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CORDIERITE-INDIALITE RELATIONS

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ABSTRACT. It was recently found that minerals in structurally intermediate states between indialite (hexagonal) and common cordierite (pseudohexagonal) exist in nature as well as in artificial products. The structurally intermediate minerals show distinctive X-ray diffraction patterns and optical properties. This finding has led to a serious revision of our knowledge of the minerals of the cordierite group.

On heating at high temperatures, cordierite is transformed into indialite continuously through all gradations. Probably the transformation is of order-disorder type. The stability relations of the minerals of the cordierite group have been determined. The existence of high and low modifications in indialite as well as in cordierites is discussed.

A revised structural classification of the minerals of the cordierite group is presented in the concluding section of this paper.

INTRODUCTION

Indialite is a hexagonal mineral, polymorphic with cordierite (Miyashiro and Iiyama, 1954; Miyashiro and others, 1955). Miyashiro and others (1955, p. 204) wrote: "The existence of crystals in some structurally intermediate state between indialites and cordierites is not impossible, as the crystal structures of cordierites are derived by slight deformations from those of indialites. However, we have not found such an example."

In the summer of 1955, Prof. M. Sambonsugi of Hukusima University sent a mineral from a granitic pegmatite at Sugama in Hukusima Prefecture to Prof. H. Kuno of Tokyo University for identification. The mineral was given to me for examination and I came to the conclusion that it is structurally intermediate between indialite and common cordierite. This finding prompted me to resume a study of cordierite and indialite with special attention to the intermediate states.

Soon I found that such structurally intermediate minerals are not rare either in nature or in artificial products, and it was only from lack of due attention that the intermediate minerals had not been found. All gradations appear to exist between indialite and common cordierite. Structurally intermediate minerals show distinctive X-ray diffraction pattern and optical properties. Heating experiments have clarified the stability relations of the minerals of the cordierite group. The relations between indialite and cordierite resemble those between sanidine and microcline discussed by Goldsmith and Laves (1954a, 1954b).

Though Miyashiro and others (1955) discussed the existence of high and low modifications in cordierite as well as in indialite, the problem is discussed from this new point of view in this paper.

DISTORTION INDEX

Indialite is iso-structural with beryl, whereas the structure of cordierite may be derived by slight distortion from that of indialite. X-ray diffractograms for indialite and cordierite show a general similarity. The pattern in the range of 2θ between 29° and 30° for CuKα radiation is the most distinctive. In this range, at least three peaks (possibly four or five peaks) appear in cordierite, while all these peaks are united to form a single peak in indialite, as shown in figure 1. The three highest peaks of the cordierite pattern between

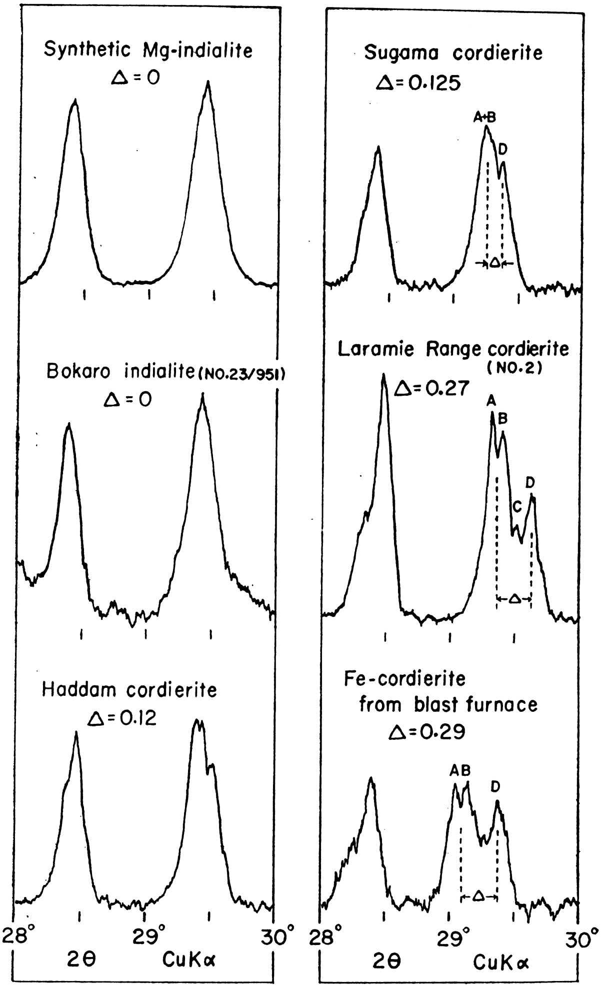

Fig. 1. X-ray diffractograms of indialites and cordierites.

29° and 30° are designated as *A*, *B*, and *D* from the lower angle to the higher. A fourth peak which may appear between the peaks *B* and *D* is designated as *C*. (Probably the peaks *A*, *B*, and *D* represent the reflections (511), (421), and (131), respectively, of CuKα_1 radiation. The peak *C* is probably due to the reflection (421) of CuKα_2 radiation. The corresponding single peak of indialite represents the $(12\bar{3}1)$ reflection.)

The spaces between *A*, *B*, and *D* increase with the degree of distortion of the cordierite structure. In indialite all these spaces are equal to zero. Therefore, these spaces or some quantities related to them can be used as an index to represent the degree of distortion. It has been found that the following value Δ is the most convenient as an index of the degree of distortion:

$$\Delta = 2\theta_D - \frac{2\theta_A + 2\theta_B}{2}$$

where $2\theta_A$, $2\theta_B$, and $2\theta_D$ indicate the deviation angles, in degrees, of the peaks *A*, *B*, and *D*, respectively, for $CuK\alpha_1$ radiation. This value, called the ***distortion index*** in this paper, is equal to zero for indialite, and increases continuously as the distortion increases. The maximum value of the distortion index has been found to be of the order of 0.29-0.31 for any Fe^{+2}/Mg ratio of the mineral.

