

## VIOLET-COLORED DIOPSIDE FROM SOUTHERN BAFFIN ISLAND, NUNAVUT, CANADA

CHRISTOPHER D.K. HERD<sup>§</sup> AND RONALD C. PETERSON

*Department of Geological Sciences, Queen's University, Kingston, Ontario K7L 3N6, Canada*

GEORGE R. ROSSMAN

*Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125, U.S.A.*

### ABSTRACT

Diopside with an unusual violet color from southern Baffin Island, Nunavut, Arctic Canada, is found in calc-silicate lenses, associated with marialite, pargasite, phlogopite, calcite, apatite, titanite, talc, chlorite, plagioclase and quartz. It occurs as massive aggregates of roughly equant grains. Basal parting is evident, and pyroxene cleavage is subtle. Indices of refraction are  $n_{\alpha}$  1.670(1),  $n_{\beta}$  1.675(1), and  $n_{\gamma}$  1.695(1), and  $2V_Z$  is equal to 57.6(5)° at 589 nm. Pleochroism is nonexistent.  $D_{\text{calc}} = 3.30 \text{ g/cm}^3$ . Cell dimensions determined from powder X-ray diffraction are  $a$  9.730(4),  $b$  8.873(3),  $c$  5.275(2) Å,  $\beta$  105.95(3)°. A single-crystal X-ray structural refinement was performed to determine bond lengths and angles. The empirical formula, based on results of electron-microprobe analyses and absorption spectroscopy indicating 0.30 wt.% H<sub>2</sub>O in the structure, is  $(\text{Ca}_{0.96}\text{Na}_{0.04})(\text{Mg}_{0.86}\text{Al}_{0.06}\text{Fe}^{2+}_{0.05}\text{Ti}^{4+}_{0.02})(\text{Si}_{1.89}\text{Al}_{0.11})\text{O}_{5.93}\text{OH}_{0.07}$ . The unusual color is due to intervalence charge-transfer between Fe<sup>2+</sup> and Ti<sup>4+</sup> at the M1 site, and is observed owing to the low overall concentration of Fe in the diopside. Cathodoluminescence indicates that Mn<sup>2+</sup> is present in the M1 site. Absorption spectroscopy demonstrates that Mn<sup>3+</sup> does not contribute to the violet color.

*Keywords:* diopside, violet color, spectroscopy, intervalence charge-transfer, clinopyroxene, Baffin Island, Nunavut, Canada.

### SOMMAIRE

Nous décrivons un échantillon de diopside violacé provenant du sud de l'île de Baffin, au Nunavut, dans l'Arctique canadien, prélevé d'une lentille de calc-silicates et associé à marialite, pargasite, phlogopite, calcite, apatite, titanite, talc, chlorite, plagioclase et quartz. Le diopside forme des agrégats massifs de grains équidimensionnels. Un plan de séparation (001) est évident, mais les plans de clivage sont subtiles. Les indices de réfraction sont  $n_{\alpha}$  1.670(1),  $n_{\beta}$  1.675(1), et  $n_{\gamma}$  1.695(1), avec  $2V_Z$  égal à 57.6(5)° à 589 nm. Il n'y a aucun pléochroïsme. La densité calculée est de 3.30 g/cm<sup>3</sup>. Les paramètres réticulaires ont été déterminés par diffraction X sur poudre:  $a$  9.730(4),  $b$  8.873(3),  $c$  5.275(2) Å,  $\beta$  105.95(3)°. Un affinement de la structure utilisant un cristal unique a été fait afin de déterminer les longueurs de liaison et les relations angulaires. La formule empirique, fondée sur les résultats d'analyses à la microsonde électronique et les spectres d'absorption, qui indiquent la présence de 0.30% (poids) de H<sub>2</sub>O dans la structure, serait  $(\text{Ca}_{0.96}\text{Na}_{0.04})(\text{Mg}_{0.86}\text{Al}_{0.06}\text{Fe}^{2+}_{0.05}\text{Ti}^{4+}_{0.02})(\text{Si}_{1.89}\text{Al}_{0.11})\text{O}_{5.93}\text{OH}_{0.07}$ . La couleur inhabituelle serait due au transfert intervalence des charges impliquant le Fe<sup>2+</sup> et le Ti<sup>4+</sup> sur le site M1, phénomène observable à cause de la faible teneur en fer dans cet échantillon. D'après la cathodoluminescence, le Mn<sup>2+</sup> est présent au site M1. Les spectres d'absorption montrent que le Mn<sup>3+</sup> ne contribue pas à la couleur violette.

(Traduit par la Rédaction)

*Mots-clés:* diopside, couleur violette, spectroscopie, transfert intervalence des charges, clinopyroxène, île de Baffin, Nunavut, Canada.

