

## LETTER

# Ultrapotassic clinopyroxene from the Kumdy-Kol microdiamond mine, Kokchetav Complex, Kazakhstan: Occurrence, composition and crystal-chemical characterization

LUCA BINDI,<sup>1,\*</sup> OLEG G. SAFONOV,<sup>2</sup> VASILY O. YAPASKURT,<sup>3</sup> LEONID L. PERCHUK,<sup>3</sup> AND SILVIO MENCHETTI<sup>1</sup>

<sup>1</sup>Dipartimento di Scienze della Terra, Università di Firenze, Via La Pira 4, I-50121, Florence, Italy

<sup>2</sup>Institute of Experimental Mineralogy, Moscow district, 142432, Chernogolovka, Russia

<sup>3</sup>Department of Petrology, Moscow State University, Vorobievsky Gory, 119899, Moscow, Russia

## ABSTRACT

We report data on the composition and crystal structure of the most K-rich (3.61 wt% K<sub>2</sub>O) natural clinopyroxene yet discovered. The studied crystal was found as a tiny inclusion in garnet from a garnet-clinopyroxene rock of the Kumdy-Kol microdiamond mine, Kokchetav complex, Northern Kazakhstan. Microprobe analysis yields the formula (Ca<sub>0.61</sub>Fe<sub>0.13</sub>Mg<sub>0.04</sub>Mn<sub>0.01</sub>K<sub>0.17</sub>Na<sub>0.05</sub>)(Al<sub>0.61</sub>Mg<sub>0.39</sub>)(Si<sub>1.61</sub>Al<sub>0.39</sub>)O<sub>6.00</sub>. Lattice parameters are:  $a = 9.773(1)$ ,  $b = 8.926(1)$ ,  $c = 5.269(1)$  Å,  $\beta = 105.75(1)^\circ$ . The structure was refined up to  $R_{\text{all}} = 2.42\%$  using 982 independent reflections. Substitution of K for Ca causes significant modification of the average structure. No evidence for an additional M2' position was found. Crystal-chemical characteristics are compared with published data on both natural and synthetic K-bearing clinopyroxenes.

## INTRODUCTION

Clinopyroxene containing up to 1.7 wt% of K<sub>2</sub>O is a characteristic feature of certain inclusions in diamonds. Such K-rich clinopyroxene (hereafter Kcpx) inclusions (e.g., Bishop et al. 1978; Harlow and Veblen 1991) have also been encountered in some eclogitic and peridotitic xenoliths (Reid et al. 1976; Jaques et al. 1990). Until now, the maximum concentration of K<sub>2</sub>O, 2.34 wt%, was reported for clinopyroxene megacrysts from a K-rich hawaiite from Australia (Ghorbani and Middlemost 2000). However, experimental studies of model and natural systems at  $P > 5$  GPa (Perchuk et al. 2002) have shown that 2.34 wt% is not a limit for the K<sub>2</sub>O content in clinopyroxene. Chudinovskikh et al. (2001), Safonov et al. (2001, 2002), and Bindi et al. (2002), reported 5.50–5.75 wt% K<sub>2</sub>O in clinopyroxene in the run products in both carbonate-silicate and aluminosilicate systems at 7 GPa.

Sobolev and Shatsky (1990) first described clinopyroxene containing up to 1.5 wt% K<sub>2</sub>O as inclusions in garnets from fine-grained diamondiferous garnet-clinopyroxene rocks of the Kokchetav UHP Complex, Northern Kazakhstan. Similar clinopyroxene relics in garnet, containing up to 1.2 wt% K<sub>2</sub>O, were studied in detail by Perchuk et al. (1995, 1996, 2002) and Perchuk and Yapaskurt (1998) in coarse-grained Grt-Cpx aluminosilicate rocks of the Kumdy-Kol microdiamond mine of the same complex. Thus far, the Kokchetav UHP rocks represent the only occurrence of K-bearing clinopyroxene (Kcpx) in a crustal environment. Kcpx of the Kokchetav Grt-Cpx carbonate-bearing and carbonate-free rocks differs in composition from Kcpx of kimberlites and lamproites. First of all, Kcpx from the Kokchetav rocks show wide variations of Mg no. [ $100 \cdot \text{Mg}/(\text{Mg} + \text{Fe})_{\text{atomic}}$ ] from about 40 in Fe-rich Grt-Cpx rocks

