

*Location of argon and water in cordierite.*

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*Summary.* Evaluation of X-ray powder diffraction data shows that argon atoms (radius 1.9 Å) lie at the centres of the large holes in the cordierite structure. The reflection intensities for hydrous cordierite differ from those for anhydrous cordierite but to a lesser degree than those for argon-bearing cordierite. Although analysis is uncertain, it appears that the smaller water molecules (radius 1.4 Å) do not occupy either the centres of the six-membered rings or the centres of the large cavities. It is possible that they may be attached to the walls of the large cavities or occur partly as hydroxyl groups in the framework. Single-crystal X-ray analysis is necessary to resolve this problem.

FOR more than fifty years there has been uncertainty about the occurrence of water in chemical analyses of natural cordierite, and it is only recently that progress has been made in the solution of this problem. It is now firmly established that water may indeed be incorporated in the cordierite structure (Sugiura, 1959; Iiyama, 1960; Schreyer and Yoder, 1960) and causes concomitant variations of physical properties of the mineral. Much confusion in the earlier work stems from the fact that these variations could not be separated from other independent variations of cordierite properties mainly caused by mutual substitution between various cations, principally magnesium and ferrous iron; furthermore, cordierite may undergo a high-low structural change<sup>1</sup> thought, but not proved, to result from order-disorder of the one aluminium and five silicon atoms that form each ring of tetrahedra

<sup>1</sup> A new nomenclature for this structural change was proposed by Schreyer and Schairer (1961) using the prefixes high, 'low', and intermediate state. This usage should not be confused with that of Miyashiro (1957), who had named high- and low-cordierite what should, with our present knowledge, be called anhydrous and hydrous cordierite.

(Miyashiro, 1957; Schreyer and Schairer, 1961); this truly polymorphic variation is quite independent of the compositional variations.

Despite considerable advances there are still a number of uncertainties concerning the mineralogy of cordierite. One of them is the role played by water in the crystal structure: there are indications, based on calculation of cell contents, rate of weight loss with temperature, and infra-red absorption analysis, that part may occur as molecular water in the channels and the remainder in the form of hydroxyl groups replacing oxygen atoms. It was of considerable interest, therefore, that cordierite could be synthesized containing high amounts of argon firmly held in its structure (Schreyer, Yoder, and Aldrich, 1960). Because of its inert nature the argon atoms cannot substitute for any element present in the cordierite structure but must occupy previously empty positions.

In the course of the present investigation X-ray diffraction data for synthetic anhydrous, hydrous, and argon-bearing cordierites were used to give information on the location of water and argon in the cordierite structure. Because the synthetic material was inappropriate for single-crystal studies, it was necessary to collect the data by powder techniques.

After the initial proposal by Gossner (1928), the crystal structure of cordierite was established by Byström (1942) to be isostructural with beryl. It consists of six-membered rings of tetrahedra, each ring containing one Al and five Si atoms. The rings are joined together by Al atoms in tetrahedral coordination and Mg atoms in octahedral coordination. The method of linkage is very elegant but can hardly be appreciated fully without examination of a model built of spheres. In the absence of such a model, fig. 1 serves as a partial substitute. Each six-membered ring has the shape of a cogwheel with six teeth, each formed by a pair of projecting oxygen atoms. The cogwheels interlock in the (001) plane to form layers of pseudohexagonal symmetry. Three oxygen atoms from three adjoining cogwheels are bonded to an Mg atom and form one face of an octahedron, while two oxygen atoms from adjoining cogwheels form half of a tetrahedron occupied by an Al atom. The cogwheels of the next layer are rotated through  $20^\circ$  to  $30^\circ$  with respect to the first layer, permitting the outer oxygen atoms of one cogwheel to fill in the gaps between the outer atoms of cogwheels of adjacent layers. This rotation permits three oxygen atoms to form a triangle rotated  $60^\circ$  about the triad mentioned earlier, thus forming a complete octahedron about a magnesium atom: in a similar way, tetrahedra are formed about the aluminium atoms linking adjacent layers together. The final result is a structure tightly bonded in all three directions.