### INTRODUCTION

We describe here the physical, optical, crystallographic, chemical and spectroscopic properties of violet-colored diopside, the most abundant mineral in a

meter-scale calc-silicate lens, located about 1 km west of Crooks' Inlet, on the south coast of Baffin Island, Nunavut (UTM 391490, 6998420), in Arctic Canada. The lens is contained within a white, grey-weathering marble unit that forms a layer up to 200 meters thick in

<sup>§</sup> *Current address:* Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, New Mexico 87131, U.S.A. *E-mail address:* herdc@unm.edu

the Paleoproterozoic Lake Harbour Group (Jackson & Taylor 1972). The current state of knowledge of the regional geology is summarized by Scott *et al.* (1997) and St-Onge *et al.* (2000).

Deer *et al.* (1978) listed the range of possible colors of diopside as white, pale green, or dark green, and stated that more iron-rich members are more deeply colored. Clinopyroxene of a violet hue seems to be relatively rare. Titanogite exhibits violet pleochroism (*e.g.*, Manning & Nickel 1969), and may be purplish brown or black in hand specimen (Deer *et al.* 1978). A variety of clinopyroxene informally known as "violan" or "violane", most recently described by Mottana *et al.* (1979), has a deep violet color, and in essence consists of Mn-rich omphacite or an intergrowth of omphacite and disordered *C2/c* impure diopside. A spectral study of synthetic and natural Mn-substituted diopside was done by Hålenius & Skogby (1996).

Optical absorption spectroscopy is now commonly recognized as an efficient means of determining the local symmetry of the anionic environment around the cation (Burns 1993), and the distribution and valence states of the more abundant transition metals in virtually any crystal structure. This approach also provides a physical means of quantifying color in a wide variety of minerals.

In the present study, we determine the composition of the Baffin Island diopside in terms of major and minor elements, characterize the effect of the minor elements on crystal structure, and determine whether the observed color can be explained by incorporation of these minor elements.

## OBSERVATIONS AND EXPERIMENTAL METHODS

### *Mineral assemblages*

The mineral assemblage in the host marble is typically calcite  $\pm$  diopside (green)  $\pm$  forsterite  $\pm$  spinel  $\pm$  graphite. The assemblage in the calc-silicate lens consists of mainly violet diopside and cream-colored marialite, with subordinate brown pargasite and yellow-brown phlogopite. Also present are minor calcite, blue apatite in idiomorphic prismatic crystals, fine-grained titanite, talc, chlorite and plagioclase. Quartz is intergrown with or included within the major minerals.

### *Physical and optical properties of the diopside*

Diopside typically comprises over 50% of the calc-silicate assemblage in the lens. Grains are 0.5 to 2 mm across, and equant, although some coarser poikiloblasts were observed in thin section.

Fresh grains of diopside are violet to pale brown, homogeneous, and have a vitreous luster. The violet color is retained upon crushing, and the powder is light violet to pink. In thin section, the mineral is colorless and nonpleochroic in plane-polarized transmitted light.

Basal parting is evident, but the typical set of cleavages is not obvious.

Turbid areas in some grains appear to be due to the presence of mineral inclusions, alteration minerals, and fluid inclusions, as seen in thin section. Relict amphibole is present in the core of some grains. Alteration products, including talc, chlorite, and possibly amphibole or a phyllosilicate after amphibole, are present throughout the thin section, and the latter is prominent along planes of fluid inclusions. Fluid inclusions are elongate parallel to [001], as observed by Philippot & Selverstone (1991), confined to planes, and have broken open since formation, such that they are now devoid of fluid. The fluid may therefore have been responsible for formation of alteration products along these planes during retrograde metamorphism.

The density could not be determined owing to the presence of inclusions and products of alteration. The calculated density, based on the electron-microprobe data and unit-cell volume determined from X-ray powder-diffraction data, is 3.30 g/cm<sup>3</sup>.

The mineral is biaxial positive, with a  $2V_z$  angle of 57.6(5)° at 589 nm, as determined using spindle-stage microscopy and the program EXCALIBR (Bloss *et al.* 1981). Values of  $2V$  were calculated from extinction data at 470 nm [56.5(8)°], 546 nm [55.6(5)°], 589 nm [57.6(5)°], and 650 nm [59(1)°].

Indices of refraction (Table 1) were determined by the Becke line method using immersion oils and orientation by spindle-stage techniques.

### *X-ray diffraction*

Cell parameters were determined on powder in a capillary tube 0.5 mm in diameter with germanium-monochromatized CuK $\alpha_1$  X-radiation, using a Stoe diffractometer operated at 45 kV and 32 mA, with a silicon internal standard. A full-range (6° < 2 $\theta$  < 90°) pattern was obtained at a step rate of 0.02° every 15 seconds. The *d*-values of 38 peak positions, indexed using Rietveld analysis, were used to refine the cell parameters with the aid of the CELSIZ least-squares program (Hay 1995). Cell parameters are shown in Table 1, with results from Clark *et al.* (1969) for comparison.

