

Compositions and unit-cell parameters of synthetic non-stoichiometric tschermakitic clinopyroxenes

BERNARD J. WOOD AND C. M. B. HENDERSON

Department of Geology, University of Manchester
Manchester, M13 9PL, England

Abstract

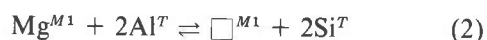
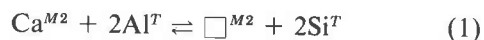
Clinopyroxenes with substantial numbers of *M1* and *M2* vacancies have been synthesized at 1300–1450°C and 25.0–32.3 kbar from compositions on the joins $\text{CaAl}_2\text{SiO}_6\text{--SiO}_2$ and $[(\text{CaAl}_2\text{SiO}_6)_{0.7}(\text{CaMgSi}_2\text{O}_6)_{0.3}]\text{--SiO}_2$. The non-stoichiometry, which is a stable phenomenon, is of much greater extent in clinopyroxenes on the latter join. In a composition which yielded clinopyroxene and quartz the pyroxene has the formula $\text{Ca}_{0.95}^{M2}(\text{Mg}_{0.28}\text{Al}_{0.68})^{M1}(\text{Al}_{0.49}\text{Si}_{1.51})^T\text{O}_6$ with a small predominance of *M2* over *M1* vacancies. If anorthite and quartz coexist with the pyroxene the vacancies are exclusively in *M2*.

Powder diffraction patterns of the product clinopyroxenes were indexed in the space group *C2/c*. A stoichiometric clinopyroxene with an atomic $\text{Al}/(\text{Al}+\text{Mg})$ ratio of 0.81 gave the cell parameters: $a = 9.635$ (1), $b = 8.722$ (2), $c = 5.2815$ (4) Å, $\beta = 106.18$ (1)°, $V = 426.26$ (6) Å³. A clinopyroxene of the same $\text{Al}/(\text{Al}+\text{Mg})$ ratio but with substantial *M1* and *M2* vacancies (formula above) has a considerably smaller cell volume: $a = 9.588$ (2), $b = 8.720$ (2), $c = 5.2638$ (6) Å, $\beta = 106.45$ (2)°, $V = 422.10$ (8) Å³.

The degree of non-stoichiometry increases with increasing pressure due to two factors. Firstly, the non-stoichiometric pyroxenes have relatively small cell volumes and, secondly, increasing pressure favors increasing Al_2O_3 solubility in the pyroxene and aluminous clinopyroxene can more readily accept *M1* and *M2* vacancies than alumina-free pyroxenes.

Introduction

Several experimental studies have shown that clinopyroxenes may deviate to some extent from the expected stoichiometry (*M1*) (*M2*) $T_2\text{O}_6$ at high temperatures. In the system CaO--MgO--SiO_2 , diopsidic clinopyroxenes exhibit small amounts of solid solution towards either SiO_2 or Mg_2SiO_4 , depending on bulk composition (Kushiro, 1972; Howells and O'Hara, 1975; Mori and Green, 1976). Preliminary work on aluminous systems (Kushiro, 1969; Wood, 1976) indicated that the presence of large amounts of $\text{CaAl}_2\text{SiO}_6$ component greatly facilitates the solution of excess SiO_2 in clinopyroxene. The solution mechanism presumably involves coupled substitutions which produce vacancies in the *M2* and *M1* crystallographic sites rather than the entry of Si into octahedral coordination, e.g.:



Mao (1971) showed that jadeitic pyroxenes synthesized at high pressure in the system $\text{NaAlSi}_2\text{O}_6\text{--CaAl}_2\text{Si}_2\text{O}_8$ could contain up to 7 weight percent excess SiO_2 .

Some naturally-occurring clinopyroxenes also exhibit significant amounts of non-stoichiometry. Cawthorn and Collerson (1974) found that the cation sums of natural clinopyroxenes decrease progressively from 4.0 (calculated to 6 oxygens) as the Al^{VI} contents of the pyroxenes increase. Sobolev *et al.* (1968) found marked deficiencies in the cation sums of highly aluminous (omphacitic) clinopyroxenes from grosspydite xenoliths. Smyth (1977) has recently reported the presence of more than 17 percent $\text{Ca}_{0.5}\text{AlSi}_2\text{O}_6$ component in clinopyroxenes from grosspydite inclusions in kimberlite pipes.

