Ultrahigh potassium content in the clinopyroxene structure: an X-ray single-crystal study

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Abstract: The crystal structures and chemical compositions of two crystals of clinopyroxene (labelled K1 and K2) synthesized in the model system $CaMgSi_2O_6$ - $KAlSi_2O_6$ at 7 GPa, have been investigated. Quantitative analysis leads to the following formulae: $(Ca_{0.75}K_{0.23}Mg_{0.02})(Mg_{0.73}Al_{0.27})(Si_{1.97}Al_{0.03})O_{6.00}$ and $(Ca_{0.90}K_{0.07}Mg_{0.03})(Mg_{0.86}Al_{0.14})(Si_{1.94}Al_{0.06})O_{6.00}$, for K1 and K2 respectively. Lattice parameters are: $a = 9.803(2)$, $b = 8.985(2)$, $c = 5.263(1)$ Å, $\beta = 105.69(1)°$ for K1 and $a = 9.744(1)$, $b = 8.904(2)$, $c = 5.273(1)$ Å, $\beta = 106.14(1)°$ for K2. The structures were refined to $R_{all} = 1.16$ and 2.02 %, respectively, using 982 independent reflections. Substitution of K for Ca causes strong modifications to the average structure, mainly a lengthening of the M2-O3C1 bond distance and a shortening of the T-O3A1 bond distance. The crystal K1 shows the largest volume for a M2 polyhedron ever reported for the clinopyroxene structure with divalent cations in this site. No evidence was found for a small cation such as Mg coexisting with Ca in the M2 site that might act as a structural stabilizer for the accommodation of K in the clinopyroxene structure.
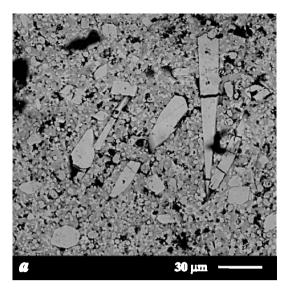
Key-words: potassium-bearing clinopyroxene, structure refinement, single-crystal X-ray diffraction, synthetic crystals, chemical analysis.

Introduction

The crystal chemical explanation for potassium avoidance of clinopyroxene at ambient pressure is that K^+, with an ionic radius of 1.51 Å (Shannon, 1976), is too large to be accommodated in the M2 site of the clinopyroxene structure. However, Harlow (1997) calculated that the polyhedral compressibility of K^+ is relatively large and at pressures in excess of 5 GPa the potassium ion might easily substitute for Ca^{2+} or Mg^{2+}. In order to preserve charge balance in the structure, introduction of K^+ into the M2 site should be accompanied by the simultaneous replacement of $(Mg, Fe)^{2+}$ in the M1 site by a trivalent cation (*e.g.* Al, Cr) by the following scheme $Ca_{M2}(Mg, Fe)_{M1} \Leftrightarrow K_{M2}(Al, Cr)_{M1}$. This scheme is supported by the direct correlation of K content with that of trivalent cations in both natural and synthetic clinopyroxenes (*e.g.* Edgar & Vukadinovic, 1993; Perchuk *et al.*, 1996; Safonov *et al.*, 2001). It reflects a presence in the clinopyroxene solid solution of the fictive K-jadeite $(KAlSi_2O_6)$ and K-kosmochlor $(KCrSi_2O_6)$ end-members. In addition, Harlow (1996) proposed that more K can enter the M2 site in the constrained structure of pyroxene if smaller adjacent cations (*e.g.* Mg) are present so as to reduce the average cation size. Harlow (1998) proposed the so-called "subway rider" model of crystal chemistry at high pressures to explain this effect. However, the increase of enstatite and

jadeite contents leads to an appreciable decrease in molar volume of clinopyroxene that could prevent K incorporation. The presence of Al and Cr in M1 site of the diopside structure also dramatically affects potassium incorporation. The effect of Cr in clinopyroxene on K uptake was previously established for chromium-diopsides (Harlow & Veblen, 1991; Harlow, 1997). Nevertheless, Luth (1992) showed that Cr was no more effective than Al in stabilizing of K in the clinopyroxene structure. Indeed, Luth (1995) succeeded in synthesis of clinopyroxene with 3 wt. % of K_2O in the system $CaMgSi_2O_6$ - $KAlSi_2O_6$.