Fig. 1 shows channels parallel to the  $c$ -axis with a radius of about  $1.4 \text{ \AA}$  formed by stacks of the six-membered rings of oxygen atoms. Actually this radius applies only to the narrowest parts of the channels which widen out to a radius of  $2.2 \text{ \AA}$  between successive rings.

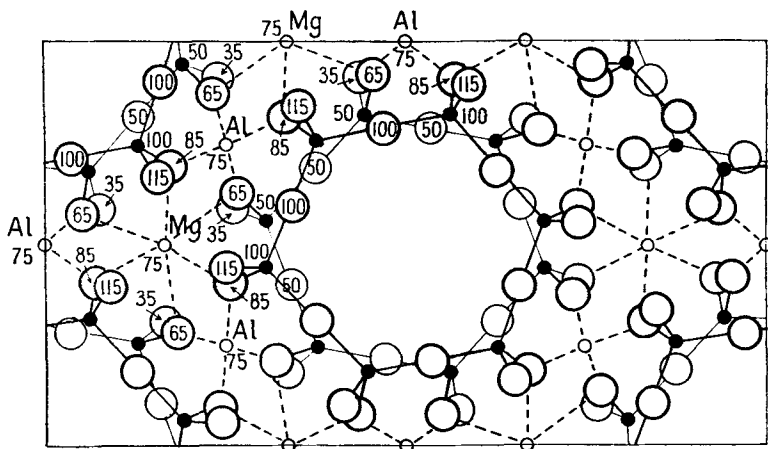


FIG. 1. Structure of cordierite as determined by Byström (copied with permission from his 1942 paper). The projection is taken down the  $c$ -axis with the  $a$ -axis moving horizontally from the upper left-hand corner and the  $b$ -axis moving in the same plane towards the reader. The large circles are oxygen atoms and the small black circles are silicon or aluminium atoms in the ratio 5 to 1. The figures denote the levels of the atoms in % of  $c$ . Superimposed oxygen atoms are symmetrically displaced. Note how successive six-membered rings are rotated by about  $25^\circ$ .

Fig. 2 shows these relations more clearly: the channels consist of strings of almost spherical cavities with an average radius of about  $2.2 \text{ \AA}$  linked by the apertures of  $1.4 \text{ \AA}$  radius. Thus if an atom or molecule can pass through the constrictions, there are large holes for it to occupy.

The argon atom with radius about  $1.92 \text{ \AA}$  fits the cavity easily, and examination of the X-ray data confirms this position. The water molecule with radius about  $1.4 \text{ \AA}$  is much too small for the cavity, and many positions are possible including the centre of a six-membered ring, positions to one side of a cavity where contact can be made with four or five oxygen atoms, or perhaps floating in the middle of a cavity. If the water is incorporated during the growth of the crystal it is possible that it exists in the form of hydroxyl groups replacing oxygen atoms of the framework, with a suitable adjustment of the charged cations. If the water is incorporated after growth of the crystal, such a substitution

appears to be very difficult, because the cations and oxygen atoms should be almost immovable after formation of the crystal.

*Samples.* For the present investigation three samples were used: anhydrous cordierite, hydrous cordierite, and argon-bearing cordierite. The initial starting material for all three samples was glass of the composition  $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ .

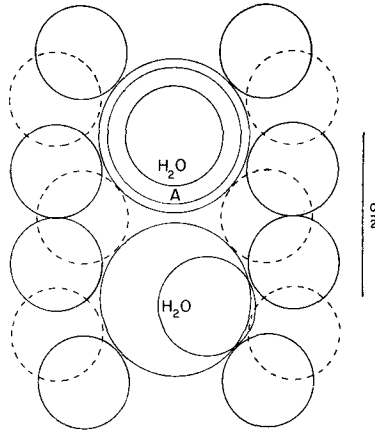


FIG. 2. Section through a channel in cordierite. Oxygen atoms have been assigned a radius of 1.35 Å, water molecules 1.4 Å, and argon atoms 1.92 Å. Note that successive levels of oxygen atoms are rotated 30° about the *c*-axis and that this diagram, therefore, is intentionally simplified. Examination of a solid model shows that the channels almost have rotational symmetry so that this figure although technically non-planar is a good approximation to the truth. The largest circles give a measure of the space available in each cavity. In the lower cavity a possible position is given for a water molecule attached to the cavity wall.