Cordierite showing the maximum degree of distortion is called ***perdistortional cordierite*** in this paper, whereas the minerals structurally intermediate between indialite and perdistortional cordierite are called ***subdistortional cordierite***. Thus the distortion index of the minerals of the cordierite group is as follows:

Cordierite	Perdistortional cordierite	$\Delta \geqslant 0.29$
	Subdistortional cordierite	$0.29 > \Delta > 0$
Indialite		$\Delta = 0$

In some subdistortional cordierites (for example, in the Sugama cordierite of fig. 1), the peaks *A* and *B* cannot be resolved from each other, thus making an apparently single peak. In such cases, the reading of the united peak of *A* and *B* may be considered to represent $(2\theta_A + 2\theta_B)/2$, because the peaks *A* and *B* usually have similar heights. Then the distortion index of such a mineral is equal to the space between the united peak and the peak *D*. When a sample has a small Δ value and especially when a sample is composed of a mixture of cordierites with small variable Δ values, the resolution of the peaks *A*, *B*, and *D* from one another is bad. Thus, it is not rare that all the peaks *A*, *B*, and *D* are united to form an apparently single peak, broader than a true single peak. The nature of such samples can be inferred from the width of the peak.

The complete indexing of the powder diffraction data of many cordierites with various compositions and Δ values has been performed by Mr. T. Iiyama and published in a separate paper (Iiyama, 1956).

The distortion is probably due to some order-disorder change of the Si and Al atoms in the cordierite-indialite rings Si_5AlO_{18}. Probably the disordered arrangement produces the hexagonal symmetry of indialite, while an ordered arrangement produces the lower symmetry of perdistortional cordierite. Subdistortional cordierite represents an intermediate degree of order. Thus, the distortion index is probably a measure of the degree of order. Rearrangements of Al, Mg, and Fe^{+2} atoms between the rings may accompany the order-disorder transition.

OBSERVED DISTORTION INDICES OF NATURAL CORDIERITES

Introductory Statement

The distortion index and optical properties were measured on various natural cordierites and indialite, as shown in table 1. The possible magnitudes of error are ±0.01 for Δ, ±5° for 2V, and ±0.003 for β. The $(Fe^{+2} + Mn) \times 100/(Mg + Fe^{+2} + Mn)$ ratios given in the last column were calculated

TABLE 1

The Distortion Indices and Optical Constants of Natural Cordierites and Indialite

Locality	Host rock and mode of occurrence	Δ	2V about X	β_D	$\frac{Fe^{+2}+Mn}{Mg+Fe^{+2}+Mn}\times 100$
Bokaro, India	Fused sediments	0.00-ca. 0.31	0°-ca.90°		
Asama, Japan	Xenolith in andesite	0.30	92°	1.544	
Etna, Italy	Xenolith in 1669 lava	0.29			
Kasyo-to near Taiwan	Crystals in andesite	0.25	88°	1.537	
Seto, Japan	Xenocrysts in granite-porphyry	0.27		1.542	
Laramie Range, Wyoming (no. 1)	Metamorphic deposit	0.27	77°-88°	1.548	About 33.0*
Laramie Range, Wyoming (no. 2)	Metamorphic deposit	0.27	77°	1.541	11.1
Orijärvi, Finland	Metamorphic rock	0.27	89°	1.536	15.9
Sori, Japan	Biotite-cordierite-hornfels	0.27	70°	1.555	
Komagane, Japan	Sillimanite-cordierite-biotite gneiss	0.27			
Micanite, Colo.	Sillimanite-cordierite-biotite gneiss	0.26	88°		
Tanzawa, Japan	Metasomatic cordierite-biotite rock	0.245			
Sarurugawa, Japan	Porphyroblasts in gneiss	0.21	80°	1.550	
New Haven, Conn.	Pegmatite	0.26	72°	1.544	22.6
Mont Bity, Madagascar	Quartz vein	0.26	68°	1.544	22.2
Risör, Norway	Pegmatite (?)	0.25	84°	1.535	
Hitati, Japan	Quartz vein	0.25	68°	1.546	21.9
Guilford, Conn.	Pegmatitized gneiss	0.24	75°	1.546	
Dosi, Japan	Pegmatite	0.23	66°	1.566	76.7**
Micanite, Colo.	Pegmatite	0.13	49°	1.568	
Sugama, Japan	Pegmatite	0.125	55°	1.574	70.3
Haddam, Conn.	Pegmatite	0.12	42°	1.560	33.6

* Estimated from FeO = 7.06% alone.

