

## Apparent Effects of Molecular Water on the Lattice Geometry of Cordierite

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### Abstract

Changes in the distortion index ( $\Delta$ ) of cordierite are a measure of lattice geometry and are only related to Al-Si ordering insofar as Al and Si distributions affect the lattice parameters. Available structure refinements, infrared absorption data, and dehydration experiments suggest a model in which molecular water and perhaps alkalis distort the lattice geometry, and thereby  $\Delta$ , in a manner dependent on the existing state of Al-Si order in six-membered rings. The proposed model predicts that ordering considerations with respect to molecular water in the structure may bear on the accuracy of thermochemical calculations involving cordierite at elevated temperature and pressure.

### Introduction

The widespread occurrence of cordierite,  $(\text{Fe,Mg,Mn})_2\text{Al}_4\text{Si}_6\text{O}_{18} \cdot n\text{H}_2\text{O}$ , in regional metamorphic terrain, contact aureoles, and less commonly in igneous parageneses has generated considerable interest in the thermochemical stability of this mineral. Experimental and theoretical efforts in this direction, however, are complicated by an incomplete understanding of the relative importance of Al-Si ordering and of the effect of water on the pressure-temperature stability relationships. The importance of the latter effect on zeolites and other hydrous minerals (Greenwood, 1961; Fyfe, Turner, and Verhoogen, 1958) is well documented, but only recently have the relevant experimental data for cordierite become available. Studies by Newton (1972) clearly illustrate the profound effect of relatively small amounts of zeolite-like water on the pressure stability of Mg-cordierite. The terminal breakdown pressure of the anhydrous phase to form enstatite, sillimanite, and quartz at 830°C is 7.7 kbar, whereas the terminal pressure of the same reaction involving hydrous cordierite ( $n_{\text{H}_2\text{O}} = 0.7$ ) is increased to 11.2 kbar. Chernosky (1973) shows that the entropy contribution of water to cordierite during the hydrothermal breakdown of clinocllore would substantially increase the standard free energy and enthalpy of formation. Discrepancies in other experimental data involving the partitioning of Fe and Mg between cordierite and garnet (Hensen and Green, 1971, 1973; Currie, 1971) are attributed to differing

water contents in cordierite (Wood, 1973; Weisbrod, 1973) which further illustrate the importance of this component.

Despite the recognized importance of zeolite-like water in cordierite, there is as yet little understanding of the structural mechanism by which these effects are accomplished. Part of the problem stems from the interpretation of the distortion index ( $\Delta$  index) as determined by X-ray diffraction techniques (Miyashiro, 1957; Schreyer and Schairer, 1961; Zeck, 1969). Miyashiro (1957) first recognized that cordierites from different geologic environments were characterized by differences in the relative positions of the 131, 421, and 511 reflections. A representative diffractogram using  $\text{CuK}\alpha_1$  is shown in Figure 1. In similar cordierites heated to near their incongruent melting point at one atmosphere, the three reflections merge to one, and the  $\Delta$  index is zero. The conventional interpretation of this (Miyashiro *et al.*, 1955) assumes that cordierites with large distortion indices typically occur in regionally metamorphosed terrain characterized by slow heating and cooling. Under such conditions an ordered intracrystalline distribution of cations is likely. In contrast, the dimensionally hexagonal form ( $\Delta = 0$ ) called indialite (Miyashiro *et al.*, 1955) occurs in chilled environments in which disordered structural states are more likely. By analogy with early studies of Al-Si ordering relationships in alkali feldspars (Barth, 1934), the interpretation of the  $\Delta$  index as a parameter to measure Al-Si distributions in tetrahedral sites of cordierite came into being. Subse-

quent studies (Meagher and Gibbs, 1965; Gibbs, 1966; Langer and Schreyer, 1969) led to criticism of this interpretation, but various structural classifications of cordierite based on the distortion index are still retained. Mg-cordierites with varying distortion indices have been synthesized (Schreyer and Schairer, 1961; Schreyer and Yoder, 1964) and suggest that a continuum of chemical or structural states exists between low cordierite (maximum distortion) and high cordierite (minimum distortion).