In contrast to Cr-rich clinopyroxenes, the problem of potassium content in the essentially Al-rich clinopyroxenes is very intriguing. Al-rich, Cr-free, potassium-bearing (up to 1.5 wt. % K_2O) clinopyroxenes are known from the Kokchetav ultra-high pressure rocks (Sobolev & Shatsky, 1990; Perchuk *et al.*, 1996). Al in the M1 site induces a compaction effect in the clinopyroxene structure and the unit-cell volumes of Al-rich high-pressure clinopyroxenes (jadeite or Ca-eskolaite) are significantly smaller than those of Cr-diopside or even pure diopside (*e.g.* Oberti & Caporuscio, 1991). The opposite effect of K incorporation (Harlow, 1997) should drastically modify the structure of Al-rich clinopyroxene. The question is how much K_2O can coexist in Al-rich clinopyroxene and which structural modifications accompany the solubility of $KAlSi_2O_6$ into diopside.
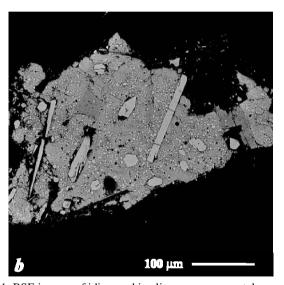
Fig. 1. BSE images of idiomorphic clinopyroxene crystals, coexisting with garnet (small idiomorphic equant grains in the matrix), produced in the runs (*a*) 688 (1310 °C, 60 mol. % $KAlSi_2O_6$) and (*b*) 650 (1350 °C, 70 mol. % $KAlSi_2O_6$). CamScan electronic microscope.

The major purpose of the present study was to provide crystal-chemical characteristics of Al-rich clinopyroxenes containing 1.6 and 5.0 wt. % K_2O and $(Ca + K)_{M2} = 0.97$-0.98 a.p.f.u. synthesized in the model system $CaMgSi_2O_6$ - $KAlSi_2O_6$ at 7 GPa, and to verify the "subway rider" effect (Harlow, 1998).

Experimental and structure refinements

Two small crystal fragments (labelled K1 and K2), handpicked under a reflected light microscope from the run products (Fig. 1) synthesized by Safonov *et al.* (2001), were used for the X-ray diffraction study and electron microprobe analysis. In order to determine the real symmetry of the selected clinopyroxene crystals, we decided to perform a test data collection of the whole Ewald sphere up to $2\theta_{Mo\text{-}K\alpha} =$

Table 1. Crystal data and experimental details.

	K1	K2
cell parameters	$a = 9.803(2)$ (Å)	$a = 9.744(1)$ (Å)
	$b = 8.985(2)$ (Å)	$b = 8.904(2)$ (Å)
	$c = 5.263(1)$ (Å)	$c = 5.273(1)$ (Å)
	$\beta = 105.69(1)°$	$\beta = 106.14(1)°$
	$V = 446.29(1)$ (Å³)	$V = 439.46(1)$ (Å³)
crystal size (μm)	40x30x60	30x30x40
wavelength	Mo-$K\alpha$	Mo-$K\alpha$
	(26 mA x 50 kV)	(26 mA x 50 kV)
theta-range (°)	1-35	1-35
scan mode	ω	ω
scan width (°)	2.50	2.50
scan speed (°/min)	1.65	2.06
independent refl.	982	982
refl. with Fo>4σ(Fo)	844	878
R_{merge} (%)	3.71	3.39
R_{obs} (%)	1.11	1.89
R_{all} (%)	1.16	2.04

Table 2. Atomic coordinates and equivalent isotropic-displacement parameters with their standard deviations in parentheses.