The anhydrous cordierite was synthesized at atmospheric pressure by devitrifying the glass at 1000° C for 3 days, then at 1180° C for 3 days, and finally at 1380° C for 7 days.

Argon-bearing cordierite was obtained by subjecting a sample of the anhydrous cordierite synthesized in the above manner to an argon atmosphere at 10 000 bars, 900° C, for 5 hours. After this treatment the mean refractive index of the cordierite had changed from  $1.524 \pm 0.003$  to  $1.547 \pm 0.003$ . Gravimetric and mass spectrometric analyses indicated an argon content of 2 to 3 weight % (Schreyer, Yoder, and Aldrich, 1960).

Hydrous cordierite was synthesized by subjecting previously crystallized anhydrous cordierite to a water pressure of 10 000 bars at 700° C

for 67 hours. The mean refractive index of this hydrous cordierite was  $1.546 \pm 0.003$ . On the basis of a determinative curve for hydrous Mg-cordierite published by Schreyer and Yoder (1960) this would indicate a water content of about 2.75 weight %.

The three samples employed exhibited identical structural states. In the nomenclature of Schreyer and Schairer (1961) they were 'low'-cordierites with a distortion index of  $0.25^\circ$ .

TABLE I. X-ray data of Mg-cordierites  $Mg_2Al_4Si_5O_{18} \cdot X$ .  $I_E$ , anhydrous ( $1000^\circ C$ , 3 days +  $1180^\circ C$ , 3 days +  $1380^\circ C$ , 7 days);  $I_A$ , argon-bearing (10 000 bars,  $900^\circ C$ , 5 hours);  $I_H$ , hydrous (10 000 bars,  $700^\circ C$ , 67 hours). Cu-K $\alpha$  radiation.

<i>hkl</i>	<i>d</i>	$2\theta$	$I_E$	$I_A$	$I_H$	<i>hkl</i>	<i>d</i>	$2\theta$	$I_E$	$I_A$	$I_H$
200	8.53	10.36	100	63	100	241	2.267	39.72	1	2	2
110	8.45	10.46	95	61	94	204	2.254	39.97	1	4	2
310	4.91	18.05	30	15	27	423	2.234	40.34	3	4	3
020	4.86	18.24	14	7.5	11	133	2.225	40.50	2	3	2
002	4.67	18.99	17	11	17	622	2.171	41.56	4	9	6
400	4.27	20.85	1	7	4	042	2.156	41.87	1	3	2
220	4.22	21.06	—	6	2	900	2.130	42.40	< 1	—	—
112	4.09	21.73	72	43	64	712	2.107	42.88	7	3.5	6
312	3.381	26.33	56	100	70	532	2.099	43.05	6	3	4
022	3.369	26.43	48	84	54	242, 333	2.091	43.22	5	3.5	5
510	3.217	27.70	< 1	5	2	224	2.044	44.28	2	< 1	1
420	3.206	27.80	1	7	3	820	1.951	46.50	2	2	2
402	3.149	28.32	40±	66	45	730	1.946	46.64	4	3	3.5
222	3.132	28.47	64	98	77	802	1.938	46.80	3	4	3
511	3.041	29.34	53	62	62	150	1.932	46.98	2	2	2
421	3.033	29.42	53	62	60	442	1.924	47.20	3	4	3
131	3.012	29.63	40	47	45	821	1.911	47.52	1	1	1
300	2.840	31.47	1	2	2	151	1.892	48.05	1	—	—
600	2.812	31.80	—	3	—	424	1.888	48.15	2	2	1
512	2.650	33.79	16	12	16	713	1.882	48.33	5	5	5
422	2.644	33.87	18	11	18	533	1.875	48.52	7	7.5	7
132	2.631	34.05	9	5	8.5	243	1.870	48.66	7	7	8
620	2.452	36.61	3.5	6.5	5	910	1.860	48.93	3	3±	3
040	2.430	36.96	4.5	5	6	640	1.847	49.30	2	2.5	2.5
332	2.410	37.28	3	< 1	1	350	1.839	49.51	2	3	3
621	2.373	37.88	1	< 1	< 1	115	1.825	49.93	1	1	1
004	2.334	38.54	11	16	14	641	1.811	50.33	2	2.5	2.5
711	2.292	39.27	2	2	2	604, 351	1.804	50.54	5	6	5
531	2.278	39.52	2	2	2	334	1.798	50.74	6	8	6

