Apparent effects of molecular water on the lattice geometry of cordierite: a discussion

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When Miyashiro (1957) introduced the distortion index \( \Delta = 2\theta_{\text{131}} - (2\theta_{\text{151}} + 2\theta_{\text{421}}) / 2 \) as a measure for the deviation of orthorhombic cordierites, \((\text{Mg,Fe})\text{Al}_{2}[\text{AlSiO}_{4}]_{3}\), from hexagonal lattice geometry, he suggested that "the distortion is probably due to some order-disorder changes of the Si and Al atoms in cordierite-indialite rings." On the basis of experimental work, Schreyer and Schairer (1961) and Schreyer and Yoder (1964) showed for Mg-cordierite that the magnitude of \( \Delta \) is, for most practical purposes, at conditions below the melting point, a function of heating time, \( \Delta \) increasing with run duration. Thus, comparing this behavior with the development and nature of triclinicity values of feldspars, it seemed that the increasing "orthorhombicity" of cordierites is indeed caused by a gradual ordering process in the structure. When Gibbs (1966) published his structure refinement of an orthorhombic low-cordierite, \((\text{Mg,Fe})_{2}\text{Al}_{4}\text{Si}_{5}\text{O}_{16}\), redefining this mineral as a framework silicate with pronounced Al/Si order, the problem of the variable lattice geometry of cordierite seemed to be largely solved. However, complications arose again when cordierites with apparently identical Al/Si distributions were found to exhibit different \( \Delta \) values (Meagher, 1967). Moreover, the increase in the \( \Delta \) index of Mg-cordierites upon heating turned out to be related to changes in the infrared properties only in the range of relatively small \( \Delta \) values (Langer and Schreyer, 1969). Stout (1975) has opened the discussion again by postulating that water molecules trapped within the cordierite structure reduce the degree of distortion caused by Al/Si order.

In our view, Stout's conclusion does not take into account a number of facts previously determined through synthesis experiments and is not in agreement with results of physical measurements pertaining to the behavior of isolated water molecules trapped in silicates. For the following discussion the relevant observations on water in cordierite as reported in the literature are repeated briefly.

Smith and Schreyer (1962) have shown that water molecules are incorporated in the almost spherical cavities (2.2 Å average radius) lying between two six-membered \((\text{Al}_{5}\text{Si}_{10}\text{O}_{26})\) tetrahedral rings stacked parallel to \( c \). The rings themselves form narrow passages of about 1.40 Å radius separating the individual cavities from each other. The cordierite structure (Byström, 1942, Gibbs 1966) contains one cavity per formula unit, \((\text{Mg,Fe})_{2}\text{Al}_{5}\text{Si}_{10}\text{O}_{26}\).

Because the Van der Waals radius of oxygen is 1.40 Å (Pauling, 1960) and the apparent radius of the water molecules in crystals is 1.70 Å (Remy, 1970), it is unlikely that more than one water molecule can be accommodated in one cavity, and hence, the maximum water content should be one molecule per formula unit or about 3 weight percent \( \text{H}_{2}\text{O} \). Indeed, analyses of natural cordierites (Leake, 1960) show rarely higher but often lower \( \text{H}_{2}\text{O} \) contents. Farrell and Newnham (1967) concluded from their IR-absorption spectra obtained with polarized radiation on oriented single crystal slabs "that many of the \((\text{H}_{2}\text{O}^-)\) molecules lie in the \((010)\) plane with the \( H-H \) direction parallel to \( c \)."

Following the more prevalent axial labelling for cordierite with \( a \approx b \sqrt{3} \) this plane would be (100).

Stout's paper contains mainly five arguments in support of an effect of molecular water on the lattice geometry of cordierite, and they are treated separately here:

(1) Stout writes: "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." The present authors reject this argument, because the observed increase in refraction must obviously be due to the incorporation of additional refracting matter in...
previously open sites as required by the Gladstone-Dale relationship. Simple calculations performed on this basis by Schreyer and Yoder (1964, Fig. 12) actually yielded good agreement between theory and experiment.

