

On the  $p$ - $T$  Diagrams of the Trimorphic Minerals of  
 $Al_2SiO_5$  with a Special Reference to Andalusite and  
Cyanite as a Geological Thermometer or  
a Geological Piezometer

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**Abstract**

By calculating the Gibbs free energy difference between the trimorphic minerals  $Al_2SiO_5$ , sillimanite, andalusite, and cyanite, are drawn the  $p$ - $T$  diagrams, and it is found that andalusite is stable in the area of high temperature and low pressure, cyanite is stable in the area of high pressure and low temperature, and sillimanite is stable in the intermediate area. It is pointed out thermodynamically that the  $p$ - $T$  diagram may be affected by impurities included in the minerals. In the last part of this paper, are made two estimates as an application of the  $p$ - $T$  diagrams that the temperature of granite magma yielding andalusite as a contact mineral is higher than 1760°K, and that the isotropic part of the pressure produced by a dynamo-metamorphism forming cyanite is greater than about 50,000 atm.

**Introduction**

It is well-known that sillimanite, andalusite, and cyanite are trimorphic minerals with a chemical composition of  $Al_2SiO_5$ . An investigation of the stability correlation of these three minerals under the atmospheric pressure was already undertaken by F. NEUMANN<sup>1)</sup> standing on the thermodynamics.

But geologists require to investigate the correlation of these three minerals under any isotropic pressure  $p$  (atm) and at any temperature  $T$  (°K).

For doing this, we may introduce the Gibbs free energy, as the second law of thermodynamics shows that a mineral characterized by the smallest Gibbs free energy is the most stable under the given conditions of  $p$  and  $T$ . Here let us use the following thermodynamical quantities :

$G$ : Gibbs free energy	in cal/mol
$H$ : Enthalpy	in cal/mol
$U$ : Internal energy	in cal/mol
$S$ : Entropy	in cal/°K/mol

$C_p$ :	Heat capacity at a constant pressure	in cal/°K/mol
$V$ :	Volume	in cal/atm/mol
$v$ :	Volume	in cm <sup>3</sup> /mol

And let us represent the above quantities for sillimanite, andalusite, and cyanite by suffixes  $s$ ,  $a$ , and  $c$  respectively, for example  $G_a$  for the Gibbs free energy of andalusite.

As Gibbs free energy is defined by

$$G = H - TS = U + pV - TS,$$

a small change of  $dG$  is

$$dG = Vdp - SdT.$$

Therefore,  $G$  is a function of  $T$  and  $p$ ,

$$G = G(p, T), \quad (3)$$

and we have

$$\left(\frac{\partial G}{\partial p}\right)_T = V, \quad \left(\frac{\partial G}{\partial T}\right)_p = -S. \quad (4), (5)$$

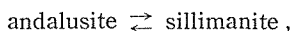
Let us introduce the Gibbs free energy differences given by

$$\Delta G_{a-s} = G_a - G_s, \quad (6)$$

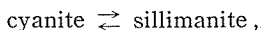
and

$$\Delta G_{c-s} = G_c - G_s. \quad (7)$$

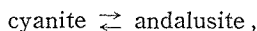
If we know numerical values of  $\Delta G_{a-s}$  and  $\Delta G_{c-s}$ , we can determine the differences between any two values of  $G_a$ ,  $G_c$ , and  $G_s$ , so that we can know the mineral of the smallest Gibbs free energy. Also signs of  $\Delta G_{a-s}$  and  $\Delta G_{c-s}$  decide respectively the directions of the reactions



and



and that of the difference of  $\Delta G_{a-s}$  and  $\Delta G_{c-s}$  does that of the reaction



as

$$\Delta G_{c-a} = G_c - G_a = \Delta G_{c-s} - \Delta G_{a-s}. \quad (8)$$

#### The stability's correlation under the atmospheric pressure

The heat capacity  $C_p$  at a constant pressure is connected with the entropy and the enthalpy by

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}, \quad \left(\frac{\partial H}{\partial T}\right)_p = C_p. \quad (9)$$

By taking definite integral of the right sides of (9) from  $T=0$  to  $T=T$  for a constant

pressure of  $p=1$  atm, we can obtain the expressions of the two differences  $S(1, T) - S(1, 0)$  and  $H(1, T) - H(1, 0)$ . And putting  $H(1, T)$  and  $S(1, T)$  thus obtained into (1), the Gibbs free energy  $G(1, T)$  takes the form

$$G(1, T) = \int_0^T C_p dT - T \int_0^T \frac{C_p}{T} dT + H(1, 0), \quad (10)$$

as  $G(1, 0) = H(1, 0)$  and  $S(1, 0) = 0$ .

