

*BeO in pegmatitic cordierite*

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*Summary.* Several cordierites from pegmatites were found by emission spectroscopy to contain as much as 0.7 wt. % of BeO. Structural crystallographic considerations suggest that the beryl molecule,  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ , may have appreciable solubility in the structure of cordierite. Some hydrothermal experiments carried out on this assumption indicated about the same amount of BeO substitution in the magmatic temperature range as is shown by the pegmatite cordierites. The natural BeO-bearing cordierites have distinctive infra-red absorption properties, which are reproduced in the synthetic solid solutions.

IT is shown in the present study that some cordierites from pegmatites contain considerable amounts of BeO. This phenomenon, although it has not been reported previously, is not surprising in view of the close structural relation between cordierite, orthorhombic  $(\text{Mg}, \text{Fe})_2\text{Al}_4\text{Si}_5\text{O}_{18}$ , and beryl, hexagonal  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$  (Gossner, 1928; Bragg, 1930). Both structures are characterized by six-membered rings of tetrahedrally coordinated cations enclosing a large structural channel, which is the probable location of the varying amounts of loosely held water that almost all natural cordierite contains (Smith and Schreyer, 1962).

At least one of the six ring cations in cordierite is  $\text{Al}^{3+}$ , which fact probably gives rise to the departure from hexagonal symmetry in cordierite (Schreyer and Schairer, 1961). A recent structural determination reveals that the six-membered ring is probably made of 4  $\text{SiO}_4^{4-}$  tetrahedra and 2  $\text{AlO}_4^{5-}$  tetrahedra (G. V. Gibbs, to be published). Varying amounts of disorder among silicon and aluminum atoms in a  $T_9\text{O}_{18}$  framework of tetrahedra can give rise to a symmetry variation that culminates in a truly hexagonal structure in the case of complete disordering. Hydrothermally synthesized Mg-cordierites and those synthesized in air below  $1300^\circ\text{C}$  from glass are hexagonal. A natural hexagonal cordierite found in altered shale adjacent to a burning coal seam has been called *indialite* (Miyashiro *et al.*, 1955).

A X-ray spectrographic *distortion index* ( $\Delta = 2\theta_{131} - \frac{1}{2}(2\theta_{511} + 2\theta_{421})$ ) for copper radiation conveniently measures the degree of departure from

hexagonal symmetry in cordierite (Miyashiro, 1957). Many natural metamorphic cordierites have  $\Delta = 0.20$  or more, while cordierites from pegmatites often have a very low  $\Delta$  of the order of 0.12. Synthetic anhydrous Mg-cordierites formed from glass of the 2:2:5 composition at temperatures between 1300° and 1400° in long runs show  $\Delta$ 's as large as 0.25 (Schreyer and Schairer, 1961). For the case of vanishing distortion index, cordierite (or indialite) may be said to be isostructural with beryl.

A few experiments were performed in the present study to determine approximately the extent of BeO substitution in Mg-cordierite and its dependence on temperature. The results indicate that BeO content of pegmatite cordierite may provide a useful geothermometer for pegmatites.

*Analyses of minerals.* The cordierites studied in the present paper include samples from Haddam, Connecticut (pegmatite; Oppenheimer, 1914); Micanite, Colorado (pegmatite; Heinrich, 1950); Bjordan, Norway (pegmatite); Mont Bity, Madagascar (quartz vein; Miyashiro *et al.*, 1955); New Haven, Connecticut (pegmatite; Iiyama, 1956), and Laramie Range, Wyoming (metasomatic; Newhouse and Hagner, 1949). The cordierite from Bjordan has not previously been described; its unit cell constants are  $a$  16.994,  $b$  9.824,  $c$  9.353 Å. The minerals were analyzed for BeO with the emission spectrograph by Oiva Joensuu, Miami University, Marine Experiment Station. Microscopically selected clear chips from large crystals were analysed; the possibility of beryl inclusions was therefore rendered quite small. The cordierites containing BeO as a major constituent were the Haddam (0.52 wt. %), the Bjordan (0.12 %), and the Micanite (0.70 %). If a binary cordierite-beryl join is assumed, the molar percentages of beryl in solid solution are: Haddam, 4.3 %; Bjordan, 0.8 %; and Micanite, 5.7 %.

*Experimental Techniques.* Glasses of Mg-cordierite and beryl composition were prepared by melting reagent grade oxides together at 1550° C for several hours in a platinum crucible. The temperature was sufficient to avoid crystalline phases. Each glass was ground to a very fine powder, mixed several times under acetone and remelted. The procedure was repeated three times for each glass to affect homogenization. Precautions were taken in handling the BeO because of its high toxicity.