** The original specimen described by Shibata (1936).

TABLE 2
Chemical Compositions of Cordierites

	I	II	III	IV
SiO_2	48.04	47.09	46.99	44.64
Al_2O_3	33.41	34.86	32.72	29.96
TiO_2	0.06	0.03	0.10	n.d.
Fe_2O_3	0.01	0.11	0.16	2.72
FeO	5.04	2.59	7.12	11.02
MnO	0.20	0.05	0.42	1.86
MgO	10.32	11.92	8.38	3.08
CaO	<0.04	0.04	0.06	0.02
Na_2O	1.12	0.78	0.85	2.05
K_2O	0.30	tr.	0.30	0.75
H_2O_+	1.81	2.21	3.07	3.85
H_2O_-	0.23	0.65	0.05	
Total	100.58	100.33	100.22	99.95
α_D	1.539	1.536	1.551	1.560
β_D	1.544	1.541	1.560	1.574
γ_D	1.547	1.546	1.562	1.578
2V about X	68°	77°	42°	55°
Dispersion (about X)	Weak, $v>r$	Very weak, $v>r$	Weak, $v>r$	Weak, $v>r$
Δ	0.26	0.27	0.12	0.125

I: Cordierite from Mont Bity, Madagascar. Analyzed by H. Haramura.
II: Cordierite from Laramie Range, Albany County, Wyoming ("Laramie Range cordierite no. 2"). Analyzed by T. Katsura and H. Haramura.
III. Cordierite from Haddam, Connecticut. Analyzed by H. Haramura.
IV: Cordierite from Sugama, Hukusima Prefecture, Japan. Analyzed by an analyst of the Geological Survey of Japan (Sambonsugi, 1956).

from chemical analyses, four of which are shown in table 2. The observed values of Δ range from 0.00 to 0.31.

The Laramie Range cordierite no. 2, which has a very low Fe^{+2}/Mg ratio, shows $\Delta = 0.29$ after heating at 1000°C for 10 minutes. The Asama cordierite shows $\Delta = 0.30$. The Kasyo-to cordierite, heated at 900°C for 60 minutes, shows $\Delta = 0.31$. An artificial cordierite with a very high Fe^{+2}/Mg ratio shows $\Delta = 0.29$, as will be stated later in detail. Thus, we may consider that the maximum value of the distortion index is of the order of 0.29-0.31 for any Fe^{+2}/Mg ratio.

Distortion Index and Optical Angle

There exists a close relation between the distortion index and optical angle as shown in figure 2. Generally speaking, the larger the distortion index, the larger the optical angle about X. The chemical composition (or the high-low transition to be discussed later) has only a very little effect on the optical angle.

Distortion Index and Refractive Indices

There exists also a relation between the distortion index and refractive indices. Figure 3 shows the relation in cordierite from metamorphic rocks, pegmatites and quartz veins. Two cordierites with the distortion indices of 0.12 and 0.125 have much higher refractive indices than other cordierites with distortion indices of 0.25-0.27 and with nearly same Fe^{+2}/Mg ratios. The smaller the distortion index, the higher the refractive indices, so far as all the other factors remain constant.

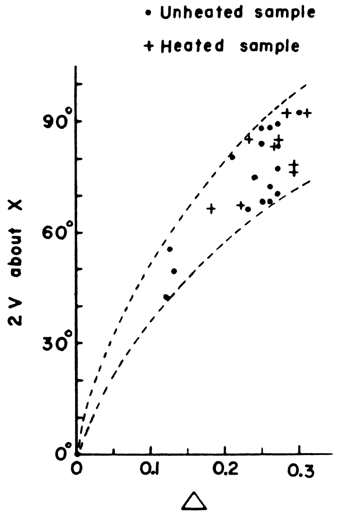

Fig. 2. The relation between the distortion index and optical angle of cordierites and indialite.

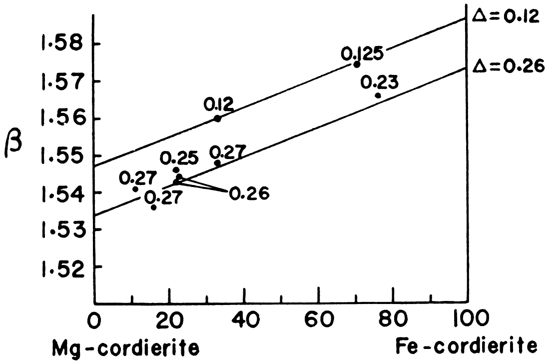

Fig. 3. The relation between the composition and β index of cordierites from metamorphic rocks, pegmatites and quartz veins (i.e. low cordierites). The numerals associated with the points represent the Δ value.

Distortion Index and Modes of Occurrence

Certain samples from volcanic rocks belong to the group of perdistortional cordierite, while the remaining sample belongs to the group of subdistortional cordierite. All the samples from metamorphic rocks, pegmatites, and quartz veins belong to the group of subdistortional cordierite.

It is noteworthy that subdistortional cordierite with $\Delta > 0.20$ was found in metamorphic rocks as well as in pegmatites and quartz veins, while subdistortional cordierite with $\Delta < 0.20$ was found characteristically in pegmatites.

INDIALITE AND CORDIERITE FROM BOKARO COALFIELD

In previous papers (Miyashiro and Iiyama, 1954; Miyashiro and others, 1955, p. 193-194), it was stated that the cordierite-like mineral in fused sediments (so-called para-lava) of Bokaro coalfield, India, was actually indialite. Now I have re-examined two specimens of the fused sediments with special attention to the structurally intermediate states. Thus it has been revealed that some of the cordierite-like crystals are true indialite, but others are subdistortional cordierites with variable Δ values.

Specimen No. 23/951

This specimen contains numerous minute colorless crystals embedded in glass. Most of them do not show twinning. According to conoscopic observations, some of them are completely or nearly uniaxial negative. In other crystals, the central portion is uniaxial negative, whereas the marginal portion is biaxial with optical angles about X smaller than 40°. The refractive indices are $\omega_D = 1.539$ and $\varepsilon_D = 1.534$.