F. NEUMANN measured the heat capacities  $C_p$  and the heats of reaction with hydrofluoric acid for sillimanite, andalusite, and cyanite, and he computed the Gibbs free energy differences  $\Delta G(1, T)_{a-s}$  and  $\Delta G(1, T)_{c-s}$  under the atmospheric pressure, by being based upon the equation (10). In Fig. 1 are shown the  $\Delta G(1, T)$  diagrams thus determined by F. NEUMANN.

In Fig. 1 the  $\Delta G(1, T)_{a-s}$  curve decreases with increasing temperature and intersects the temperature-axis at  $1760^\circ K$  ( $1487^\circ C$ ), but the  $G(1, T)_{c-s}$  curve steadily increases positively.

The  $\Delta G(1, T)_{a-s}$  curve shows that sillimanite is more stable than andalusite in a temperature range between  $0^\circ K$  to  $1760^\circ K$ , as in this range we have  $G(1, T)_s < G(1, T)_a$ , but is unstable for temperatures above  $1760^\circ K$ , and that sillimanite is in equilibrium with the andalusite at  $1760^\circ K$ .

To this equilibrium temperature NEUMANN has estimated an error of  $\pm 180^\circ K$  due to experimental errors.

The  $\Delta G(1, T)_{c-s}$  curve shows that cyanite is more unstable than sillimanite in all temperatures above  $0^\circ K$  and no equilibrium points exist for the cyanite-sillimanite system.

As from (8)  $\Delta G(1, T)_{c-a} = \Delta G(1, T)_{c-s} - \Delta G(1, T)_{a-s}$ , the  $\Delta G(1, T)_{c-a}$  curve should positively increase with increasing temperature more steeply than the curve of  $\Delta G(1, T)_{c-s}$  does, that is, cyanite is more unstable than andalusite.

As  $G(1, T)_a = G(1, T)_s + \Delta G(1, T)_{a-s}$  and  $G(1, T)_c = G(1, T)_s + \Delta G(1, T)_{c-s}$ , Fig. 1 gives us  $G(1, T)_s < G(1, T)_a < G(1, T)_c$  in the temperature range from  $0^\circ K$  to  $1760^\circ K$ . Therefore, sillimanite is the most stable among the trimorphic minerals of  $Al_2SiO_5$  in this temperature range and under the atmospheric pressure.

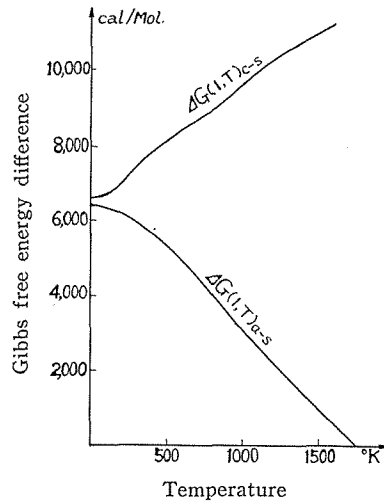


Fig. 1. Temperature dependency of Gibbs free energy difference for cyanite-sillimanite and that for andalusite-sillimanite systems (after F. NEUMANN)

### Volumes per mol $v$ of sillimanite, andalusite, and cyanite

For later usage let us calculate here the volumes per mol of sillimanite, andalusite, and cyanite from their densities and the molecular weight  $161.98 \text{ gm}$  of  $Al_2SiO_5$ , giving

	density		volume $v$	
sillimanite	3.24	$\text{gm}/\text{cm}^3$	50.0	$\text{cm}^3/\text{mol}$
andalusite	3.16~3.2		51.4~50.6	
cyanite	3.56~3.67		45.5~44.1	

