Low-Ca augite from experimental alkali basalt at 18 kbar: Structural variation near the miscibility gap

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ABSTRACT

The crystal chemical configuration of an experimental subcalcic augite sample crystallized from an alkali olivine basalt at 18 kbar and 1320 °C was studied by means of single-crystal X-ray diffractometry and electron microprobe analysis. The investigated sample shows an exceptionally low Ca content (0.487 atoms per formula unit, or apfu), the lowest ever recorded for a quadrilateral pyroxene of ascertained $C2/c$ space-group symmetry. Low Ca is associated with relatively high [4]Al (0.232 apfu) and [6]Al (0.207 apfu) and moderate Na (0.080 apfu) contents. Thus, the cation substitution mechanism appears to be quite different from that found in natural clinopyroxene phenocrysts from volcanic rocks, as well as in megacrysts from alkaline volcanics. The uncommon chemical composition requires peculiar structural arrangements that produce an exceptionally small and distorted M2 polyhedron and an uncommonly regular tetrahedron and that involve strong cell volume reduction.

The structural variations in $C2/c$ pyroxenes with decreasing Ca + Na content are described in detail and provide evidence of the role of structural constraints in determining the presence of the miscibility gap. High pressure and temperature conditions and rapid quenching appear to be crucial for the stability of such a distorted M2 site configuration as that shown by the studied sample. The relatively high [4]Al and, despite the high-pressure origin, moderate Na contents arise from specific structural stability requirements.

INTRODUCTION

A methodology that combines single-crystal X-ray structural refinement and electron microprobe analysis of the same crystal (Dal Negro et al., 1982) allowed detailed definition of intracrystalline constraints in clinopyroxenes from various magmatic environments. This approach to the crystal chemistry of clinopyroxene demonstrated that intracrystalline relationships can be used as sensitive genetic indicators (e.g., Dal Negro et al., 1989a). Hydrostatic pressure has been shown to be crucial for the crystal chemical response of clinopyroxene during magma crystallization (e.g., Dal Negro et al., 1989b), but so far its effects have been verified only qualitatively in natural samples. A first attempt to relate crystal chemistry precisely to physicochemical conditions was made by Manoli and Molin (1988), who refined the structure of a clinopyroxene from an experimental lunar basalt (Green et al., 1975) synthesized at 12 kbar and 1320 °C. The present work provides additional data on high-pressure clinopyroxene through a detailed study of the crystal chemical configuration of an experimental subcalcic augite sample crystallized from an alkali olivine basalt at 18 kbar and 1320 °C (Green and Ringwood, 1967). The extreme chemical and structural features of the studied pyroxene are also used to outline the intracrystalline variations in $C2/c$ pyroxene in a portion of the compositional field not previously investigated and to provide evidence of the role of structural constraints in determining the presence of the high-Ca and low-Ca pyroxene miscibility gap.

CRYSTAL SEPARATION AND ANALYTICAL METHODS

The crystal studied here is from the experimental mount 6-12 (expt. no. 132) from the pioneering work of Green and Ringwood (1967) on the genesis of basaltic magmas. The probe mount was prepared from a glass of alkali olivine basalt composition formed at 18 kbar and 1320 °C (60 min), some 5 °C below the liquidus temperature. Uncommonly large (2–300 μm), well-crystallized clinopyroxene is the only primary crystalline phase, occurring together with glass and rare quenched clinopyroxene (Green and Ringwood, 1967).

A small fragment (ca. 150 μm) of a clinopyroxene crystal was hand-picked under a microscope directly from the probe mount and checked for optical homogeneity. The selected fragment was tested for diffraction quality by scanning a few of its intense reflections. All reflections showed sharp peak profiles. X-ray diffraction data were obtained on a computer-controlled Siemens AED II four-circle diffractometer with MoKα radiation monochromatized with a flat graphite crystal. Equivalent pairs, hkl and $h\bar{k}l$, were measured to $\theta \leq 30°$ using the ω-scan mode. No reflections that violated space group $C2/c$ were observed. Intensities were corrected for absorption follow-