(2) Comparing two natural cordierites both exhibiting complete Al/Si order, i.e. that from Guilford (Gibbs, 1966; \( \Delta = 0.24^\circ \)) and that from Haddam (Meagher, 1967; \( \Delta = 0.12^\circ \)), with regard to their water contents and \( \Delta \) indices, Stout argues “the Haddam cordierite ... has more water ..., and less distortion....” For a more comprehensive comparison it is necessary to emphasize that the Haddam cordierite, in contrast to the Guilford cordierite, contains beryllium (Newton, 1966), which must be substituting for Al or Si in the tetrahedral framework. Povondra and Langer (1971 a,b) have studied experimentally the introduction of Be into both anhydrous and hydrous Mg-cordierites and found evidence that Be is introduced into cordierite predominantly through the substitution \( \text{Be}^{2+} + \text{Na}^+ \rightarrow \text{Al}^{3+} \), and that the Haddam cordierite contains the necessary amount of Na to explain its Be content on the basis of this substitution. Moreover they discovered that incorporation of Be + Na tends to decrease the orthorhombic distortion of the cordierite. Certainly for fixed conditions and durations of runs the orthorhombic distortion decreased with increasing Na, Be contents (Povondra and Langer, 1971a, Fig. 2). Thus the relatively low \( \Delta \) index of the Haddam cordierite may easily be explained on the basis of its Na + Be content alone, and water may be without significance.

(3) The conclusion of Farrell and Newnham (1967) concerning the preferred orientation of \( \text{H}_2\text{O} \) molecules in the cordierite channels as cited above leads Stout (1975) to the statement “that coordination between the protons and \( \text{O}_4 \) is likely.” He continues that this oxygen atom, which belongs to the \( (\text{Al}_2\text{Si}_4\text{O}_{18}) \) ring lying between Si and Al atoms, “has a locally unsatisfied charge which makes it a likely acceptor for hydrogen bonding to the water molecule.” On this basis he suggests “a model ... in which \( \text{O}_4 \) is kinked into the open channels due to its coordination with molecular water.”

In our opinion any significant distortion of a tetrahedral silicate framework by molecular water would require very strong hydrogen bonding with estimated energies of several kilocalories per mole \( \text{H}_2\text{O} \). However, the available information on the properties of water molecules in cordierite as well as in beryl do not support hydrogen bond energies of this magnitude: nuclear magnetic resonance results (Tsang and Ghose, 1972) reveal that “at room temperature the vibrational amplitudes of water molecules in cordierite and beryl are quite large and vibrate rather freely inside the large (ca. 2.2 \( \text{Å} \) radius) spherical cavities.” Indeed, the frequencies of the \( \text{H}_2\text{O} \) stretching fundamental vibrations in cordierite are much nearer to those of free water molecules in the gaseous state than to the values of liquid water (Table 1), in which the strength of the hydrogen bond is somewhere between 1.3 and 4.5 kcal/mole, depending on the definition of hydrogen bonding energy and the method of its determination (Eisenberg and Kautzmann, 1969). From this, it seems clear that any hydrogen bonding energy of \( \text{H}_2\text{O} \) molecules in cordierite can only amount to some 0.4-1.8 kcal/mole.