The values of  $v$  can be computed from the volumes of unit cells of these minerals and the numbers of atoms (Al:8, Si:4, O:20)<sup>2)</sup>, giving

	Volume of unit cell	Volume $v$
sillimanite	$323.3 \pm 2.4 \text{ \AA}^3$	$49.0 \pm 0.4 \text{ cm}^3/\text{mol}$
andalusite	$340.7 \pm 2.2$	$51.6 \pm 0.4$
cyanite	$287.0 \pm 2.0$	$43.5 \pm 0.4$

From the above two results let us employ the following values being valid for the atmospheric pressure and the room temperature:

$$\left. \begin{array}{l}
 \text{sillimanite} \quad \bar{v}_s = 49.3 \text{ cm}^3/\text{mol} \\
 \text{andalusite} \quad \bar{v}_a = 51.3 \\
 \text{cyanite} \quad \bar{v}_c = 43.8
 \end{array} \right\} \quad (11)$$

### Stability correlation of $Al_2SiO_5$ minerals for any pressure and temperature

$T$  being held constant, (4) gives rise to

$$G(p, T) = G(1, T) + \int_1^p V(p, T) dp. \quad (12)$$

As  $V=0.0242 \times v$ , the Gibbs free energy difference between any two of the trimorphic minerals is given by from (12)

$$\Delta G(p, T) = \Delta G(1, T) + 0.0242 \int_1^p \Delta v(p, T) dp. \quad (13)$$

The numerical value of  $\Delta G(1, T)$  in (13) for a given temperature can be found from the Neumann curves of  $\Delta G(1, T)$  shown in Fig. 1. But regrettably we does not know how  $\Delta v(p, T)$  varies with  $p$  and  $T$ . We might assume in a first approximation that the volume  $v$  of a silicate mineral is not so greatly influenced by large changes in pressure and temperature, unless its crystal structure changes. Because its compressibility is of the order of  $10^{-12} \text{ cm}^2/\text{dyne}$  and its thermal volumetric dilatation is that of  $10^{-5}/^\circ K$ ; the former indicates 1% volume decrease due to increase of 10,000 atm, and the latter 1% volume increase due to

a temperature increase of  $1,000^\circ K$ . We may write  $v(p, T) = \bar{v} + v'(p, T)$  where  $v' \ll \bar{v}$  from the above considerations. Then the volume difference  $\Delta v$  is

$$\Delta v_{a-s} = (\bar{v}_a - \bar{v}_s) + (v'_a - v'_s), \quad \text{etc. } (c-s, c-a), \quad (14)$$

where  $\bar{v}_a - \bar{v}_s = 2.0$ ,  $\bar{v}_c - \bar{v}_s = -5.5$ ,  $\bar{v}_c - \bar{v}_a = -7.5 \text{ cm}^3/\text{mol}$ .

When a pressure change of 10,000 atm or a temperature change of  $1,000^\circ C$  occurs, the above said values of compressibility and thermal volumetric dilatation produce a value of about  $0.5 \text{ cm}^3/\text{mol}$  for the absolute values of  $v'_a$ ,  $v'_s$ , and  $v'_c$ . As their signs are the same for the same pressure and temperature changes, the differences  $|v'_a - v'_s|$ ,  $|v'_c - v'_s|$ , and  $|v'_c - v'_a|$  will be less than  $0.5 \text{ cm}^3/\text{mol}$ . Therefore we may put in the first approximation

$$\left. \begin{aligned} \Delta v_{a-s} &\doteq \bar{v}_a - \bar{v}_s = 2.0, & \text{cm}^3/\text{mol} \\ \Delta v_{c-s} &\doteq \bar{v}_c - \bar{v}_s = -5.5, & \text{,,} \\ \Delta v_{c-a} &\doteq \bar{v}_c - \bar{v}_a = -7.5, & \text{,,} \end{aligned} \right\} \quad (15)$$

But these approximations (15) will become erroneous for much greater changes of pressure and temperature over 10,000 atm and  $1,000^\circ K$  respectively. As will be seen later on, we employ a pressure range of  $0 \sim 80,000 \text{ atm}$  and a temperature range of  $0 \sim 2,000^\circ K$ , and therefore, our results estimated for the higher extrimities of these ranges should be seen as quasi-quantitative, excepting the results for  $p=0$  which is independent of  $\Delta v$ 's (cf. (13), (15), (16), ..., (21)).

