

## The high temperature behavior of water and carbon dioxide in cordierite and beryl

ROGER D. AINES AND GEORGE R. ROSSMAN

*Division of Geological and Planetary Sciences  
California Institute of Technology  
Pasadena, California 91125*

### Abstract

We have studied the behavior of molecular water and carbon dioxide in the channels of cordierite and beryl at temperatures up to 900°C using high temperature infrared spectroscopy. Above 400°C water that is structurally bound in the channels begins partitioning into an unbound state with the characteristics of a gas. The process is fully reversible and involves both type I and type II water in both minerals. Dehydration occurs after most of the water is in this unbound state, and channel cations are no longer coordinated by the type II water molecules. These cations can then move to the wall of the channel or be expelled from the channel, opening the channel for dehydration of the water contained in it. This behavior is contrasted with that of muscovite, in which the hydroxide shows no change in speciation and only slight changes in its spectroscopic properties at temperatures below the dehydration point. CO<sub>2</sub> in the channels of cordierite does not undergo major changes in bonding at high temperatures. Although all the water in the cordierite was released, about 40% of the CO<sub>2</sub> remained after heating to 800°C. Heating to 900°C was required to expel all CO<sub>2</sub>. This is indicative of the tighter wedging of CO<sub>2</sub> in the channels. Because of an equilibrium among type I, type II, and unbonded gas-like water at high temperature, the concentration of type I alone serves as an indicator of the water fugacity. The type II concentration only responds to the number of channel cations and need not be considered in water fugacity calculations. Cordierites with greater numbers of channel cations will effectively close to re-equilibration at higher temperatures, making them more suitable as indicators of water and carbon dioxide fugacity.

### Introduction

The potential use of cordierite as a water and carbon dioxide fugacity indicator in rocks has generated much current interest in the thermodynamics and structural properties of the gases contained in its channels. Cordierite and beryl are also of interest as models for extremely small channel zeolites and for the behavior of water trapped in small cavities in other minerals. We report here studies of the behavior of the channel water and carbon dioxide in these two minerals at temperatures up to 900°C. The primary tool used in this study was high temperature infrared spectroscopy on oriented, natural, single crystals.

Cordierite and beryl are structurally similar, containing (Si,Al)<sub>6</sub>O<sub>18</sub> and Si<sub>6</sub>O<sub>18</sub> rings which define channels parallel to the *c* axis. The most common contents of these channels are water, carbon dioxide, and alkali cations (Wood and Nassau, 1967; Armbruster and Bloss, 1980; Cohen et al., 1977; Hawthorne and Cerny, 1977; Zimmerman, 1981). In both minerals water can assume two orientations in the channel (Wood and Nassau, 1967;

Goldman et al., 1977). Type I water has its H–H vector parallel to *c*, and type II has its H–H vector perpendicular to *c* (Fig. 1). The presence of an alkali cation seems to predispose any adjacent water molecule to reside primarily in the type II orientation, while in the absence of a cation the type I orientation is preferred. These positions are not rigid. Carson et al. (1982) used NMR to demonstrate that individual water molecules can hop between the two orientations in cordierite. A rotational IR spectrum is observed in beryl (Wood and Nassau, 1967) which is also consistent with motion of this type. The fact that type I and type II water molecules are distinct on an IR time scale (about 10<sup>-12</sup> seconds) but indistinct on an NMR time scale (about 10<sup>-6</sup> seconds) indicates a residence time in the bonded state that is somewhere between these values at room temperature.

The crystallographic and thermodynamic status of water in cordierite will have a substantial effect on any attempt to use cordierite as a water fugacity indicator. Experimental work (e.g., Johannes and Schreyer, 1981; Armbruster and Bloss, 1982) has emphasized Mg-cordier-

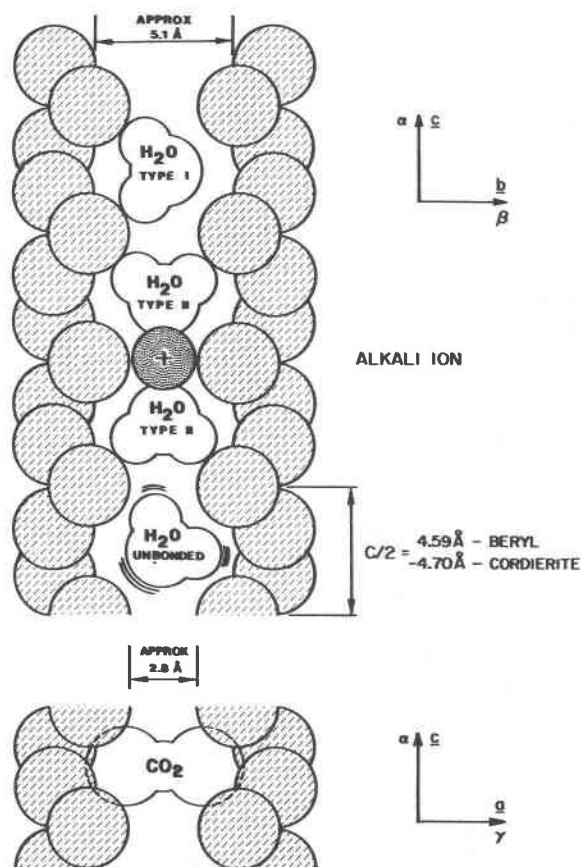


Fig. 1. Schematic representation of the orientations of channel constituents.

ite with no channel cations and no type II water. The theoretical model of the H<sub>2</sub>O-cordierite system by Martignole and Sisi (1981) also considers only one water site. A thermal release study by Zimmerman (1981) of the gases contained in cordierites from different origins did not consider the presence of multiple water sites or the influence of channel cations on release patterns. The relationship between the two types of water, channel cations, and also carbon dioxide in the channels must be understood before these studies can be confidently applied to natural systems. Such an understanding can be advanced by studying the channel constituents at the temperatures of cordierite formation.