Intensities *I* were obtained by measuring the peak height above background on a diffractometer chart, and scaling each pattern so that the strongest peak has an intensity of 100. Because of the pseudo-hexagonal symmetry, there are many overlapping peaks, which might appear as single lines in low-resolution patterns.

*Experimental.* Tables I and II contain X-ray powder data collected on a Norelco Geiger-counter diffractometer for the three samples of synthetic cordierite. Experimental conditions were as nearly as possible identical for each diffractometer record, permitting an accurate comparison. Peak positions for all three samples were equal within experimental error. The cell dimensions were  $a = 17.06_2$ ,  $b = 9.72_1$ ,  $c = 9.33_9$  Å. All reflections were indexed on the basis of space group *Cccm*. Because

of serious overlapping of peaks caused by the pseudohexagonal symmetry, it was not possible to obtain reliable integrated values of intensities for overlapping peaks, especially in the region where resolution of the  $\alpha_1$ ,  $\alpha_2$  doublet begins. It was possible to record peak intensities for individual reflections (table I) but when integrating intensities it was often necessary to carry the integration over two or more peaks. Detailed experimental conditions were: radiation, filtered Cu-K; scanning rate,  $\frac{1}{4}^\circ$  per minute; time constant, 8 sec.

The divergence angle of  $1^\circ$  gave a beam that just covered the rectangular smear mounts at  $2\theta = 15.0^\circ$  and was fully intercepted by the sample at higher angles. Assuming the sample to be infinitely thick (a good approximation) the relation between the observed intensity  $I$  and the observed structure amplitude  $|F_{\text{obs}}|$  is:

$$I = \text{constant } |F_{\text{obs}}|^2 \left( \frac{1 + \cos^2 2\theta}{\sin 2\theta} \right) \frac{p}{\sin \theta}$$

for reflections with  $2\theta > 15^\circ$ , and

$$I = \text{constant } |F_{\text{obs}}|^2 \left( \frac{1 + \cos^2 2\theta}{\sin 2\theta} \right) p$$

for reflections with  $2\theta < 15^\circ$  (Brindley and Gillery, 1956).  $p$  is the multiplicity factor for the reflection, and in the space group *Cccm* of cordierite is 2 for reflections with two zeros such as 200, 4 for reflections with one zero such as 310, and 8 for reflections with no zeros such as 312. By means of the above equations, peak intensities for anhydrous cordierite (table I) were converted into values of  $|F_{\text{obs}}|$  (table II). Because the value of the constant is not known, the values of  $|F_{\text{obs}}|$  could only be placed on a relative scale at this stage.

Structure amplitudes,  $F_{\text{calc}}$ , for anhydrous cordierite were calculated from the atomic coordinates given by Byström using the program developed by Shiono of the University of Pittsburgh for an IBM 650 computer. Empirical scattering factors, assuming half-ionization, and based on the calculations of Berghuis *et al.*, were used. Serious discrepancies were found between  $F_{\text{calc}}$  and  $|F_{\text{obs}}|$ , but these were resolved when it was found that Byström had listed erroneous values. The coordinates  $x_{10}$  and  $y_{10}$  given by Byström for one oxygen atom in general position as  $-0.681$  and  $0.405$  should be changed respectively to  $0.070$  and  $-0.405$ . Comparison of the values of  $|F_{\text{obs}}|$  and the new values of  $F_{\text{calc}}$  (table II), after applying a linear scaling factor to the former, proved to be satisfactory, showing that the atomic coordinates used by

TABLE II. Calculated and observed structure amplitudes. Intensities:  $I_E$ , anhydrous;  $I_A$ , argon-bearing;  $I_H$ , hydrous; int., integrated.