Then we get from (13) and (15),

$$\Delta G(p, T)_{a-s} = \Delta G(1, T)_{a-s} + 0.0484p, \quad (16)$$

$$\Delta G(p, T)_{c-s} = \Delta G(1, T)_{c-s} - 0.133p, \quad (17)$$

$$\Delta G(p, T)_{c-a} = \Delta G(1, T)_{c-a} - 0.182p, \quad (18)$$

by putting  $p-1=p$  as  $p \gg 1$ .

The condition of the equilibrium,  $\Delta G=0$ , gives us from (16), (17), and (18)

$$p = -\frac{\Delta G(1, T)_{a-s}}{0.0484} \quad \text{for the system andalusite-sillimanite,} \quad (19)$$

$$p = \frac{\Delta G(1, T)_{c-s}}{0.133} \quad \text{for the system cyanite-sillimanite,} \quad (20)$$

$$p = \frac{\Delta G(1, T)_{c-a}}{0.182} \quad \text{for the system cyanite-andalusite.} \quad (21)$$

The  $p-T$  diagrams shown in Figs. 2 and 3 have been obtained from (19), (20), and (21). The stable regions of the minerals are shown in the figures by writing their names.

As seen in Fig. 1, F. NEUMANN does not draw the  $\Delta G(1, T)_{a-s}$  curve beyond  $1760^\circ K$ . Therefore, in drawing the  $p-T$  diagram of  $\Delta G_{a-s}=0$ , the values of  $\Delta G(1, T)_{a-s}$  needed for temperatures above  $1760^\circ K$  has been estimated by an natural extrapolation of the Neumann curve for  $\Delta G(1, T)_{a-s}$ .

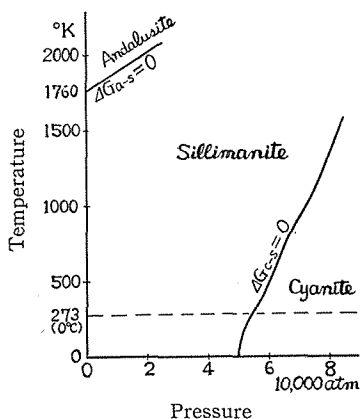


Fig. 2.  $p$ - $T$  diagrams of andalusite-sillimanite and cyanite-sillimanite systems

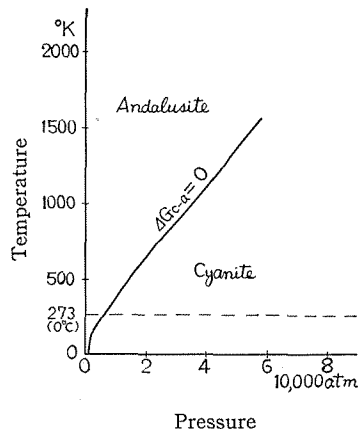


Fig. 3.  $p$ - $T$  diagram of cyanite-andalusite system

### $p$ - $T$ diagram and impurities

The three curves in the  $p$ - $T$  diagrams (Figs. 2 and 3) obtained by  $\Delta G=0$  naturally involve certain errors arising from the errors in the adopted values of  $\Delta G(1, T)$  and  $\Delta v(p, T)$  shown in (13). The errors in the adopted values of  $\Delta v(p, T)$  have been disregarded by the discussion in the previous section, and here let us consider the effects of an error in  $\Delta G(1, T)$  due to impurities the minerals may involve.

A mineral includes usually some elements as impurities differing from those indicated by its molecular formula. The impurities may give rise to certain strain in the crystal lattice, so that certain change would be produced not only in the potential energy and the kinetic energy of the crystal lattice, but in all the thermodynamical quantities. Let us denote the Gibbs free energy of a pure mineral by  $G$  and the increment of that due to the addition of impurities by  $g$ , and then the Gibbs free energy of a mineral including impurities,  $G'$ , is represented by  $G'=G+g$ , where perhaps  $|g|\ll|G|$ .