We have carried out experiments at high pressures on compositions in the $\text{CaO--Al}_2\text{O}_3\text{--SiO}_2$ and $\text{CaO--MgO--Al}_2\text{O}_3\text{--SiO}_2$ systems in order to establish the maximum extent of non-stoichiometry in aluminous clinopyroxenes and to determine the effects of this non-stoichiometry on unit-cell dimensions.

Experimental methods

Experiments were performed at high pressures and temperatures in an 0.5 inch diameter piston-cylinder apparatus. The pressure cell consisted of pyrex and talc sleeves outside the graphite heater with inserts of AlSiMag G222 (trade name of 3M Company, Ltd.) and a Pt capsule of approximate dimensions 0.20" × 0.20" inside the heater. The experiments were brought to pressure and temperature using the piston-out procedure (Johannes *et al.*, 1971), and the temperature was controlled with a Pt/Pt87Rh13 thermocouple situated on top of the capsule.

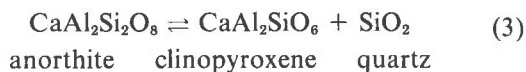
Starting compositions on the join [(CaAl₂SiO₆)_{0.7}(CaMgSi₂O₆)_{0.3}]-SiO₂ were glasses made from mixtures of MgO, γ-Al₂O₃, SiO₂ (glass), and CaCO₃. Glasses on the join CaAl₂SiO₆-SiO₂, which were prepared in a similar manner, contained small amounts of corundum. In one case the starting material consisted of crystalline phases which had been synthesized from glasses of appropriate compositions.

Product clinopyroxenes were analyzed with an AEI Electron Microscope Microanalyser (EMMA IV) using the correction procedures described by Cliff and Lorimer (1975). The EMMA IV is fitted with a Kevex energy-dispersive analysis system which enables quantitative determination of the ratios of elements present in the specimen. For the high Al₂O₃ pyroxenes produced in this study synthetic anorthite and Dobruva dravite (USNM 103791) were used as standards.

Cell parameters were determined by X-ray powder diffraction methods using a Philips PW 1050 diffractometer. Cu radiation was used (CuKα = 1.54178; CuKα₁ = 1.54051Å), Si was added as internal standard (a = 5.43065Å) and samples were scanned at 0.25° 2θ/min. Reflections were indexed assuming a C2/c space group (Hays, 1966; Okamura *et al.*, 1974) and cell parameters were calculated by least-squares methods. Reflections used included $\bar{2}21$, 310, $\bar{3}11$, 002, $\bar{1}31$, 221, 311, 112, 022, 330, $\bar{3}\bar{3}1$, $\bar{4}21$, $\bar{1}\bar{3}2$, 510, 150, $\bar{3}13$, $\bar{2}23$, $\bar{1}33$.

Results

The breakdown reaction of anorthite at high pressure:



is situated at 1430°C at approximately 34 kbar. However, this reaction is metastable with respect to melting reactions in the system CaO-Al₂O₃-SiO₂ at these

Table 1. Experiments in the systems CaO-Al₂O₃-SiO₂ and CaO-MgO-Al₂O₃-SiO₂

Sample	P kbar	T °C	Time (Hrs)	Starting Composition*	Products**
CaTs 1	27.0	1450	2.5	S ₀ Glass + Cor	Cpx, Gt, Cor
CaTs 2	25.0	1420	4.0	S ₂ Glass + Cor	Cpx, Gt
CaTs 3/2	30.0	1420	2.7	S ₅ Glass + Cor	Cpx, Gt, An
CD 1	31.5	1340	2.0	S ₀ Glass	Cpx, Gt, (Cor?)
CD 2	31.5	1340	2.0	S ₄ Glass	Cpx, Gt
CD 3/2	32.3	1340	1.3	S ₁₁ Glass	Cpx, Gt, Qz
C 28	25.0	1300	1.5	D ₂₅ ^A ₆₀ Q ₁₅ Glass ^a	Cpx, An, Qz
C 196	25.0	1300	2.5	Cpx, An, Qz ^b	Cpx, An, Qz

* S_x refers to x wt % SiO₂ in excess of that required for stoichiometric pyroxene.