### Experimental method

Single crystal samples of previously studied cordierite (Goldman et al., 1977) and beryl (Goldman et al., 1978) were used. The cordierite, #5 in Goldman et al. (1977), is from a metamorphic pegmatite near Manitouwadge, Ontario, Canada (Pye, 1957). The beryl, #8 in Goldman et al. (1978), is from Brazil. Analytical data for the cordierite are given in Table 1; additional data are given by Goldman et al. (1977). Data for the

beryl are given by Goldman et al. (1978). Both samples are homogeneous at microprobe detection limits.

Infrared spectra were obtained in the 4000 cm<sup>-1</sup> to 1200 cm<sup>-1</sup> region using a Perkin-Elmer model 180 grating infrared spectrophotometer using techniques described by Goldman et al. (1977) for room temperature spectra. The same doubly polished oriented single crystal slabs were used for all measurements. At higher temperatures similar methods were used, but the sample was mounted in an evacuated, Pt<sub>80</sub>Rh<sub>20</sub> wound tube furnace which was placed in the spectrophotometer. The beam from the spectrometer passes through KCl windows in a vacuum jacket and down the length of the tube furnace, which is 2.5 cm in diameter and 12 cm long. Approximately 10 mm<sup>2</sup> of sample, in the form of an unsupported section, 20–40 μm thick is exposed to the spectrometer beam. The sample, mounted on a stainless steel aperture using stainless steel straps, sits in the middle of the furnace. The sample temperature reported for these experiments is measured in the stainless steel sample mount adjacent to the sample since the sample is too fragile to support a thermocouple. In experiments with a 5 mm thick quartz slab with thermocouples mounted in the sample, the aperture was 10°C hotter than the sample.

One doubly polished beryl slab was used. This was an ac section 40 μm thick. Two cordierite slabs were used; one optimized for H<sub>2</sub>O observation, a bc (βα) section 60 μm thick, and one optimized for CO<sub>2</sub> observation, an ab (γβ) section 16 μm thick. The ab section contained a simple {130} twin. About 20% of the slab was not an ab section, therefore, and the polarizations E||a and E||b are mixed slightly.

Spectra obtained from the beryl, the bc cordierite and the muscovite section were digitized to produce Figures 2, 3, and 6. Data from the ab cordierite section were collected in digital form using a computer interface and were used directly to produce Figures 4 and 5. This was necessitated by the low intensity of the H<sub>2</sub>O bands and the CO<sub>2</sub> rotational bands in this section, which was optimized for the CO<sub>2</sub> stretching peak.

The effects of black body radiation by the furnace and sample

Table 1. Cordierite analytical data

	wt. %
Na <sub>2</sub> O	0.33
MgO	10.44
Al <sub>2</sub> O <sub>3</sub>	33.31
SiO <sub>2</sub>	48.88
K <sub>2</sub> O	0.02
CaO	0.13
TiO <sub>2</sub>	0.09
MnO	0.15
FeO	5.29
Subtotal	98.44
H <sub>2</sub> O type I	0.81*
	0.77**
H <sub>2</sub> O type II	0.43**
CO <sub>2</sub>	0.42*
Total	100.06†

\*H<sub>2</sub>O and CO<sub>2</sub> concentrations determined spectroscopically using powdered sample. Powder ε type I H<sub>2</sub>O = 210 ± 10, ε CO<sub>2</sub> = 6000 ± 500 (l mole<sup>-1</sup> cm<sup>-1</sup>). Standards were two synthetic cordierites provided and analyzed by W. Johannes and W. Schreyer, their #s 97A and 98A.

\*\*H<sub>2</sub>O type I and II concentrations using single crystal ε values of 204 and 256 (l mole<sup>-1</sup> cm<sup>-1</sup>) from Goldman et al. (1977).

†Calculated using %H<sub>2</sub>O from single crystal calibration (\*\*).

are eliminated by double chopping of the spectrometer beam; the pure emission spectrum of the sample and furnace is subtracted electronically from the observed absorption spectrum, yielding the actual absorption spectrum. The subtraction becomes impractical above 900°C because the intensity of the black body radiation becomes much greater than that of the spectrometer beam. This causes the thermopile detector to behave nonlinearly, and is evidenced as an apparent phase shift in the sample and reference beam. This phase shift was checked at all temperatures and is not an important factor until 800°C; above this the absorbance measurements become increasingly nonlinear. All absorbance values reported here and shown in the figures are accurate to within approximately  $\pm 2\%$ , verified using standard absorption screens.

### Results

Infrared spectra were obtained in the  $3600\text{ cm}^{-1}$  region where stretching modes of water occur, in the  $1600\text{ cm}^{-1}$  region where the bending mode occurs, and in the  $2300\text{ cm}^{-1}$  region where  $\text{CO}_2$  absorbs. Beryl was studied between  $-180^\circ$  and  $700^\circ\text{C}$  and cordierite was studied between  $35^\circ$  and  $915^\circ\text{C}$ .

### Beryl

Figure 2 shows the  $\epsilon$ -spectrum ( $E||c$ ) of the beryl between  $35^\circ$  and  $700^\circ\text{C}$ . The peaks are indexed according to Wood and Nassau (1968). For type I water, absorptions occur at:  $3694\text{ cm}^{-1}$  in  $\epsilon$ , ( $\nu_3$ , asymmetric stretching),  $3555\text{ cm}^{-1}$  in  $\omega$ , ( $\nu_1$ , symmetric stretching), and  $1595\text{ cm}^{-1}$  in  $\omega$ , ( $\nu_2$ , bending). For type II water, the corresponding absorptions occur at:  $3655\text{ cm}^{-1}$  in  $\omega$ ,  $3592\text{ cm}^{-1}$  in  $\epsilon$ , and  $1628\text{ cm}^{-1}$  in  $\epsilon$ . Both type I and type II water are present, which is consistent with the alkali content of this sample (Goldman et al., 1977). Figure 1B also shows an overtone absorption of a lattice mode, at  $1929\text{ cm}^{-1}$ . No  $\text{CO}_2$  absorptions were detected in the infrared spectrum of this sample.