(e.g., Perchuk et al. 1996) to above 90 in Mg-rich Grt-Cpx rocks and dolomite marbles, whereas Mg no. of Kcpx from kimberlites and lamproites never falls below 70. In addition, clinopyroxenes of the mantle-derived rocks usually contain high concentrations of Na and Cr (e.g., Jaques et al. 1990; Harlow and Veblen 1991). The peculiar feature of Kcpx from Grt-Cpx rocks of the Kokchetav Complex is the very low concentration of Na (<1 wt% of Na<sub>2</sub>O) and the absence of Cr. Moreover, K commonly dominates over Na in these Kcpx (Perchuk et al. 1996).

Here we report compositional and structural data on a unique Al-rich ultrapotassic (3.61 wt% K<sub>2</sub>O) clinopyroxene, recently discovered in the Kokchetav rocks. The major purpose of the present study is to provide crystal-chemical characteristics of this clinopyroxene crystal, and to compare these data with those of Mg-rich Kcpx from kimberlites (Harlow 1996) and synthetic Kcpx (Bindi et al. 2002).

## GEOLOGICAL SETTING AND PETROGRAPHY OF THE STUDIED ROCK SAMPLE

The Kumdy-Kol mine is situated in the Western part of the Kokchetav Complex (Lavrova et al. 1999). The geological position of Grt-Cpx rocks within the complex is thoroughly described in numerous books and papers (e.g., Dobrozhineckaya et al. 1994; Perchuk et al. 1995; Dobretsov et al. 1995; Shatsky et al. 1999; Lavrova et al. 1999). These rocks form interlayers, boudins, and lenses in garnet-biotite diamondiferous gneisses and schists metamorphosed under amphibolite-facies conditions. A metamorphic age of the host gneisses and schists is 524–535 Ma (Shatsky et al. 1999).

A representative sample of Fe-rich, diamond-free garnet-clinopyroxene rock of the Kumdy-Kol mine (Kum-39) was chosen for a detailed study of the Kcpx inclusions in garnets. The sample is a coarse-grained rock mainly composed of

\* E-mail: lbindi@steno.geo.unifi.it

clinopyroxene and garnet (see also Perchuk et al. 1996). Titanite, apatite, quartz, and calcite are common accessory minerals, whereas chlorite, epidote, and albite are present only as secondary minerals. Clinopyroxene in the matrix of the rock forms prismatic grains. Cores of large clinopyroxene crystals contain needle-like inclusions (lamellae) of K-feldspar, whereas such lamellae are absent on the rims of the grains. Garnet forms separate euhedral grains 5–6 mm in size. K-feldspar forms rims or intergrowths with Cpx and Grt (~10–200  $\mu\text{m}$  wide) along garnet and clinopyroxene grain boundaries. Garnet contains rounded euhedral inclusions of clinopyroxene (up to 50  $\mu\text{m}$  in size), polycrystalline inclusions of calcite, and Al-rich titanite. Some Cpx inclusions are clear, but others are crowded with K-feldspar lamellae.

The characteristic compositional feature of garnets in the studied sample is the high concentration of grossular (50–58 mol%), andradite (20–30 mol%), and almandine (15–20 mol%) components, and the low content of pyrope and spessartine (<5 mol%). Garnets also contain around 1 wt%  $\text{TiO}_2$ . Garnet grains show flat profiles of all components in cores (200–300  $\mu\text{m}$ ); slight increase of Ca,  $\text{Fe}^{3+}$  and decrease of Mg at narrow rims (~50  $\mu\text{m}$ ) are observed. Mg no. of typical clinopyroxene inclusions in garnet varies within the range 0.38–0.41. These clinopyroxenes are characterized by low a  $\text{Na}_2\text{O}$  content (<0.3 wt%) and a low concentration of Al in the tetrahedral site (low CaTs content). The  $\text{K}_2\text{O}$  content in the clinopyroxene inclusions reaches 1.2 wt%. The Mg no. of matrix clinopyroxene ranges from 0.41 down to 0.35, whereas the  $\text{K}_2\text{O}$  content is below 0.2 wt%. Zoning of clinopyroxene from inclusions and matrix with respect to Mg no. and K content are identical to that described by Perchuk et al. (1996, 2002) and Perchuk and Yapaskurt (1998) for similar Grt-Cpx rock (Kum-2) from the Kumdy-Kol mine. Titanite inclusions in garnet contain up to 8 wt% of  $\text{Al}_2\text{O}_3$ .