$hkl$	$F$ calc. anhyd.	$F$ calc. 2.5% argon.	$F$ obs. anhyd. peak.	$F^2$ argon calc.	$\frac{I_E}{I_A}$ peak.	$\frac{I_E}{I_A}$ int.	$\frac{I_E}{I_H}$ peak.	$\frac{I_E}{I_H}$ int.	$\frac{I_E}{I_H}$ int.	$I_E$ int.	$I_A$ int.	$I_H$ int.
200	-172	-128	116	1.81	1.86	1.94	1.14	1.08	100.0	66.0	100.0	
110	-178	-134	79	1.76	1.82		1.15					
310	-112	-71	84	2.49	2.3	2.8	1.27	1.43	33.0	15.0	25.0	
020	-112	-81	81	2.49	2.2		1.45					
002	+125	+85	96	2.16	1.8	2.0	1.14	1.17	13.0	8.5	12.0	
400	-15	+25	26	—	—	0.06	—	0.08	0.3	6.8	3.8	
220	-37	+2	0	—	—							
112	+140	+101	120	1.92	1.96	2.43	1.28	1.38	55.0	29.0	43.0	
312	-181	-219	149	0.68	0.65	0.68	0.91	0.95	53.0	100.0	60.0	
022	-190	-228	194	0.69	0.67		1.01					
510	+56	+92	21	0.37	—	0.23	—	0.8	1.1	6.1	1.5	
420	+70	+106	30	0.44	—		—					
402	-218	-254	202	0.74	0.71	0.76	1.01	1.02	56.0	95.0	59.0	
222	-218	-253	179	0.74	0.76		0.95					
511	-161	-161	174	1.00	1.00	(1.00)	(0.98)	(1.00)	74.0	95.0	80.0	
421	+67	+67	174	1.00	1.00	(1.00)	(1.01)	(1.00)				
131	-172	-172	153	1.00	1.00	(1.00)	(1.02)					
600	+22	+56	48	0.15	—	0.5	—	0.48	0.4	1.1	0.9	
330	+13	+47	0	—	—	0.0	—	0.0	0.0	1.3	0.0	
422	+135	+101	125	1.79	1.6	2.1	1.14	1.08	20.0	12.0	20.0	
422	+130	+96	132	1.83	1.9		1.14					
132	+132	+89	94	1.75	2.1		1.1					
620	+132	+164	94	0.65	0.6	0.55	0.8	0.79	1.9	4.4	2.6	
040	+129	+161	158	0.64	1.0	1.03	0.85	1.08	3.3	4.1	3.3	
332	+44	+12	65	13.0	—	4.8	3.4	1.3	1.5	0.4	1.2	
621	+107	+107	39	1.00	—	1.6	—	1.6	0.3	0.2?	0.2?	
004	+331	+353	266	0.88	0.8	0.75	0.90	0.95	8.8	15.0	10.0	





Byström are reasonably accurate. However, some significant discrepancies occur, indicating the need for further refinement.

*Analysis.* There are four large cavities in each unit cell of cordierite. If each were occupied by argon atoms, the resulting argon-cordierite would contain 6.40 weight % of argon. However, analyses of the argon-cordierite used in this study indicated an argon content of only 2 to 3 weight %. Consequently, it was assumed at first that only half the possible sites were randomly occupied by argon atoms. Furthermore, it was assumed that the presence of argon did not affect the positions of the other atoms. Calculations of structure amplitudes for argon-bearing cordierite showed that the argon contribution would indeed produce changes of relative intensities in the same direction as those found experimentally (table II). However, the calculated changes for two argon atoms per unit cell were too small in comparison with the observed changes. Reasonable agreement was obtained for 2.5 argon atoms per unit cell. Considering the possible experimental errors and the incomplete refinement of atomic coordinates this agreement is quite good. The method of comparison was as follows: the argon atoms can lie at 0, 0, 1/4; 0, 0, 3/4; 1/2, 1/2, 1/4; and 1/2, 1/2, 3/4. As these positions make no contribution to reflections with  $l$  odd, it is possible to scale the intensities for the anhydrous and argon cordierites by using the reflections 511, 421, and 131 which are unaffected by argon. Then comparison can be made for the reflections with  $l$  even, which are affected by the argon atoms. In table II comparison is made in this manner of ratios of both peak and integrated intensities with ratios of the squares of calculated structure amplitudes. The only serious discrepancies are for weak reflections where high accuracy cannot be expected either in the measured or calculated intensities. According to an average of the scatter in table II the estimated content per unit cell of argon atoms, 2.5, is probably accurate to 0.2. This cell content would correspond to an argon content of the cordierite of about 4 weight %.