Atom	K1	K2
M2		
x	0	0
y	0.29894(2)	0.30054(2)
z	¼	¼
U_{eq}(Å²)	0.01121(6)	0.01247(5)
M1		
x	0	0
y	0.90387(3)	0.90677(3)
z	¼	¼
U_{eq}(Å²)	0.00717(10)	0.00941(10)
T		
x	0.28892(2)	0.28775(2)
y	0.09163(2)	0.09247(2)
z	0.23494(4)	0.23260(3)
U_{eq}(Å²)	0.00633(5)	0.00678(5)
O1		
x	0.11496(6)	0.11522(5)
y	0.08716(5)	0.08746(4)
z	0.15053(9)	0.14715(9)
U_{eq}(Å²)	0.01014(9)	0.00912(8)
O2		
x	0.36175(6)	0.36290(5)
y	0.24918(6)	0.24918(5)
z	0.32099(9)	0.32315(9)
U_{eq}(Å²)	0.01235(10)	0.01182(8)
O3		
x	0.32847(5)	0.34501(4)
y	0.02757(6)	0.01882(5)
z	0.97953(9)	0.98670(8)
U_{eq}(Å²)	0.00994(9)	0.01126(8)

30°. Only reflections consistent with the space group $C2/c$ were observed. Unit-cell parameters, determined by centering 25 high-θ (18-25°) reflections, are shown in Table 1. Intensity data were collected on an automated diffractometer (Enraf Nonius – CAD4) using Mo-$K\alpha$ radiation monochro-

Table 3. Anisotropic displacement parameters U_{ij} (Å^2) for K1 and K2.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K1						
M2	0.01104(9)	0.01171(9)	0.00718(8)	0	-0.00387(5)	0
M1	0.00680(16)	0.00770(15)	0.00641(16)	0	0.00079(11)	0
T	0.00610(8)	0.00727(8)	0.00562(8)	-0.00126(5)	0.00159(6)	0.00027(5)
O1	0.00702(19)	0.01338(20)	0.00987(20)	0.00083(14)	0.00201(16)	0.00081(14)
O2	0.01492(22)	0.00917(20)	0.01316(21)	-0.00844(16)	0.00412(17)	-0.00031(16)
O3	0.00882(18)	0.01357(21)	0.00762(18)	-0.00009(15)	0.00253(15)	-0.00566(15)
K2						
M2	0.01239(8)	0.01323(8)	0.00969(8)	0	-0.00044(5)	0
M1	0.00957(14)	0.00971(14)	0.00863(16)	0	0.00203(10)	0
T	0.00612(7)	0.00818(7)	0.00630(8)	-0.00033(4)	0.00214(5)	0.00084(4)
O1	0.00537(15)	0.01121(17)	0.01081(18)	0.00098(11)	0.00230(12)	0.00095(12)
O2	0.01243(18)	0.01013(16)	0.01396(20)	-0.00361(13)	0.00544(14)	0.00036(14)
O3	0.01030(16)	0.01444(18)	0.00898(18)	0.00242(13)	0.00258(13)	-0.00340(13)

matized by a flat graphite crystal. Intensities were corrected for Lorentz-polarization effects and subsequently for absorption following the semi-empirical method of North *et al.* (1968); the values of the equivalent pairs hkl and $h\bar{k}l$ were averaged. Structure refinements were performed in space group $C2/c$, starting from the atomic coordinates of diopside (Clark *et al.*, 1969), using the program SHELXL-93 (Sheldrick, 1993). Following Harlow (1996), K was assumed to substitute for Ca in M2. Because both Ca and K (M2 site), and Mg and Al (M1 site), have similar atomic numbers we applied two different refinement strategies. The first model was to refine an unconstrained site occupancy using Ca in M2 and Mg in M1; the second to refine Mg *vs.* Al (M1 site) and Ca *vs.* Mg (M2 site). The differences, in terms of mean electron number, between these two refinements were within the range of errors (first model: 19.8, 19.7 for M2 and 12.4, 12.2 for M1 for K1 and K2, respectively; second model: 19.8, 19.7 for M2 and 12.5, 12.3 for M1). The results obtained with the first model are presented here. Neutral scattering curves for Ca, K, Na, Mg, Fe, Si, O were taken from *The International Tables of X-ray Crystallography*, volume IV (Ibers & Hamilton 1974). The inspection of the difference Fourier maps revealed that maximum positive and negative peaks were 0.59 and 0.39 e$^-$/Å^3, and -0.23 and -0.52 e$^-$/Å^3 for K1 and K2, respectively. Experimental details and R indices are given in Table 1. Fractional atomic coordinates and anisotropic-displacement parameters are shown in Tables 2 and 3, respectively. Table 4[1] lists the observed and calculated structure factors.

