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Hydrous gem magnesian cordierite with inclusions of hydroxyapatite, dolomite, and rutile

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SUMMARY. An uncommon sample of a pale-blue Madagascar cordierite and its mineral inclusions of different kinds have been studied. The physical properties of the embedding cordierite are: $\alpha = 1{\cdot}528$, $\beta = 1{\cdot}522$, $\gamma = 1{\cdot}537$, $\delta = 0{\cdot}009$, $2V_\alpha = 96^\circ$, density = 2·534 g/cm^3, a = 17·082 Å, b = 9·728, c = 9·352, $\Delta = 0{\cdot}26$. The electron probe analysis gave SiO_2 = 48·64%, Al_2O_3 = 35·08, FeO = 0·70, MgO = 12·35, H_2O^+ = 2·50. This is therefore a hydrous magnesian cordierite. Its structural state is related to the shift in $\alpha, \beta, \gamma, 2V_\alpha$, and Δ with heating. Probe analyses were performed on the inclusions: hydroxyapatite, dolomite, and rutile. The occurrence of dolomite suggests the conditions of formation of the host mineral.

THE cordierite modifications can yield useful information on the genesis of this mineral because of the gradation from hexagonal to orthorhombic symmetry through the distortions of the hexagonal lattice. Furthermore, its composition and the optical and structural characteristics of these polymorphous forms vary with the degree of distortion, probably caused by the disorder-order distribution of Si and Al atoms.

The present study was undertaken to determine: the nature of the structural state of the cordierite, the mineralogical characterization of different kinds of crystals included in this mineral, and the genetic crystallization conditions of the host mineral.

Experimental. The rounded and fragmented specimens of pale-blue translucent cordierite used in this work were kindly supplied by Professor W. F. Eppler, Munich, West Germany, who reports the occurrence of this sample in a secondary deposit in Madagascar.

Optical observations showed that this cordierite, of gem size and quality, contained different kinds of inclusions, some colourless and others of a deep red-brown colour. The former showed no definite habit, while the latter were found in short prismatic crystals (fig. 1).

We first studied the cordierite, of which we also had some minute fragments free from inclusions, making it possible to conduct a complete mineralogical study.

Optical observations were carried out. In particular, the refractive indices and the optical axial angle $2V_\alpha$ were determined at room temperature: $\alpha = 1{\cdot}528 \pm 0{\cdot}003$, $\beta = 1{\cdot}532 \pm 0{\cdot}003$, $\gamma = 1{\cdot}537 \pm 0{\cdot}003$, $\delta = 0{\cdot}009$, $2V_\alpha = 96 \pm 2^\circ$.

Density was measured with heavy liquids, because of the limited amount of material available, and found to be rather low (D = 2·534 g/cm^3).

X-ray powder diffractograms of the cordierite were obtained and the diffraction angles were calibrated with those of rock salt used as an internal standard. The powder diffractogram of this cordierite varied only slightly from the standard of a sample from Risør, Norway, used by Byström (1942) for full structural determination. The agreement between the observed and calculated values of 2θ and Q was considered satisfactory. It is known that the powder pattern in the range of 2θ between 29° and 30°, for Cu-K_α radiation, is the most distinctive. The distortion index (Δ), as defined by Miyashiro (1957), was calculated and found to show a value typical of the

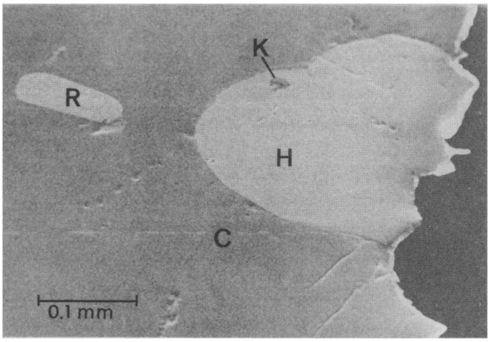


FIG. 1. Scanning electron microscope photograph of the Madagascar cordierite. A characteristic surface with some kinds of inclusions: *C*, cordierite; *H*, hydroxyapatite; *K*, K-feldspar; *R*, rutile.

subdistortional cordierites with $\Delta > 0{\cdot}20$. The unit cell parameters and the distortion index were determined by least-squares refinement of X-ray data, indexed by comparison with Iiyama's (1956) published pattern: $a = 17{\cdot}082 \pm 0{\cdot}006$ Å, $b = 9{\cdot}728 \pm 0{\cdot}005$, $c = 9{\cdot}352 \pm 0{\cdot}005$, $\Delta_{\text{obs.}} = 0{\cdot}26 \pm 0{\cdot}02^\circ$, $\Delta_{\text{calc.}} = 0{\cdot}25 \pm 0{\cdot}03^\circ$.