The single crystal of the unusual clinopyroxene (labeled KOK-1) used in this study was recovered as an inclusion in a garnet grain among other clinopyroxene inclusions. No visible differences were observed between this crystal and other extracted clinopyroxenes. Because the crystal was extracted prior to the microprobe analysis, composition of contacting garnet was not studied.

## EXPERIMENTAL METHODS

The crystal (30  $\times$  40  $\times$  55  $\mu\text{m}$ ), rounded and completely transparent and gemmy, without visible inclusions, was used for the X-ray diffraction study and electron microprobe analysis. The Kcpx crystal used for the structural study is preserved at the Dipartimento di Scienze della Terra, Università di Firenze.

A total of 25 high- $\theta$  reflections were centered and subsequently indexed yielding  $a = 9.773(1)$  Å,  $b = 8.926(1)$  Å,  $c = 5.269(1)$  Å,  $\beta = 105.75(1)^\circ$ ,  $V = 442.38(2)$  Å<sup>3</sup>. Intensity data were collected on an automated diffractometer (Bruker P4) using  $\text{MoK}\alpha$  radiation monochromatized by a flat graphite crystal. Intensities were treated for Lorentz-polarization effects and subsequently corrected for absorption following the semi-empirical method of North et al. (1968). Experimental details are given in Table 1.

**TABLE 1.** Crystal data and experimental details

	KOK-1
Space group	$C2/c$
Cell parameters	$a = 9.773(1)$ (Å) $b = 8.926(1)$ (Å) $c = 5.269(1)$ (Å) $\beta = 105.75(1)^\circ$ $V = 442.38(2)$ (Å <sup>3</sup> )
Crystal size ( $\mu\text{m}$ )	30 $\times$ 40 $\times$ 55
Wavelength	$\text{MoK}\alpha$ (26 mA $\times$ 50 kV)
theta-range ( $^\circ$ )	1–35
Scan mode	$\omega$
Scan width ( $^\circ$ )	2.50
Scan speed ( $^\circ/\text{min}$ )	1.65
Independent refl.	982
Refl. with $F_o > 4\sigma(F_o)$	869
$R_{\text{merge}}$ (%)	3.15
$R_{\text{obs}}$ (%)	2.26
$R_{\text{all}}$ (%)	2.42

Note:  $R_{\text{obs}}$  was calculated by SHELXL-93 with the instruction omit active.

## STRUCTURE REFINEMENT

The structure of KOK-1 was refined by means of the program SHELXL 93 (Sheldrick 1993). The equivalent monoclinic pairs  $hkl$  and  $h\bar{k}l$  were merged ( $R_{\text{merge}} = 3.15\%$ ) according to the symmetry of the  $C2/c$  space group. The refinement was carried out starting from the atomic coordinates of diopside (Clark et al. 1969). Following the results obtained by Harlow (1996) and Bindi et al. (2002), K was assumed to substitute for Ca in M2. Because Ca and K (M2 site), and Mg and Al (M1 site), have similar atomic numbers we decided to refine an unconstrained site occupancy using Ca in M2 and Al in M1; by means of some anisotropic full-matrix least-squares cycles, the refinement quickly converged to  $R = 2.26\%$  for 869 observed reflections [according to the criterion  $F_o > 4\sigma(F_o)$ ]. The scattering curves for neutral Ca, Al, Si, and O were taken from *International Tables for X-ray Crystallography* (Ibers and Hamilton 1974). The site-occupancy refinement for the M2 and M1 sites led to a mean electron number of 19.9 and 12.7, respectively. The inspection of the difference Fourier map revealed maximum positive and negative peaks of 0.55 and 0.49  $e/\text{Å}^3$ , respectively. Fractional atomic coordinates and anisotropic-displacement parameters are shown in Table 2. Table 3<sup>1</sup> lists the observed and calculated structure factors.