Chemical composition

The same crystals used for the intensity data collection were used for electron-microprobe analysis (EPMA) which was performed with a JEOL JXA 8600. Major and minor elements were determined at 15 kV accelerating voltage and

Table 5. Chemical composition (means and ranges of oxides in wt%) and unit formulae (on the basis of six oxygens) for synthetic K-rich clinopyroxenes.

	K1	range	K2	range
SiO$_2$	54.55	54.18-54.90	53.71	53.50-53.92
Al$_2$O$_3$	7.08	6.99-7.19	4.95	4.86-5.04
MgO	13.93	13.85-14.08	16.51	16.21-16.81
CaO	19.46	19.30-19.63	23.21	22.71-23.73
K$_2$O	5.00	4.98-5.04	1.57	1.29-1.85
total	100.02		99.95	
T *site*				
Si	1.968		1.935	
Al	0.032		0.065	
M1 *site*				
Mg	0.731		0.855	
Al	0.269		0.145	
M2 *site*				
Ca	0.752		0.896	
Mg	0.018		0.032	
K	0.230		0.072	
e^-_{M1}	12.3		12.1	
e^-_{M2}	19.6		19.7	
charge	12.007		12.008	

10 nA beam current. The matrix correction was performed with the Bence & Albee (1968) program as modified by Albee & Ray (1970). Replicate analyses of augite USNM 122142 were used to check accuracy and precision. The estimated analytical precision is: ± 0.02 for CaO and MgO, ± 0.03 for SiO$_2$, ± 0.06 for K$_2$O, and ± 0.1 for Al$_2$O$_3$. Seven or eight analyses were performed on different spots of each crystal; both crystals were found to be homogeneous within the analytical error. Chemical compositions are reported in Table 5. The mean electron numbers calculated for the site populations obtained on the basis of the chemical data (19.6, 19.7 for M2 and 12.3, 12.1 for M1 for K1 and K2, respectively) are in close agreement with those from the site-occupancy refinement (19.8, 19.7 and 12.4, 12.2 respectively).

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[1] It can be obtained from the authors or through the E.J.M. Editorial Office – Paris.

Table 6. Bond distances (Å) and angles (°) for K1 and K2.

	K1	K2
M2 site		
M2-O2	2.338(1)	2.318(1)
M2-O1	2.342(1)	2.344(1)
M2-O3C1	2.789(1)	2.612(1)
M2-O3C2	2.796(1)	2.734(1)
mean	2.566	2.502
Vp	28.09	25.85
M1 site		
M1-O2	2.045(1)	2.047(1)
M1-O1A1	2.139(1)	2.117(1)
M1-O1A2	2.106(1)	2.084(1)
mean	2.097	2.082
Vp	12.17	11.94
σ^2 (oct)	22.41	18.74
λ (oct)	1.0069	1.0057
T site		
T-O2	1.595(1)	1.586(1)
T-O1	1.642(1)	1.616(1)
T-O3A1	1.603(1)	1.635(1)
T-O3A2	1.638(1)	1.681(1)
T-Onbr	1.619	1.601
T-Obr	1.621	1.658
mean	1.620	1.629
Vp	2.156	2.205
σ^2 (tet)	31.93	20.10
λ (tet)	1.0079	1.0051
e^-_{M1}	12.0	12.2
e^-_{M2}	19.8	19.7
O3-Si-O3	111.38(1)	106.55(1)
O3-O3-O3	158.68(1)	165.51(1)
Si-O3-Si	146.50(1)	139.28(1)

Note: The mean quadratic elongation (λ) and the angle variance (σ^2) where computed according to Robinson *et al.* (1971).