We are not even sure whether hydrogen bonding of water in cordierite is present at all: the slight energy decrease of about 80 cm\(^{-1}\) in the two stretching modes of \( \text{H}_2\text{O} \) in cordierite compared with free \( \text{H}_2\text{O} \) molecules (cf. Table 1) is almost the same as that of \( \text{H}_2\text{O} \) type I (H-H \( \parallel c \)) in beryl (about -100 cm\(^{-1}\) for \( \nu_1 \) and -60 cm\(^{-1}\) for \( \nu_2 \)). This indicates that the strength of hydrogen bonds would be very nearly the same in orthorhombic cordierite and beryl for its \( \text{H}_2\text{O} \) molecules with H-H \( \parallel c \). Recent microwave spectroscopic investigations of water molecules in beryl (Rehm, 1974) revealed that \( \text{H}_2\text{O} \) type I molecules rotate nearly freely around the axis of inertia in the H-O-H plane down to a temperature of 4.2\(^\circ\)K. This excludes any hydrogen bonding of the respective molecules in beryl with certainty; furthermore, Wood and Nassau (1967, 1968) had previously presented evidence for nonhydrogen bonding of \( \text{H}_2\text{O} \) type I in beryl from their spectra. Because on the basis of spectroscopic evidence (Table 1), \( \text{H}_2\text{O}(\text{H-H} \parallel c) \) behaves almost identically in beryl and orthorhombic cordierite, it is indeed most unlikely that there is hydrogen bonding in cordierite.

In this connection it should be stressed in a general way that, for the above reasons, the term “zeolite-like water in cordierite” used by Stout is misleading. Typical zeolitic water occurs in higher (\( \text{H}_2\text{O} \)) \( \delta \) aggregates with hydrogen-bonding within relatively large cavities; it has properties very near those of liquid water which do not resemble those of the single, isolated \( \text{H}_2\text{O} \) molecules in cordierite.

(4) Regarding the hydration of cordierite, Stout refers to experimental studies by Chernosky (1973), whose “initially anhydrous starting material (\( \Delta = 0.28^\circ \)) showed a decrease of \( \Delta \) to near zero after prolonged hydrothermal treatment at various water

<table>
<thead>
<tr>
<th>Vibration of H₂O</th>
<th>Single molecules in</th>
<th>State of H₂O</th>
<th>Molecules in liquid water</th>
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<tbody>
<tr>
<td></td>
<td>Vapor</td>
<td>Cordierite</td>
<td>Type I</td>
</tr>
<tr>
<td>v₁ symmetrical stretching</td>
<td>3657</td>
<td>3580</td>
<td>3555</td>
</tr>
<tr>
<td>v₂ bending</td>
<td>1595</td>
<td>1650</td>
<td>1595*</td>
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<tr>
<td>v₃ asymmetrical stretching</td>
<td>3756</td>
<td>3680</td>
<td>3694</td>
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In a later paper, Wood and Nassau (1968) report 1542 cm⁻¹ without commenting on the earlier value. Because of this uncertainty, the variations of v₂ are not taken into account in the discussion given here.

pressures and temperatures between 575°C and 725°C.” Stout interprets this observation in favor of his hypothesis of a negative correlation between the Δ values and H₂O contents of cordierite.

Chernosky’s (1973) observation seems somewhat surprising in view of the fact that, in the many hydration experiments performed on cordierite by one of us (W. Sch.), a significant decrease of Δ after hydration has never been detected. As an example the hydrous cordierite with Δ = 0.25° referred to in Table 5 on page 320 of the paper by Schreyer and Yoder (1964) was prepared by hydration of an anhydrous cordierite previously crystallized from glass at 1300°C for 36 hours and at 1420°C for 71 hours. This anhydrous cordierite had exhibited a Δ value of 0.21°. The observed increase of Δ during hydration at 10 kbar Pₜₐₓ, 700°C, 67 hours, is in line with the statement on page 312 of the paper quoted above, that Δ increases with temperature, water pressure, and duration of the run.