### Structural Considerations

The order-disorder relationships are best understood by examining the structure of low cordierite (Fig. 2) refined by Gibbs (1966). The effect of ordering Al in  $T_5$  and Si in  $T_3$  and  $T_4$  is to lengthen  $a$  relative to  $b$  because the longer Al-O bond lengths are parallel to  $a$ . A disordered distribution of Al and Si in  $T_3$ ,  $T_4$ , and  $T_5$  equalizes the bond lengths around the six-membered rings such that the dimensional symmetry of this ring is hexagonal. The change in  $\Delta$ , however, that presumably accompanies disordering (Langer and Schreyer, 1969; Fontaine, 1969), is a measure of the shape of the lattice and is only related to Al-Si ordering insofar as the ordering affects the lattice parameters. This is seen by considering the squared expressions for  $d$  in terms of reciprocal lattice coordinates for each of the reflections that comprise the  $\Delta$  index in the orthorhombic form:

$$\frac{1}{(d_{131})^2} = 4 \frac{\sin^2 \theta}{\lambda^2} = Q_{131}$$

$$Q_{131} = a^{*2} + 9b^{*2} + c^{*2}$$

$$Q_{511} = 25a^{*2} + b^{*2} + c^{*2}$$

$$Q_{421} = 16a^{*2} + 4b^{*2} + c^{*2}$$

If we now impose the lattice restrictions for the orthohexagonal cell, that is,  $a = \sqrt{3} b$  or  $b^* = \sqrt{3} a^*$ :

$$Q_{131} = a^{*2} + 27a^{*2} + c^{*2}$$

$$Q_{511} = 25a^{*2} + 3a^{*2} + c^{*2}$$

$$Q_{421} = 16a^{*2} + 12a^{*2} + c^{*2}$$

or

$$Q_{131} = Q_{511} = Q_{421} .$$

That is, the three reflections have identical  $Q$  values when the lattice has hexagonal geometry.

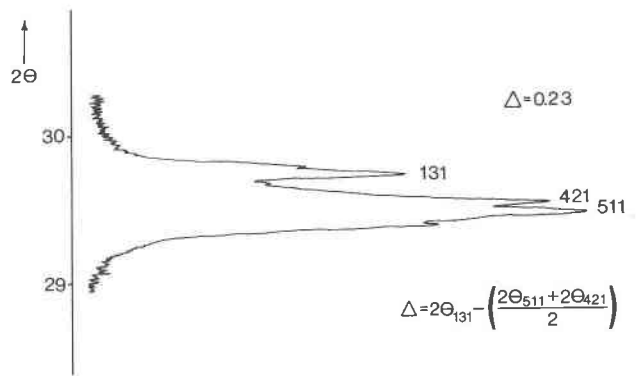


FIG. 1. Typical low cordierite from Falun, Sweden. The  $\Delta$  index was determined by averaging several values of  $2\theta_{131}$ ,  $2\theta_{511}$ , and  $2\theta_{421}$  obtained by repeated scanning through the interval  $28.5^\circ$  to  $30.5^\circ$   $2\theta$ . Radiation is  $\text{CuK}\alpha_1$ .

An examination of published lattice parameters and distortion indices of cordierite reveals a systematic relationship between the  $\Delta$  index,  $a$ , and the parameter  $(a - \sqrt{3} b)$ , this latter measuring how closely the lattice approaches orthohexagonality (Fig. 4). Indialites with  $\Delta = 0$  have  $a - \sqrt{3} b = 0$  and the shortest  $a$  cell dimensions. Intermediate and low cordierites with progressively longer  $a$  have larger  $\Delta$  indices. Since changes in the  $\Delta$  index are *directly* related to the lattice geometry, compositional changes in addition to possible order-disorder effects may be considered in understanding the real significance of the distortion index.