## CHEMICAL COMPOSITION

The same crystal used for the structure refinement was analysed by means of a Jeol JXA-8600 electron microprobe. Major and minor elements were determined at 15 kV accelerating voltage and 10 nA beam current, with variable counting times: 10 s were used for Na; 15 s for other major elements; and 40 s for the minor elements Fe, K, Mn, Ti, and Cr. The matrix correction was performed with the Bence and Albee (1968) program as modified by Albee and Ray (1970). Replicate analyses of augite USNM 122142 were used to check ac-

<sup>1</sup>For a copy of Table 3, document item AM-03-025, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items may also be available on the American Mineralogist web site at <http://www.minsocam.org>.

**TABLE 2.** Fractional atomic coordinates and anisotropic displacement parameters  $U_{ij}$  ( $\text{\AA}^2$ ) for KOK-1

	$x/a$	$y/b$	$z/c$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$	$U_{eq}$
M2	0	0.30131(4)	0.25000	0.0124(2)	0.0105(2)	0.0064(1)	0	-0.0035(1)	0	0.0110(1)
M1	0	0.90339(6)	0.25000	0.0095(3)	0.0091(3)	0.0067(3)	0	0.0016(2)	0	0.0086(2)
T	0.28752(3)	0.09211(3)	0.23187(6)	0.0073(1)	0.0083(2)	0.0051(1)	-0.0020(1)	0.0022(1)	0.0006(1)	0.0068(1)
O1	0.1148(1)	0.0867(1)	0.1462(2)	0.0074(3)	0.0117(4)	0.0119(4)	0.0006(2)	0.0031(3)	0.0007(3)	0.0103(2)
O2	0.3614(1)	0.2496(1)	0.3201(2)	0.0137(4)	0.0117(4)	0.0119(4)	-0.0074(3)	0.0066(3)	0.0004(3)	0.0118(2)
O3	0.3490(1)	0.0191(1)	0.9871(2)	0.0115(4)	0.0145(4)	0.0091(3)	-0.0062(3)	0.0025(3)	-0.0061(3)	0.0118(2)

curacy and precision. The estimated analytical precision is:  $\pm 0.02$  for CaO, FeO, and MgO;  $\pm 0.03$  for SiO<sub>2</sub> and TiO<sub>2</sub>;  $\pm 0.05$  for Cr<sub>2</sub>O<sub>3</sub>;  $\pm 0.06$  for K<sub>2</sub>O and Na<sub>2</sub>O;  $\pm 0.07$  for MnO; and  $\pm 0.1$  for Al<sub>2</sub>O<sub>3</sub>. The standards employed were: olivine (Mg), diopside (Ca), albite (Al, Si, Na), bustamite (Mn), ilmenite (Fe, Ti), sanidine (K), and chromite (Cr). The KOK-1 crystal was found to be homogeneous within the analytical error. The average chemical composition (eight analyses on different spots) is reported in Table 4 along with those of other selected Kcpx (Harlow 1996; Bindi et al. 2002). On the basis of six oxygen atoms, the formula of KOK-1 is (Ca<sub>0.61</sub>Fe<sub>0.13</sub>Mg<sub>0.04</sub>Mn<sub>0.01</sub>K<sub>0.17</sub>Na<sub>0.05</sub>)(Al<sub>0.61</sub>Mg<sub>0.39</sub>)(Si<sub>1.61</sub>Al<sub>0.39</sub>)O<sub>6.00</sub>. The mean electron numbers calculated for the site population obtained on the basis of the chemical data (19.9 for the M2 site and 12.6 for the M1 site) are in excellent agreement with those from the site occupancy refinement (19.9 and 12.7 respectively).

### CRYSTAL CHEMICAL REMARKS

On the whole, the crystal structure of KOK-1 refined in this study is topologically identical to that of the other  $C2/c$  clinopyroxenes (Cameron and Papike 1981, and references therein). Table 5 reports selected bond distances and angles for KOK-1 compared with those of other selected clinopyroxenes (Cameron et al. 1973; Harlow 1996; Bindi et al. 2002). As already pointed out by Harlow (1996) and Bindi et al. (2002), K was found to enter the M2 site.

