metamorphic marbles. Because of the content of fluorine in phlogopite, it is very reasonable to assume a pneumatolytic origin of the phlogopites in metamorphic limestones. But the occurrence of Mg-mica in ordinary regional metamorphic skarns without other pneumatolytic minerals demands a different explanation of its origin.

T. F. W. Barth has suggested that the occurrence of metamorphic phlogopite in marbles is due to a deficit of silica in the paragenesis.² But this assumption cannot always explain the fact that the Fe-rich biotite does not appear in intermediate and high grade limestones. Biotite only occurs in low grade marbles where hornblende and pyroxene are not stable and hence biotite will not react with calcite forming hornblende and diopside. But as soon as the $P,T$-conditions cross the lowest stability boundary of hornblende or diopside, biotite disappears leaving its place to lime silicates in contact with calcite.

¹ H. Ramberg loc. cit. p. 61.
Fig. 14. Sub-solidus equilibrium diagram of the biotite, calcite $\rightarrow$ potash feldspar, lime silicate parageneses. Other than the elements which are given in the fig., silica and water must be present in sufficient amount.

The Mg-rich phlogopite, on the other hand, may occur up to the highest grade of metamorphic marbles.

The biotite series will react with calcite forming lime silicates (hornblende or diopсидic pyroxen) and potash feldspar. The feldspar, hornblende side of the equation is the high temperature paragenesis. But we must assume that the pure Fe-end member reacts at considerably lower temperatures than the pure Mg-end member of the phlogopite-lepidomelane series. According to this explanation the diagram fig. 14 appears. It gives a simple and natural explanation of the occurrence of phlogopite and the absence of biotite in metamorphic marbles.

**Example 12. The hypersthene—pigeonite equilibrium.**

As the last example of sub-solidus transition we shall consider a combination of the eutectic and the isodimorphic type.

The pyroxene of the basaltic lavas, the pigeonite, is a typical illustration of such a combination type. Disregarding Al, Fe··· and Na, the pigeonite is a mixed crystal of the clinohypersthene and the diopside series:

$$(\text{Mg, Fe})_2 \text{Si}_2 \text{O}_6 \text{ and } (\text{Mg, Fe}) \text{Ca Si}_2 \text{O}_6.$$  

The Ca-free compounds occur as isodimorphic series (p. 60) the high temperature modifications of which are monoclinic and the low temperature modifications orthorhombic. Only the high temperature modifications are miscible with the diopside, forming pigeonite. Diopside has only one modification. Accordingly, there must exist a eutectic sub-solidus equilibrium between the orthorhombic hypersthene $((\text{Mg, Fe})_2 \text{Si}_2 \text{O}_6)$ and the 4-component mixed crystal: pigeonite...
Fig. 15. Equilibrium diagram of the orthopyroxene (enstatite) and the clinopyroxene (pigeonite) in solid state. The vertical plane FeSiO₃, MgSiO₃, 1140°, 995° is redrawn after Bowen and Schairer (op. cit.) The vertical plane rising from FeSiO₃, CaFeSi₂O₆ shows the equilibrium diagram of the eutectic sub-solidus phase transition between pure ferrosilite and the mixed crystal clinoferrasilite-hedenbergite. The plane rising from MgSiO₃, CaMgSi₂O₆ represents the equilibrium of eutectic type between pure enstatite and the mixed crystal clinoenstatite — diopside. Above the curved surface A, B, 1140°, 995° only pigeonite (and diopside) is stable. Below the mentioned surface pigeonite is in stable equilibrium with orthopyroxene. At point X (temperature equal to T₁° and chemical composition given by point Y) a pigeonite of composition c (or b) exists in equilibrium with rhombic hypersthene of composition a. As the temperature increases from X to Z, the pigeonite gradually grows richer in (Fe, Mg)-silicate, and at point Z the last rest of the orthopyroxene disappears.
At temperatures decreasing below the transformation point: clino­hypersthené→ortohypersthené the pigeonite must gradually get poorer in the (Mg, Fe) SiO₃ compound, which separates from the pigeonite as orthohypersthené.

But the Ca/(Mg, Fe) ratio of the pigeonite which is in stable equilibrium with orthohypersthené is not only dependent on the P,T-conditions; also the Fe/Mg-ratio in the pyroxenes play a role. Fig. 15 shows schematically the equilibrium conditions.

Even at temperatures far below the transformation point of the Ca-free pyroxenes, the pigeonitic 4-component mixture must exist, but now with a smaller amount of the (Mg, Fe)₂Si₂O₆-compound in solid solution. We have a diopsidic pyroxene with excess of Mg and Fe.

The association: orthopyroxene — clinopyroxene (pigeonite) has been discussed by many investigators (see Barth¹ and the references in his paper) but always with the conclusion that the pigeonitic pyroxenes which occur in rocks containing orthopyroxenes are metastable phases. In my opinion the two pyroxenes are, as we have seen, stable together over a wide temperature range.

Diopside and hypersthené is a common association in rocks of the charnocite-anorthosite kindred, and in rocks belonging to the granulite facies. An excess of the hypersthené-compound in the diopside of these rocks is very common.²

Under the high P,T-conditions represented by the granulite facies the equilibrium between the minerals probably is well on the way to complete adjustment. The excess of Mg- and Fe-silicate in the diopside existing together with hypersthené may accordingly appear as a usable geological thermometer and barometer within the granulite facies.