TABLE 1. INDICES OF REFRACTION AND UNIT-CELL PARAMETERS OF VIOLET DIOPSIDE FROM BAFFIN ISLAND

Sample	Baffin Diopside	Clark <i>et al.</i> , 1969
$n_x$	1.670(1)	--
$n_y$	1.675(1)	--
$n_z$	1.695(1)	--
$2V_z$ (°)	57.6 (5)	--
$D_{calc}$ (g/cm <sup>3</sup> )	3.30	3.28
a (Å)	9.730 (4)	9.746 (4)
b (Å)	8.873 (3)	8.899 (5)
c (Å)	5.275 (2)	5.251 (6)
$\beta$ (°)	105.95 (3)	105.63 (6)
V (Å <sup>3</sup> )	437.9 (7)	438.6 (3)

Indices of refraction for 589 nm and 25°C. Unit-cell parameters from X-ray diffraction.

TABLE 2. ATOMIC POSITIONS AND DISPLACEMENT PARAMETERS OF VIOLET DIOPSIDE FROM BAFFIN ISLAND

	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
O1	0.1148(2)	0.0865(2)	0.1407(4)	0.0051(8)	0.0103(9)	0.0078(9)	0.0008(7)	0.0017(6)	-0.0009(7)
O2	0.3612(2)	0.2514(2)	0.3178(4)	0.0109(9)	0.0075(9)	0.0081(8)	-0.0003(7)	0.0025(7)	0.0004(7)
O3	0.3513(2)	0.0177(2)	0.9947(3)	0.0062(8)	0.0102(9)	0.0065(9)	-0.0006(7)	0.0012(7)	-0.0028(7)
Si	0.28650(7)	0.09339(8)	0.2284(1)	0.0037(3)	0.0056(4)	0.0044(3)	0.0001(2)	0.0010(3)	-0.0005(2)
M1	0	0.9080(1)	0.25	0.0043(5)	0.0052(6)	0.0036(5)	0	0.0007(4)	0
M2	0	0.3021(1)	0.25	0.0097(4)	0.0077(4)	0.0055(4)	0	0.0006(3)	0

### Structural refinement and chemical analysis

In order to obtain bond lengths for comparison with published values, diffracted X-ray intensities were measured from a roughly spherical crystal with an average diameter of 0.25 mm using an Enraf Nonius Delft four-circle diffractometer with graphite-monochromatized MoK $\alpha$  X-radiation, at 45 kV accelerating voltage and 26 mA current. Intensities of three reflections were monitored at one-hour intervals, and variations of less than 3% were observed. A total of 2259 reflections were collected, with index ranges  $0 \leq h \leq 13$ ,  $0 \leq k \leq 12$ , and  $-7 \leq l \leq 6$  (maximum  $2\theta = 60^\circ$ ); they are consistent with space group  $C2/c$ . The data were corrected for Lorentz, polarization, spherical absorption ( $\mu = 0.002 \text{ cm}^{-1}$ ) and background effects, and reduced ( $R_{\text{sym}} = 2.4\%$ ) to 629 unique structure-factors. Structure refinements were done using XTAL3.2 software (Hall *et al.* 1992). Atomic positions and displacement parameters are given in Table 2. Bond lengths and bond-valence sums calculated according to the approach of Brown (1981) are listed in Table 3, along with data from Clark *et al.* (1969) for comparison. A table of observed and calculated structure-factors is available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

TABLE 3. SELECTED INTERATOMIC DISTANCES, BOND VALENCE SUMS, AND TETRAHEDRON CHAIN ANGLE O3-O3-O3

Atomic Distance (Å)	Baffin Diopside	Clark <i>et al.</i> , 1969	Bond Valence Sum	Baffin Diopside	Clark <i>et al.</i> , 1969
Si-O (1)	1.608(2)	1.602(2)	Si	3.92	3.97
Si-O (2)	1.590(2)	1.585(1)	M(1)	2.16	2.10
Si-O (3)	1.672(2)	1.664(2)	M(2)	1.97	1.97
Si-O (3)	1.690(2)	1.687(2)			
Average Si-O	1.639	1.634	O(1)	2.08	2.08
			O(2)	1.83	1.83
M(1)-O(1)(2x)	2.057(2)	2.065(3)	O(3)	1.94	1.97
M(1)-O(1)(2x)	2.107(2)	2.115(1)			
M(1)-O(2)(2x)	2.035(2)	2.050(1)	Bond Angle ( $^\circ$ )		
Average M(1)-O	2.066	2.077	O3-O3-O3	166.4(1)	166.38(11)
M(2)-O(1)(2x)	2.365(2)	2.360(1)			
M(2)-O(2)(2x)	2.356(2)	2.353(3)			
M(2)-O(3)(2x)	2.548(2)	2.561(2)			
M(2)-O(3)(2x)	2.708(2)	2.717(1)			
Average M(2)-O	2.494	2.498			