At high temperatures, the peaks broaden slightly and decrease in intensity. The broadening is attributable to an increase in the range of O-H  $\cdots$  O distances in the environments of the  $\text{H}_2\text{O}$  molecules brought on by thermal motion. At  $330^\circ\text{C}$  the intensity of the original peaks is diminished, and a new component is added to the spectra. There is a broad band of equal intensity in both polarizations, centered at approximately  $3650\text{ cm}^{-1}$ . This band

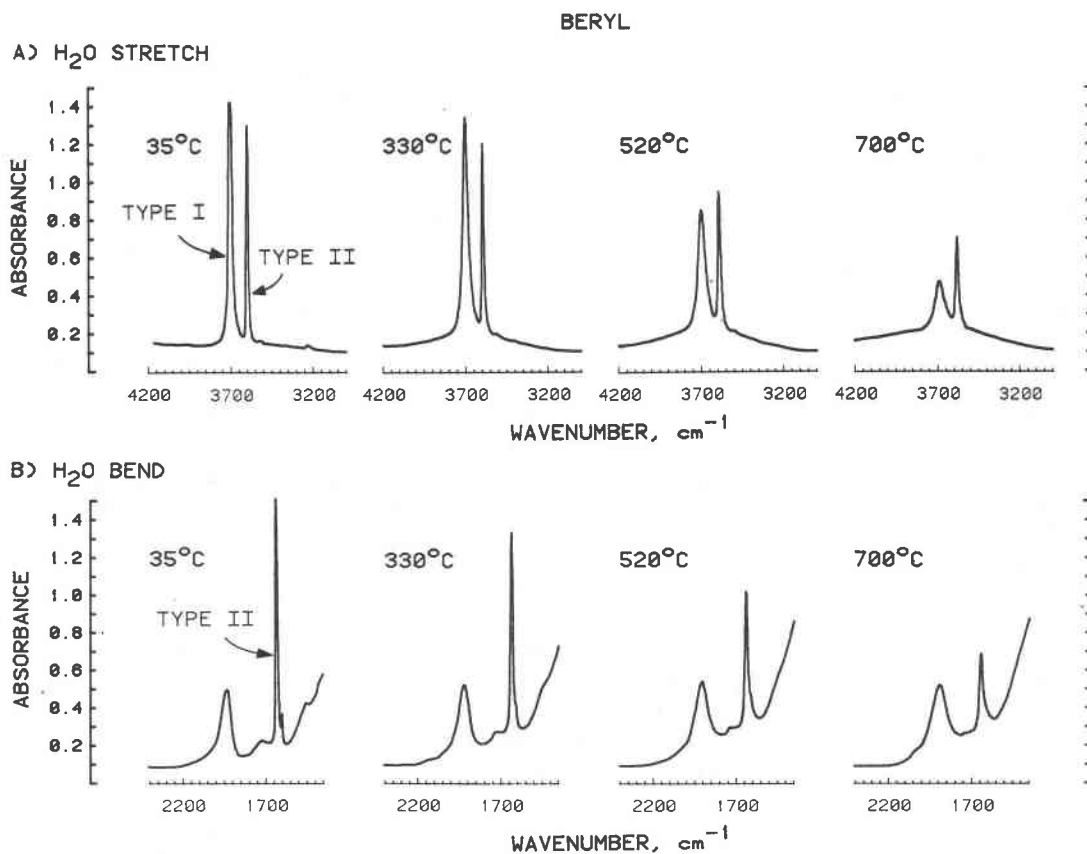


Fig. 2. Infrared spectra of a  $40\text{ }\mu\text{m}$  thick single crystal of beryl. Polarized  $E||c$ . A) O-H stretching region, B) H-O-H bending region. Labels indicate sample temperature at time of measurement. The broad band in the  $\text{H}_2\text{O}$  stretching region, centered at  $\sim 3600\text{ cm}^{-1}$ , is apparent at  $330^\circ$  but is best seen at  $700^\circ\text{C}$ .

was not apparent at 160°C. The intensity of this band increases with temperature at the expense of the sharp peaks of type I and type II water. The two water types appear to be partitioning into the state represented by the broad band. This partitioning is reversible. Upon cooling the broad band disappears and the spectra of the two water types are identical to those obtained before heating. Although both type I and type II water partition into the state resulting in the broad band, there is only evidence of a single broad band. The two water types do not partition equally into this third state; type I water enters it at lower temperatures as is evidenced by the more rapid loss of intensity of the type I stretching peak in Figure 2. It is not possible to resolve a broad band in the bending region ( $1600\text{ cm}^{-1}$ ) although the peak intensities there show similar decreases to the stretching peaks. The loss of intensity in the sharp peaks is not due to broadening, because the integrated intensity of the peaks decreases at the same rate that the integrated intensity of the broad band increases.

The sample remained at 700°C for 2 hours. When cooled and measured at 35°C, some dehydration had occurred as indicated by a loss of intensity of 15% for both water types. The relative intensities remained approximately the same as before heating.

### Cordierite

The cordierite  $\text{H}_2\text{O}$  spectra (Fig. 3) show the same features observed in the beryl spectra, but the peaks are broader and less well defined in cordierite. The indexing of the peaks, according to Goldman et al. (1977) follows the same pattern as for beryl. For type II water, absorptions occur at:  $3632\text{ cm}^{-1}$  in  $\beta$ , ( $\nu_3$ , asymmetric stretching),  $3574\text{ cm}^{-1}$  in  $\alpha$  ( $\nu_1$ , symmetric stretching), and  $1630\text{ cm}^{-1}$  in  $\alpha$ , ( $\nu_2$ , bending). For type I water absorptions occur at:  $3689\text{ cm}^{-1}$  in  $\alpha$ , (asymmetric stretching), the exact position of the  $\nu_1$  symmetric stretch is not assigned, but it occurs in  $\beta$ , and the bending mode appears in  $\beta$  as a triplet centered near  $1600\text{ cm}^{-1}$ . Figure 3B shows a silicate lattice overtone at  $1880\text{ cm}^{-1}$  similar to that in beryl, Figure 2B. The increased complexity of this band is presumably due the lower symmetry of the  $(\text{Si,Al})_6\text{O}_{18}$  rings in cordierite.