** Cpx = clinopyroxene, Gt = garnet, Cor = corundum, An = anorthite, Qz = quartz.

^a D₂₅^A₆₀Q₁₅ refers to percentages of (D)diopside, (A)northite and (Q)quartz in the glass.

^b The starting mix was crystalline and contained stoichiometric clinopyroxene of composition (CaAl₂SiO₆)_{0.68}(CaMgSi₂O₆)_{0.32}.

pressures and temperatures (Wood, unpublished data). Therefore it is not possible to determine the maximum solid solution of CaAl₂SiO₆-SiO₂ pyroxenes towards SiO₂ under conditions of quartz saturation. High values of aSiO₂ can, however, be obtained in this system by producing the assemblage pyroxene-anorthite under pressures as close as possible to reaction (3). Accordingly, experiments were made in the pressure and temperature ranges 25–32 kbar and 1420–1450°C respectively (Table 1). These experiments yielded clinopyroxenes together with small amounts of grossular and/or anorthite and/or corundum. In only one case (CaTs 1) were crystals large enough to analyze with the microprobe, other analyses being made with EMMA IV. A comparison of microprobe and EMMA analysis of clinopyroxene crystallized from CaAl₂SiO₆ composition (Table 2) demonstrates an extremely close agreement between the two analytical methods.

The compositions of the synthetic clinopyroxenes were compared with stoichiometric CaAl₂SiO₆ using the Student t-test. Although crystallized from a glass of CaAl₂SiO₆ composition, pyroxene CaTs 1 has significant (99% confidence level) deficiency of Al₂O₃ and excess of CaO relative to the end member. The excess of CaO is of the same order as that found in previous syntheses of (nominally) CaAl₂SiO₆ pyroxene (Table 2; Hays, 1966; Okamura *et al.*, 1974) and it implies the possibility of Ca occupancy of the M1 site. Pyroxene CaTs 2 does not deviate significantly from CaAl₂SiO₆ composition, even though the glass

Table 2. Compositions and cell parameters of synthetic clinopyroxenes in the system CaO-Al₂O₃-SiO₂

	Analyses, weight %						
	1	2	3	CaTs 1 (a) 8 analyses	CaTs 1 (b) 12 analyses	CaTs 2 10 analyses	CaTs 3/2 10 analyses
SiO ₂	27.55	25.1		27.2(0.9)*	27.3(1.2)	27.5(1.5)	29.0(1.1)
Al ₂ O ₃	46.74	47.6		45.4(1.1)	45.6(1.1)	46.5(1.2)	45.4(0.9)
CaO	<u>25.71</u>	<u>26.3</u>		<u>26.9(1.0)</u>	<u>27.1(1.0)</u>	<u>26.0(1.2)</u>	<u>25.6(1.5)</u>
Total	100.00	99.0		99.5	-	-	-
Cation formulae calculated for 6(0)							
T (Si)	1.00	0.93	1.034	1.00	1.00	1.00	1.05
Al	1.00	1.07	0.966	1.00	1.00	1.00	0.95
M1 Al	1.00	1.00	0.968	0.96	0.96	0.99	0.99
M2 Ca	<u>1.00</u>	<u>1.04</u>	<u>1.030</u>	<u>1.06</u>	<u>1.06</u>	<u>1.01</u>	<u>0.99</u>
Total	4.00	4.04	3.998	4.02	4.02	4.00	3.98
Cell parameters							
a, Å		9.619(3)**	9.609(3)		9.619(2)	9.614(2)	9.608(2)
b, Å		8.659(3)	8.652(2)		8.667(2)	8.663(1)	8.665(2)
c, Å		5.278(2)	5.274(2)		5.2808(7)	5.2787(5)	5.2776(5)
β°		106.14(2)	106.06(2)		106.13(3)	106.14(2)	106.19(2)
V, Å ³		422.3(2)	421.35(21)		422.87(10)	422.33(7)	421.99(10)

1. Stoichiometric CaAl₂SiO₆; 2. Hays (1966); 3. Okamura et al. (1974), CaTs 1, 2 etc. refer to experiments shown in table 1. CaTs 1(a) is a microprobe analysis, all others were performed using EMMA IV. EMMA analyses are obtained by assuming the analysis total is 100.0.

* Values in brackets are one standard deviation.