The X-ray diffractogram of the powdered rock has only one peak between 29° and 30° for CuKα radiation, as shown in figure 1. The diffraction data have been indexed completely on the basis of a hexagonal unit cell with dimensions $a = 9.812$ Å and $c = 9.351$ Å, as shown in table 5 of the paper by Miyashiro and others (1955). Thus at least most of the crystals in this specimen are considered to be indialite. Probably the uniaxial mineral is indialite and the biaxial one is subdistortional cordierite with very small Δ values.

Specimen No. 23/952

This specimen contains slightly larger crystals, which generally show complicated twinning between crossed nicols, as was described by Venkatesh (1954). The optical angle of the crystals is highly variable, ranging from a small value to nearly 90° about X.

The X-ray diffractogram has an apparently single but too broad peak between 29° and 30° for CuKα radiation, indicating that probably the crystals are subdistortional cordierites with variable Δ values. Probably the average value of Δ is about 0.15. A small number of the crystals may be true indialite or perdistortional cordierite.

Optical Angle and Optical Anomaly

The results of studies, given in the present and preceding parts of this paper, indicate that the optical angle is a fairly good indicator of the structural states in indialite as well as in cordierites. True indialite is completely uniaxial negative or at least nearly so, and the optical angle becomes generally larger with the increasing Δ values, as already shown in figure 2. Thus, the optical anomaly, if any, is not so remarkable in this case.

ARTIFICIAL INDIALITE AND CORDIERITE

The α form of $Mg_2Al_4Si_5O_{18}$, synthesized and named by Rankin and Merwin (1918), is completely or nearly uniaxial negative without twinning. Certainly it is indialite. Several later investigators, however, reported the formation of artificial "cordierite" with varied optical angles, such as 8°, 30°, 50°, and 82°, usually with twinning (Dittler and Köhler, 1938; Shand, 1943; Sugiura, 1951; Yoder, 1952).

I examined a "magnesium-cordierite" with $2V = 8°$, synthesized and described by Sugiura (1951). It is composed of radial aggregates of crystals, resembling twinning. Its unit cell was found to have a hexagonal shape within the limit of experimental error. Thus, it is either true indialite showing slight optical anomaly or subdistortional cordierite with a very small Δ value. It appears probable that twinned artificial "cordierites" with intermediate optical angles, such as 30° and 50°, are subdistortional cordierites with varied Δ values.

Richardson and Rigby (1949) and Richardson, Ball, and Rigsby (1952) described an artificial cordierite with a very high Fe^{+2}/Mg ratio from blast-furnace linings. A chemical analysis of the cordierite-bearing part showed 27.07 percent FeO and 0.68 percent MgO. It is biaxial negative, and certain crystals exhibit complicated twinning. Recently I obtained a sample of the material through the courtesy of Dr. S. O. Agrell of the University of Cambridge. The X-ray diffractogram shows that it is a perdistortional cordierite with $\Delta = 0.29$ (fig. 1).

Thus, it is probable that indialite and subdistortional and perdistortional cordierites all can be formed in artificial processes under various conditions. The conditions related probably comprise not only the temperature of formation but also the rate of crystal growth and the properties of the surrounding materials. As is shown below, indialite is stable at higher temperatures than subdistortional and perdistortional cordierites. Rapid growth of crystals may favor the formation of indialite and subdistortional cordierites with small Δ values even at temperatures where cordierites with larger Δ values are stable.

In a previous paper (Miyashiro and others, 1955, p. 191-192, 194), it was stated that the "twinning", observed between crossed nicols, of artificial "cordierites" and of Bokaro crystals might actually be a kind of apparent optical structure, genetically related to optical anomaly. At that time I regarded those twinned materials as indialite. However, it has now been clarified that they are probably subdistortional cordierite. Thus there remains no reason to doubt that the structure is true twinning. These twins are, in most cases, very complicated in shape, possibly because of variations of the Δ value in different parts of a single crystal.

HEATING EXPERIMENTS OF CORDIERITES

Introductory Statement

Each small sample of natural cordierite was heated at a certain definite temperature in an electric furnace in air and then taken out to cool. The temperature was controlled within ±20°. The distortion index, optical angle, and refractive indices were measured on the cooled samples.

The rate of structural changes appears to be influenced not only by the heating temperature but also by some unknown factors (for example, possibly by the grain size). Small pieces of cordierite, several millimeters in size, were used as samples in most cases, when available. Certain heated samples were composed of a mixture of cordierites with variable Δ values and optical properties, probably owing to a difference in the rate of structural change in different parts of the samples. In such cases, the estimated average values of Δ, 2V, and/or β are shown in the following tables.

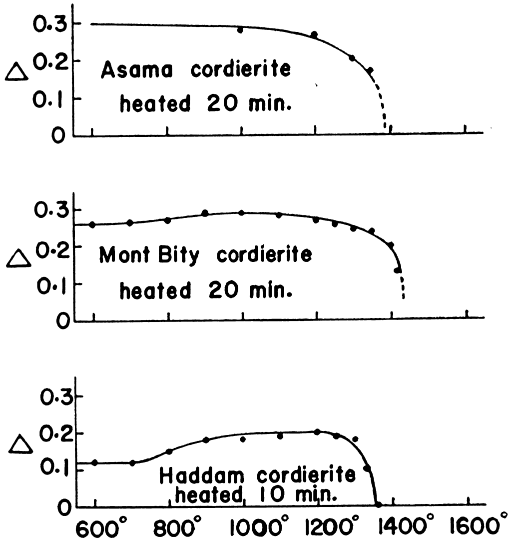

Fig. 4. The changes of the distortion index on heating.