The degree of deviation of cordierite from hexagonal symmetry is expressed by the value $(a - \sqrt{3}\,b)$ as a function of the distortion index (Iiyama, 1956), since the cell dimensions b and c seem to depend on composition only. For this cordierite we can estimate a deviation from hexagonal symmetry of about 1·36 % of the a length. The diffraction angle 2θ was measured for the 004 reflection, whose variation is suitable for estimating the $(\text{Fe}^{2+} + \text{Mn})/(\text{Mg} + \text{Fe}^{2+} + \text{Mn})$ ratio, which was found to be about 6 %.

Heating experiments were conducted in the 550–1400° ± 3 °C temperature range, and at every 100 °C the sample was put for 20 minutes in an electric furnace in air and then taken out to cool, as suggested by Miyashiro (1957). The distortion index, optical angle, and β refractive index were estimated on the cooled sample. Table I shows the changes in these physical features. The variation of the distortion index is shown in fig. 2 and the graph is characteristic of the subdistortional cordierites with $\Delta > 0{\cdot}20$ (Miyashiro, 1957). It is interesting to remark that the values of the β index and of the optical angle decreased appreciably on heating. This behaviour is typical of the low subdistortional cordierites with $\Delta > 0{\cdot}20$ (Miyashiro *et al.*, 1955; Iiyama, 1958).

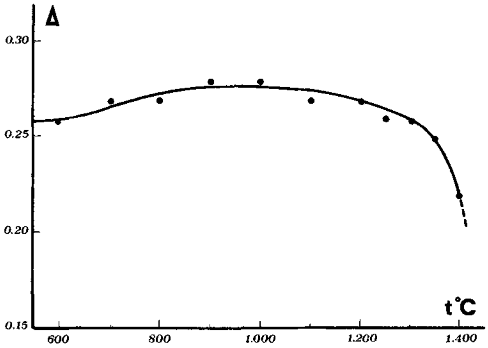
Experiments were conducted in the same temperature range and for the same time, under vacuum, with a heating X-ray powder diffractometer, for the purpose of measuring the distortion index, every 100 °C, on the whole sample being heated. The diffraction angles were calibrated by those of α-Al_2O_3, used as an internal standard for all temperatures. The graph obtained (fig. 3) shows a pattern similar to that appearing in fig. 2, but the variations in the distortion index reach considerably higher values. As it also appears from a study of Table I, it becomes quite evident that this sample belongs to the class of subdistortional cordierites with $\Delta > 0{\cdot}20$. The graphs (figs. 2 and 3) were obtained by calculating the coefficients of a fourth-degree polynomial, approximated by the least-squares method (Olivetti Program Code 9201150, 1973), and plotted by a suitable programme.

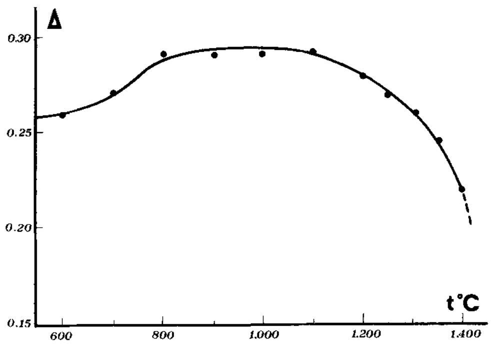
The sample, characterized by optical observations and X-ray diffraction investigations, was analysed by the infrared method. The spectrum of this cordierite was taken under the experimental

TABLE I. *Heating experiments on a Madagascar cordierite**

Temperature (°C)	Cooled sample			Heated sample
	$2V_\alpha$	β	Δ	Δ
Room temp.	96	1·532	0·26	0·26
550	102	1·529	0·26	0·26
600	103	1·528	0·26	0·26
700	104	1·527	0·27	0·27
800	106	1·526	0·27	0·29
900	106	1·526	0·28	0·29
1·000	106	1·526	0·28	0·29
1·100	108	1·525	0·27	0·29
1·200	109	1·524	0·27	0·28
1·250	109	1·524	0·26	0·27
1·300	110	1·523	0·26	0·26
1·350	110	1·523	0·25	0·24
1·400	112	1·522	0·22	0·22

* Time of heating for every experiment: 20 minutes.