In cordierite the reversible formation of the broad band at high temperatures occurs in an analogous fashion to that in beryl, but it begins at a lower temperature (200°C) as does dehydration (600°C). The same reversal in type I/type II peak intensities occurs as the temperature increases. The lower dehydration temperature of cordierite allowed us to observe it going to completion. At 600°C the integrated intensity ratio of sharp peak (types I & II) to broad band is about 3:1 (Fig. 3A). At 800°C dehydration occurred too rapidly for us to obtain a complete spectrum from the *bc* slab, however, the sharp peak to broad band ratio was approximately 5:1. As the crystal dehydrated this ratio remained approximately constant. Type I and Type II waters were lost at the same rate.

The *ab* section allowed us to obtain information on the isotropy of the broad band state. In the room temperature  $\gamma$  polarization ( $\text{E}||\text{a}$ ) there are no absorption features due to water identified as type I or II. The high temperature broad band state is isotropic, however, and is clearly seen in  $\gamma$  at 655°C (Fig. 4). (The sharp peaks seen in the  $\gamma$  spectrum are due to the slight mixing of polarizations and to minor unidentified O-H species.) At 655°C dehydration was occurring slowly. At 755°C dehydration occurred more rapidly and was complete in 2 hours. Upon cooling, all the bands attributable to types I & II water were gone.

This cordierite sample also contains  $\text{CO}_2$  in the channels, as is evidenced by a sharp peak at  $2348\text{ cm}^{-1}$  in  $\gamma$  (as assigned by Armbruster and Bloss, 1982). This peak is due to asymmetric stretching of  $\text{CO}_2$  and its polarization indicates that the  $\text{CO}_2$  molecule is oriented with its long axis parallel to the *a* axis of the crystal. This orientation has also been suggested on the basis of structural criteria (Johannes and Schreyer, 1981) and optical properties (Armbruster and Bloss, 1982) and is consistent with the orientation of  $\text{CO}_2$  in beryl (Wood and Nassau, 1967). Two sidebands occur at  $2307\text{ cm}^{-1}$  and  $2390\text{ cm}^{-1}$  in  $\beta$ . These have the characteristics of rotational, or more likely librational, sum and difference combination bands involving both the stretching motion and a coupled, hindered rotation.

The spectra of  $\text{CO}_2$  in the  $\gamma$  and  $\beta$  directions are shown in Figure 5. These directions are slightly mixed by the twin in the sample. Room temperature observation of the untwinned portion of the sample indicates that the side bands are completely polarized in  $\beta$ , and the fundamental band completely in  $\gamma$ . High temperature spectra require a large aperture, so the twinned sector had to be included in those measurements.

At high temperatures the only change apparent in the  $\text{CO}_2$  spectrum in both polarizations is a broadening of the peaks. The integrated intensity in  $\gamma$  increased about 50% as the sample is heated. In  $\gamma$  the broadening is asymmetric, with a lower energy shoulder becoming prominent. It appears that the rotational bands center on this shoulder, and not the sharper peak, at high temperature. No broad band behavior is observed. Upon cooling from below 650°C the spectra are identical to the original spectra. Beginning at 700°C some decarbonation occurs. As mentioned previously, the *ab* section was held at 755°C for 2 hours until all the  $\text{H}_2\text{O}$  was gone. Only 20% of the  $\text{CO}_2$  was lost. The sample was then heated in increments of 10° to 915°C, losing  $\text{CO}_2$  more rapidly at each step. After 20 minutes at 915° no  $\text{CO}_2$  remained. The decarbonation rate could also be observed in the *bc* section, using the rotational bands. The section was heated from 600° to 800°C quickly, and allowed to remain at 800°. This procedure resulted in a greater loss of  $\text{CO}_2$  (60%) at 800°C than was observed in the 10° stepwise heating of the *ab* section (30%).

For the purposes of comparison we also include the high temperature spectra of muscovite (Fig. 6). The single