Perdistortional Cordierite

As an example of natural perdistortional cordierite, I used a material from volcano Asama, which lies about 130 kilometers northwest of Tokyo. The cordierite occurs as small grains in xenoliths included in augite-hypersthene andesite. (A detailed petrological and mineralogical description of the cordierite-bearing xenoliths will be made by Mr. S. Aramaki of Tokyo University in the near future.)

TABLE 3

Heating Experiment of the Asama Cordierite

Temperature (°C)	Time of heating (in minutes)	Δ	2V about X	β_D
Room temp.		0.30	92°	1.544
1000	20	0.28	92°	1.547
1200	20	0.265	83°	1.552
1300	20	0.20		
1350	20	0.17		
1400	20	Decomposes		

The results of the heating experiment are summarized in table 3. On heating at high temperatures, the distortion index decreases as shown in figure 4, whereas the optical angle becomes smaller and the β index increases. The color of the mineral becomes darker and brownish. Therefore it is considered that the change in optical angle and refractive indices are due to the gradual structural change towards indialite as indicated by the decrease in Δ, as well as to the oxidation of iron. On heating at 1400°C, the mineral decomposes into liquid and mullite.

Subdistortional Cordierites with $\Delta > 0.20$

Kasyo-to cordierite.—This cordierite occurs as porphyritic individuals, up to 1 centimeter long, in andesite at Kasyo-to, a volcanic island, east of Taiwan (Ichimura, 1936). Very recently I obtained good specimens of it through the courtesy of Dr. T. P. Yen of the Geological Survey of Taiwan.

TABLE 4

Heating Experiment of the Kasyo-to Cordierite

Temperature (°C)	Time of heating (in minutes)	Δ	2V about X	β_D
Room temp.		0.25	88°	1.537
900	20	0.28		1.537
900	60	0.31	92°	1.537

The results of the heating experiment are shown in table 4. On heating at 900°C, the distortion index and optical angle about X increase, while the refractive indices remain practically unchanged. On heating at 1000°C for 20 minutes, the refractive indices still remain practically unchanged. (A more detailed study is in progress.)

Mont Bity cordierite.—This cordierite occurs in a quartz vein cutting through mica schists at Mont Bity, Madagascar. The chemical composition is shown in table 2.

TABLE 5

Heating Experiment of the Mont Bity Cordierite

Temperature (°C)	Time of heating (in minutes)	Δ	2V about X	β_D
Room temp.		0.26	68°	1.544
600	20	0.26		1.538
700	20	0.265		1.538
800	20	0.27		1.536
900	20	0.29	78°	1.536
1000	20	0.29		1.534
1100	20	0.285		1.533
1200	20	0.27	84°	1.533
1250	20	0.26		1.533
1300	20	0.245		1.533
1350	20	0.24		1.533
1400	20	0.20	84°	1.532
1415	20	0.13		

Table 5 and figure 4 show that the Δ value changes on heating and it becomes largest after heating at 900° and 1000°C. This fact may be interpreted as follows: At temperatures below 1000°C, perdistortional cordierite with Δ = about 0.29 is stable. The Mont Bity cordierite is initially in a metastable state with Δ = 0.26. On heating at 700°-1000°C, it gradually changes towards the perdistortional-cordierite state, stable at those temperatures. On heating at 900° and 1000°C for 20 minutes, the stable state is reached. On heating at and above 1100°C, the mineral gradually resumes the subdistortional-cordierite states with smaller Δ values, as such states are stable at those high temperatures. Probably it becomes indialite slightly above 1415°C. (The increase of the Δ value of the Kasyo-to cordierite on heating at 900°C, mentioned before, also may be regarded as a change to the stable state at that temperature.)

In the Asama and Kasyo-to cordierites the β index increases or remains practically unchanged on heating, whereas in the Mont Bity cordierite the β index decreases remarkably on heating. Table 5 shows that the decrease begins at so low a temperature that the change towards the perdistortional-cordierite state, mentioned above, hardly takes place. The Δ value of the sample, heated at 1250°C, is identical with that of the initial material, whereas the β index of the former is much lower than that of the latter. These facts indicate that the decrease of the β index cannot be explained by that kind of structural change alone which is revealed by the change of the Δ value. Being superposed on this kind of structural change, probably another kind also takes place. Thus, as regards the latter kind of structural change, we can distinguish probably two modifications in cordierite, regardless of the Δ value. They are called *low and high cordierites.* High cordierite has much lower refractive indices than low with the same Δ value and composition. The structural change from low to high cordierite also appears to take place gradually through intermediate states.

Initially the Mont Bity mineral is low cordierite, whereas the Asama and Kasyo-to minerals are high cordierite formed at fairly high temperatures under volcanic conditions, and hence they do not show any decrease in β index on heating. Natural cordierite emits water on heating. The relation of this fact to the high-low transition was discussed in another paper (Miyashiro and others, 1955, p. 200-201).

Laramie Range cordierite no. 2.—This cordierite occurs in a metasomatic deposit in meta-norite in the Laramie Range, Albany County, Wyoming (Newhouse and Hagner, 1949). As shown in table 2, it has a very low Fe^{+2}/Mg ratio. It is suitable for heating experiments for long periods at high temperatures, for the oxidation of iron has probably little effect on the properties of this mineral.