Discussion

Harlow (1996) showed that K entered the M2 site of the clinopyroxene structure. The assignment of K to M2 is required both to account for the electron density at that site and to justify the strong increase of the M2-O distances (Table 6) relative to diopside. The M2 site in the crystals that we have studied is dominated by Ca (0.75-0.90 a.p.f.u.) and K (0.07-0.23 a.p.f.u.) with minor amounts of Mg (0.02-0.03 a.p.f.u.). The value of the <M2-O> distance for K2 (2.502 Å) is very similar to that observed for natural K-rich diopside (2.504 Å; Harlow, 1996), whereas the geometry of the M2-polyhedron of K1 shows specific characteristics never previously reported for the clinopyroxene structure. The mean <M2-O> value of 2.566 Å exceeds by far those observed in natural crystals and in synthetic Sr-bearing clinopyroxene-type analogues (Ca, Sr)MgSi$_2$O$_6$ (2.500-2.511 Å; Benna, 1982; Benna *et al.*, 1987). The increase of the M2-O distances is not isotropic; the longer distances, in particular M2-O3C1, increase the most while there is a slight shortening of the M2-O1 distance. In addition, the entry of K in M2 causes geometrical changes to the adjacent M1 site. For the synthetic Sr-clinopyroxenes Benna *et al.* (1987) observed
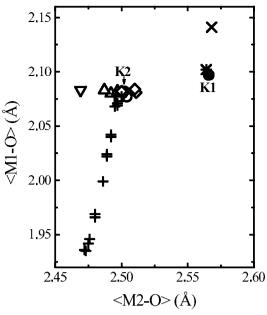

Fig. 2. Values of <M1-O> distances in *C2/c* clinopyroxenes plotted against <M2-O> distances. The filled circle refers to the synthetic clinopyroxene crystals of this study. Open symbols are literature data, as follows: circle, natural K-rich diopside (Harlow, 1996); square, diopside (Cameron *et al.,* 1973); down triangle, Di$_{66}$En$_{34}$ (Tribaudino *et al.,* 1989); up triangles, Di$_{100}$, Di$_{90}$En$_{10}$, Di$_{80}$En$_2$ (Bruno *et al.*, 1982); diamonds, (Ca,Sr)-clinopyroxenes (Benna *et al.*, 1987); crosses (+) natural clinopyroxenes of the augite-jadeite join (Boffa Ballaran *et al.*, 1998); star, NaScSi$_2$O$_6$ (Hawthorne & Grundy, 1973); cross (x), NaInSi$_2$O$_6$ (Hawthorne & Grundy, 1974).

that an increase of the size of the M2 site, due to the large Sr cation, resulted in a slight increase of the <M1-O> bond length. Similar and more enhanced behaviour is observed in the structure of the K1 crystal, in which the large K cation induces a strong increase of the M1-polyhedral volume (12.17 Å^3) and of the <M1-O> distance (2.097 Å). This value is notably larger than the 2.040 Å, calculated on the basis of the site occupancy (using <Mg-O> = 2.081 Å, Bruno *et al.*, 1982; <Al-O> = 1.930 Å, Dal Negro *et al.*, 1982).

In the synthetic compounds NaScSi$_2$O$_6$ (Hawthorne & Grundy, 1973) and NaInSi$_2$O$_6$ (Hawthorne & Grundy, 1974) the same but reversed interaction between M1 and M2 polyhedra is observed. Indeed, the size of the M1 occupant (Sc or In) is able to affect the size of M2 which shows <M2-O> distances (2.564 and 2.568 Å, respectively) similar to that found in K1 (2.566 Å) and significantly longer than those expected for a polyhedron fully occupied by Na (2.469 Å for NaAlSi$_2$O$_6$, Cameron *et al.*, 1973; 2.489 Å for NaCrSi$_2$O$_6$, Clark *et al.*, 1969; 2.518 Å for NaFeSi$_2$O$_6$, Clark *et al.*, 1969). On the other hand, the large M2 polyhedron observed in the structures of NaScSi$_2$O$_6$ and NaInSi$_2$O$_6$ differs from that of K1 in the distribution of the individual M2-O distances (6+2 and 8-fold coordination, respectively).