TABLE 1. Selected structural refinement data of the 6-12 clinopyroxene

Obs. refl.	539	M2-O2 (Å)	2.215(2)
R (%)	3.1	M2-O1	2.258(2)
		M2-O3C1	2.582(2)
a (Å)	9.689(1)	M2-O3C2	2.833(2)
b	8.824(2)	M2-O$_{mean}$	2.472(6)
c	5.280(1)	V_{M2} (Å³)	24.54(1)
β (°)	107.60(1)	Δ**	0.482
V (Å³)	430.26		
		T-O2 (Å)	1.602(2)
	B_{eq} (Å²)	T-O1	1.629(1)
M1	0.99	T-O$_{nbr}$	1.615
M2	1.89	T-O3A1	1.655(2)
T	1.10	T-O3A2	1.664(3)
O1	1.32	T-O$_{br}$	1.660
O2	1.74	V_T (Å³)	2.237(3)
O3	2.23	λ_{tet}^*	1.0051
		σ_{tet}^{2*}	21.45
M1-O2 (Å)	2.000(2)	kink (°)	166.7
M1-O1A2	2.031(2)		
M1-O1A1	2.127(2)		
M1-O$_{mean}$	2.053(4)		
V_{M1} (Å³)	11.42(1)		
λ_{oct}^*	1.0075		
σ_{oct}^{2*}	22.51		

Note: standard deviations are given in parentheses.
* Octahedral and tetrahedral angle variances (σ^2) and elongations (λ) from Robinson et al. (1971).
** The M2 distortion parameter from Dal Negro et al. (1982).

TABLE 4. Chemical data (wt%) and site partitioning (apfu) of the 6-12 clinopyroxene

		M1	
SiO₂	49.16(0.61)	Mg	0.693
Al₂O₃	10.35(0.68)	Fe²⁺	0.030
FeO	8.01(0.26)	Fe³⁺	0.034
MgO	17.60(0.41)	[6]Al	0.207
MnO	0.20(0.06)	Ti	0.034
TiO₂	1.26(0.16)	Cr	0.002
Cr₂O₃	0.06(0.04)	Total	1.000
CaO	12.63(0.30)	R^{3+}	0.277
Na₂O	1.14(0.07)		
Total	100.41		
		M2	
Si	1.768	Ca	0.487
[4]Al	0.232	Na	0.080
Total	2.000	Fe²⁺	0.177
		Mg	0.250
		Mn	0.006
		Total	1.000
		Ca + Na	0.567

Note: standard deviations are given in parentheses.

ing the semiempirical method of North et al. (1968), and the values of equivalent pairs were averaged. Structural refinement was carried out in space group $C2/c$ without chemical constraints using the Strucsy Package program (Stoe, Germany). Reflections with $I \geq 3\sigma_I$ were considered as observed and were given unit weight. All structural sites were considered as fully occupied. Atomic scattering curves were taken from the *International tables for X-ray crystallography* (Ibers and Hamilton, 1974) and Tokonami (1965); fully ionized atomic scattering curves were adopted for M2 (Ca²⁺ and Na⁺) and M1 (Mg²⁺ and Fe²⁺) sites, and partially ionized factors were adopted for Si (Si²·⁵⁺) and O (O¹·⁵⁻). In the first stages of the refinement, isotropic displacement parameters were used. Atomic coordinates, anisotropic displacement parameters, M1 and M2 site occupancies, scale factor, and the secondary extinction coefficient (Zachariasen, 1963) were allowed to vary until the shifts were less than the least-squares difference of the corresponding parameters. The final cycles were performed using anisotropic displacement parameters. After convergence, difference-Fourier synthesis showed significant residual electron density of about 0.6 Å from the M2 sites, corresponding to the M2′ site (e.g., Dal Negro et al., 1982). The M2′ site was assigned the Fe²⁺ atomic scattering curve, and its displacement parameter was fixed equal to the equivalent isotropic displacement parameter of M2. Further least-squares cycles were carried out varying alternatively the unconstrained M2′ occupancy and all the other parameters. When refinement reached convergence, the conventional discrepancy R factor was equal to 3.1%. Selected crystallographic parameters are given in Table 1. Atomic co-

ordinates and anisotropic displacement parameters are given in Table 2.[1] Calculated and observed structure factors are given in Table 3.[1]