The thermal behavior of this mineral is similar to that of the Mont Bity (table 6). Initially it is in a metastable state with Δ = 0.27. On heating at 1000° and 1100°C, it changes to the stable state with Δ = 0.29. On heating at and above 1200°C, the mineral resumes subdistortional-cordierite states with gradually smaller Δ values, which are stable at those temperatures. Probably it becomes indialite eventually at a temperature above 1420°C. (Recently

TABLE 6

Heating Experiment of the Laramie Range Cordierite No. 2

Temperature (°C)	Time of heating (in minutes)	Δ	2V about X	β_D
Room temp.		0.27	77°	1.541
1000	10	0.29	77°	1.530
1000	60	0.29		1.531
1100	60	0.29		
1200	60	0.27		1.530
1400	10	0.24		
1400	60	0.24		
1400	240	0.24		
1420	240	0.21		

Sugiura and Kuroda (1955) made a heating experiment of this specimen. They declared that this cordierite changed to indialite on heating at 1400°C. However, judging from the X-ray diffractogram shown in figure 2 of their paper, it appears to me that the material they obtained by the heating is not indialite but actually a mixture of subdistortional cordierites with variable Δ values.)

The β index decreases on heating. Before heating, $\Delta = 0.27$ and $\beta = 1.541$. After heating at 1200°C, $\Delta = 0.27$ and $\beta = 1.530$. These two samples, with the same Δ value, have different β index. Therefore, it is considered that the initial material is low cordierite, and the heated sample is high cordierite.

Table 6 shows that the mineral reaches the stable state by heating only for 10 minutes. Further heating for a longer period does not cause any more noticeable change in Δ value.

The Laramie Range cordierite no. 1 with a higher Fe^{+2}/Mg ratio ($FeO = 7.06\%$) shows a decrease of about 0.005 in the refractive indices on heating at 1000°C for 10 minutes (Miyashiro and others, 1955, p. 198).

Subdistortional Cordierites with $\Delta < 0.20$

Haddam cordierite.—This cordierite occurs in pegmatite cutting through biotite gneiss at Haddam, Connecticut (Heinrich, 1950, p. 177-178). The chemical composition is shown in table 2.

Table 7 and figures 4 and 5 show the results of the heating experiment. They may be interpreted as follows: Initially the cordierite is in a metastable state with $\Delta = 0.12$. On heating at 700°-1200°C, it changes into states with larger Δ values, which are more stable at those temperatures. The Δ value of the heated samples is largest after heating at 1200°C. However, the state of perdistortional cordierite has not been reached in these heat treatments. Eventually on heating at 1360°C, it becomes indialite. On heating at 1380°C, it decomposes into liquid and mullite.

On heating, the β index decreases gradually probably owing to the two kinds of structural change: one from low cordierite towards high and the other of the changing Δ type.

TABLE 7

Heating Experiment of the Haddam Cordierite

Temperature (°C)	After heating for 10 minutes, Δ	2V about X	β_D	After heating for 60 minutes Δ
Room temp.	0.12	42°	1.560	0.12
600	0.12		1.560	0.12
700	0.12		1.560	0.145
800	0.15		1.547	
900	0.18		1.542	0.15
1000	0.18	66°	1.542	0.19
1100	0.19		1.542	
1200	0.20		1.541	0.20
1250	0.19			0.175
1300	0.18			0.10
1330	0.10			Very small
1360	0.00			0.00
1380	Decomposes			Decomposes

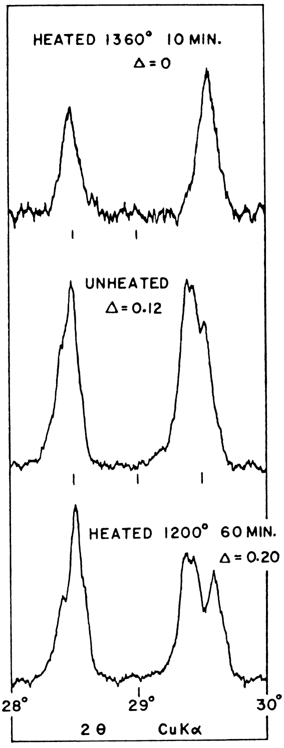

Fig. 5. X-ray diffractograms of unheated and heated samples of the Haddam cordierite.

The state of perdistortional cordierite is much more difficult to reach in the heat treatment of subdistortional cordierite with $\Delta<0.20$ than in that of subdistortional cordierite with $\Delta>0.20$.

The amount of decrease in β index on heating is much larger in subdistortional cordierites with $\Delta<0.20$ than in subdistortional cordierites with $\Delta>0.20$. For example, it is 0.019 in the Haddam cordierite, whereas it is of the order of 0.005-0.011 in subdistortional cordierites with $\Delta>0.20$, as shown before.

Sugama cordierite.—This cordierite occurs in a granitic pegmatite cutting through gneissic hornblende-biotite granodiorite and metamorphic rocks at Sugama near Isikawa, about 200 kilometers north-northeast of Tokyo (Sambonsugi, 1956). Cordierite samples from various parts of the pegmatite mass do not show any noticeable difference in the Δ value. The cordierite has a very high Fe^{+2}/Mg ratio, as shown in table 2.

TABLE 8
Heating Experiment of the Sugama Cordierite

Temperature (°C)	After heating for 10 minutes			After heating for 40 minutes	After heating for 60 minutes
	Δ	2V about X	β_D	Δ	Δ
Room temp.	0.125	55°	1.574	0.125	0.125
500	0.125			0.125	0.125
700	0.135		1.574	0.135	0.135
800	0.22		1.555		
900	0.22		1.555	0.22	0.26
1000	0.22	67°	1.555		
1100	0.22		1.555	0.20	
1150	0.15			0.17	
1175				0.05	
1200	0.00			0.00	
1250	Decomposes			Decomposes	

The results of the heating experiment are shown in table 8. The thermal behavior of this cordierite is similar to that of the Haddam. Initially the cordierite is in a metastable state with $\Delta = 0.125$. On heating at 700°-1000°C, it changes into states with larger Δ values, which are more stable at those temperatures. On heating above 1100°C, the Δ value becomes gradually smaller again. Eventually on heating at 1200°C, it becomes indialite. On heating at 1250°C, it decomposes into liquid, mullite, etc. The remarkable decrease in the β index on heating indicates that the initial material is low cordierite.