** Values in brackets are standard errors of cell parameters : a, b x 10³; c x 10⁴; β, V x 10².

starting material contained 2 percent excess SiO₂. A further increase in the SiO₂ content of the starting material (CaTs 3/2) produced a small but significant (99% confidence level) increase in the SiO₂ content of the pyroxene, with corresponding decrease in Al₂O₃. The non-stoichiometry could not, however, be increased beyond the excess of SiO₂ of 1.5 weight percent observed in CaTs 3/2 (Fig. 1). This is equivalent to the presence of 0.05 atoms Si per formula unit in excess of the 1.00 atom of the stoichiometric composition (Table 2).

The maximum degree of non-stoichiometry towards SiO₂ should occur for clinopyroxenes coexisting with quartz. The assemblage clinopyroxene-quartz is not stable in the system CaO-Al₂O₃-SiO₂ (Wood, unpublished data), but it may be stabilized by the addition of MgO. We therefore proceeded by crystallizing starting compositions on the join [(Ca Al₂SiO₆)_{0.7}(CaMgSi₂O₆)_{0.3}]-SiO₂.

Clinopyroxene CD 1 was crystallized from a glass of composition (CaAl₂SiO₆)_{0.7}(CaMgSi₂O₆)_{0.3} and

does not deviate significantly from a stoichiometric pyroxene of formula CaMg_{0.32}Al_{1.36}Si_{1.32}O₆. (The slight difference between starting and product compositions can probably be ascribed to the presence of small amounts of garnet and corundum amongst the products.) The non-stoichiometries of pyroxenes CD 2 and CD 3/2 are, however, significant at the 99.9 percent confidence level. Thus, samples CD 1, CD 2, and CD 3/2 define a linear compositional trend of increasing SiO₂ (Fig. 1), and demonstrate the large non-stoichiometry towards SiO₂ possible in high-pressure clinopyroxenes. CD 3/2 coexists with quartz and has nearly 6 weight percent excess SiO₂.

The cell formulae of these pyroxenes (Table 3) were calculated by assuming that the excess Si enters the tetrahedrally-coordinated (T) sites. Sufficient Al was added to Si to make the T group add up to 2.00 atoms. The remaining Al was assumed to be in the M1 sites together with Mg, while the M2 sites contain only Ca. As Si increases, total Al decreases but Al in M1 remains constant at 0.68 atoms. Mg and Ca also

decrease, leading to decreasing occupancy of *M1* and *M2* sites. The linear compositional trend for these pyroxenes (Fig. 1) has almost constant values for the atomic ratios $Mg/(Ca + Mg)$ and $Al/(Al + Mg)$ (Table 3). As $Mg/(Ca + Mg)$ is essentially constant, *M2* vacancies must predominate over *M1* vacancies.

Two experiments on anorthite-rich compositions C28 and C196 (Table 1), produced aluminous clinopyroxene and quartz together with anorthite. EMMA-IV analyses of the product clinopyroxenes (Table 4) demonstrate that they also deviate markedly from the expected pyroxene stoichiometry, but that all vacancies are in *M2* positions. These pyroxenes have lower $Al/(Al + Mg)$ ratios (Table 4) than those of the CD series of pyroxenes (Table 3), even though they were synthesized from more aluminous starting compositions; this is due to their synthesis at lower pressures (Table 1).

The unit-cell parameters of the clinopyroxenes are given in Tables 2, 3, and 4 and show significant variations depending on the degree of non-stoichiometry present. The almost stoichiometric Ca-tschermak's pyroxene (CaTs 2) has very similar cell parameters to those reported by Clark *et al.* (1962) and Hays (1966) (Table 2). The presence of excess

SiO_2 in CaTs 3/2 causes a small but significant decrease in *a* and *V*, but *b* and *c* show little change. Sample CaTs 1 has significantly larger cell parameters than CaTs 2, as might be expected for its relatively Ca-rich composition.