Similar calculations for water molecules are inconclusive. If the water molecules occupied the same positions as the argon atoms, the change of intensity for each reflection would be in the same sense as for argon cordierite but not quite as large because the number of electrons in the 2.75 weight % of H<sub>2</sub>O would be less than in the 4 weight % of argon determined by the above X-ray analysis. Intensity changes should average about one-half or two-thirds of those found for the argon cordierite. Examination of table II shows that changes of intensities greater than experimental error do occur when water is introduced into

anhydrous cordierite. However, they are much less than one-half or two-thirds of those found for the argon cordierite. It is quite certain, therefore, that the water molecules are not rigidly fixed in the centres of the cavities, but it is not possible to draw any definite conclusion on the present evidence concerning their positions. One interpretation of the present data is that the water molecules occupy positions around the surface of the cavities such that the average position is at the centre of the cavities. This would explain why the deviations of the intensities tend to lie in the same direction for the argon and hydrous cordierites. Another interpretation might be that only part of the water in cordierite is situated in the channels. However, the evidence for both interpretations is quite inconclusive, and a rigorous conclusion must await single-crystal X-ray analysis. No conclusion can be reached on the basis of the present data concerning the possibility of occurrence of part of the water as hydroxyl groups in the framework; indeed it is possible that even the most refined single-crystal X-ray techniques would not permit detection of this type of substitution.

*Discussion.* It is of interest to speculate why the content of argon is found by X-ray analysis to be larger than that revealed by weight-loss experiments, and why it is still less than the theoretical maximum content. Blockage of the six-membered rings by impurities, or high activation energy for passage of the argon atoms ( $1.9 \text{ \AA}$ ) through the rings ( $1.4 \text{ \AA}$ ), or both, may be the answer. It is not unlikely that faults in the crystal structure such as the presence of a few alkali atoms may block some of the six-membered rings. If two blocks occur in any channel all atoms or molecules lying between the blocks are trapped. It is for this reason that in the field of zeolite molecular sieves great importance is attached to the difference between those zeolites with intersecting and those with non-intersecting channels. So in alkali-bearing cordierite it is possible that some of the argon cannot leave the structure until it is completely destroyed by heating; also it is possible that parts of the structure form free of argon and that argon cannot reach these parts after growth. However, the glass from which the cordierite used in this study was synthesized contains a minimum amount of alkalis (not more than 0.05 weight %; Schreyer and Schairer, 1961), and refractive index measurements indicate that all the argon can be expelled by heating this cordierite to  $1000^{\circ} \text{C}$  for 15 minutes.

A factor of considerable interest in the interpretation of weight-loss experiments is the occurrence of different sizes of six-membered rings. Even in the most highly-ordered cordierites there should be some rings

in which there are more or less than one aluminium atom. Because of the difference in the Si-O and Al-O distances (1.60 and 1.78 Å), this would lead to rings of different sizes. The energy barrier for passage through a constriction varies greatly with size, and a change of 0.1 Å in the diameter of a constriction may lead to a tenfold decrease of diffusion, or in an extreme case to the difference between acceptance or rejection. Consequently, observations of water molecules coming off at a variety of temperatures do not necessarily mean that there are different ways in which water molecules are bound in the structure; they may result merely from energy barriers of varying height. Furthermore, there should be differences in the diffusion rates of argon and water from cordierites of different structural states.

An obvious extension of this work is the examination of single crystals of cordierite to obtain further data on the position of water molecules, to test the possibility of sodium and potassium atoms occupying the centres of the six-membered rings or the surfaces of the cavities, and to test whether the high-'low' relation is caused by order-disorder of the Al and Si atoms. Such studies are under way by Dr. G. V. Gibbs of the University of Chicago.

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