The crystal fragment was subsequently mounted on a glass slide and polished for WDS microprobe analysis with a Cameca Camebax system, operating at 15 kV and 15 nA with a count time of 5 s for major and 10 s for minor elements. The Cameca-PAP program was used to convert elemental X-ray counts into weight-percent oxides. The crystal was analyzed at 11 spots. Analyses are conservatively believed to be precise to ca. ±1% (relative) for major and ca. ±5% (relative) for minor elements. Neither inclusions nor significant zoning was detected. The program of Papike et al. (1974) was used to convert weight-percent oxides into atoms per formula unit (apfu) and to estimate the Fe³⁺ content with the charge balance method. Site occupancies were calculated according to the method of Dal Negro et al. (1982), assigning Ca²⁺, Na⁺, and the small fraction of Mn²⁺ to M2, R^{3+} (= [6]Al³⁺ + Cr³⁺ + Ti⁴⁺ + Fe³⁺) to M1, and Si and [4]Al to T. Electron densities of M2 and M1 sites calculated from crystal chemical partitioning ($e_{M2+M1} = 31.84$) are in good agreement with those estimated on the basis of site occupancy refinement ($e_{M2+M2'+M1} = 31.64$). Average chemical analysis and crystal chemical partitioning are given in Table 4.

DISTINCTIVE CHEMICAL AND STRUCTURAL CHARACTERISTICS

The most striking characteristic of the studied sample is its exceptionally low Ca content (0.487 apfu); this value is the lowest ever reported for a quadrilateral pyroxene of ascertained $C2/c$ space-group symmetry. The low Ca is associated with relatively high [4]Al (0.232 apfu) and

[1] Tables 2 and 3 may be ordered as Document AM-94-558 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street, NW, Suite 330, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.
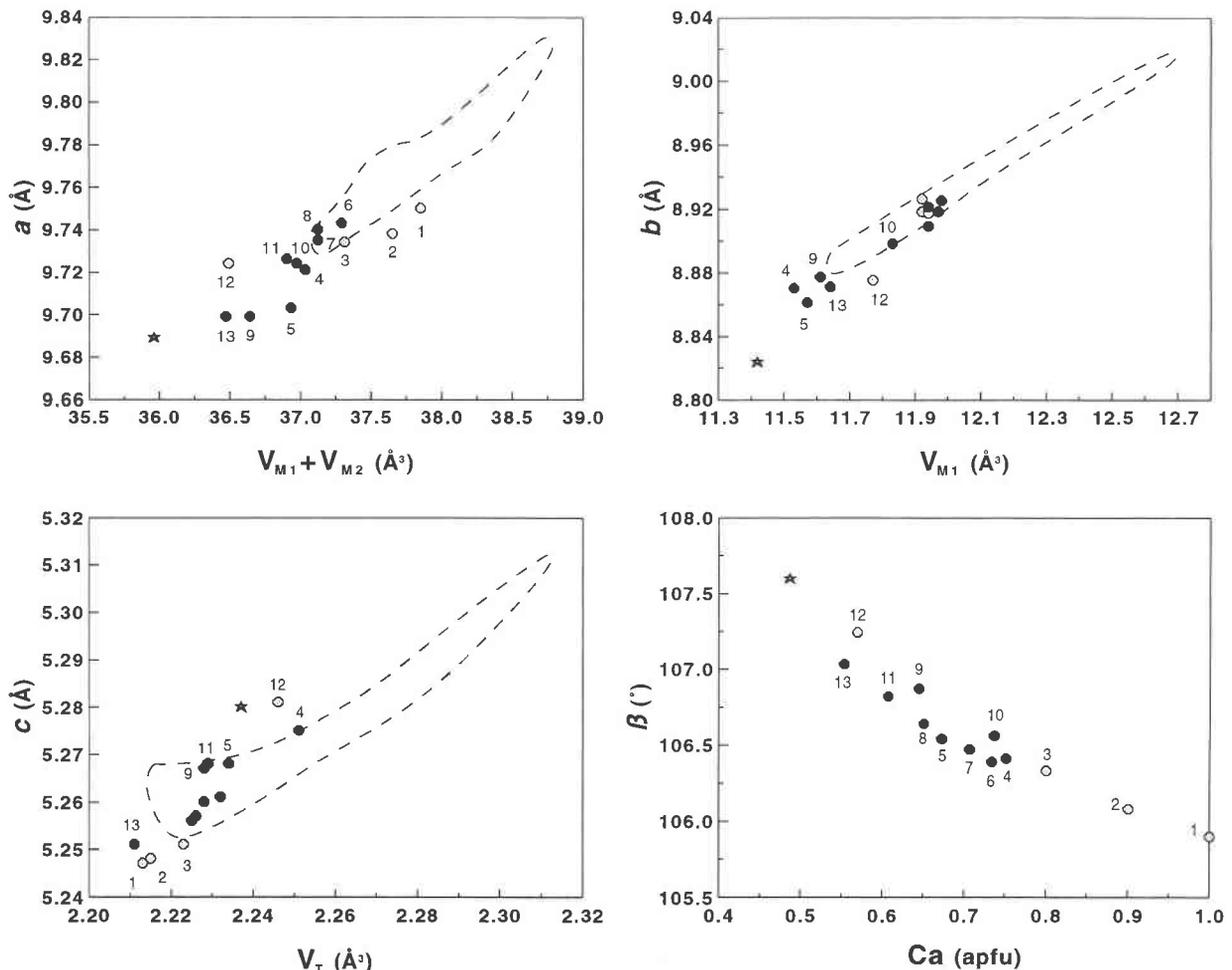
Fig. 1.   Cell parameters in low-Ca clinopyroxenes. Star = 6-12 clinopyroxene (this work); circles = natural (solid) and synthetic (shaded) clinopyroxenes with varying Ca content (Table 5). Volcanic clinopyroxene fields (dashed line), from Dal Negro et al. (1989b), are shown for comparison. The a and b edges are essentially controlled by the M1 and M2 sizes, and the c edge mainly depends on the tetrahedral volume. The close correlation between β and Ca content shows a slightly nonlinear character.