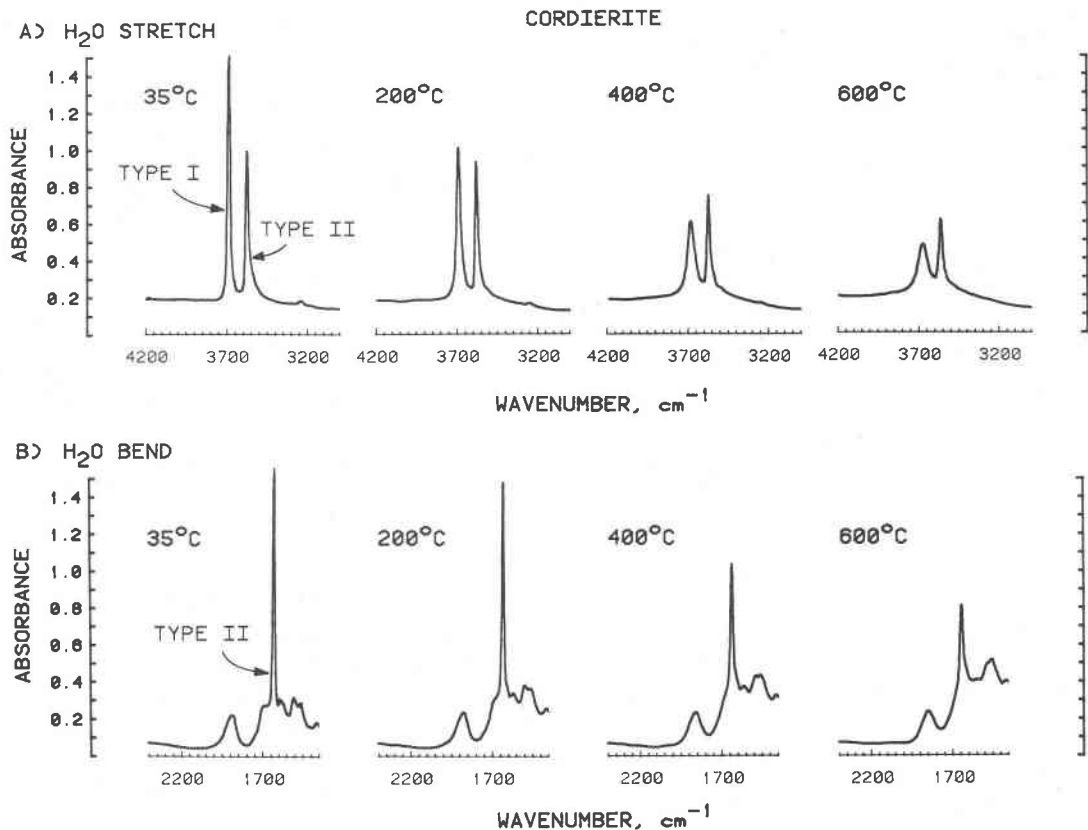


Fig. 3. Infrared spectra of a 60  $\mu\text{m}$  thick single crystal of cordierite (optimized for H<sub>2</sub>O observations). Polarized E||c ( $\alpha$ ). A) O–H stretching region, B) H–O–H bending region. Labels indicate temperature of sample at time of measurement. The broad band is centered at  $\sim 3600\text{ cm}^{-1}$  as in beryl, but is spread over a wider range of energies and therefore is less intense at  $3600\text{ cm}^{-1}$  (see Fig. 4).

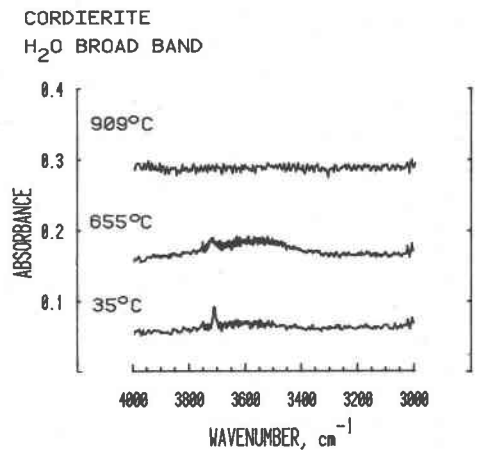


Fig. 4. Infrared spectra of a 16  $\mu\text{m}$  thick single crystal of cordierite. Polarized E||a ( $\gamma$ ). The broad absorption present at 655° disappears after the sample dehydrates at 755°C. The 909°C spectrum shows that the high temperature broad band absorption is caused by H<sub>2</sub>O and that it disappears after dehydration. Labels indicate temperature of sample at time of measurement. Peak at  $3740\text{ cm}^{-1}$  is caused by a minor, unidentified hydrous species. Baseline corrected to remove elements of the  $\beta$  spectrum mixed in by a twin in the sample.

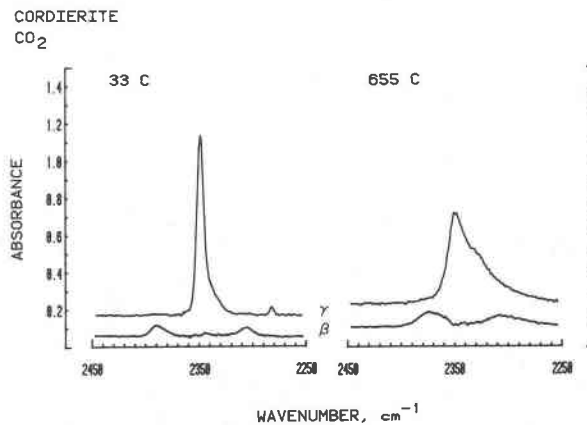


Fig. 5. Infrared spectra of a 16  $\mu\text{m}$  thick single crystal of cordierite, the same crystal as Fig. 4, showing the absorptions due to CO<sub>2</sub>. Polarized E||a ( $\gamma$ ) and E||b ( $\beta$ ). Labels indicate sample temperature at time of measurement.  $\beta$  spectra have been baseline corrected to remove elements of the  $\gamma$  spectra mixed in due to a twin in the sample.  $\gamma$  spectra are uncorrected.

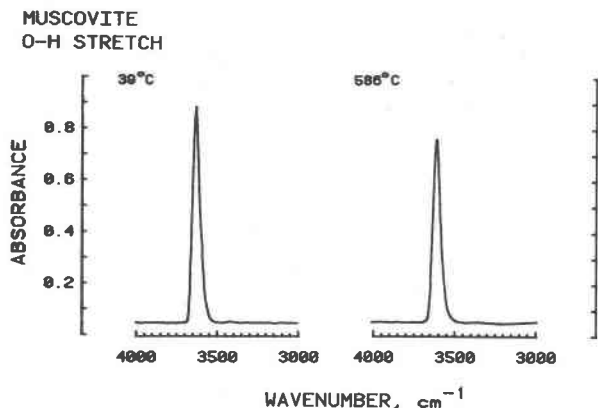


Fig. 6. Infrared spectra of a single crystal cleavage flake of muscovite 11  $\mu\text{m}$  thick. The 586° spectrum was obtained 150° below the dehydration point. Polarized approximately E||a. Labels indicate temperature at time of measurement.

hydroxide group gives a single peak, and no broad band is observed at high temperature. The peak shifts slightly to lower energies (from  $3625\text{ cm}^{-1}$  to  $3612\text{ cm}^{-1}$ ), and is slightly broadened at high temperature. The integrated intensity is approximately constant. At  $700^\circ\text{C}$  the sample was observed during dehydration, and no spectroscopic changes other than loss of intensity occurred during this process. We have also observed topaz, quartz, and feldspar at high temperatures and seen no evidence of the formation of a broad band, or of large intensity decreases prior to dehydration. This indicates that many of the changes observed in the beryl and cordierite spectra, in particular the formation of the broad band, are not general characteristics of high temperature.