Wavelength-dispersion (WDS) chemical analyses were done using a JEOL 733 Superprobe at the Department of Earth and Planetary Sciences, University of New Mexico, operated at 15 kV and a beam current of 20 nA. A diopside standard was used for Si, Cr, Mg, and Ca, an augite standard for Al, Ti, and Na, an olivine standard for Fe, and a spessartine standard for Mn. The average composition derived from the results of 24 analyses on five grains and the corresponding structural formula, normalized to six atoms of oxygen + OH, are given in Table 4. No zonation was observed in back-scattered electron imaging or core-to-rim WDS analyses. Manganese and Cr were sought but not found.

Determination of a structural formula was done following the criteria outlined by Papike (1987), by normalizing compositions to 12 negative charges. Sufficient aluminum was allotted to the tetrahedral site so that the sum is equal to 2 atoms per formula unit, *apfu*. The remainder of the aluminum, along with Mg, Fe<sup>2+</sup> and Ti, were assigned to the M1 site, and Ca and Na to the M2 site, on the basis of cation size. The structural formula is  $(\text{Ca}_{0.96}\text{Na}_{0.04})(\text{Mg}_{0.86}\text{Al}_{0.06}\text{Fe}^{2+}_{0.05}\text{Ti}^{4+}_{0.02})(\text{Si}_{1.89}\text{Al}_{0.11})(\text{O},\text{OH})_6$ , under the assumption that OH groups are present (see below).

TABLE 4. CHEMICAL COMPOSITION OF VIOLET DIOPSIDE FROM BAFFIN ISLAND

Wt. %	BAFFIN ISLAND			Clark <i>et al.</i> , 1969
	Baffin Diopside <sup>a</sup>	Atomic Proportions <sup>b</sup>	Baffin Diopside	
SiO <sub>2</sub>	52.33	Si	1.890	1.97
Al <sub>2</sub> O <sub>3</sub>	4.03	<sup>IV</sup> Al	0.106	nr <sup>d</sup>
		<sup>VI</sup> Al	0.065	0.01
TiO <sub>2</sub>	0.60	Ti	0.016	nr <sup>d</sup>
Cr <sub>2</sub> O <sub>3</sub>	bdl <sup>e</sup>	Cr	---	--
FeO	1.76	Fe	0.053	0.01
MnO	bdl <sup>e</sup>	Mn	---	--
MgO	15.96	Mg	0.861	1.01
CaO	24.63	Ca	0.960	0.99
Na <sub>2</sub> O	0.50	Na	0.035	0.02
H <sub>2</sub> O	0.30	OH	0.072	--
TOTAL	100.11	TOTAL <sup>c</sup>	3.986	4.01

<sup>a</sup>Average result of 24 electron-microprobe analyses on five grains

<sup>b</sup>Atoms per formula unit, based on 6 (O,OH)

<sup>c</sup>Below detection limit of 0.03 wt%

<sup>d</sup>Not reported.

<sup>e</sup>Cations only.

## Cathodoluminescence

Cathodoluminescence (CL) spectra were collected at the University of Massachusetts, using electron excitation from a Nuclide Luminoscope (R) ELM-2A, and recorded with a Gamma Scientific model 3000 AR scanning spectroradiometer and a more recent model NM-3 monochromator system, as described in Roeder *et al.* (1987). A yellow-orange (577 nm) CL with low CL efficiency was observed (Fig. 1).

## Thermal stability of the color

Several grains displaying prominent color were heated in a platinum crucible, in air, at 790°C for 3 hours. No change in the violet color was observed.

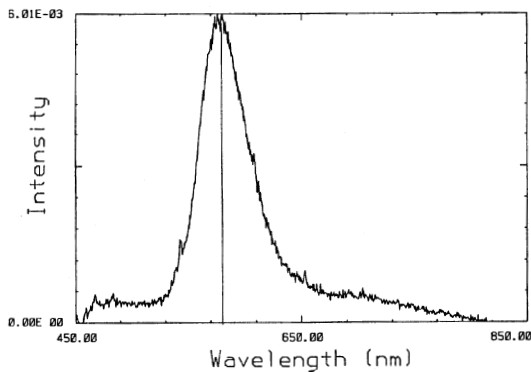


FIG. 1. Cathodoluminescence spectrum of Baffin Island diopside, with maximum intensity at about 577 nm, corresponding to a dull yellow-orange color (courtesy A.N. Mariano).