In our problems, then, the Gibbs free energy difference is given by,

$$\Delta G'_{a-s} = (G_a - G_s) + g_a - g_s, \quad \text{etc.},$$

where  $(G_a - G_s)$ ,  $g_a$ , and  $g_s$  may be of the same order of magnitude and  $g_a$  and  $g_s$  may be different in signs. In fact,  $G_a - G_s$  is far smaller than  $G_a$  or  $G_s$ ; the former is  $10^3 \sim 10^4$  as seen from Fig. 1 and the latter  $10^5 \sim 10^6$  as estimated from the value of enthalpy at ordinary state,  $-H \approx 650 \text{ Kcal/mol}$  for  $Al_2SiO_5$  minerals.

It is, therefore, noteworthy that assumptions of

$$|g_a - g_s| \ll |G_a - G_s| \quad \text{and} \quad \Delta G'_{a-s} \approx G_a - G_s$$

are erroneous, that is the Gibbs free energy difference of the minerals including impurities may be not approximately equal to that of the pure minerals. Therefore the impurities would play an important rôle in affecting the equilibria between the trimorphic minerals.

The three mineral samples employed by F. NEUMANN may have included some impurities of different kinds and in different amounts. If this view point is not wrong, the Neumann curves of  $\Delta G(1, T)$  (Fig. 1) may be looked upon as different in certain amount from those of the pure minerals. As the  $p-T$  diagrams shown in Figs. 2 and 3 have been derived from the said Neumann curves, these diagrams may be looked upon as different from the corresponding diagrams of the pure minerals or synthesized ones including no impurities.

It is really an important thing to clarify the effects of the impurities in a quantitative manner. But from the stand point of interpretation of a geological phenomenon in a given area, what we need is the  $p-T$  diagram of the natural minerals sampled in this area which may involve impurities. And it is expected that the  $p-T$  diagrams may change in certain amount from place to place, as the impurities may change in quality and also in quantity from place to place where the minerals responsible to these diagrams have been sampled.

### Applications to geological phenomena

In the first place let us mention the following five geological and mineralogical facts which the  $p-T$  diagram (Fig. 2) seems to be able to interpret:

(1) Andalusite occurs always in contact metamorphic rocks changed from shaly rocks. This fact suggests that andalusite has been produced at high temperatures.

(2) Sillimanite occurs in gneiss and crystalline schist, and cyanite does in crystalline schist highly dynamo-metamorphosed. This facts suggest that sillimanite and cyanite have been produced under high pressures.

(3) Densities of cyanite, sillimanite, and andalusite under normal pressure and temperature are respectively 3.56~3.67, 3.24, and 3.16~3.2  $gm/cm^3$ . Crystal structure of cyanite has oxygen atoms arranged in closest packing<sup>2)</sup>. These facts would suggest that pressures under which the three minerals were originally formed were in an increasing order of andalusite  $\rightarrow$  sillimanite  $\rightarrow$  cyanite.

(4) Sillimanite occurs more frequently than the other two minerals do. This suggests that the stable area in the  $p-T$  diagram of sillimanite is broader than those of the other two minerals.

(5) Andalusite occurring in pegmatite is frequently found under a microscope and even by naked eyes as changed into sillimanite. This suggests that a temperature decrease undergone by andalusite after its formation at a high temperature inverted it into sillimanite which is stable in low temperatures.

In a laboratory, nobody can yet succeed in inverting sillimanite into andalusite by heating the former. It is generally accepted that when sillimanite is heated

under the atmospheric pressure, it decomposes into mullite+liquid  $\text{SiO}_2$  at a temperature of  $1818^\circ\text{K}$  ( $1545^\circ\text{C}$ ). This temperature is nearly equal to the andalusite-sillimanite equilibrium temperature at the atmospheric pressure,  $1760^\circ\text{K}$  ( $1487^\circ\text{C}$ )  $\pm 180^\circ\text{K}$  determined by F. NEUMANN. He explains that the sillimanite  $\rightarrow$  andalusite inversion by heating at 1 atm can not take place, as the sillimanite has disappeared due to its decomposition which would have taken place at the temperature lower than the inversion temperature, and he suggests by taking into consideration the error of  $\pm 180^\circ\text{K}$  that the equilibrium temperature may be somewhat higher than  $1818^\circ\text{K}$  ( $1545^\circ\text{C}$ ). The discrepancy between  $1818^\circ\text{K}$  and  $1760^\circ\text{K}$  might be attributed to an effect of difference in impurities included in the two samples employed in the determination of these two temperatures. However, the present authors propose an other interpretation contrary to F. NEUMANN that the equilibrium temperature may be by certain amount lower than the decomposition temperature of  $1818^\circ\text{K}$  being in the vicinity of  $1760^\circ\text{K}$  and that the sillimanite  $\rightarrow$  andalusite inversion takes place so slowly that the experimental heating can easily reach to the decomposition temperature.