The glasses were crystallized in two ways. Crystallization in the dry way was carried out by holding the glass at  $1300^\circ \pm 15^\circ$  in air in a platinum crucible for 200 hours. Hydrothermal crystallization was accomplished at 700° C and 1000 bars in runs of two weeks duration seeded with a trace of the Haddam cordierite. Both methods yielded

well-crystallized cordierite or beryl or both as the only phases identifiable microscopically and with X-ray diffraction.

Spacings of the crystallized products were determined by X-ray scanning of the major diffraction spectra with a General Electric spectrometer at a rate of  $\frac{1}{4} 2\theta$  per minute using a quartz internal standard. The  $d$ -spacings were converted into unit-cell constants with a least-square programme written by Charles Burnham.

Infra-red absorption spectra of the powdered samples in KBr pellets in the range 7 to 15  $\mu$  were taken with a Beckman IR-7 NaCl prism instrument and in the range 15 to 30  $\mu$  with a Perkin-Elmer 301 grating instrument.

All of the synthetic cordierites could be satisfactorily indexed as hexagonal, within the limits of experimental error. Table I lists unit-cell data of Mg-cordierites and cordierite-beryl solid solutions prepared in various ways.

*Unit-cell data of Mg-indialites.* There is no distinguishable difference in unit-cell constants between the hydrothermal Mg-indialite and the anhydrous material prepared at 1300° (table II). The Mg-cordierite of  $\Delta$  0.25 prepared by Schreyer and Schairer (1961) has a very slightly smaller unit-cell volume. The ' $\alpha$ -Mg<sub>2</sub>Al<sub>4</sub>Si<sub>5</sub>O<sub>18</sub>' prepared by Miyashiro *et al.* (1955) by devitrifying glass at 1200° C has a slightly smaller  $a$ -axis and larger  $c$ -axis than the present anhydrous Mg-indialite of run 2, as has the product of Schreyer and Schairer (1961) prepared by devitrifying glass at 1000° C for 16 hours. The phenomena of small  $a$ -axis and large  $c$ -axis are shown to extreme in the material synthesized by Iiyama (1956) in short runs below 1100°.

It may be concluded from the foregoing data that Mg-indialite prepared at temperatures near 1300° for sufficient lengths of time from on-composition Mg-cordierite glass has the same unit-cell constants as hydrothermally synthesized Mg-indialite. Other authors have shown that water content does not affect the unit-cell size of cordierite appreciably (Miyashiro *et al.*, 1955; Iiyama, 1956). The data on natural cordierites given by Iiyama (1956) lead to a cell-volume of 775.5 Å<sup>3</sup> for  $\Delta = 0$ , if a short extrapolation to zero iron content is made. The unit-cell volume of well-crystallized Mg-indialite may therefore be taken as 776.5  $\pm$  1.5 Å<sup>3</sup>.

*Unit-cell data of solid solutions and beryl.* The hydrothermally synthesized beryl (table I) has unit-cell constants identical with those of a natural beryl specimen. The unit-cell constants of Mg-indialite were considerably affected by BeO content of the starting glass. If Vegard's

TABLE I. Synthetic cordierite and beryl data

Run	Glass Composition (wt. %)	T	P <sub>H<sub>2</sub>O</sub> bars	Time hrs.	Resulting material	a	c	V
1	Mg-cord.	720° C	1000	368	cordierite	9.802 ± 0.005 Å	9.350 ± 0.004 Å	777.9 ± 0.8 Å <sup>3</sup>
2	Mg-cord.	1300	0	216	cordierite	9.802 ± 0.003	9.342 ± 0.002	777.4 ± 0.4
3	beryl	700	1000	416	beryl	9.218 ± 0.002	9.213 ± 0.006	678.0 ± 0.4
4	85 % Mg-cord. 15 % beryl	700	1000	456	cordierite + trace beryl	9.778 ± 0.005	9.339 ± 0.004	773.2 ± 0.7
5	85 % Mg-cord. 15 % beryl	1300	0	216	cordierite	9.753 ± 0.006	9.328 ± 0.005	768.5 ± 1.0
6	55 % Mg-cord. 45 % beryl	700	1000	456	cordierite + beryl	$\left\{ \begin{array}{l} 9.769 \pm 0.004 \\ (\text{cordierite}) \\ 9.216 \pm 0.003 \\ (\text{beryl}) \end{array} \right.$	9.333 ± 0.004	771.3 ± 0.6
7	55 % Mg-cord. 45 % beryl	1300	0	216	cordierite + beryl	$\left\{ \begin{array}{l} 9.700 \pm 0.004 \\ (\text{cordierite}) \\ 9.252 \pm 0.008 \\ (\text{beryl}) \end{array} \right.$	9.297 ± 0.004	757.6 ± 0.7
							9.230 ± 0.014	684.2 ± 1.0