## Discussion

### Speciation of water at high temperature

The formation at high temperature of a state of water which yields a broad band IR spectrum is most easily explained by postulating that water can exist in beryl and cordierite in both bound and unbound states. The bound states are types I and II. The unbound state has the characteristics of a gas, with a typical gas IR spectrum which is broad and isotropic. The formation of this gas-like state is reversible, with the type I/type II ratio the same before and after heating. This suggests that although the gas-like water molecules are not bound, they are confined to the ring voids that they occupy at low temperature. The motion of the gas-like molecules is distinct from the fluctuational motion that Carson et al. (1982) observed in cordierite, and from the motion resulting in the librational bands in beryl (Wood and Nassau, 1967). These motions are restricted to the plane defined by the type I-type II orientations (the bc plane in cordierite), and would only result in the interconversion of the

two types. The formation of the gas-like state results in a water molecule that can assume any orientation in the channel.

Our observation of gas-like water is consistent with high temperature X-ray diffraction work on cordierite done by Hochella et al. (1979). They refined the structure of an Mg-rich cordierite (poor in channel cations) at  $24^\circ$ ,  $375^\circ$ , and  $775^\circ\text{C}$ . At  $375^\circ$  the peak in the electron density map ascribed to oxygen in channel water broadens in the a direction, the large axis of the cavity. At  $775^\circ\text{C}$  the peak disappeared, but it reappeared upon cooling, with some dehydration having occurred. Hochella et al. attribute the disappearance at  $775^\circ\text{C}$  to thermal motion, which is consistent with our postulated gas-like state. At this temperature the water is almost completely in the broad band state. The broadening at  $375^\circ\text{C}$  could either be due to type I - type II interconversion motion, or to the formation of the gas-like state.

### Dehydration mechanism

The close association between the formation of the gas-like  $\text{H}_2\text{O}$  state in cordierite, and the onset of dehydration, is probably not coincidental. Just below the point of dehydration ( $600^\circ\text{C}$ ) the ratio of unbound to bound water is 3:1 (Fig. 3). During dehydration at  $700^\circ\text{C}$  to  $800^\circ\text{C}$  (not shown) it is higher, 5:1 or greater. Both values are approximate due to difficulty integrating the overlapping bands. In beryl, which is known to dehydrate at higher temperatures than cordierite, (e.g., Brown and Mills, manuscript), the partitioning of bound into unbound states is delayed relative to cordierite. At  $700^\circ\text{C}$  in beryl the ratio of unbound to bound water is only 2:1 (Fig. 2), and only minor dehydration occurred.

This close association between the unbound water and dehydration can be explained using a model involving the hydration of channel cations. It is now accepted that the intermediate size channel cations such as  $\text{Na}^+$  and  $\text{Fe}^{3+}$  reside in the center of the  $(\text{Si,Al})_6\text{O}_{18}$  rings in both minerals (Hawthorne and Cerny, 1977; Hochella et al., 1979; Brown and Mills, manuscript). This is the most restricted point in the channel. These cations are then coordinated by two type II water molecules, one above and one below in the channel (Goldman et al., 1977; Hawthorne and Cerny, 1977). Our data suggest that the dehydration of beryl and cordierite proceeds when these coordinating water molecules are partitioned into the gas-like state. We propose that the coordinating water molecules hold the cation in its central position, where it completely plugs the channel. When the water molecules are partitioned into the gas-like state and are removed from their coordinating positions, the cation is released and moves into the larger part of the channel, releasing the other contents of the channel. Such motion of  $\text{Fe}^{3+}$  to the walls of the channels in dehydrated cordierite was proposed by Goldman et al. (1977) on the basis of optical spectra.

When enough of the channel cations are simultaneously not coordinated, dehydration can occur. We interpret the pervasive cracking of both minerals at temperatures above the normal dehydration point as due to build up of gas pressure in the channel as larger continuous volumes with unplugged cations form. If, however, the dehydration point is not exceeded greatly, the equilibrium between diffusion down the channel and the release of coordinated channel cations allows dehydration to occur without cracking.

### *Decarbonation mechanism*

During the heating of cordierite, no CO<sub>2</sub> is lost before H<sub>2</sub>O, but a substantial amount remains after all the H<sub>2</sub>O is gone. This is probably due to tight wedging of CO<sub>2</sub> in the cavity, as described by Johannes and Schreyer (1981). This tight wedging appears to cause CO<sub>2</sub> to diffuse slowly along the channel, and considerably higher temperatures are required to remove CO<sub>2</sub> than H<sub>2</sub>O, 900° vs. 750°C. The different rates of CO<sub>2</sub> loss in the two sections we studied appear to be due to the heating rates. The section heated rapidly to 800° lost considerably more CO<sub>2</sub> up to that point than the one heated gradually to that point. One explanation for this is that some CO<sub>2</sub> is swept out by the H<sub>2</sub>O in the rapidly heated sample, but that when the heating rate is more gradual water diffuses down the channels without carrying CO<sub>2</sub> with it. Zimmerman's (1981) data support this. Using mass spectrometric analysis of the gas released from continuously heated cordierites he observed smooth water release curves, with release generally beginning at around 500°C and reaching a maximum near 700°C. In contrast CO<sub>2</sub> and CH<sub>4</sub> were released in two pulses, the first corresponding to the initial release of water, and the second not occurring until 900°C.

CO<sub>2</sub> does not appear to undergo any changes in speciation or bonding prior to decarbonation. Our observations are consistent with simple diffusional loss, but at a much slower rate than H<sub>2</sub>O. This reflects the fact that CO<sub>2</sub> is wedged in the larger part of the channel while H<sub>2</sub>O is held in largely by weak hydrogen bonds and by cations plugging the channel. The effective length of the linear CO<sub>2</sub> molecule is 4.96 Å (Wood and Nassau, 1967), while the effective diameter of the H<sub>2</sub>O molecule is only 3.40 Å (Langer and Schreyer, 1976).