The M2 site in KOK-1 is dominated by Ca (0.61 atoms per formula unit = afu), K (0.17 afu), and Fe<sup>2+</sup> (0.13 afu), with minor amounts of Na, Mg, and Mn ( $\Sigma_{Na,Mg,Mn} = 0.09$  afu). The value of the  $\langle M2-O \rangle$  distance (2.502 Å) is intermediate between that of a natural K-rich diopside (2.504 Å; Harlow 1996) and that of pure diopside (2.498 Å; Cameron et al. 1973). Despite the higher content of K<sub>2</sub>O for KOK-1 (3.61 wt%) with respect to that of K2 (1.57 wt%; Bindi et al. 2002), we observed the same value of the  $\langle M2-O \rangle$  distance (2.502 Å). This similarity is probably due to the combined effect of the lower Ca<sub>M2</sub> and higher (Mg + Fe)<sub>M2</sub> content in the present sample. As already outlined by Bindi et al. (2002) for the synthetic K-rich crystals, the increase of the M2-O distances in KOK-1 is not isotropic. The longest distances, in particular M2-O3C1, show the greatest increase whereas the M2-O1 distance shortens only slightly.

The most prominent feature accompanying the entry of K in M2 is the induced geometrical modification of the adjacent M1 site. The large K cation induces a strong increase of the M1-polyhedral volume (11.97 Å<sup>3</sup>) and of the  $\langle M1-O \rangle$  distance (2.085 Å). This value is notably larger than 1.989 Å, calculated on the basis of the site occupancy. This feature is evident from Figure 1, where the observed  $\langle M1-O \rangle$  distances are plotted against the calculated  $\langle M1-O \rangle$  distances for several  $C2/c$

**TABLE 4.** Electron microprobe analyses (means and range in wt% oxides) and atomic ratios (on the basis of six oxygen atoms) for KOK-1 and comparisons with other Kcpx from literature

	KOK-1	range	K1	K2	K18a
SiO <sub>2</sub>	43.92	43.12–44.09	54.55	53.71	54.3
TiO <sub>2</sub>	0.03	0.00–0.07	–	–	0.01
Al <sub>2</sub> O <sub>3</sub>	23.15	22.97–23.37	7.08	4.95	0.68
Cr <sub>2</sub> O <sub>3</sub>	0.02	0.00–0.05	–	–	2.44
Fe <sub>2</sub> O <sub>3</sub>	–	–	–	–	0.17
FeO	4.12	3.95–4.28	–	–	1.76
MnO	0.29	0.19–0.38	–	–	0.08
MgO	7.84	7.11–8.06	13.93	16.51	17.5
CaO	15.66	15.01–15.97	19.46	23.21	20.3
Na <sub>2</sub> O	0.66	0.54–0.74	–	–	0.33
K <sub>2</sub> O	3.61	3.55–3.68	5.00	1.57	1.57
Total	99.30	–	100.02	99.95	99.1
			<b>T site</b>		
Si	1.607	–	1.968	1.935	1.992
Al	0.393	–	0.032	0.065	0.008
			<b>M1 site</b>		
Mg	0.392	–	0.731	0.855	0.880
Fe <sup>2+</sup>	–	–	–	–	0.024
Al	0.606	–	0.269	0.145	0.021
Fe <sup>3+</sup>	–	–	–	–	0.005
Cr	0.001	–	–	–	0.070
Ti	0.001	–	–	–	0.000
			<b>M2 site</b>		
Ca	0.614	–	0.752	0.896	0.798
Fe <sup>2+</sup>	0.126	–	–	–	0.036
Mg	0.036	–	0.018	0.032	0.070
Mn	0.009	–	–	–	0.000
K	0.168	–	0.230	0.072	0.073
Na	0.047	–	–	–	0.023
$\epsilon_{M1}$	12.6	–	12.3	12.1	13.3
$\epsilon_{M2}$	19.9	–	19.6	19.7	19.4
charge	12.001	–	12.007	12.008	11.992