Micanite cordierite.—This cordierite occurs in a granitic pegmatite cutting through Precambrian biotite gneiss at the Micanite district in Colorado (Heinrich, 1950). Prof. E. Wm. Heinrich of the University of Michigan kindly gave me specimens of the cordierite, together with a cordierite-bearing country rock.

The pegmatite cordierite shows $\Delta = 0.13$. On heating at 1000°C for 20 minutes, the Δ value becomes 0.22. The β index is 1.568 before heating and 1.549 after heating.

It is of some interest to note that the cordierite in the country rock (sillimanite-cordierite-biotite gneiss) shows $\Delta = 0.26$.

STABILITY RELATION OF CORDIERITE AND INDIALITE

According to the heating experiments of the preceding chapter, perdistortional cordierite ($\Delta = 0.29$-0.31) represents the state stable at low temperatures, and subdistortional cordierites are stable at higher temperatures. At still higher temperatures, indialite ($\Delta = 0$) is stable. Eventually at a very high temperature, indialite decomposes into liquid and crystals (mullite and probably in some cases tridymite). The structural changes take place by heating only for 10 to 20 minutes in many cases.

The temperatures of structural changes and decomposition become lower with increasing Fe^{+2}/Mg ratio as shown in table 9. Judging from the studies of Rankin and Merwin (1918) and of Schairer and Yagi (1952),the decomposition temperatures of pure Mg- and Fe-indialites are 1470° and 1210°C respectively. Thus, we obtain the equilibrium diagram of the system $Mg_2Al_4Si_5O_{18}$—$Fe_2Al_4Si_5O_{18}$ as shown in figure 6.

TABLE 9

Temperatures of Structural Changes and Decomposition

	$\frac{(Fe^{+2}+Mn)\times 100}{Mg+Fe^{+2}+Mn}$	Boundary between perdistortional and subdistortional cordierite	Boundary between subdistortional cordierite and indialite	Decomposing temperature
Laramie Range cordierite no. 2	11.1	Between 1100° and 1200°C	Above 1420°C	?
Mont Bity cordierite	22.2	Between 1000° and 1100°C	Slightly above 1415°C	?
Haddam cordierite	33.6	?	1350°C	1370°C
Sugama cordierite	70.3	?	1180°C	Between 1200° and 1250°C

This diagram gives some informations on conditions of formation of cordierites and indialite. However, it must be emphasized that there are reasons to believe that various structural modifications of cordierite and indialite are formed metastably in many cases in artificial processes as well as in nature. Thus, not only the stability relations but also the mechanism and velocity of crystallization must be taken into consideration for understanding the modes of formation and occurrence of the minerals of the cordierite group.

The manner of change of distortion index with temperature, as shown in figure 4, resembles that of long-range order with temperature in alloys. This fact supports the view that the cordierite-indialite transformation is of the order-disorder type, and the distortion index is a good measure of the degree of order.

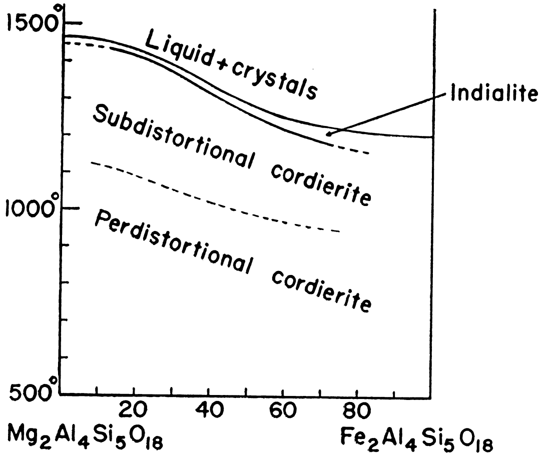

Fig. 6. The equilibrium diagram of the system $Mg_2Al_4Si_5O_{18}$—$Fe_2Al_4Si_5O_{18}$. (The distinction between high and low modifications is not shown in this diagram. "Indialite" and "subdistortional cordierite" of this diagram represent the high modifications, while "perdistortional cordierite" represents both the high and low modifications.

HIGH AND LOW CORDIERITES

In a previous section I pointed out evidence to indicate that the materials from volcanic rocks of Asama and Kasyo-to are high cordierite, while the materials from metamorphic rocks, pegmatites, and quartz veins are low cordierite. (In this paper the term metamorphic rocks does not connote the inclusions in igneous rocks.) Corroborative evidences on this problem will be discussed below.

If we compare the Haddam and Sugama cordierites heated around 900°-1200°C with low cordierites with $\Delta = 0.26$ or so of similar compositions, the former minerals have smaller Δ values (0.18-0.22) and much lower refractive indices than the latter ones whose β index is shown in figure 3. This is contrary to the tendency that the smaller the distortion index of cordierites from metamorphic rocks, pegmatites and quartz veins, the higher the refractive indices. This fact cannot be explained until we recognize that the heated samples belong to the group of high cordierite which has much lower refractive indices than cordierite from metamorphic rocks, pegmatites, and quartz veins (i.e. low cordierite), when they have the same chemical composition.