In Figure 2, the <M1-O> distance is plotted against <M2-O> for several *C2/c* clinopyroxenes. The values for K1, NaScSi$_2$O$_6$, and NaInSi$_2$O$_6$ clearly lie beyond the main trend. In turn, the values of the K2 crystal are close to those observed by Harlow (1996) and those found by Benna *et al.*
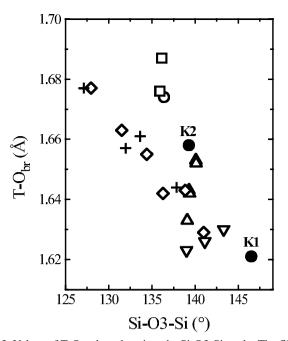
Fig. 3. Values of T-O_{br} plotted against the Si-O3-Si angle. The filled circles refer to the synthetic clinopyroxene crystals of this study. Empty symbols refer to published data (Cameron & Papike, 1981). Circles, natural K-rich diopside (Harlow, 1996); squares, $C2/c$ pyroxenes with general formula $CaM^{2+}Si_2O_6$; up triangles, $C2/c$ pyroxenes with general formula $NaM^{3+}Si_2O_6$; down triangles, $C2/c$ pyroxenes with general formula $LiM^{3+}Si_2O_6$; diamonds, $Pbca$ pyroxenes; crosses, $P2_1/c$ pyroxenes.

(1987) for synthetic Sr-pyroxene. Significant variations can also be observed for the T site. As documented by Oberti & Caporuscio (1991) for mantle clinopyroxenes, an increase of the M2-O3 bond lengths corresponds to a decrease of the only other bond distance involving O3 (*i.e.* T-O3), in order to maintain the charge balance on O3. The crystal K1 exhibits the shortest T-O3A1 (1.603 Å) and the longest T-O1 (1.642 Å) distance ever reported for a clinopyroxene structure, thus resulting in T-O_{br} = 1.621 Å and T-O_{nbr} = 1.619 Å. In general, the mean of the bridging distances is larger than that of the non-bridging distances, and the difference between the two values is smallest for the $C2/c$ Li-pyroxenes with monovalent M2 cations and largest for the $C2/c$ Ca-pyroxenes with divalent M2 cations. However, several approaches were suggested to explain the variation of the T-O_{br} distances. According to Clark *et al.* (1969), the increase in bridging distances in $C2/c$ pyroxenes is directly related to the strength of the M2-O bond distances. Brown *et al.* (1969) and Gibbs *et al.* (1972) rationalized the variation of the T-O bond lengths by covalent bonding models such as the extended Hückel molecular orbital theory. Cameron & Papike (1981) reported that the variation of the bond lengths in the tetrahedral site could be attributed to the effects of geometrical factors, such as O3-Si-O3 and Si-O3-Si angles. In general, these authors showed that shorter T-O bonds were associated with larger Si-O3-Si angles. Figure 3 shows the diagram proposed by Cameron & Papike (1981), where a negative correlation of the data is evident. The data of the

crystal K1 fall within the trend showing the largest Si-O3-Si angle.

To some extent, the general features described for K1 can be observed also for the structure of the K2 crystal. In fact, the K2 crystal shows a longer M2-O3C1 distance (2.612 Å) than synthetic diopside (2.561-2.573 Å; Cameron *et al.*, 1973; Bruno *et al.*, 1982). Consequently, a shortening of the T-O3A1 distance (1.635 Å) occurs as well.

Harlow (1996) proposed that large K cations could be incorporated into the M2 site of the pyroxene structure provided some smaller cations (*e.g.* Mg) were present so as to reduce the average cation size. This hypothesis seems to be contradicted by the present study in which only a minor amount of Mg was found in the K1 and K2 crystals. This low Mg-content also accounts for the absence of the M2' site in the structures of these crystals. Rossi *et al.* (1987) showed that the occupancy of the additional M2' position in clinopyroxenes decreased with the increase of Ca+Na (a.p.f.u.) and completely disappeared at Ca + Na > 0.95 (a.p.f.u.). The evidence from the current study is therefore against the hypothesis of the stabilizing role of small cations (*i.e.* Mg) on K in the clinopyroxene structure.

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