The cell parameters of CD 1 (Table 3) are almost identical to those of a synthetic pyroxene of nominal composition $(CaAl_2SiO_6)_{0.7}(CaMgSi_2O_6)_{0.3}$ (Newton *et al.*, 1977). As the amount of Si in excess of the stoichiometric amount increases, *a*, *c*, and *V* decrease, β increases, and *b* shows little significant change (Fig. 2). Similar deviations occur between the cell parameters of C28 and those of a stoichiometric pyroxene of the same $Al/(Al + Mg)$ ratio (Table 4). These trends are comparable to those for non-stoichiometric tschermakitic pyroxenes crystallized from compositions on the join $CaMgSi_2O_6$ - $CaAl_2Si_2O_8$ (Kushiro, 1969), except that the latter samples show substantial decreases in *b* as well as *a* and *V*. However, Mao (1971) extrapolated the cell parameters for synthetic jadeitic pyroxenes with excess SiO_2 to the $CaAl_2Si_2O_8$ composition, and found that the *b* parameter showed a much smaller reduction than *a*, *c*, and *V* relative to the parameters for Hays' (1966) $CaAl_2SiO_6$ pyroxene.

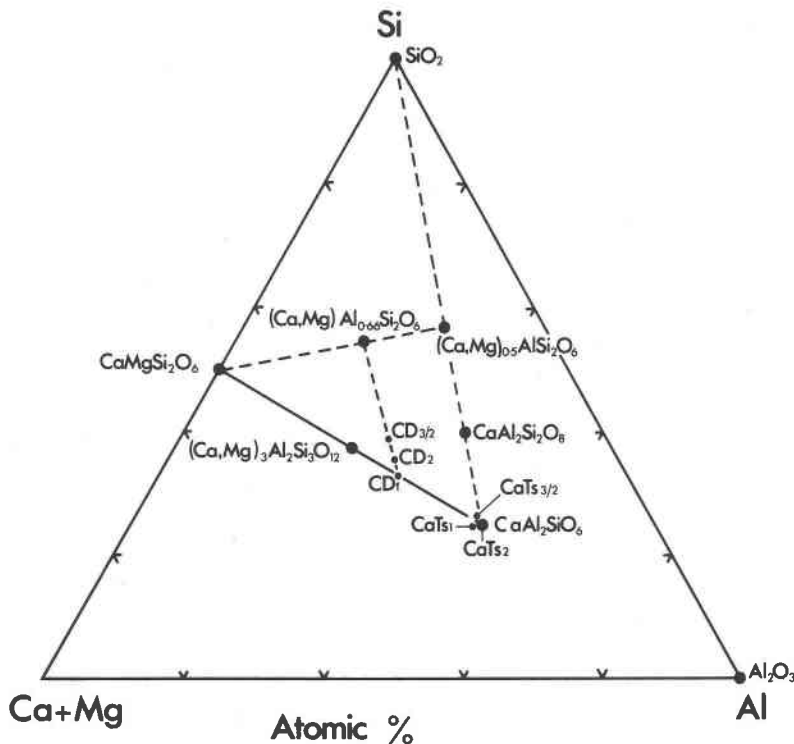


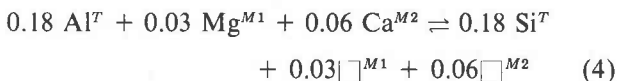
Fig. 1. Compositions of analyzed synthetic pyroxenes in the system Ca and/or Mg-Al-Si (atomic). Various pyroxene end-members and other compositions of interest are also shown.

Table 3. Compositions and cell parameters of synthetic clinopyroxenes crystallized from glasses on the join $[(\text{CaAl}_2\text{SiO}_6)_{0.7}(\text{CaMgSi}_2\text{O}_6)_{0.3}]\text{-SiO}_2$