FIGS. 2 and 3: FIG. 2 (*top*). Heating experiment. The changes of the distortion index (Δ) on the cooled sample. FIG. 3 (*bottom*). Heating experiment. The changes of the distortion index (Δ) on the sample measured while heated.

TABLE II. *Microprobe analyses of the Madagascar cordierite and its inclusions*

Cordierite		Hydroxyapatite		Dolomite		Rutile	
SiO_2	48·64	FeO*	0·18	FeO*	0·22	TiO_2	98·79
TiO_2	—	MnO	0·15	MnO	—	SnO_2	—
Al_2O_3	35·08	MgO	0·57	MgO	21·08	SiO_2	—
FeO*	0·70	CaO	55·31	CaO	31·20	Cr_2O_3	—
MnO	0·06	SrO	—	CO_2†	46·80	V_2O_3	—
MgO	12·35	Na_2O	—			Al_2O_3	0·15
CaO	0·71	K_2O	—			Nb_2O_5	—
Na_2O	0·18	P_2O_5	42·14			Ta_2O_5	—
K_2O	0·07	F	—			FeO*	0·90
H_2O^+	2·50	Cl	tr.			MnO	0·10
H_2O^-	0·23	H_2O^+	n.d.			H_2O	n.d.
		H_2O^-	n.d.				
Total	100·52		98·35		99·30		99·94

Numbers of ions on the basis of:

18(O)			26(O, OH, F, Cl)			6(O)			2(O)		
Si	4·666	6·00	P	6·201	6·20	Mg	0·978	2·02	Si	—	1·00
Al	1·334		Mg	0·148	10·5	Fe^{2+}	0·006		Cr	—	
Al	2·632	2·63	Fe^{2+}	0·026		Mn	—		Ti	0·991	
Ti	—		Mn	0·022		Ca	1·040		Ta	—	
Mg	1·765	1·94	Na	—		C	1·988		Nb	—	
Fe^{2+}	0·056		Ca	10·302					Sn	—	
Mn	0·005		Sr	—					Fe^{2+}	0·010	
Na	0·033		F	—	tr.				V	—	
Ca	0·073		OH	n.d.							
K	0·009		Cl	tr.							

* Total iron as FeO.
† Calculated.

conditions selected by Langer and Schreyer (1969); it shows a marked splitting of bands A, B, D, E, F, and C between the measured wavelengths from 7 to 40 μm, characteristic of these cordierites. The pattern of the graph was found to be quite similar to that reported by the above-cited authors for the low cordierites with $\Delta = 0{\cdot}24$.

Microprobe analyses were performed on pure cordierite and its inclusions, in order more fully to investigate compositional variations (Table II). All iron is calculated as FeO.

The study of the experimental data showed, in the host mineral, a low FeO content, in contrast to a high MgO content. The value of the $(Fe^{2+}+Mn)/(Mg+Fe^{2+}+Mn)$ was quite low: 5·8 %, characteristic of a Mg-cordierite, in substantial agreement with the above deductions. The sample was also checked for MnO and TiO_2, whose contents were found to be, respectively, quite low and almost indeterminable. The ignition loss was determined thermogravimetrically on a fragment of pure cordierite at 850 °C and was found to be appreciable (2·50 %). The insufficient sample did not permit analysis by mass spectrometer of the gases liberated during heating. Therefore the weight loss was attributed totally to H_2O^+. Alkali ions, Na and K, were present but not in appreciable amounts.

The clear and colourless inclusions were then examined. They could be further subdivided into greyish-green rounded crystals (maximum size: 0·30 × 0·20 mm), negative uniaxial, and greyish individuals (maximum size: 0·10 × 0·06 mm), negative uniaxial, with high birefringence and refraction indices close to those of the host mineral.