Probably the transition from low to high cordierite also is of order-disorder type and takes place gradually through intermediate states. The reverse change has not been noticed in my experiments. It is interesting that this transition has only a very little effect on the optical angle, as shown in figure 2.

The refractive indices of low cordierite increase with decreasing Δ. Therefore, indialite ($\Delta = 0$) should have higher refractive indices than low cordierite. However, we know that indialites synthesized in dry melt experiments (i.e. the α-forms of $Mg_2Al_4Si_5O_{18}$ and $Fe_2Al_4Si_5O_{18}$) have much lower refractive indices than low cordierites of the same compositions. Therefore, we must suppose another form of indialite ($\Delta = 0$) with much higher refractive indices than the above-mentioned form of indialite, as the limiting case of decreasing Δ value in low cordierite. Thus, the form of indialite from dry melt (the α-form) may be called *high indialite*, whereas another form of indialite with much higher refractive indices may be called *low indialite*. Through intermediate states, high indialite is probably continuous to high perdistortional cordierite, whereas low indialite may be supposed to be continuous to low perdistortional cordierite.

Yoder (1952) synthesized what appears to be high subdistortional cordierite ($2V = 30°$) by the hydrothermal method at temperatures above 830°C, while he obtained similar crystals ($2V<45°$) with much higher refractive indices by the same method at temperatures below 830°C. The latter is probably a low subdistortional cordierite with a small Δ value. (This material was called the β-form by Karkhanavala and Hummel (1953).)

The high-low transition point of cordierites is probably lower than 830°C, at least in most cases. Therefore, we come to the conclusion that low perdistortional cordierite, high perdistortional cordierite, high subdistortional cordierite, and high indialite are probably stable at successively higher temperatures. Low indialite and low subdistortional cordierite are probably unstable in all cases.

The relation between the refractive indices and chemical composition in high cordierite is discussed in other papers (Miyashiro and others, 1955, fig. 2: Iiyama, 1956).

FORMATION OF LOW SUBDISTORTIONAL CORDIERITE

All the examined cordierites from metamorphic rocks, pegmatites, and quartz veins belong to the class of low subdistortional cordierite, which is unstable as noted above. Probably they were formed as a metastable phase at temperatures so low that the change from the metastable to the stable state could not take place during and after their formation. Low subdistortional cordierites with Δ values smaller than 0.20 occur characteristically in pegmatites, and have Fe^{+2}/Mg ratios larger than 3/7, so far as I am aware. The rapid growth of big crystals and higher Fe^{+2}/Mg ratios in pegmatites may favor the formation of metastable cordierites with such small Δ values.

The lowest limit of temperature at which natural subdistortional cordierite changes into perdistortional on heating should represent the highest possible temperature of its formation. Tables 5, 7, and 8 show that such a change takes place at a temperature as low as 700°C within 1 hour in those cordierites, whereas the Haddam cordierite, heated at 600°C for 7 hours, shows little appreciable change in Δ. These data suggest that the metastable cordierites were formed at temperatures lower than 700°C.

There is, however, a serious defect in this reasoning. The pressures of water vapor and oxygen, under which natural cordierites are formed, differ from those of water vapor and oxygen in the laboratory. Therefore, the manner of emission of water and oxidation on heating in the laboratory must differ from the corresponding phenomena in nature. This difference must have some effect on the temperature and ease of structural changes. Since the magnitudes of these effects are not known, it is impossible to determine the temperature of formation of natural cordierite by simple heating.

The conditions and mechanism of formation of metastable cordierite will be discussed in a later paper.

CONCLUSION

I am presenting below a revised structural classification of the members of the cordierite group of minerals on the basis of the investigation described in this paper.

In order to understand the variations in the structural states of these minerals, the following four limiting forms are to be set forth:

(1) High indialite (identical with the α-form synthesized by Rankin and Merwin, 1918). It is hexagonal ($\Delta = 0$) and stable at very high temperatures. It occurs in fused sediments of Bokaro coalfield in India.

(2) Low indialite (supposed). It is hexagonal ($\Delta = 0$) and unstable at all temperatures. It has been found neither in nature nor in artificial products.

(3) High perdistortional cordierite. It is pseudohexagonal ($\Delta = 0.29$-0.31) and stable at medium temperatures. It was found in xenoliths in andesite from Asama, and also in blast-furnace linings.

(4) Low perdistortional cordierite (supposed). It is pseudohexagonal ($\Delta = 0.29$-0.31) and stable at low temperatures. It has been found neither in nature nor in artificial products, though I expect that it will be found in some metamorphic rocks.

There exist many materials in structurally intermediate states between indialites and perdistortional cordierites. Thus, most of the natural as well as artificial "cordierites" belong to either of the following two classes:

(5) High subdistortional cordierite (intermediate between high indialite and high perdistortional cordierite). It is pseudohexagonal ($0.29>\Delta>0$) and stable at high temperatures. It was found in andesite from Kasyo-to, and also in fused sediments from Bokaro coalfield. Most cordierites in industrial materials may belong to this class.

(6) Low subdistortional cordierite (intermediate between low indialite and low perdistortional cordierite). It is pseudohexagonal ($0.29>\Delta>0$) and unstable at all temperatures. Most cordierites, if not all, in ordinary metamorphic rocks, pegmatites, and quartz veins belong to this class.

The nature of the μ-form of Rankin and Merwin (1918) is not clear. What was called the β-form by Karkhanavala and Hummel (1953) is probably a low subdistortional cordierite with a small Δ value. In this classification I have ignored the existence of intermediate states between high and low modifications in cordierite as well as in indialite, because otherwise the classification would become too complicated.

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