[6]Al (0.207 apfu) and moderate Na (0.080 apfu) contents. The cation substitution mechanism appears to be quite different from that found in natural clinopyroxenes from volcanic rocks, in which a strong positive correlation between Ca and [4]Al occurs (Dal Negro et al., 1982), as well as in megacrysts from alkaline volcanics, in which relatively low Ca and high [6]Al are coupled with high Na occupancies (Dal Negro et al., 1989b).

This uncommon chemical composition requires peculiar structural arrangements. The very low $(Ca + Na)_{M2}$ content produces an exceptionally small and distorted M2 polyhedron: $V_{M2} = 24.54$ Å^3 and $\Delta_{M2} = 0.482$ [Δ = M2-O3C2 − (M2-O3C1 + M2-O1 + M2-O2)/3 (Dal Negro et al., 1982)]. The high content of small-sized and highly charged R^{3+}_{M1} cations (Table 4), mainly [6]Al, is in turn responsible for the small volume of the M1 polyhedron ($V_{M1} = 11.42$ Å^3) and its large distortion (see λ_{oct} and σ^2_{oct} in Table 1). The tetrahedron remains relatively large ($V_T = 2.237$ Å^3) because of its high [4]Al content. Low M1 and M2 volumes require

strong cell-volume reduction. The very low value of the cell volume (430.3 Å^3) results from short a and b cell edges, mainly related to the size of the M1-M2 layers, and the uncommonly large β angle; the c edge is relatively long owing to the high tetrahedron volume (Fig. 1). In particular, the value of β, which is related to Ca content (Takeda, 1972b), is the largest ever found in $C2/c$ quadrilateral pyroxenes; only two crystals, a megacryst from kimberlite (McCallister et al., 1974) and a synthetic sample crystallized at 12 kbar from an experimental lunar basalt (Manoli and Molin, 1988), showed a β angle larger than 107° (107.03 and 107.24°, respectively).

The extreme chemical and structural features of our pyroxene allowed us to outline the intracrystalline relationships of $C2/c$ pyroxene in a portion of the compositional field not previously investigated. In the next section, data from the 6-12 pyroxene are compared with data from 13 natural and synthetic clinopyroxene samples with decreasing Ca + Na and variable Na (0.000–

TABLE 5.   Selected chemical data (apfu) for 13 clinopyroxenes with varying Ca + Na content