Law and a binary cordierite–beryl join are assumed, Mg-indialite takes in 7.1 mol. % of beryl according to run 6 and 5.8 % according to run 4. The figures are in qualitative agreement with the measured amounts in pegmatitic cordierites. At 700° beryl takes in no appreciable amount of Mg-cordierite. At 1300° Mg-indialite takes in 21.0 mol. % of beryl according to run 7 and beryl takes in 5.7 mol. % of Mg-cordierite. Evidence bearing on the assumption of a binary cordierite–beryl join is summarized below.

TABLE II. Unit-cell constants of synthetic Mg-indialites

Method of preparation (by crystallizing glass)	Source	<i>a</i>	<i>c</i>	<i>V</i>
Hydrothermal, 720°, 1000 bars, 368 hrs.	present	9.802 Å	9.350 Å	777.9 Å <sup>3</sup>
Hydrothermal, 720°, 2000 bars, unknown time	Miyashiro <i>et al.</i> (1955)	9.792	9.349	776.9
Dry, 1300°, 216 hrs.	present	9.802	9.342	777.4
Dry, 1200°, unknown time	Miyashiro <i>et al.</i> (1955)	9.782	9.365	776.7
Dry, 1000°, 16 days	Schreyer and Schairer (1961)	9.770	9.352	773.7
Dry, 1100°, unknown time	Iiyama (1956)	9.777	9.358	775.3
Dry, 1100°, unknown time	Iiyama (1956)	9.742	9.394	772.7

*Infra-red absorption data of synthetic Mg-indialites* are shown in fig. 1. No marked differences exist between the patterns of hydrothermal and anhydrous Mg-indialite except for a somewhat stronger pattern for the hydrothermal material, which is probably owing to better crystallinity. Slight but definite shifts to shorter wavelength are shown in some of the peaks of the run 4 material, especially peaks F and G, indicating cation substitution effects on lattice vibration frequencies (Hafner and Laves, 1961). The peaks resulting from a small amount of beryl in the charge are marked (B). The data for natural cordierites are given in fig. 2. The patterns for the BeO-bearing cordierites are distinct from the others, and show the slight but definite shift to shorter wavelength of the peaks at 16 to 18  $\mu$ .

#### *Mineralogic interpretation*

Beryllium may enter the cordierite structure in a number of ways. The simplest substitution would be BeSi for AlAl; a theoretical limit of substitution would occur when all of the tetrahedrally coordinated Al is replaced by Be and Si, corresponding to the formula  $Mg_2Be_2Si_7O_{18}$ ; this would give about 8 % BeO by weight. The amount given by the natural