	Analyses, weight %			
	1*	CD 1 12 analyses	CD 2 14 analyses	CD 3/2 15 analyses
SiO ₂	35.89	36.3(1.8)	39.3(1.7)	42.1(1.6)
Al ₂ O ₃	32.79	31.9(1.0)	29.9(0.9)	27.9(1.0)
MgO	5.56	5.8(0.5)	5.5(0.4)	5.2(0.4)
CaO	25.76	26.0(1.6)	25.3(1.4)	24.8(1.5)
Cation formulae calculated for 6(0)				
T	(Si 1.30 Al 0.70	1.32 0.68	1.41 0.59	1.51 0.49
M1	(Al 0.70 Mg 0.30	0.68 0.31	0.68 0.30	0.68 0.28
Sum M1	1.00	0.99	0.98	0.96
M2 Ca	1.00	1.01	0.97	0.95
Cation sum	4.00	4.00	3.95	3.91
Mg/(Ca+Mg)	0.231	0.235	0.236	0.228
Al/(Al+Mg)	0.824	0.814	0.809	0.807
Cell parameters				
a	9.6357(14)**	9.635(1)	9.609(1)	9.588(2)
b	8.7245(20)	8.722(2)	8.725(2)	8.720(2)
c	5.2816(18)	5.2815(4)	5.2729(5)	5.2638(6)
β	106.205(10)	106.18(1)	106.31(1)	106.45(2)
V	426.361(114)	426.26(6)	424.25(7)	422.10(8)
* Calculated composition of stoichiometric $(\text{CaAl}_2\text{SiO}_6)_{0.7}\text{-}(\text{CaMgSi}_2\text{O}_6)_{0.3}$.				
** Cell parameters from Newton et al. (1977) for clinopyroxene of nominally stoichiometric composition $(\text{CaAl}_2\text{SiO}_6)_{0.7}\text{-}(\text{CaMgSi}_2\text{O}_6)_{0.3}$.				

Discussion and conclusions

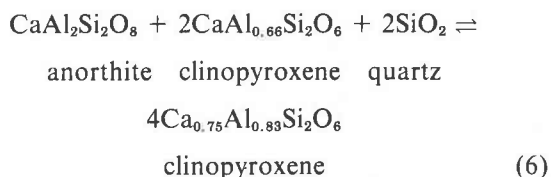
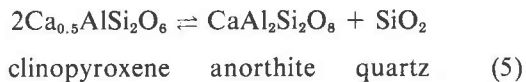
The cation formulae of the pyroxenes synthesized from compositions on the join $[(\text{CaAl}_2\text{SiO}_6)_{0.7}(\text{CaMgSi}_2\text{O}_6)_{0.3}]\text{-SiO}_2$ indicate that solution of excess SiO₂ leads to the introduction of vacancies in both M1 and M2 sites. Comparison of the formulae for pyroxenes CD 1 and CD 3/2 suggests a coupled substitution close to:



This substitution indicates that vacancies in M2 are approximately twice as abundant as those in M1. The linear compositional trend (Fig. 1) for the pyroxenes showing this substitution can be extrapolated to the pyroxene "molecule" $(\text{Ca,Mg})\text{Al}_{0.66}\text{Si}_2\text{O}_6$ (Fig. 1). As this linear trend retains an almost constant value for $\text{Mg}/(\text{Ca} + \text{Mg})$, the solid solution can be considered to be between the end members stoichiometric

$\text{Ca}^{M2}(\text{Mg}_{0.3}\text{Al}_{0.7})^{M1}(\text{Si}_{1.3}\text{Al}_{0.7})\text{O}_6$ and non-stoichiometric $\text{Ca}_{0.77}^{M2}(\text{Mg}_{0.23}\text{Al}_{0.66})^{M1}\text{Si}_2\text{O}_6$.

In clinopyroxenes saturated with anorthite (C28, C196, Table 4) the cation vacancies occur only in the M2 positions. The differences between these compositions and the CD series discussed above can be understood by considering the following equilibria:



Reactions (5) and (6) involve the hypothetical pyroxenes $\text{Ca}_{0.5}\text{AlSi}_2\text{O}_6$ (M2 vacancies only), $\text{CaAl}_{0.66}\text{Si}_2\text{O}_6$ (M1 vacancies only), and $\text{Ca}_{0.75}\text{Al}_{0.83}\text{Si}_2\text{O}_6$ (M2 and M1 vacancies). If anorthite is absent,

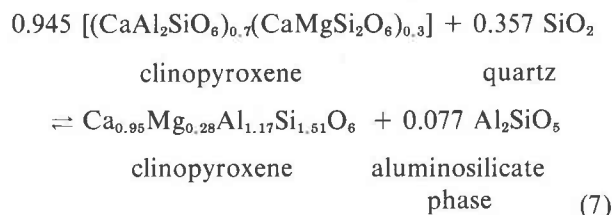
Table 4. Compositions and cell parameters of synthetic clinopyroxenes crystallized from glasses on the join