Several questions remain concerning the high temperature behavior of CO<sub>2</sub>. We do not have satisfactory explanations for the appearance of the low energy shoulder in the  $\gamma$  spectrum, or for the behavior of the rotational-librational bands which center on it and grow in intensity along with it. Certain possibilities may be ruled out, however. The shoulder does not represent a broad band state, since it only appears in  $\gamma$ . Likewise, the librational bands are only in  $\beta$ . This means the CO<sub>2</sub> molecule is to some degree in a state of different energy, but it is still highly oriented. When coupled with the rapid equilibration and reversibility of the sharp band to shoul-

der conversion, this orientation of the CO<sub>2</sub> molecule suggests that it remains in the same channel site at high temperatures.

### *Orientation of water and its effect on the structure*

Early models of water in cordierite and beryl emphasized rigid positions. It is apparent that this is not the case, and that depending on the time scale of the observation water in cordierite can be in motion in two ways: the hopping between types I and II seen by Carson et al. and the random motion of the gas-like state proposed here. The room temperature predominance of rotational bands that are consistent with the hopping motion, and the lack of rotational bands corresponding to motion in other directions, indicates that it is the predominant motion at low temperatures. In beryl, an additional motion at room temperature has been observed by Rehm (1974) using microwave spectroscopy, this being the rotation of type I molecules around the crystallographic *c* axis such that the water always occupies symmetrically equivalent positions in the channel. In both minerals the random motion of gas-like water molecules predominates at high temperatures, but may occur to a small extent at all temperatures. These motions appear to contribute to the difficulty in resolving the positions of water molecules by diffraction techniques. It is not possible to directly reconcile the neutron diffraction data taken at room temperature by Hochella et al. (1979) with the IR data by appealing to these motions, however. They report positions which cannot be considered to be averages over the positions and motions described here. It seems likely that the extreme differences in time scale for IR vs. diffraction measurements ( $\sim 10^{-12}$  vs.  $\sim 10^3$  seconds) allows for the diffraction methods to be observing a long term average not predictable by spectroscopic methods.

The apparent effect of channel H<sub>2</sub>O on the structure and properties of cordierite can be substantial (Stout, 1975; Hochella et al., 1979) but as Langer and Schreyer (1976) have pointed out, the absorption energies of the stretching modes indicate a lack of strong hydrogen bonds. We suggest that the coupling mechanism between the lattice properties and the presence of water is the coordination of channel cations by water. By holding the cations in the intra-ring position type II water can have a substantial effect on the structure in an indirect fashion.

### *Implications for the use of cordierite as a petrogenetic indicator*

An important limitation in the use of cordierite as a water fugacity indicator is the difficulty in accounting for both type I and type II water. The required task of experimentally calibrating the entire range of possible H<sub>2</sub>O, CO<sub>2</sub>, and alkali contents for cordierite would be immense, and some simplification is called for. We suggest that since the low temperature type I/type II ratio reflects accurately the high temperature ratio, it is only necessary to consider the concentration of type I water in

order to arrive at the original water fugacity. Type II water, as well as type I, is originally incorporated in an equilibrium form with the gas-like state, and two type II waters will coordinate each channel cation at low temperature. This leaves the remaining sites to be filled by type I H<sub>2</sub>O or CO<sub>2</sub>, as well as possible exotic species like the rare gases. The equilibrium at high temperatures between type I, type II, and gas-like water assures that the final low temperature concentration of type I water is an accurate reflection of the original H<sub>2</sub>O fugacity.

The ease with which type I and type II waters may be distinguished using IR spectroscopy makes this the ideal technique for petrologic application of cordierite as an H<sub>2</sub>O-CO<sub>2</sub> fugacity indicator. We suggest the following method. Since type II H<sub>2</sub>O seems to only respond to the number of channel cations, it is not considered and the number of sites taken up by it are subtracted from the total available sites. These sites are filled by type I H<sub>2</sub>O, CO<sub>2</sub>, other constituents, or they are empty. A simple model ignores the other constituents because of the complexity of their partitioning into the crystal. This leaves type I H<sub>2</sub>O, CO<sub>2</sub>, and empty sites to be considered, and these are exactly the parameters considered and calibrated by Johannes and Schreyer (1981). The implicit assumptions in this technique are: (1) there are no important channel constituents aside from H<sub>2</sub>O, CO<sub>2</sub>, and cations of intermediate size; (2) all channel cations are coordinated by two type II H<sub>2</sub>O molecules; (3) once the sites filled by type II H<sub>2</sub>O are removed from consideration, the remaining sites are filled by H<sub>2</sub>O and CO<sub>2</sub> as if there were no channel cations or type II H<sub>2</sub>O present.

The concentration of the important channel constituents, that is, types I and II H<sub>2</sub>O, CO<sub>2</sub>, and empty sites, will be easily determined by IR spectroscopy. The powder spectrum of the cordierite used in this study is shown

in Figure 7. The two water types are well resolved from each other. CO<sub>2</sub> (not shown) also is resolved at 2348 cm<sup>-1</sup>. Only 2 mg of sample are required for this technique, and our experience indicates that it can be a quantitative technique provided uniform sample handling procedures are followed. All that is required are good calibrations of molar absorptivities. Two major advantages to this technique over bulk analytical techniques are: (1) the type I/type II H<sub>2</sub>O ratio and the type I H<sub>2</sub>O/CO<sub>2</sub> ratio may be very accurately determined, and (2) very small samples, or even petrographic thin sections may be used in the measurement, allowing studies of disequilibrium and zonation. This will also allow the hydrous impurities common in cordierite (e.g., Zimmerman, 1981) to be rigorously excluded from the measurement.

The formation of variable lengths of interconnected open channel due to the partitioning of type II water into the unbound state will have a substantial effect on the observed closing temperatures and equilibration rates for cordierite. The diffusion rates for H<sub>2</sub>O and CO<sub>2</sub> through a channel that is mostly plugged will be much lower than the rate through a channel that is mostly open. As the length of interconnected open stretches approaches the thickness of the mineral grain, rapid equilibration is expected to occur. This has been observed by Goldman et al. (1977) who found that finely ground cordierite dehydrates at about 500°C while large crystals do not dehydrate until 800°C, and that the difference could not be attributed solely to diffusional path lengths. Selkregg and Bloss (1980) describe a cordierite with high Na and Be content which is resistant to dehydration, presumably because the number of plugs still in the channel at any temperature is higher than for other cordierites. The differences in dehydration temperatures reported by Zimmerman (1981) (400° to 800°C for crushed samples) are probably not due to the origin of the cordierites, as he suggests. It is more likely that they are a reflection of the channel cation content of the samples, which were not reported.