This suspicion was confirmed by Meagher's (1967) refinement of the Haddam cordierite. A comparison of the tetrahedral cation-oxygen bond lengths be-

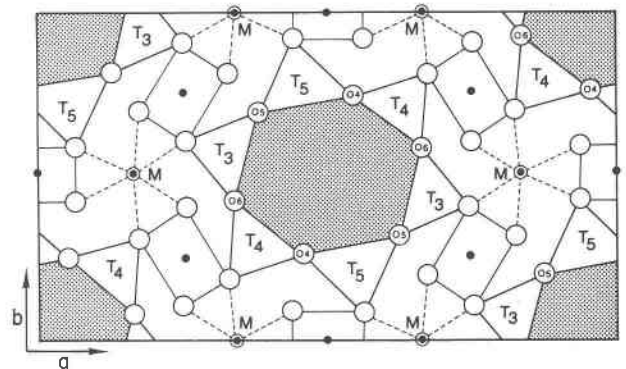


FIG. 2. The crystal structure of the Guilford cordierite (Gibbs, 1966) viewed down the  $c$  axis. Open circles represent oxygen; small closed circles represent Al-rich,  $T_1$  and  $T_2$  sites. Larger solid circles (M) represent Fe, Mg, Mn octahedral sites. In the six-membered rings,  $T_5$  is Al-rich and  $T_3$  and  $T_4$  are Si-rich. Oxygen 4 ( $O_4$ ), coordinated to  $T_4$  and  $T_6$ , is situated near (010) and has a locally unsatisfied charge. Molecular water occupies the shaded regions.

tween Gibbs' Guilford cordierite and the Haddam cordierite indicates that the two have the same Al-Si ordering. The  $\Delta$  indices, however, are not the same. The Guilford cordierite has  $\Delta = 0.24$ , and the Haddam cordierite has  $\Delta = 0.12$ . As this difference is apparently not due to Al-Si ordering, compositional controls are immediately suspect.

### Effects of Channel Constituents

A detailed study made by Harwood and Larson (1969) includes FeO/(FeO + MgO) ratios for cordierites that exhibit a range of  $\Delta$  indices from a contact aureole in the Cupsuptic Quadrangle, Maine. The  $\Delta$  indices increase from 0.23 to 0.29 toward the pluton. Harwood and Larson conclude that this variation is independent of MgO/(MgO + FeO) and  $\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{SiO}_2)$  in the 52 specimens examined.<sup>1</sup>

<sup>1</sup> Their data strongly suggest that other chemical parameters have more significant effects on the structure. In particular, they conclude that the systematic decrease of Be from 15 to 7 ppm toward the quartz monzonite pluton has no measurable effect on the  $\Delta$  indices, but rather it may reflect the ability of cordierite in various structural states to accommodate Be. Newton (1966) shows that the introduction of Be in the structure of synthetic Mg-indialite leads to systematic changes in lattice parameters, but the effect of Be on an ordered or partially ordered cordierite in which the parameter  $(a - \sqrt{3}b)$  is free to vary has yet to be evaluated.

TABLE 1. Chemical Analyses of the Guilford Cordierite and the Haddam Cordierite

	Guilford*	Haddam**
SiO <sub>2</sub>	48.1 wt %	47.0 wt %
Al <sub>2</sub> O <sub>3</sub>	33.5	32.2
BeO	--	0.5
TiO <sub>2</sub>	--	0.1
Fe <sub>2</sub> O <sub>3</sub>	--	0.2
FeO	5.3	7.1
MnO	0.2	0.4
MgO	10.0	8.4
CaO	0.3	0.1
Na <sub>2</sub> O	0.5	0.9
K <sub>2</sub> O	0.1	0.3
Li <sub>2</sub> O	0.3	--
H <sub>2</sub> O	1.4	2.5
TOTAL	99.7	99.6

\* Gibbs (1966)

\*\* Iiyama (1956); Meagher (1967)

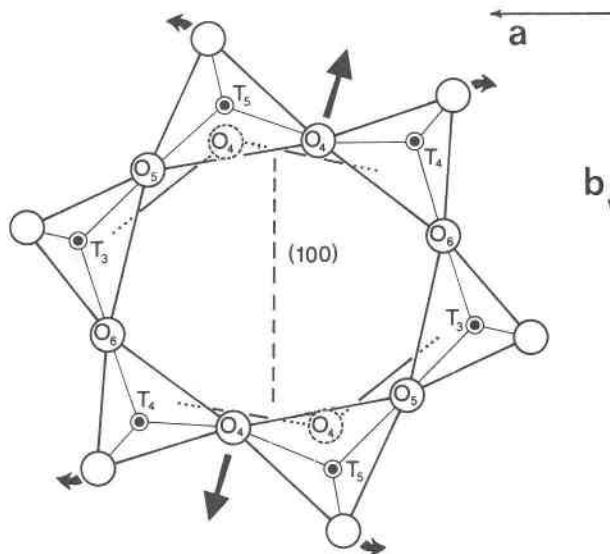


FIG. 3. Proposed model for the lattice distortion of ordered cordierite due to presence of molecular water. Dehydration increases the O<sub>4</sub>-O<sub>4</sub> distance across the open channel with concomitant increase of *a* relative to *b*.