	1 Di100	2 Di90	3 Di80	4 BU-11	5 NO-15	6 TH-11	7 TH-4	8 TH-9	9 PC 135	10 PC 133	11 12052	12 190/3	13 1600E4
[4]Al	0.000	0.000	0.000	0.152	0.105	0.041	0.035	0.066	0.117	0.066	0.214	0.208	0.026
Ca	1.000	0.900	0.800	0.751	0.673	0.734	0.707	0.651	0.645	0.737	0.607	0.569	0.553
Na	0.000	0.000	0.000	0.092	0.116	0.000	0.000	0.000	0.094	0.022	0.000	0.000	0.118
Ca + Na	1.000	0.900	0.800	0.843	0.789	0.734	0.707	0.651	0.739	0.759	0.607	0.569	0.671
R^{3+}	0.000	0.000	0.000	0.202	0.224	0.027	0.022	0.038	0.203	0.085	0.176	0.134	0.117

Note: sources of data: 1–3 = Bruno et al. (1982); 4–8 = Dal Negro et al. (1989b); 9–10 = Salviulo et al. (1992); 11 = Takeda (1972a); 12 = Manoli and Molin (1988); 13 = McCallister et al. (1974).

0.118 apfu) and [4]Al (0.000–0.214 apfu) contents (Table 5).

Structural changes in low-Ca $C2/c$ pyroxenes

Takeda (1972b) studied the structural changes in four clinopyroxene samples with $(Ca + Na)_{M2}$ content as low as 0.61 apfu and provided evidence of the crucial role of the M2 polyhedron in determining the presence of the miscibility gap. He pointed out the continuous decrease in the short M2-O1,O2 distances and the sharp and non-linear increase in the long M2-O3C2,C1 distances, causing a strong polyhedral distortion toward the Ca-poor end. He also suggested that a further decrease in $(Ca + Na)_{M2}$ would result in unstable fourfold coordination for the M2 cation. The present data extend the compositional field of low-Ca clinopyroxenes and enable direct verification of Takeda's (1972b) predictions.

Figure 2 shows the changes in M2-O distances with decreasing $(Ca + Na)_{M2}$ content. Takeda's (1972b) basic considerations are essentially confirmed. Nevertheless, some previously unreported peculiarities can be recognized for the M2-O3 distances. In Na-free crystals, the intermediate M2-O3C1 distance increases nonlinearly with decreasing Ca^{2+}_{M2} to a maximum value of 2.643 Å for $Ca_{M2} = 0.61$ apfu and then decreases. The effect caused by Na^+_{M2} is a shortening of this distance to provide the charge balance to the O3 atom (cf. Dal Negro et al., 1984), the contraction becoming more marked as the $(Ca + Na)_{M2}$ content decreases. Lengthening becomes crucial for M2-O3C2, which reaches a record value of 2.833 Å in the 6-12 pyroxene. Na^+_{M2} and Ca^{2+}_{M2} show similar effects on this distance. Figure 2 suggests that the influence of [4]Al in the most subcalcic crystals is to prevent excessive lengthening of the M2-O3C2 distance, which would probably not be compatible with a $C2/c$ symmetry. This would explain the high [4]Al content in the two most subcalcic pyroxenes. Unfortunately, the scarcity of crystals poor in Ca and [4]Al does not allow this hypothesis to be confirmed, yet the very existence of pyroxenes low in [4]Al with Ca < ≈0.65 appears to be unlikely.

The local charge imbalance caused by low $(Ca + Na)_{M2}$ on the O3 atom also affects the geometry of the tetrahedron (Fig. 3). Although the T-O1,O2 (T-O$_{nbr}$) are strictly related to Si → [4]Al substitution, low-Ca clinopyroxenes show significantly shorter T-O3A1,A2 (T-O$_{br}$) relative to Ca-rich volcanic ones. The studied 6-12 pyroxene shows the lowest value of T-O$_{br}$ ever reported (1.660 Å), about

0.020 Å lower than in volcanic samples with similar [4]Al contents. Relative to lunar synthetic and natural clinopyroxenes (Manoli and Molin, 1988; Takeda, 1972a), the presence of Na$^+$ in the M2 site of the studied sample (0.080 apfu) increases the charge imbalance on the O3 atom and requires a greater contraction of the longest tetrahedral distances (Fig. 3). The M2 population also affects the internal angles of the tetrahedron (Fig. 3) so that low $(Ca + Na)_{M2}$ contents induce an overall greater regularity in the T polyhedron (cf. Bruno et al., 1982).