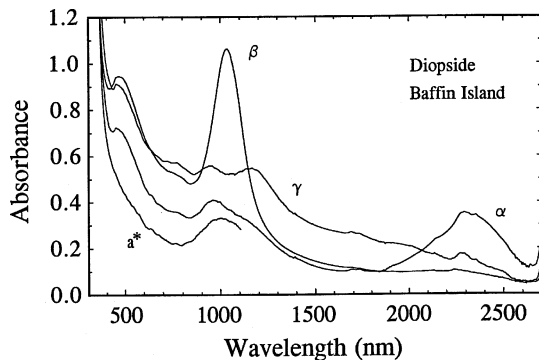


FIG. 2. Optical absorption spectra of diopside from Baffin Island. A partial spectrum in the  $a^*$  direction shows that the 480 nm band assigned to  $\text{Fe}^{2+}-\text{Ti}^{4+}$  intervalence charge-transfer does not occur in this direction. All spectra normalized to 1.0 mm thickness.

## Optical and infrared absorption spectroscopy

Polarized optical absorption spectra were recorded in the range 300 to 5000 nm. All work was performed on oriented crystals of 0.4 to 1.1 mm thickness, at 23°C. Optical spectra in the 300–1100 nm region were acquired with a home-built single-beam silicon diode array spectrometer operating at 1.2 nm resolution. Polarization was achieved with an air-spaced Glan–Thompson calcite polarizer placed in front of the sample. In the 1000–5000 nm region, a Nicolet 60SX Fourier-transform infrared (FTIR) spectrometer was used with a W source,  $\text{CaF}_2$  beam splitters, InSb detector, and a Glan–Foucault style  $\text{LiIO}_3$  polarizer. Spectra were acquired through clear regions in the sample, which varied from 400 to 600  $\mu\text{m}$  in diameter as defined by pinhole apertures placed next to the sample. The spectra are shown in Figures 2 and 3.

## DISCUSSION

## Structural analysis

Unit-cell dimensions reflect cation substitution in pyroxenes, as summarized by Cameron & Papike (1981). The diopside from Baffin Island is similar in an approximate sense to “end-member” diopside studied by Clark *et al.* (1969) (Tables 1, 4). Differences above the  $2\sigma$ -level exist in cell dimensions (Table 1) and some bond lengths (Table 3). These slight discrepancies can be explained by the greater extent of incorporation of Fe, Al and Ti relative to that in the diopside of Clark *et al.* (1969) (Table 4). For example, the incorporation of Ti and Al into the  $M1$  site reduces the average  $M1$  radius from the ideal value of 0.72 Å (that of Mg) to 0.71 Å (this is only slightly offset by the substitution of 0.05 *apfu*  $\text{Fe}^{2+}$  with  $r_{M1} = 0.78$  Å). A strong positive correlation between  $M1$  radius and the  $a$  and  $b$  cell dimensions

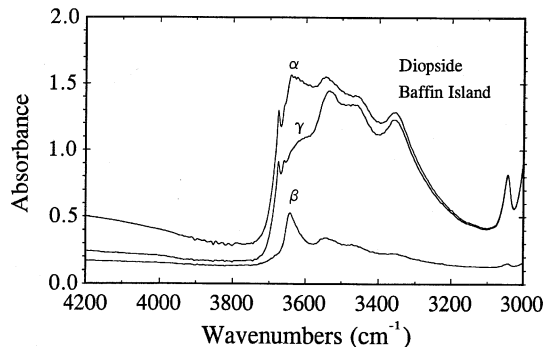


FIG. 3. Infrared spectra in the OH region of diopside from Baffin Island, showing that there is a significant amount of OH in this pyroxene. All spectra are normalized to 1.0 mm thickness.