	Analyses, weight %		
	2*	C 28 21 analyses	C 196 15 analyses
SiO ₂	38.95	43.6 (1.8)	42.6 (2.4)
Al ₂ O ₃	27.67	26.3 (1.5)	27.4 (2.4)
MgO	7.60	7.2 (1.0)	6.8 (0.7)
CaO	25.78	22.9 (0.9)	23.3 (0.9)
Cation formulae calculated for 6 (0)			
T	(Si 1.41 Al 0.59	1.55 0.45	1.52 0.48
M1	(Al 0.59 Mg 0.41	0.65 0.38	0.66 0.36
Sum M1	1.00	1.03	1.02
M2 Ca	1.00	0.87	0.89
Cation sum	4.00	3.90	3.91
Mg/(Ca+Mg)	0.291	0.304	0.288
Al/(Al+Mg)	0.742	0.741	0.760
Cell parameters			
a	9.649**	9.616 (2)	
b	8.750	8.754 (2)	
c	5.281	5.2718 (8)	
β	106.25	106.42 (2)	
V	428.1	425.66 (10)	
* Calculated composition of stoichiometric clinopyroxene of formula $(\text{CaAl}_2\text{SiO}_6)_{0.59}(\text{CaMgSi}_2\text{O}_6)_{0.41}$.			
** Estimated from results of Newton et al. (1977).			

reaction (5) will tend to be displaced to the right, removing $M2$ vacancies, and reaction (6) to the left, creating $M1$ vacancies at the expense of $M2$ vacancies. As the activity of anorthite is increased towards saturation, (5) is displaced to the left (creating $M2$ vacancies) and (6) to the right, creating $M2$ vacancies at the expense of $M1$ vacancies. Pyroxenes C28 and C196 coexist with anorthite and have a much greater predominance of $M2$ over $M1$ vacancies than do CD1, 2, and 3/2.

Experiment C196 produced non-stoichiometric clinopyroxene from crystalline stoichiometric pyroxene (CD1), anorthite, and quartz. This demonstrates that the non-stoichiometry discussed here is a stable rather than a metastable phenomenon.

The introduction of excess SiO_2 and the creation of vacancies appear to be favored by increasing pressure. This is partly because, in anorthite-bearing assemblages, the $\text{CaAl}_2\text{SiO}_6$ content of the pyroxene and hence the possibility of creating vacancies increases with increasing pressure. In addition, if one considers a reaction to produce pyroxene CD3/2 from quartz and stoichiometric pyroxene:



it is found that, whichever aluminosilicate phase the excess Al_2SiO_5 enters (*e.g.* kyanite or garnet), the volume change will be negative. Hence increasing pressure stabilizes the non-stoichiometry.

Although we have indexed our samples in the space group $C2/c$ it should be pointed out that this requires complete Al-Si disorder on tetrahedral sites and hence contravenes the Al-avoidance principle. Newton *et al.* (1977) found that the excess enthalpies of mixing of clinopyroxenes on the join $\text{CaAl}_2\text{Si}_2\text{O}_6$ - $\text{CaMgSi}_2\text{O}_6$ are consistent with complete Al-Si disorder at low Al contents, but that there may be some Al-Si order at the $\text{CaAl}_2\text{SiO}_6$ end of the series. We are unable, however, with the powder diffraction methods we have used, to deduce whether or not there might be any Al-Si order in our samples. In support of our indexing, Okamura *et al.* (1974) found that (nominally) pure $\text{CaAl}_2\text{SiO}_6$ pyroxene also gave space group $C2/c$. Although pyroxenes with Al-Si order could still statistically yield the $C2/c$ space