The complex relationship between M2 cations and O3 atoms also involves a significant distortion of the tetrahedral chains with varying $(Ca + Na)_{M2}$ content. In Na-
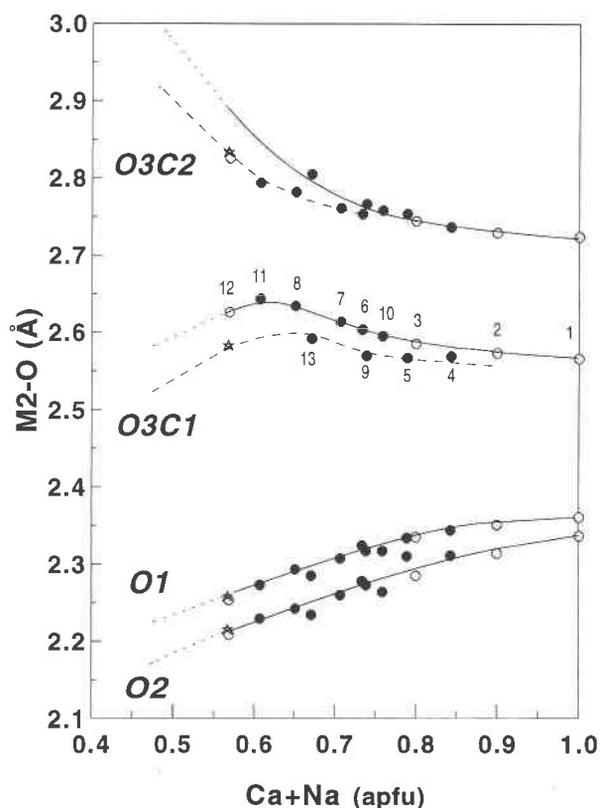
Fig. 2. M2-O distances in $C2/c$ pyroxenes with Ca + Na content. Solid and dashed lines for M2-O3 distances refer approximately to Na = 0.000 and Na = 0.100 apfu trends (C1) and to [4]Al = 0.000 and [4]Al = 0.200 trends (C2), respectively. Symbols are as in Fig. 1.
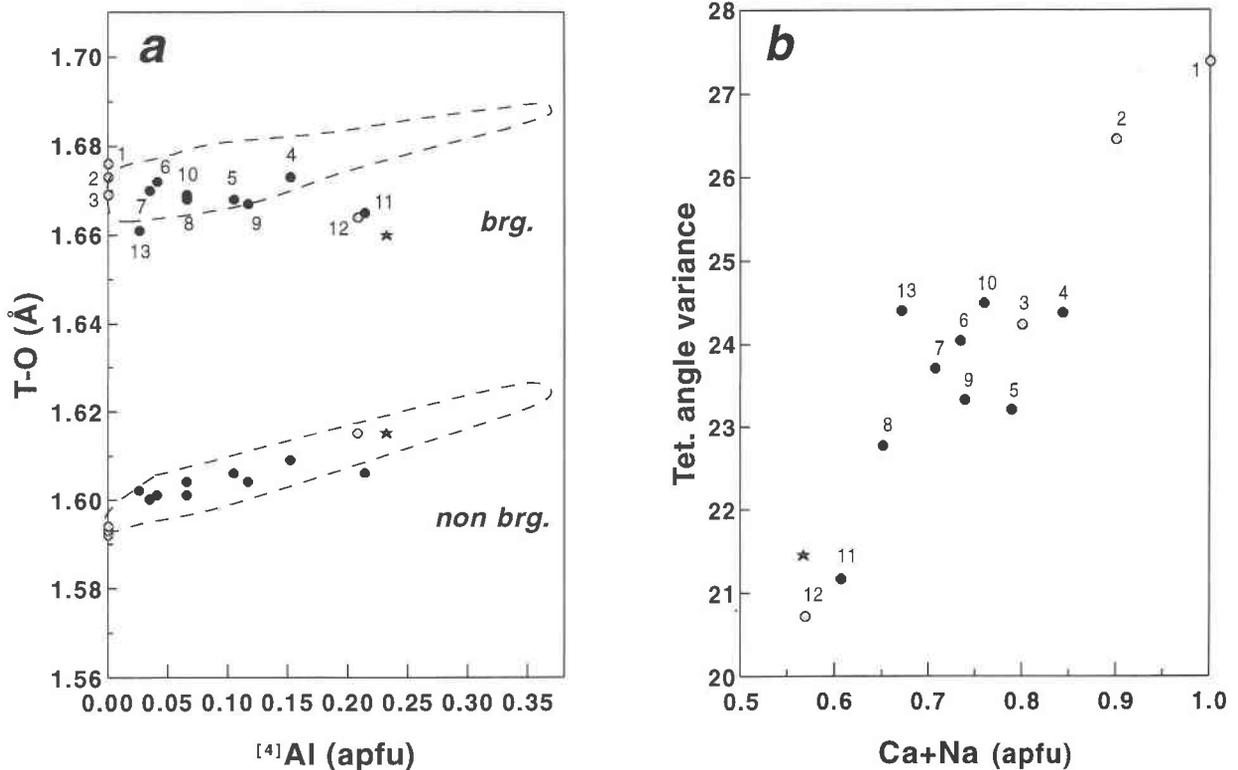
Fig. 3.   (a) T-O distances vs. $^{[4]}$Al content in $C2/c$ pyroxenes. Dashed line = volcanic clinopyroxene field from Dal Negro et al. (1989b). (b) Tetrahedral angle variance (Robinson et al., 1971) vs. the Ca + Na content in $C2/c$ pyroxenes. Symbols are as in Fig. 1.
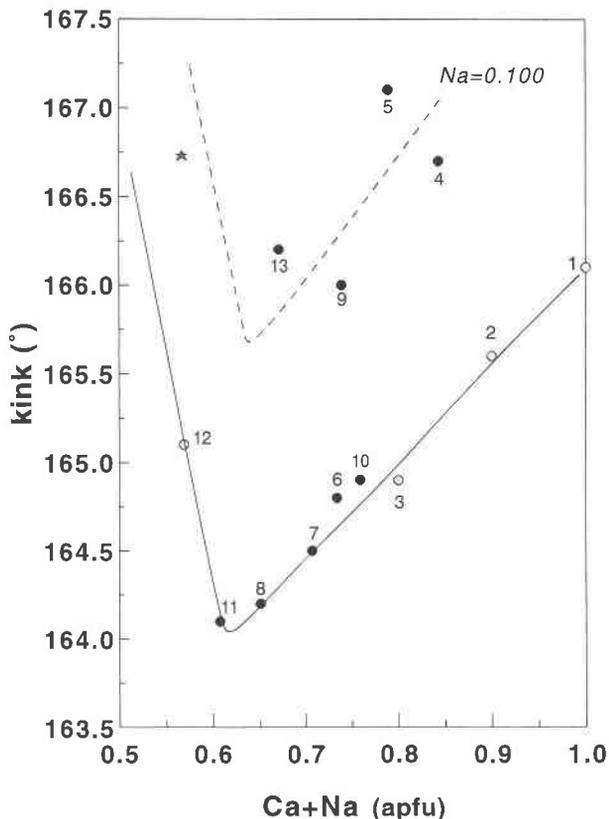
free crystals, the O3-O3-O3 kink angle (Fig. 4) decreases linearly with Ca to a minimum value of about 164° for $Ca_{M2} = 0.61$ apfu. With a further decrease in Ca, the kink angle sharply increases because of concurrent M2-O3C1 contraction and strong lengthening of M2-O3C2 (Fig. 2). The shift of Na-bearing crystals from the Na-free trend is related to the shortening of M2-O3C1 (Fig. 2).