in  $C2/c$  pyroxenes has been demonstrated by Ribbe & Prunier (1977). Therefore, the smaller  $a$  and  $b$  cell dimensions of the diopside in this study can be explained by the smaller average  $M1$  radius. A direct correlation between  $M1$  radius and the  $c$  cell dimension is not found, but  $\text{csin}\beta$  and  $M1$  radius are positively correlated (Ribbe & Prunier 1977). This correlation does not explain the slightly smaller  $c$  dimension of the Clark *et al.* (1969) diopside, which has a larger  $M1$  radius than the diopside in this study. Alternatively, Turnock *et al.* (1973) showed that the  $a$ ,  $b$  and  $c$  cell dimensions increase with increasing Fe content of the clinopyroxene. The 1.76 wt.% FeO in the Baffin Island diopside is apparently sufficient to increase the  $c$  cell dimension relative to that in end-member diopside. If Fe incorporation similarly increases the  $a$  and  $b$  cell dimensions, the increase is overwhelmed by the shortening due to the incorporation of Al and Ti at  $M1$ . The effect of Fe incorporation is apparently greater on the  $c$  dimension than it is on the  $a$  and  $b$  dimensions. It is difficult to determine whether bond lengths are similarly affected by incorporation of Al, Ti and Fe. Although the differences are small (on the order of 0.01 Å), the difference in average bond-length between Baffin Island diopside and the Clark *et al.* diopside (Table 3) is greatest for the  $M1$ -O bonds. This is apparently a reflection of the incorporation of 0.14 *apfu* of non-Mg cations into the  $M1$  site of the Baffin diopside. The Na contents of the two samples of diopside are similar (Table 4), which leads to a close match in average  $M2$ -O bond lengths (Table 3).

#### *Cause of color and absorption spectra*

Fifteen possible causes of color are listed in Nassau (1987). However, color most commonly involves trace amounts of transition elements or color centers (vacancies or charge imbalances in the structure). Heating has been shown to free electrons trapped in color centers and to reverse color caused by this feature (Nassau 1987). Since no change in color occurred during heating, we can conclude that color centers do not contribute in any significant way to the observed color. Cathodoluminescence and absorption spectroscopy have shed light on the distribution of trace elements in the Baffin Island diopside. Conclusions regarding the cause of the violet color can be made from absorption spectra.

Two emission bands in the CL spectrum of diopside have been attributed to  $\text{Mn}^{2+}$  activation (Walker 1985).  $\text{Mn}^{2+}$  activation at the eightfold  $M2$  sites gives rise to a yellow-orange CL with low luminescence-efficiency, whereas  $\text{Mn}^{2+}$  activation at the sixfold  $M1$  sites gives rise to red CL, with low efficiency. Since only the yellow-orange CL was observed (Fig. 1), we have concluded that a trace amount of  $\text{Mn}^{2+}$  is present at the  $M2$  site only. Manganese was not detected by electron-microprobe analysis, but the CL spectrum suggests that <0.03 wt.% Mn (the detection limit for this element with the electron microprobe used) is present at the  $M2$  site.

The optical spectrum of the violet diopside (Fig. 2) has dominant absorption bands near 1050 nm in  $\beta$  and 2300 nm in  $\alpha$  orientations. They arise from  $\text{Fe}^{2+}$  in the  $M2$  site and are comparable to those found in many clinopyroxenes (Rossman 1980). Bands near 940 and 1165 nm in the  $\gamma$  orientation correspond to absorption from  $\text{Fe}^{2+}$  in the  $M1$  site and are also routinely found in the spectra of clinopyroxenes. A weak band near 770 nm is comparable to the 770–790 nm  $\text{Fe}^{2+}$ - $\text{Fe}^{3+}$  intervalence charge-transfer band in clinopyroxenes such as augite and hedenbergite (Amthauer & Rossman 1984).

The color is strongly influenced by the broad absorption band at about 480 nm, which is present in the  $\alpha$ ,  $\beta$  and  $\gamma$  orientations. Figure 2 shows that this band is nearly absent when the polarization coincides with the  $a^*$ -direction (where the E-vector is perpendicular to both the  $b$  and  $c$  axes). This finding agrees with the observation that when the sample is viewed down the  $c$  axis, the sample is most colored in the  $b$  direction and nearly colorless when viewed perpendicular to  $c$ .

In some cases, pink to red color is associated with manganese, which is present in the Baffin Island diopside. The possibility that the 480 nm band is due to  $\text{Mn}^{3+}$  is ruled out by comparing the spectral data with the spectra of synthetic diopside doped with  $\text{Mn}^{3+}$  (Hålenius & Skogby 1996). The  $\text{Mn}^{3+}$  bands occur at distinctly longer wavelengths than 480 nm.  $\text{Mn}^{2+}$  bands are intrinsically weak and would not be expected to be observable under these conditions. Comparison of the Baffin Island diopside spectrum to that of chromian diopside (Taran *et al.* 1994) similarly shows that  $\text{Cr}^{3+}$  is not a factor in this case.

An absorption band with similar wavelength and polarization properties was observed in the spectrum of aluminous clinopyroxene from the Angra dos Reis (ADOR) meteorite (Mao *et al.* 1977). In the spectrum of this pyroxene, absorption is centered at 480 nm and is nearly absent in the  $a^*$  direction. Dowty (1978) showed that this dependence on orientation indicates intervalence charge-transfer (IVCT) between cations at the  $M1$  sites. In agreement with the spectra of the ADOR pyroxene, we propose that the interaction between  $\text{Fe}^{2+}$  and  $\text{Ti}^{4+}$ , both at the  $M1$  site, leads to the coloring of the Baffin Island diopside. The high absorbance of the IVCT band at 480 nm relative to the bands corresponding to ferrous iron in clinopyroxene (at 940, 1050, and 1165 nm) allows for the unusual coloring to be observed. This effect can be attributed to the relatively high Ti and low  $\text{Fe}^{2+}$  contents of the diopside (0.016 and 0.053 *apfu*, respectively; Table 4).