Note: K1 and K2 from Bindi et al. (2002); K18a from Harlow (1996).

clinopyroxenes. The calculated  $\langle M1-O \rangle$  distances were computed using  $\langle Mg-O \rangle = 2.081$  Å, Bruno et al. 1982;  $\langle Al-O \rangle = 1.930$  Å,  $\langle Ti-O \rangle = 1.960$  Å, Dal Negro et al. 1982;  $\langle Cr-O \rangle = 2.020$  Å, Ungaretti et al. 1981;  $\langle Fe^{2+}-O \rangle = 2.130$  Å,  $\langle Fe^{3+}-O \rangle = 2.025$  Å, Cameron et al. 1973). The values for KOK-1 (this study), and K1 and K2 (Bindi et al. 2002) clearly fall off the main trend. It can be noted, however, that the value for K1 (K = 0.23 afu) deviates less from the trend than that of KOK-1 (K = 0.17 afu). This feature can be due to the different Al content in the tetrahedral site (0.03 and 0.39 afu for K1 and KOK-1, respectively). A higher proportion of Al<sub>T</sub> leading a chain of larger tetrahedra, indeed, might favour an enlargement of the M1 site as well.

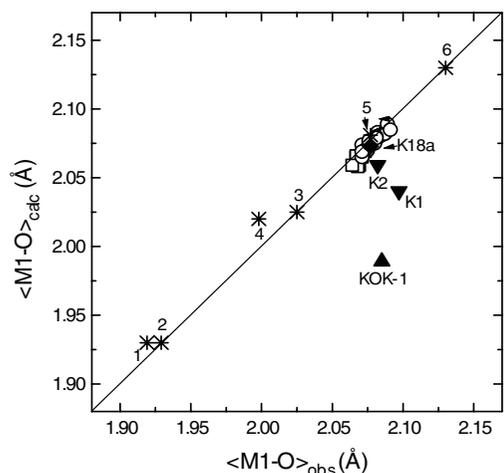
Significant variations are observed for the T site, as well. The crystal KOK-1 exhibits a  $\langle T-O \rangle$  distance (1.640 Å) notably lower than that expected for Al-rich tetrahedra (1.665 Å,

**TABLE 5.** A comparison of selected bond distances (Å) and inter-atomic angles (°)

	KOK-1	K1	K2	K18a	Di <sub>100</sub>
<b>M2 site</b>					
M2-O2	2.347(1)	2.338(1)	2.318(1)	2.338(2)	2.353(3)
M2-O1	2.358(1)	2.342(1)	2.344(1)	2.375(3)	2.360(1)
M2-O3C1	2.601(1)	2.789(1)	2.612(1)	2.574(2)	2.561(2)
M2-O3C2	2.704(1)	2.796(1)	2.734(1)	2.729(2)	2.718(2)
Mean	2.502	2.566	2.502	2.504	2.498
l $\rho$	25.86	28.09	25.85	25.89	25.76
<b>M1 site</b>					
M1-O2	2.032(1)	2.045(1)	2.047(1)	2.047(2)	2.050(1)
M1-O1A1	2.137(1)	2.139(1)	2.117(1)	2.126(1)	2.115(1)
M1-O1A2	2.086(1)	2.106(1)	2.084(1)	2.057(1)	2.065(2)
Mean	2.085	2.097	2.082	2.077	2.077
l $\rho$	11.97	12.17	11.94	11.84	11.85
$\sigma^2$ (oct)	22.89	22.41	18.74	18.77	17.37
$\lambda$ (oct)	1.0072	1.0069	1.0057	1.0058	1.0053
<b>T site</b>					
T-O2	1.591(1)	1.595(1)	1.586(1)	1.594(2)	1.585(1)
T-O1	1.625(1)	1.642(1)	1.616(1)	1.610(2)	1.602(2)
T-O3A1	1.648(1)	1.603(1)	1.635(1)	1.665(2)	1.665(2)
T-O3A2	1.694(1)	1.638(1)	1.681(1)	1.683(2)	1.687(2)
T-Onbr	1.608	1.619	1.601	1.602	1.594
T-Obr	1.671	1.621	1.658	1.674	1.676
mean	1.640	1.620	1.629	1.638	1.635
l $\rho$	2.246	2.156	2.205	2.238	2.221
$\sigma^2$ (tet)	20.62	31.93	20.10	25.39	28.56
$\lambda$ (tet)	1.0053	1.0079	1.0051	1.0059	1.0067
$e_{M1}$	12.7	12.0	12.2	13.2	12.0
$e_{M2}$	19.9	19.8	19.7	19.5*	20.0
O3-O3-O3	165.25(1)	158.68(1)	165.51(1)	165.9(1)	166.4(1)
Si-O3-Si	136.62(1)	146.50(1)	139.28(1)	136.4(1)	135.93(9)