The curve of  $\Delta G_{c-s}=0$  (Fig. 2) indicates that the pressure at which cyanite is stable at the room temperature is greater than 55,000 atm which is a pressure realizable in a laboratory, a pressure at a depth of about 200 km bellow the earth's surface.

Whereas the  $p-T$  diagram (Fig. 2) indicates that at the ordinary temperature and pressure andalusite and cyanite are unstable and sillimanite is stable, the former two minerals do exist at the earth's surface as sillimanite does. This fact may be explained by a quenching of andalusite and cyanite due to reduction of temperature and that of pressure respectively. If this interpretation is not wrong, we may assume that the speeds of andalusite  $\rightarrow$  sillimanite and cyanite  $\rightarrow$  sillimanite inversions are slower than the speeds of reduction of temperature and pressure respectively. When on the contrary the latter speeds are sufficiently slow to allow these inversions, these two minerals can be inverted completely into sillimanite, remaining no traces of andalusite and cyanite. And when the speeds are intermediate, andalusite and cyanite accompany sillimanite.

Both andalusite and cyanite can be utilized, as will be mentioned in the following, as a geological thermometer or a geological piezometer under a understanding that when the pressures or temperatures at which these mineral were originally formed in certain place in the earth's crust are given, the temperatures or pressures at this place can be estimated by the aid of the  $p-T$  diagram (Fig. 2).

**An example of a geological thermometer:** The depth of the bottom of the continental granitic layer is about 15 km below sea-level according to the modern seismology. Therefore, the granitic intrusion in the continental crust may have taken place in the region above this depth, where pressure is smaller than 4,000 atm. When andalusite occurs in metamorphic rocks in contact with granite, the temperature of the granite magma may be inferred to have been not less than  $1760^\circ\text{K}$  ( $1487^\circ\text{C}$ ), as can be estimated from Fig. 2. This estimate is interesting



when compared with the temperature range of  $1100^\circ\sim 1800^\circ\text{C}$  estimated by H. ITÔ<sup>3)</sup> for the granite magma of Kitashirakawa granite, Kyoto, Japan.

**An example of a geological piezometer:** The pressure under which cyanite is stable is higher than 50,000 *atm* as can be seen in Fig. 2. This pressure is a pressure prevailing at a depth of 180 *km* below sea-level. Below this depth the material is already ultra basic and cyanite hardly exists owing to scarcity of aluminum element. Cyanite frequently occurs in dynamo-metamorphic rocks. If it could be assumed that dynamo-metamorphism has not taken place in the deeper part of the earth's crust, then the temperature at which cyanite has been formed may not be very high. However, it is certain that this temperature has been above  $0^\circ\text{K}$  ( $-273^\circ\text{C}$ ). Therefore, it can be inferred from the  $p-T$  diagram of  $\Delta G_{c-s}=0$  (Fig. 2) that the isotropic part of the pressure which a dynamo-metamorphism has produced to form cyanite has been greater than about 50,000 *atm*. This pressure value, however, should be looked upon as quasi-quantitative according to the statements given to the approximations of (15).

**N. B.** After finishing the manuscript of this paper, the present authors have come to notice a paper by S. C. CLARK, Jr. et al.<sup>4)</sup> The experimental result reported by them for the cyanite-sillimanite equilibrium relation shows a qualitative agreement but a quantitative disagreement with our present result. The present authors would like to make an inquiry into this disagreement. However, at present they tentatively have an opinion that this disagreement might be due to difference between impurities in the natural mineral specimens upon which our calculation is based and those in the synthesized ones CLARK et al have dealt with.

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