IV. THE SUB-SOLIDUS REACTIONS IN MIXED CRYSTALS, AND THE FACIES CLASSIFICATION OF ROCKS

A definite mineral facies represents a definite P,T-interval within which the rocks have crystallized or recrystallized. The different facies are characterized by the stability field of their critical or typomorphic minerals. Since these index minerals usually are solid solutions of common rock-forming minerals the phase-transitions

of solid solutions, as discussed above, are of great importance in establishing the border lines between the several facies.

We shall now briefly go through the normal regional metamorphic mineral facies.1

1. The transition: green schist facies \(\rightarrow\) epidote amphibolite facies.

In the green schist facies the association: talc—calcite is stable. By crossing the P,T-border line against the epidote amphibolite facies, talc and calcite react forming actinolite (p. 55). But this transformation "point" varies with the Fe/Mg-ratio in the paragenesis. In Fe-rich environments the transformation point lies lower than in Mg-rich environments; i.e. at high Mg/Fe-ratio the green schist paragenesis: talc-calcite exists at higher temperatures than does the amphibolite facies index mineral: actinolite at lower Mg/Fe-ratio, (fig. 9). The whole isomorphous actinolitic series is therefore not suitable as a basis for distinguishing between the two facies. The Fe/Mg-ratio of the actinolite which shall characterize the transition: green schist facies \(\rightarrow\) epidote amphibolite facies must be defined.

The transformation: talc \(\rightarrow\) anthophyllite lies between the two above mentioned facies. This transition is also highly dependent on the Fe/Mg-ratio, (fig. 8 p. 54).

The transformation: chlorite \(\rightarrow\) almandine probably lies at the P,T-condition under consideration. Here the Fe/Mg-ratio is not the only factor; also the Mn-contents of the paragenesis are of the greatest importance, as shown on p. 64.

2. The transition: epidote amphibolite facies \(\rightarrow\) amphibolite facies.

According to Eskola,2 the epidote amphibolite facies is characterized by unstability of any amount of anorthite in the plagioclase. All the "anorthite molecule" exists in the epidote minerals. These conditions, however, occur only at very low temperature; surely far below the temperature which Eskola thought to be the highest stability temperature of the epidote amphibolites — the rocks which have given the facies its name.

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1 P. Eskola, in Barth, Correns and Eskola loc. cit. p. 334—360.
2 P. Eskola, Loc. cit. p. 357.
I will therefore propose to fix the lowest P, T-boundary of the epidote amphibolite facies by the association: \textit{Epidote} — \textit{An}_{10} \textit{Ab}_{90}, and the highest P, T-boundary by the association: \textit{Epidote}—\textit{An}_{80} \textit{Ab}_{20}. Below \textit{An}_{10}, I propose to put green schist facies, and above \textit{An}_{80} we put amphibolite facies which reaches up to the highest P, T-values at which common hornblende is stable.

3. The transition: amphibolite facies $\Rightarrow$ granulite facies.

The association \textit{pyrope-almandine garnet} and \textit{potash feldspar} is critical for the granulite facies. On crossing the borderline into the amphibolite facies the two mentioned minerals react, forming biotite (p. 58—60). According to the explanations on p. 59 the reaction point is highly influenced by the Mn/(Fe, Mg) ratio of the paragenesis. Some amount of Mn in the garnet stabilizes the association: garnet—potash feldspar at P, T conditions lower than usual.

Another critical transformation between the two last mentioned facies is the reaction: \textit{bronzite $\Leftrightarrow$ anthophyllite} (or cummingtonite). This transformation is also dependent on the Fe/Mg-ratio of the rocks (p. 62).

4. The transition: sanidinite facies $\Rightarrow$ hornfels facies.

\textit{Pigeonite} is a critical mineral in the sanidinite facies (diabase facies). By the transition to hornfels facies, or to granulite facies also, the pigeonite decomposes, forming diopsidic pyroxene and hypersthene. As discussed in example 12 p. 64 the decomposition point varies greatly with the Ca/(Fe, Mg)-ratio and also with the Fe/Mg-ratio of the paragenesis.

The importance of the eutectic and the isodimorphic types of sub-solidus phase transition for the facies classification of rocks is best understood by considering the equilibrium diagrams figs. 6—15.

Of course, one must remember that most of the diagrams are more or less hypothetical. They give the principal features of the sub-solidus equilibrium, the exact mineralogical and chemical data can only be found by very accurate paragenetical and chemical studies of metamorphic rocks.
Another thing of the greatest significance in connection with the diagrams shown in this paper is the mutual dependence of pressure and temperature during the metamorphism. It seems as if there exists a normal regional metamorphism during which \( P \) and \( T \) vary sympathetically. High grade metamorphism therefore means that both \( P \) and \( T \) are high, low grade that both \( P \) and \( T \) are low.

The equilibrium diagrams represent conditions during this normal regional metamorphism. The fields I, II, III and IV in the different diagrams represent the green schist facies, the epidote amphibolite facies, the amphibolite facies and the granulite facies respectively. And since every mineral facies has its definite \( P,T \)-field it is obvious that the borderlines between the different facies cannot coincide with reaction or transformation points in all diagrams. In diagram 9, for instance, the transition: talc $\leftrightarrow$ Mg-tremolite coincides with the boundary between epidote amphibolite facies and amphibolite facies. In diagram 7 the same boundary represents no discontinuous point, but is characterized by the association epidote—\( \text{An}_{85}\text{Ab}_{65} \), and so on.

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