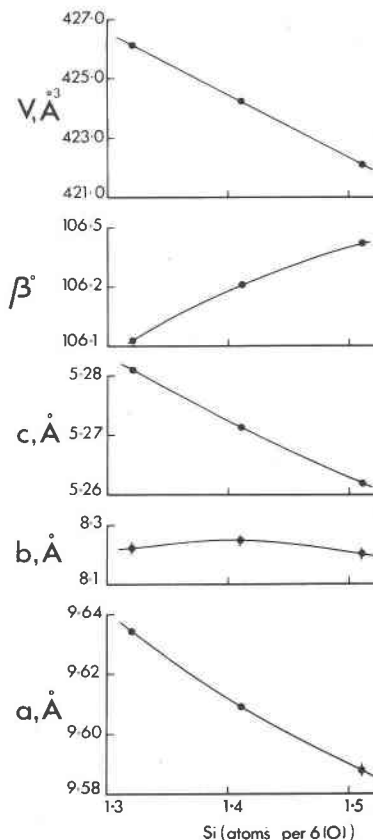


Fig. 2. Cell parameters *vs.* atoms of Si per 6(O) for pyroxenes crystallized from glasses on the join $[(\text{CaAl}_2\text{SiO}_6)_{0.7}(\text{CaMgSi}_2\text{O}_6)_{0.3}] - \text{SiO}_2$. Error bars are shown where these are larger than the symbol size.

group by X-ray diffraction (Okamura *et al.*, 1974), such ordering would not substantially affect our results.

Acknowledgements

We thank Professor J. Zussman for comments on this paper. The study was supported by the Natural Environment Research Council of Great Britain. Dr. P. E. Rosenberg kindly supplied a small specimen of the Dobruva dravite standard.

References

- Cawthorn, R. G. and K. D. Collerson (1974) The recalculation of pyroxene end-member parameters and the estimation of ferrous and ferric iron content from electron microprobe analyses. *Am. Mineral.*, 59, 1203-1208.
- Clark, S. P. Jr., J. F. Schairer and J. de Neufville (1962) Phase relations in the system $\text{CaMgSi}_2\text{O}_6$ - $\text{CaAl}_2\text{SiO}_6$ - SiO_2 at low and high pressure. *Carnegie Inst. Wash. Year Book*, 61, 59-68.
- Cliff, G. and G. W. Lorimer (1975) The quantitative analysis of thin specimens. *J. Microsc.*, 103, 203-207.
- Hays, J. F. (1966) Stability and properties of the synthetic pyroxene $\text{CaAl}_2\text{SiO}_6$. *Am. Mineral.*, 51, 1524-1529.

- Howells, S. and M. J. O'Hara (1975) Palaeogeotherms and the diopside-enstatite solvus. *Nature*, 254, 406-408.
- Johannes, W., P. M. Bell, H. K. Mao, A. L. Boettcher, D. W. Chipman, J. F. Hays, R. C. Newton and F. Seifert (1971) An interlaboratory comparison of piston-cylinder pressure calibration using the albite-breakdown reaction. *Contrib. Mineral. Petrol.*, 32, 24-38.
- Kushiro, I. (1969) Clinopyroxene solid solutions formed by reactions between diopside and plagioclase at high pressures. *Mineral. Soc. Am. Spec. Pap.* 2, 179-191.
- (1972) Determination of liquidus relations in synthetic silicate systems with electron probe analysis: the system forsterite-diopside-silica at 1 atmosphere. *Am. Mineral.*, 57, 1260-1271.
- Mao, H. K. (1971) The system jadeite ($\text{NaAlSi}_2\text{O}_6$)-anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) at high pressures. *Carnegie Inst. Wash. Year Book*, 69, 163-168.
- Mori, T. and D. H. Green (1976) Subsolvus equilibria between pyroxenes in the CaO-MgO-SiO_2 system at high pressures and temperatures. *Am. Mineral.*, 61, 616-625.
- Newton, R. C., T. V. Charlu and O. J. Kleppa (1977) Thermochemistry of high pressure garnets and clinopyroxenes in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$. *Geochim. Cosmochim. Acta*, 41, 369-377.
- Okamura, F. P., S. Ghose and H. Ohashi (1974) Structure and crystal chemistry of calcium Tschermak's pyroxene CaAlAlSiO_6 . *Am. Mineral.*, 59, 549-557.
- Sobolev N. V. Jr., I. K. Kuznetsova and N. I. Zyuzin (1968) The petrology of grosopydite xenoliths from the Zagodochnaya kimberlite pipe in Yakutia. *J. Petrol.*, 9, 253-280.
- Smyth, J. R. (1977) Peraluminous omphacite: cation vacancies in upper mantle pyroxenes (abstr). *Trans. Am. Geophys. Union*, 58, 523.
- Wood, B. J. (1976) Mixing properties of tschermakitic clinopyroxenes. *Am. Mineral.*, 61, 599-602.

Manuscript received, April 8, 1977; accepted for publication, August 1, 1977.