M1-O distances are virtually unaffected by the M2 population (Fig. 5). The very high R^{3+} content of the studied pyroxene causes a marked shortening of the M1-O2 and M1-O1A2 distances, in contrast with the fairly constant M1-O1A1 trend (cf. Carbonin et al., 1991).

DISCUSSION

Mellini et al. (1988) cast doubts on the existence of subcalcic augite as single phases at subsolidus temperatures. TEM/EDS showed that they are the result of microprobe analyses that were contaminated by the presence of lamellar pigeonite exsolution and spinodal decomposition. Mellini et al. (1988) and Carbonin et al. (1991) suggested that the minimum Ca content in natural $C2/c$ clinopyroxenes is about 0.6 apfu.

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Fig. 4.   Variation of the O3-O3-O3 kink angle with Ca + Na content. Dashed line is the approximate trend for Na = 0.100 apfu. The complex relationship is the result of M2 polyhedron distortion in low-Ca samples (see text). Symbols are as in Fig. 1.
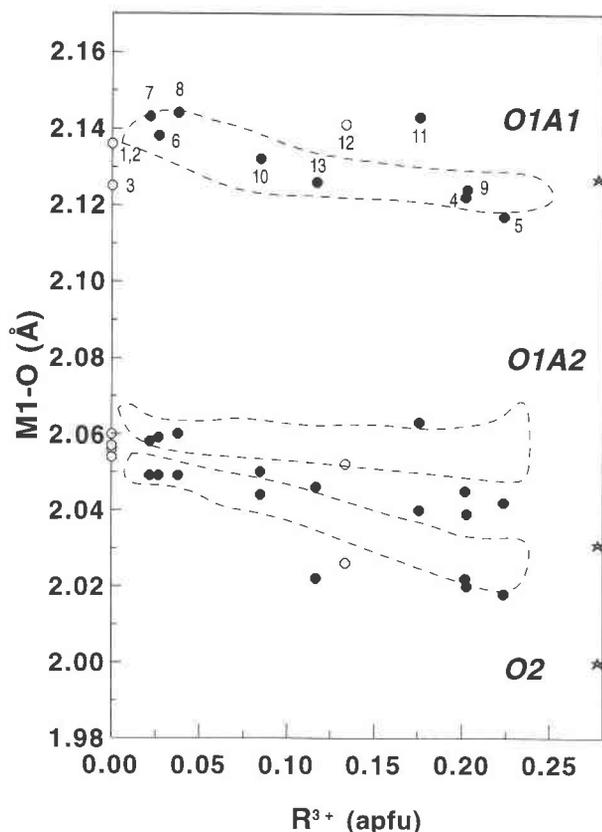
Fig. 5. M1-O distances vs. the R^{3+} content in $C2/c$ pyroxenes. Symbols are as in Fig. 1. Dashed lines show fields of clinopyroxenes from basic volcanics (Dal Negro et al., 1989b).

The consistency of $(Ca + Na)_{M2}$ vs. M2-O trends (Fig. 2), together with the absence of $h + k = 2n + 1$ reflections, strongly suggests the chemical and structural homogeneity of the 6-12 pyroxene (cf. Mellini et al., 1988), extending the possible compositional field of $C2/c$ clinopyroxenes at least to Ca ≈ 0.5 apfu (Ca + Na = 0.567 apfu). Nevertheless, it should be stressed that the 6-12 pyroxene was synthetically produced at very special conditions. High pressure (18 kbar) and temperature (1320 °C) appear to be crucial for the stability of such a distorted M2 site configuration as that shown by the studied sample. The significant positional disorder (see the high displacement parameters, B_{eq}, in Table 1) reflects the different geometries of Ca-bearing and Ca-free asymmetric units, resulting in significant fine-scale distortions. Rapid quenching, such as that commonly achieved in experimental charges, is expected to be essential for the maintenance of chemical and structural homogeneity in clinopyroxenes with Ca + Na < 0.6 apfu. Although high pressure and temperature conditions are easily reached in deep natural environments, the cooling rates of terrestrial rocks are probably much too low for pyroxenes like 6-12 to be found as metastable phases since they would decompose very rapidly during magma ascent.

The relatively high [4]Al content (0.232 apfu), which contrasts with the positive Ca vs. [4]Al relationship com-

monly found in natural volcanic clinopyroxenes (e.g., Dal Negro et al., 1982), arises from structural stability requirements. High Si occupancies in the T site would dramatically enhance M2-O3C2 lengthening in clinopyroxenes with $(Ca + Na)_{M2} < 0.6$ apfu (Fig. 2) and would cause serious problems for the maintenance of lattice periodicity. Doubts are cast on the effective meaning of many published synthetic clinopyroxene analyses characterized by Ca + Na contents of 0.5 apfu (or even lower) and [4]Al occupancies lower than 0.2 apfu (e.g., Green and Ringwood, 1967; Thompson, 1974). These possibly result from contaminated microprobe analyses arising from associated calcic (augite) and subcalcic (pigeonite?) phases (cf. Mellini et al., 1988).

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