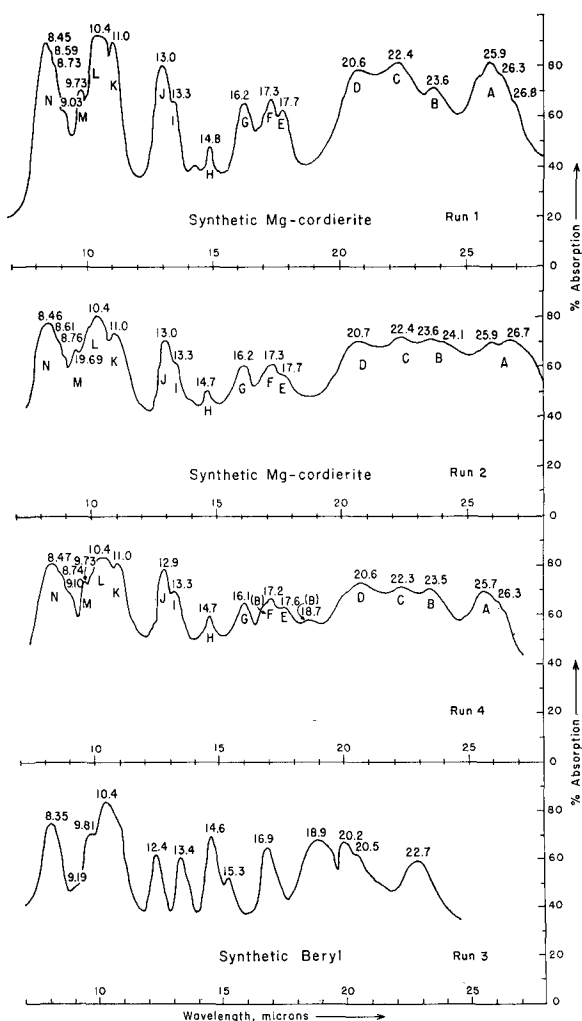


FIG. 1. Infra-red absorption spectrograms of synthetic Mg-cordierite, beryl and Mg-cordierite-beryl solid solution. The run numbers refer to table I.

and synthetic samples is much less than this. Another possibility is the substitution  $Be_3Si$  for  $Mg_2Al_2$ ; that is, that the cordierite-beryl join is binary. A third possibility is the three-cation exchange  $BeAl_2$  for  $Mg_2Si$ .

The run on glass of composition 45 % beryl, 55 % Mg-cordierite at 1300° provides some evidence to support the hypothesis of a binary

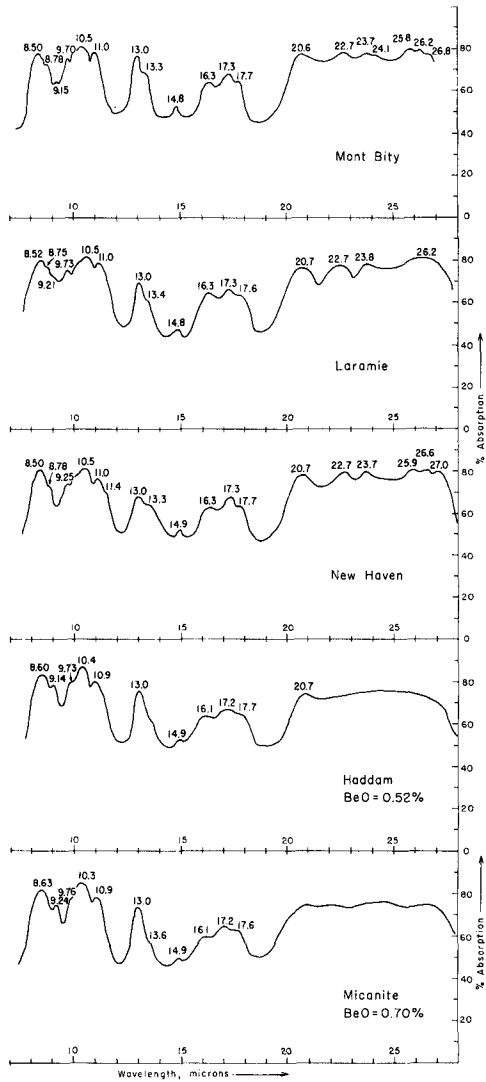


FIG. 2. Infra-red absorption spectrograms of natural cordierites.

cordierite-beryl join, in that no phases other than cordierite and beryl could be detected in the charge. If the substitution mechanism is  $\text{BeSi}$  for  $\text{AlAl}$  a certain amount of mullite would have to appear. If the substitution mechanism were  $\text{BeAl}_2$  for  $\text{Mg}_2\text{Si}$ , such phases as forsterite and phenakite ( $\text{Be}_2\text{SiO}_4$ ) would be expected to appear.

A full chemical analysis is available for the Haddam cordierite (Iiyama, 1956). On the assumption that BeO is separated with  $Al_2O_3$ , the analysis slightly favours the hypothesis of a binary cordierite–beryl join, although the result is not clear cut.

It is probable that many or most cordierites from pegmatites will be found to be rich in BeO. Pegmatitic cordierite is fairly common; 50 occurrences have been summarized by Heinrich (1950). If it can be established that the join cordierite–beryl is binary, the possibility exists of using cordierite as a geologic thermometer for pegmatites: the amount of BeO in the cordierite would indicate a minimum temperature for crystallization of the pegmatite.

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*Note added in proof:* A pegmatitic cordierite of BeO content 1.9 wt. % from Věžná, Czechoslovakia, has recently been described (Černý and Povondra, *Neues Jahrb. Min.*, 1966, *Monatsh.* pp. 36–44). The analyses indicate the substitution (Na, K) + Be → Al.

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