CO<sub>2</sub> also probably acts as a partial plug in the channels, and may affect H<sub>2</sub>O equilibration rates. The much lower diffusion rates for CO<sub>2</sub> movement through the channels indicate that water will be more readily equilibrated experimentally in cordierite than CO<sub>2</sub>. This is in agreement with the findings of Johannes and Schreyer (1981), who found that CO<sub>2</sub> moved in and out of synthetic, alkali-free cordierite at a much lower rate than H<sub>2</sub>O, and that increased CO<sub>2</sub> content inhibited H<sub>2</sub>O equilibration in high pressure, high temperature hydrothermal equilibration studies. Because of the interplay between diffusion and the coordination of channel cations, it should be more difficult to experimentally introduce equilibrium amounts of H<sub>2</sub>O and CO<sub>2</sub> into cordierites with channel cations present, and conversely the best natural cordierites for use as petrogenetic indicators will be those with high channel alkali contents because they will have comparatively high closing temperatures.

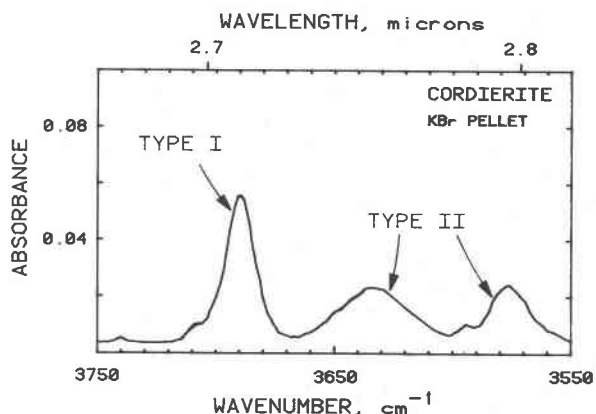


Fig. 7. Infrared spectra of cordierite powder, 2.07 mg in 200 mg of KBr pressed into a 1 cm radius pellet. Baseline due to H<sub>2</sub>O trapped in the KBr has been subtracted. Spectra of this type could be used to measure H<sub>2</sub>O concentration and speciation in cordierite.



### Acknowledgments

We would like to thank R. H. Currier for the cordierite, W. Johannes and W. Schreyer for providing analyzed samples of synthetic cordierite and for helpful discussions concerning the use of cordierite as a petrogenetic indicator, and E. M. Stolper for a critical review. This work was funded in part by NSF Grant EAR 79-19987.

### References

- Armbruster, T. and Bloss, F. D. (1980) Channel CO<sub>2</sub> in cordierites. *Nature*, 286, 140–141.
- Armbruster, T. and Bloss, F. D. (1982) Orientation and effects of channel H<sub>2</sub>O and CO<sub>2</sub> in cordierite. *American Mineralogist*, 67, 284–291.
- Carson, D. S., Rossman, G. R., and Vaughan, R. W. (1982) Orientation and motion of water molecules in cordierite: a proton nuclear magnetic resonance study. *Physics and Chemistry of Minerals*, 8, 14–19.
- Cohen, J. P., Ross, F. K. and Gibbs, G. V. (1977) An X-ray and neutron diffraction study of hydrous low cordierite. *American Mineralogist*, 62, 67–78.
- Goldman, D. S., Rossman, G. R. and Dollase, W. A. (1977) Channel constituents in cordierite. *American Mineralogist*, 62, 1144–1157.
- Goldman, D. S., Rossman, G. R. and Parkin, K. M. (1978) Channel constituents in beryl. *Physics and Chemistry of Minerals*, 3, 225–235.
- Hawthorne, F. C. and Cerny, P. (1977) The alkali metal positions in Cs–Li beryl. *Canadian Mineralogist*, 15, 412–421.
- Hochella, M. F. Jr., Brown, G. E. Jr., Ross, F. K. and Gibbs, G. V. (1979) High-temperature crystal chemistry of hydrous Mg- and Fe-cordierites. *American Mineralogist*, 64, 337–351.
- Johannes, W. and Schreyer, W. (1981) Experimental introduction of CO<sub>2</sub> and H<sub>2</sub>O into Mg-cordierite. *American Journal of Science*, 281, 299–317.
- Langer, K. and Schreyer, W. (1976) Apparent effects of molecular water on the lattice geometry of cordierite: a discussion. *American Mineralogist*, 61, 1036–1040.
- Martignole, J. and Sisi, J. (1981) Cordierite–garnet–H<sub>2</sub>O equilibrium: a geologic thermometer, barometer, and water fugacity indicator. *Contributions to Mineralogy and Petrology*, 77, 38–46.
- Pye, E. G. (1957) Geology of the Manitouwadge area. Ontario Department of Mines Reports 66, part VIII, 1–114.
- Rehm, H. J. (1974) Paraelektrische Resonanz und dielektrische Dispersion von Wasser in Beryll-Einkristallen. *Zeitschrift für Naturforschungen*, 29A, 1558–1571.
- Selkregg, K. R. and Bloss, F. D. (1980) Cordierites: compositional controls of  $\Delta$ , cell parameters, and optical properties. *American Mineralogist*, 65, 522–533.
- Stout, J. H. (1975) Apparent effect of molecular water on the lattice geometry of cordierite. *American Mineralogist*, 60, 229–234.
- Wood, D. L. and Nassau, K. (1967) Infrared spectra of foreign molecules in beryl. *Journal of Chemical Physics*, 47, 2220–2228.
- Zimmermann, J. L. (1981) The liberation of H<sub>2</sub>O, CO<sub>2</sub>, and hydrocarbons from cordierites: kinetics, structural sites, and petrogenetic implications. *Bulletin de Minéralogie*, 104, 325–338.

*Manuscript received, March 3, 1983;  
accepted for publication, September 20, 1983.*