#### *Infrared absorption spectra*

Absorption bands near 3645 (prominent in  $\beta$ ), 3535 ( $\alpha, \gamma$ ), 3465 ( $\alpha, \gamma$ ) and 3350  $\text{cm}^{-1}$  ( $\alpha, \gamma$ ) shown in Figure 3 are from  $\text{OH}^-$  groups in the pyroxene and have previously been observed in diopside (Skogby *et al.* 1990).

Their intensity, calculated by the method of Skogby *et al.* (1990), corresponds to 0.30 wt.% as H<sub>2</sub>O. This value is high compared to most of the natural samples of pyroxene examined by Skogby *et al.* (1990). Atomic proportions based on 12 negative charges, assuming that all OH is structurally bound within the diopside, are shown in Table 2. With OH, the formula becomes (Ca<sub>0.96</sub>Na<sub>0.04</sub>) $\Sigma$ <sub>1.00</sub>(Mg<sub>0.86</sub>Al<sub>0.06</sub>Fe<sup>2+</sup><sub>0.05</sub>Ti<sup>4+</sup><sub>0.02</sub>) $\Sigma$ <sub>0.99</sub>(Si<sub>1.89</sub>Al<sub>0.11</sub>) $\Sigma$ <sub>2</sub>O<sub>5.93</sub>OH<sub>0.07</sub>. The sharp absorption bands near 3675 and 3660 cm<sup>-1</sup> in the  $\alpha$  and  $\gamma$  spectra, both obtained from the same (010) slab, indicate some alteration of the pyroxene, possibly to an amphibole or other hydrous phase.

#### *Implications for the conditions of formation of the diopside*

Relict amphibole in the cores of some diopside grains testifies to the prograde transition into the granulite facies of metamorphism. The association with apparently relict amphibole and the hydrous nature of the diopside indicate that the calc-silicate lens (and, by inference, the host marble) reached peak pressures and temperatures above the transition to granulite facies of metamorphism. The reaction pargasite + 7 quartz + 3 meionite = albite + 10 anorthite + 4 diopside + 3 CO<sub>2</sub> + H<sub>2</sub>O occurs at a maximum of 600°C at  $X(\text{CO}_2) = 0.8$  and a pressure of 10 kbar (calculated using TWEEQU; Berman & Brown 1992). However, a reduction in the activity of meionite (end-member) will raise the maximum temperature of this reaction. The composition of scapolite associated with diopside was estimated using birefringence, and determined to be approximately 70 ( $\pm 10\%$ ) marialite. Assuming ideality, then, and a meionite activity of 0.3, the maximum temperature of the above reaction is 850°C (calculated using TWEEQU; Berman & Brown 1992). This value represents the approximate upper temperature limit of the granulite-facies transition for the calc-silicate assemblage, with an estimated uncertainty of at least  $\pm 100^\circ\text{C}$ .

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#### REFERENCES

- AMTHAUER, G. & ROSSMAN, G.R. (1984): Mixed valence of iron in minerals with cation clusters. *Phys. Chem. Minerals* **11**, 37-51.
- BERMAN, R.G. & BROWN, T.H. (1992): Thermobarometry with estimation of equilibration state [TWEEQU]; a software package for IBM or compatible personal computers. *Geol. Surv. Can., Open File Rep.* **2534**.
- BLOSS, F.D., RIESS, R.D. & ROHRER, M.W. (1981): *The Spindle Stage: Principles and Practice*. Cambridge University Press, Cambridge, U.K.
- BROWN, I.D. (1981): The bond valence method: an empirical approach to chemical structure and bonding. In *Structure and Bonding in Crystals II* (M. O'Keeffe & A. Navrotsky, eds.). Academic Press, New York, N.Y. (1-30).
- BURNS, R.G. (1993): *Mineralogical Applications of Crystal Field Theory* (second ed.). Cambridge University Press, Cambridge, U.K.
- CAMERON, M. & PAPIKE, J.J. (1981): Structural and chemical variations in pyroxenes. *Am. Mineral.* **66**, 1-50.
- CLARK, J.R., APPLEMAN, D.E. & PAPIKE, J.J. (1969): Crystal-chemical characterization of clinopyroxenes based on eight new structure refinements. In *Pyroxenes and Amphiboles: Crystal Chemistry and Phase Petrology*. *Mineral. Soc. Am., Spec. Pap.* **2**, 31-50.
- DEER, W.A., HOWIE, R.A. & ZUSSMAN, J. (1978): *Rock-Forming Minerals*. **2A**. *Single-Chain Silicates*. John Wiley & Sons, New York, N.Y.
- DOWTY, E. (1978): Absorption optics of low-symmetry crystals – application to titanite clinopyroxene spectra. *Phys. Chem. Minerals* **3**, 173-181.
- HÄLENIUS, U. & SKOGBY, H. (1996): Crystal field spectra of trivalent manganese in synthetic and natural (Na<sup>+</sup>-Mn<sup>3+</sup>)-substituted diopside. *Eur. J. Mineral.* **8**, 1231-1240.
- HALL, S.R., FLACK, H.D. & STEWART, J.M., eds. (1992): *XTAL3.2 Reference Manual*. University of Western Australia, Perth, Australia.
- HAY, D. (1995): *CELSIZ Program*. CSIRO Division of Materials Science and Technology, Clayton, Australia.
- JACKSON, G.D. & TAYLOR, F.C. (1972): Correlation of major Aphebian rock units in the northeastern Canadian Shield. *Can. J. Earth Sci.* **9**, 1650-1669.