The possible effects of molecular water on the lattice distortion of cordierite should be seriously considered, particularly in view of the fact that the major chemical difference between the Guilford and Haddam cordierites (Table 1) is in their water contents. Schreyer and Yoder's observation (1964) that the refractive indices of cordierite increase with higher water content suggests that molecular water held within the large six-membered rings may have an effect on the structure. Iiyama (1960) found that upon dehydration of natural cordierites, the mean refractive indices decreased. Published cordierite analyses (Leake, 1960) show that the maximum water content is close to 3 wt percent. If one water molecule occupies each cage between the constrictions in the open channels formed by the six-membered rings, the saturated water content based on structural considerations alone is one H<sub>2</sub>O per formula unit or very nearly three wt percent.

From infrared absorption data, Farrel and Newnham (1967) measured the characteristic stretching frequencies and bending mode of molecular water in cordierite. Using oriented single crystals, they demonstrated conclusively that the plane of the water molecule is aligned parallel to (100) and nearly parallel to the plane that contains O<sub>4</sub> in the six-membered rings (Gibbs, 1966). The H-H vector is parallel to *c* so that coordination between the protons and O<sub>4</sub> is likely. Oxygen 4 (Fig. 3) has particular importance because of its coordination

TABLE 2. RMS Amplitudes of Vibration for Two- and Three-Coordinated Oxygen Atoms in the Guilford Cordierite\*

Two-coordinated oxygen		Three-coordinated oxygen	
Atoms	rms amplitude of vibration	Atoms	rms amplitude of vibration
O4	0.056 Å	O1	0.058 Å
O5	0.091	O2	0.055
O6	0.082	O3	0.062

\* Gibbs (1966)

between Si and Al atoms. It has a locally unsatisfied charge which makes it a likely acceptor for hydrogen bonding to the water molecule. The anomalously low *rms* amplitude of vibration of O<sub>4</sub> (Table 2) as compared to normal values for two-coordinated oxygen (O<sub>5</sub> and O<sub>6</sub>) in the six-membered rings further suggests that O<sub>4</sub> has additional coordination. The conclusion of Smith and Schreyer (1960) and Gibbs (1966) that the water molecule is positioned near the periphery of the six-membered rings is consistent with such coordination and with a configuration of minimum electrostatic energy (Baur, 1965). It follows that in truly orthorhombic cordierite H<sub>2</sub>O is ordered, whereas in hexagonal cordierite or beryl (Wickersheim and Buchanan, 1959) H<sub>2</sub>O is disordered or randomly oriented about *c* because of the symmetrical equivalence of surrounding tetrahedra (Gibbs, Breck, and Meagher, 1968).

This evidence suggests a model (Fig. 3) in which O<sub>4</sub> is kinked into the open channels due to its coordination with molecular water. The magnitude of lattice distortion that could be achieved in this manner depends directly on the amount of H<sub>2</sub>O present. The direction of distortion and its effect on the cell parameters and the  $\Delta$  index are more difficult to assess. Comparison of interatomic distances in the refined structures of the Guilford (Gibbs, 1966) and Haddam (Meagher, 1967) cordierites suggests that the channels collapse somewhat around the *c* axis in the presence of water, decreasing *a* with respect to *b* (Fig. 3). The net effect for a given structural state would be to decrease the  $\Delta$  index in the presence of molecular water. This is consistent with relative  $\Delta$  index and H<sub>2</sub>O contents of the Haddam and Guilford cordierites (Fig. 4). Thus in the Guilford cordierite ( $\Delta = 0.24$ ) the O<sub>4</sub>-O<sub>4</sub> distances (Fig. 3) across the channels parallel to *b* and normal to *c* are 15 percent shorter than the O<sub>6</sub>-O<sub>6</sub> and O<sub>5</sub>-O<sub>5</sub> distances more nearly parallel to *a*. The Haddam cordierite ( $\Delta = 0.12$ ) has more water (Table 1) and less distortion (Fig. 4).