The microprobe analyses conducted on the former kind of inclusion indicated that this was apatite (Table II). The ascertained absence of fluorine and the small amount of chlorine suggested a hydroxyapatite. Also present in these crystals were minute grains (maximum size: 0·02 × 0·01 mm) with a considerable content of Si, Al, and K, and a very small amount of Ca. In accordance with the optical observations, we concluded that these inclusions were probably K-feldspar.

The greyish inclusions showed a composition very close to pure $CaMg(CO_3)_2$, with a small amount of FeO (0·22 %) and traces of MnO. The CO_2 content was calculated by difference, bearing in mind the crystallochemical formula (Table II).

The red-brown inclusions were made up of short prismatic crystals (maximum size: 0·10 × 0·03 mm), positive uniaxial, with a very high relief and refraction indices higher than cordierite. Their composition (Table II) was found to be essentially TiO_2 (98·79 %) with small amounts of FeO, Al_2O_3, and MnO. This was therefore rutile, the polymorph of TiO_2, the smallest in volume and the commonest in nature.

Discussion. The significant points brought out in this study of gem cordierite from the Madagascar area make it possible to formulate some genetic hypotheses.

The variations of Δ, of the refractive index β, and of the angle between optical axes with heating make it possible to recognize the degree of polymorphism of this sample and to define it as low subdistortional cordierite (Miyashiro, 1957).

Schreyer and Schairer (1961) found it convenient to subdivide the structural state of cordierite solely on the basis of the distortion index, because the difference in refractive indices were due to compositional rather than polymorphic variations. The sample, therefore, appears to be a low cordierite. The chemical composition and the infrared investigations show that this is a Mg-cordierite and, in particular, a hydrous cordierite (Schreyer and Yoder, 1964), corresponding to Miyashiro's low cordierites (1957).

The cell-edge values obtained are in satisfactory agreement with those reported by Byström (1942) and by Gibbs (1966) for the low cordierites.

The relationships among β, the $(Fe^{2+}+Mn)/(Fe^{2+}+Mn+Mg)$ ratio, the distortion index, and the unit-cell dimensions suggest that the sample is presumably of typical metamorphic, pegmatitic, and quartz-vein origin, as can be inferred from a study of the graphs by Iiyama (1958) and Miyashiro (1957).

The measurement of the distortion index by heating X-ray powder diffractometry showed considerable sensitivity and selectivity (figs. 2 and 3).

It is a known fact that cordierite of the medium grade of metamorphism can exist up to temperatures of more than 500 °C (Winkler, 1976). The pattern of the graphs in figs. 2 and 3 suggests that the formation temperature of this cordierite is certainly lower than 900 °C.

The pressure-temperature field of stability of Mg-cordierite has also recently been studied by various researchers (Ashworth and Chinner, 1978; Hensen, 1977; Hensen and Green, 1972; Holdaway and Lee, 1977; Newton, 1972; Thompson, 1976) who found temperatures between 500 and 850 °C and pressures between 4 and 6·5 kbar. However, the maximum possible value of P cannot be inequivocably defined.

The mineral inclusions in this cordierite are: hydroxyapatite, dolomite, K-feldspar, and rutile. Beyond its gemmological significance, the identification of these uncommon and certainly protogenetic inclusions has permitted a better definition of the conditions of formation of the host mineral. In particular, scarce and minute rounded grains of dolomite, since they present no trace of reabsorption, suggest temperatures not greater than 600-50 °C.

The scarcity of carbonate, by comparison with the embedding cordierite, would suggest low molar fractions of CO_2 in the fluid phase, which permits the supposition that only H_2O^+ settled in the canals of the cordierite.

The temperatures would imply barometric pressures of about 6 kbar, as can be deduced from the works of Hensen (1977), Newton (1972), and Schreyer (1976).

Furthermore, although dolomite and K-feldspar are not in contact, it can be assumed that P and T were not high enough to permit the reaction: dolomite + K-feldspar + H_2O = phlogopite + calcite + CO_2. Such temperatures oscillate, at 6 kbar, between 520 and 565 °C for X_{CO_2} between 0 and 0·38 (Puhan, 1978).

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