- MANNING, P.G. & NICKEL, E.H. (1969): A spectral study of the origin of color and pleochroism of a titanite from Kaiserstuhl and of a riebeckite from St. Peter's Dome, Colorado. *Can. Mineral.* **10**, 71-83.
- MAO, H.K., BELL, P.M. & VIRGO, D. (1977): Crystal-field spectra of fassaite from the Angra dos Reis meteorite. *Earth Planet. Sci. Lett.* **35**, 352-356.
- MOTTANA, A., ROSSI, G., KRACHER, A. & KURAT, G. (1979): Violan revisited: Mn-bearing omphacite and diopside. *Tschermaks Mineral. Petrogr. Mitt.* **26**, 187-201.
- NASSAU, K. (1987): The fifteen causes of color: the physics and chemistry of color. *Color Research and Application* **12**, 4-26.
- PAPIKE, J.J. (1987): Chemistry of the rock-forming silicates: ortho, ring, and single-chain structures. *Rev. Geophys.* **25**, 1483-1526.
- PHILIPPOT, P. & SELVERSTONE, J. (1991): Trace-element-rich brines in eclogitic veins; implications for fluid composition and transport during subduction. *Contrib. Mineral. Petrol.* **106**, 417-430.
- RIBBE, P.H. & PRUNIER, A.R., JR. (1977): Stereochemical systematics of ordered C2/c silicate pyroxenes. *Am. Mineral.* **62**, 710-720.
- ROEDER, P.L., MACARTHUR, D., MA, XIN-PEI, PALMER, G.R. & MARIANO, A.N. (1987): Cathodoluminescence and microprobe study of rare-earth elements in apatite. *Am. Mineral.* **72**, 801- 811.
- ROSSMAN, G.R. (1980): Pyroxene spectroscopy. In *Pyroxenes* (C.T. Prewitt, ed.). *Rev. Mineral.* **7**, 93-115.
- SCOTT, D.J., ST-ONGE, M.R., WODICKA, N. & HANMER, S. (1997): Geology of the Markham Bay – Crooks Inlet area, southern Baffin Island, Northwest Territories. *Geol. Surv. Can., Current Res.* **1997C**, 157-166.
- SKOGBY, H., BELL, D.R. & ROSSMAN, G.R. (1990): Hydroxide in pyroxene: variations in the natural environment. *Am. Mineral.* **75**, 764-774.
- ST-ONGE, M.R., WODICKA, N. & LUCAS, S.B. (2000): Granulite- and amphibolite-facies metamorphism in a convergent-plate-margin setting: synthesis of the Quebec–Baffin segment of the Trans-Hudson orogen. *Can. Mineral.* **38**, 379-398.
- TARAN, M.N., LANGER, K., PLATONOV, A.N. & INDUTNY, V.V. (1994): Optical absorption investigation of Cr<sup>3+</sup> ion-bearing minerals in the temperature range 77–797 K. *Phys. Chem. Minerals* **21**, 360-372.
- TURNOCK, A.C., LINDSLEY, D.H. & GROVER, J.E. (1973): Synthesis and unit cell parameters of Ca–Mg–Fe pyroxenes. *Am. Mineral.* **58**, 50-59.
- WALKER, G. (1985): Mineralogical applications of luminescence techniques. In *Chemical Bonding and Spectroscopy in Mineral Chemistry* (F.J. Berry & D.L. Vaughan, eds.). Chapman & Hall, London, U.K. (103-140).

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