The effect of dehydration (Fig. 3) in the proposed model is to increase the O<sub>4</sub>-O<sub>4</sub> distance across the channel and thereby to straighten the T<sub>5</sub>-O<sub>4</sub>-T<sub>4</sub> angle. This apparently forces the T<sub>5</sub> and T<sub>4</sub> tetrahedra apart and lengthens *a* relative to *b*. In view of the fact that the molar volume of the Haddam cordierite is slightly less than that of the Guilford, the proposed model also predicts that hydrous cordierite should have a higher pressure stability than its anhydrous equivalent. This is consistent with the observation that the refractive indices generally decrease as cordierite is dehydrated, and with the experimental results of Newton (1972).

The presence of other channel constituents, such as Na<sup>+</sup> and K<sup>+</sup>, in positions where coordination with O<sub>4</sub> is likely could have the same distorting effect as molecular water. By analogy with beryl, Folinsbee (1941) concluded that the presence of alkalis in the cavities increases the refractive indices of cordierite, which is the same effect as that observed in the presence of molecular water. In this regard it should be noted that both Na<sub>2</sub>O and K<sub>2</sub>O are slightly higher in the analysis of the Haddam cordierite compared to the Guilford cordierite (Table 1).

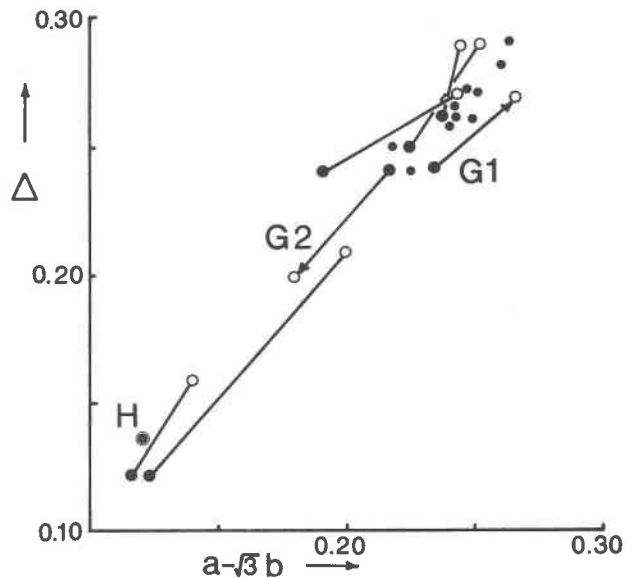


FIG. 4. The relationship between the  $\Delta$  index and  $(a - \sqrt{3}b)$ , a parameter which measures the extent to which the cordierite lattice departs from orthohexagonality. Unheated specimens (large solid circles) connected by solid lines to their dehydrated equivalents (open circles) are from Iiyama (1960). Specimen G1 is a Guilford cordierite from the Dana Collection, Harvard University, after dehydration (solid circle) at 900°C as part of this study. Specimen G2 is Guilford cordierite (Meagher, 1967) partially disordered from its initial state (solid circle) by heating at 1400°C. Smaller solid circles represent untreated cordierites from Iiyama (1960). Specimen H is Haddam cordierite.