Notes: KOK-1 this study; K1 and K2 from Bindi et al. (2002); K18a from Harlow (1996); Di<sub>100</sub> from Cameron et al. (1973). The mean quadratic elongation ( $\lambda$ ) and the angle variance ( $\sigma^2$ ) were computed according to Robinson et al. (1971).

\*  $e_{M2 + M2'}$ .



**FIGURE 1.** Values of the observed  $\langle M1-O \rangle$  distances plotted against the calculated  $\langle M1-O \rangle$  distances for several  $C2/c$  clinopyroxenes. Solid upward-triangle refers to the natural clinopyroxene crystal of this study (KOK-1); solid downward-triangles refer to synthetic ultrapotassic clinopyroxenes K1 and K2 (Bindi et al. 2002); filled diamond refers to natural K-rich diopside K18a (Harlow 1996). Open symbols are as follows: squares refer to natural clinopyroxenes from Monte Vulture Volcano (Bindi et al. 1999), circles refer to natural clinopyroxenes from ultrapotassic rocks from Central Italy (Cellai et al. 1994); stars (1–6) refer to pure end-members reported by Cameron et al. (1973): 1 = spodumene, 2 = jadeite, 3 = acmite, 4 = ureyite, 5 = diopside, 6 = hedenbergite.

considering a tetrahedral occupancy of  $Si_{1.61}Al_{0.39}$ ). The low value of the mean tetrahedral distance for KOK-1 is due to the shortening of T-O3A1 caused by a lengthening of the M2-O3C1 bond length. An increase of the M2-O3 distances indeed, corresponds to a decrease of the only other bond distance involving O3 (i.e., T-O3), in order to maintain its charge balance.

Harlow (1996) proposed that large K cation 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 was contradicted by the structural study on synthetic Kcpx carried out by Bindi et al. (2002): only a minor amount of  $Mg_{M2}$  was found in the K1 and K2 crystals. The low Mg content also accounted for the absence of the M2' site in the structures of these crystals. In the sample studied here, although some cations smaller than Ca (e.g., Mg and  $Fe^{2+}$ ) are present, no evidence for the additional M2' position (Rossi et al. 1987) was found. A careful analysis of the shape of the electron density at M2, as well as of the anisotropic displacement parameters of M2, did not reveal substantial differences between K1 and KOK-1.

#### ORIGIN OF THE ULTRA-POTASSIC CPX INCLUSIONS IN GARNET

Unfortunately, we do not have data on the composition of garnet in contact with the unique clinopyroxene. However, the striking difference in composition between this clinopyroxene inclusion and the other clinopyroxenes from the rock implies that this Kcpx probably is not in thermodynamic equilibrium with other minerals in the rock. Only qualitative speculation on the  $P$ ,  $T$ , and bulk composition of its formation is possible.

The Mg no. of the Kcpx (77) is significantly higher than the Mg no. of other clinopyroxenes of the rock, and other Kcpx inclusions in garnet (38–41) as well. However, the Mg no. is close to that of the Kcpx (85–95) from some Mg-rich Grt-Cpx and dolomitic carbonate-silicate rocks of the Kumdy-Kol locality (e.g., Sobolev and Shatsky 1990; Lavrova et al. 1999). The presence of Mg-rich Kcpx in a relatively Fe-rich rock implies a genetic similarity among these groups of rocks. A high CaTs content of the Kcpx implies its crystallization at high temperature in the absence of garnet because the equilibrium  $2Grs + Prp = 3CaTs + 3Di$  is displaced significantly to the right with increasing temperature. In addition, the extremely high K content of Kcpx is evidence for its crystallization in equilibrium with the essentially K-rich melt or fluid at high pressure (>5 GPa).