The experimental results of Chernosky (1973) quoted by Stout (1975) have since been published in detail, and indeed Chernosky (1974) reports a decrease of the distortion index from Δ = 0.28° to a very small or unmeasurable value (Δ <0.10°) during the bracketing experiments performed in his study. However, the key for the proper interpretation of this finding lies in the nature of the bracketing experiment itself, in which the stability curve of clinohore was determined using crystalline mixes consisting of equal amounts of synthetic clinohore and of the synthetic high-temperature assemblage, that is of (anhydrous) cordierite + forsterite + spinel. Obviously cordierite can only be preserved and thus become hydrated on the high-temperature side of the reaction, where additional cordierite is formed at the expense of pre-existing clinohore. From all previous experience (Schreyer and Yoder 1964) it is clear that this newly-formed cordierite can only exhibit very low Δ values due to the relatively low temperatures, water pressures, and run durations applied. Thus the run product obtained must consist, in addition to forsterite + spinel, of a mixture of essentially two cordierites with different structural states: (1) the high-Δ starting material, and (2) the low-Δ cordierite formed as a breakdown product of clinohore. The superposition of the peaks of these two cordierites will lead to an apparent predominance of the low-Δ phase, masking the well-separated peaks of the high-Δ phase still present. The net result observed in the powder X-ray pattern would thus be one broad peak without obvious splitting, and this can well be misinterpreted in favor of a decrease of Δ. On the basis of these considerations we find it hard to accept Chernosky’s (1974) observation as supporting evidence for Stout’s hypothesis.

(5) Citing earlier heating experiments by Iiyama (1960) and preliminary data of his own, Stout reports that with the dehydration of cordierite at 900°C and 1 atmosphere “the Δ index increases by 0.03 to 0.09.” As indicated at the very beginning of this discussion it is well known from earlier work (Schreyer and Schairer, 1961; Schreyer and Yoder, 1964) that Δ increases with heating time. Thus Iiyama’s (1960) and Stout's
(1975) findings could simply be interpreted as a result of a higher degree of Al/Si order in the tetrahedral framework of cordierite. Admittedly heating for two hours at 900°C, 1 atm does not cause a significant change of Δ in pure anhydrous Mg–cordierite (Schreger and Schairer, 1961). However, this may be different for natural water-bearing cordierites of much more complicated compositions involving the presence of Fe³⁺, Fe⁴⁺ as well as Na within the structural channels. Yet the difficulty arises that the Guilford cordierite heated by Stout is nearly Al/Si ordered (Gibbs, 1966). Although no straightforward alternative interpretation valid for the Δ increase in all the cordierites mentioned by Stout is at hand, several possibilities can be mentioned:

(A) Based on the structure determination of Gibbs (1966), the Guilford cordierite exhibits only 96 percent Al/Si ordering. In addition there might be long-range disorder which was not detected in the determination of the mean structure. From a combined infrared and powder X-ray study, Langer and Schreyer (1975) had concluded that increases of Δ in late stages of the ordering process starting with Δ > 0.17° may be due solely to increasing long-range order. Thus the relatively small Δ increase (0.03) of the Guilford cordierite upon heating may be due to continued overall structural ordering after all.

(B) The structural mechanism and the kinetics of the dehydration process of cordierite are only very poorly understood at present, especially for cordierites containing additional channel-filling ionic species, e.g. Na⁺, acting as blockages. At any rate, from a comparison with the water-diffusion mechanism in silica glass (Drury et al., 1962; Roberts and Roberts, 1966), which involves intermittent breakage of Si–O bonds, some rearrangement of the silicate framework during dehydration seems possible. Thus, in contrast to Stout’s hypothesis of a static influence of H₂O molecules on the cordierite framework, it would be the dynamics of the dehydration process which might cause an increase of Δ.

(C) It is likely that natural cordierites containing ferrous iron will undergo oxidation during the heating in air as performed by Iiyama (1960) and Stout (1975), and more magnesian cordierites plus hematite and other phases should form. Thus the mere compositional change of the cordierite phase would lead to changes of lattice geometry even without affecting the state of Al/Si order.

In summary, considering all the data available at present we cannot find any supporting evidence for Stout’s assumption of “apparent effects of molecular water on the lattice geometry of cordierite.”

References


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