### Heating Experiments

The proposed model was tested by heating cordierite at a temperature below that required to disorder Al and Si in the six-membered rings but above that required to volatilize the channel constituents. Iiyama (1960) made a similar study in an attempt to show that some of the water in cordierite was hydroxyl. His data, as well as preliminary data on the Guilford cordierite measured as a part of this study, are presented in Figure 4. Dehydration was accomplished by heating each specimen at 900°C for two hours in a one-atmosphere oven. A sixth specimen (this study) of Guilford cordierite (sample G1, Fig. 4) was heated under identical conditions for the same period of time. Its H<sub>2</sub>O content was measured by a method described by Wilkins and Sabine (1973) to insure that complete dehydration was achieved. In all six specimens that were dehydrated in this manner, the  $\Delta$  index increases by 0.03 to 0.09, the *a* cell dimension increases, and  $a\sqrt{3}b$  increases. Hydrothermally prepared cordierite ( $\Delta = 0.19$ ) calcined in a one-atmosphere oven for 24 hours (Newton, 1972) shows an increase of  $\Delta$  to 0.23. The effect of progressive hydration to decrease the  $\Delta$  index is demonstrated by Chernosky's (1973) experimental studies. His initially anhydrous starting material ( $\Delta = 0.28$ ) showed a decrease of  $\Delta$  to near zero after prolonged hydrothermal treatment at various water pressures and temperatures between 575°C and 725°C.

An indication of the changes in these parameters at

TABLE 3. Tetrahedral Site Occupancies as Based on Mean T-O Distances for Unheated and Heated Guilford Cordierite

Tetrahedron	Mean T-O distance	% Al
unheated*		
T <sub>3</sub>	1.611	0
T <sub>4</sub>	1.612	0
T <sub>5</sub>	1.744	96
heated**		
T <sub>3</sub>	1.633	16
T <sub>4</sub>	1.634	17
T <sub>5</sub>	1.682	51

\* Gibbs (1966)

\*\* Meagher (1967)

higher temperatures where significant disordering of Al and Si is likely to take place is given by specimen G2 (Fig. 3). The closed circle represents the untreated Guilford cordierite studied by Gibbs (1966) and the open circle represents the same specimen after heating ( $\Delta = 0.20$ ) in a controlled atmosphere at 1400°C (Meagher, 1967). A comparison of cation-oxygen bond lengths of the heated and unheated specimen (Table 3) shows that disordering of Al and Si has occurred, and has caused a change in lattice geometry (Fig. 4) just opposite to that caused by dehydration.

### Discussion

I conclude that the  $\Delta$  index of cordierite is a function of at least two variables. Al-Si ordering within the tetrahedral rings tends to increase the  $\Delta$  index whereas increasing the water content tends to decrease the  $\Delta$  index relative to that of anhydrous forms. A third variable, not as yet fully evaluated, is the disordering of H<sub>2</sub>O independent of Al-Si distribution. Disordered water ought to have the same effect on lattice distortion as less water since statistically fewer molecules will lie in (100) planes at the centers of 6-membered rings. Various combinations of these variables may account for the ambiguous interpretations of the distortion index under natural and experimental conditions.

It is important to note that the effects of Al-Si ordering and water content on the  $\Delta$  index are not independent. The preferred orientation of the water molecule parallel to (100) depends on the symmetry of the Al-Si distribution in the six-membered rings. If that distribution is orthorhombic, then the net distortion due to channel constituents is orthorhombic and shows up in the  $\Delta$  index. But if the structure is disordered so that the six-membered rings have hexagonal symmetry, then the resulting distortion due to water content also has hexagonal symmetry and therefore has no effect on the  $\Delta$  index. According to this model, variable amounts of molecular water in hexagonal indialite or disordered cordierite will have no effect on ( $a\sqrt{3}b$ ) or on the  $\Delta$  index. This agrees with Newton's (1966) conclusions regarding the effect of water in synthetic Mg-indialites.

For petrologic purposes, the  $\Delta$  index based on the model proposed here may prove useful. Because of its unique structural position and electrical neutrality, H<sub>2</sub>O in cordierite must be considered an independently variable component. In regionally metamorphosed terrain where there is little evidence for steep temperature gradients, the variation of  $\Delta$  in-

dices may give a preliminary indication of gradients in the chemical potential of H<sub>2</sub>O that may be reflected in water contents of cordierite at the time of metamorphism. Such an interpretation becomes more complicated in geological environments where there is evidence for steep temperature gradients, since the  $\Delta$  index may be a measure of the combined effects of Al-Si ordering and water content.

Lastly, the model proposed here may provide a firmer basis for thermochemical calculations involving cordierite at elevated pressure and temperature. The configurational entropy contribution by Al-Si disordering will be coupled with a disordered distribution of molecular water providing temperatures do not exceed that required for dehydration. These effects are presently being evaluated, and will be discussed in a subsequent communication.

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