Potassic Kcpx with  $K_2O > 3.0$  wt% was synthesized in some ultra-potassic systems (e.g., Harlow 1997, 1999; Chudinovskikh et al. 2001; Safonov et al. 2002) over the temperature range of 1200–1600 °C and pressure range of 7–11 GPa. The high content of  $K_2O$  in the coexisting melts (11–14 wt% in aluminosilicate melt and 14–33 wt% in carbonate melt/fluid) is the major characteristic of the systems involving Kcpx (e.g., Harlow 1997; Safonov et al. 2002). Another characteristic feature of the melts coexisting with the synthetic Kcpx is relatively high  $SiO_2$  content (activity), which provokes the formation of the Ca-Eskola component instead of the Ca-Tschermak end-member (e.g., Harlow 1999; Chudinovskikh et al. 2001; Safonov et al. 2002). Taking into account these observations, a possible reason for the formation of CaTs-rich Kcpx in the Kokchetav rocks is the

low SiO<sub>2</sub> content (activity) and, probably, the high Al<sub>2</sub>O<sub>3</sub> content in the coexisting melt/fluid.

Discussion on the origin of this K-rich melt/fluid in the Kokchetav Complex is beyond the present study. However, occurrence of such Kcpx agrees with the hypothesis that Kcpx of both the Grt-Cpx and carbonate-silicate rocks from the Kokchetav Complex was crystallized at liquidus of single deep-seated K-rich carbonate-silicate magma (Perchuk and Yapaskurt 1998; Perchuk et al. 2002). From this point of view, we can conclude that the unique Al-rich Kcpx is a relic of the earliest high-temperature (probably liquidus) crystallization of a K- and Al-rich silica undersaturated melt at pressures above 5 GPa.

### ACKNOWLEDGMENTS

The authors thank Filippo Olmi (CNR—Istituto di Geoscienze e Georisorse sez. di Firenze) for his help in the microprobe analyses. The study was supported by M.U.R.S.T., cofinanziamento 2001, project “Structural complexity and properties of minerals: microstructures, modularities, modulations”, the CNR—Istituto di Geoscienze e Georisorse sez. di Firenze, the Russian Foundation for Basic Research (project 01-05-64775), the Program for young scientists of the Russian Academy of Science (project no. 323), the Program for Support of Young Scientists of the Russian Academy of Science, the Program “Leading Russian Scientific Schools” (project 00-15-98519). We are also grateful to Roberta Oberti, George Harlow, Robert Downs, and Robert Dymek for their careful and helpful reviews.

### REFERENCES CITED

- Albee, A.L. and Ray, L. (1970) Correction factors for electron probe analysis of silicate, oxides, carbonates, phosphates, and sulphates. *Analytical Chemistry*, 48, 1408–1414.
- Bence, A.E. and Albee, A.L. (1968) Empirical correction factors for the electron microanalysis of silicate and oxides. *Journal of Geology*, 76, 382–403.
- Bindi, L., Cellai, D., Melluso, L., Conticelli, S., Morra, V., and Menchetti, S. (1999) Crystal chemistry of clinopyroxene from alkaline undersaturated rocks of the Monte Vulture Volcano, Italy. *Lithos*, 46, 259–274.
- Bindi, L., Safonov, O.G., Litvin, Y.A., Perchuk, L.L., and Menchetti, S. (2002) Ultrahigh potassium content in the clinopyroxene structure: an X-ray single-crystal study. *European Journal of Mineralogy*, 14, 929–934.
- Bishop, F.C., Smith, J.V., and Dawson, J.B. (1978) Na, K, P and Ti in garnet, pyroxene and olivine from peridotite and eclogite xenoliths from African kimberlites. *Lithos*, 11, 155–173.
- Bruno, E., Carbonin, S., and Molin, G. (1982) Crystal structure of Ca-rich clinopyroxenes on the CaMgSi<sub>2</sub>O<sub>6</sub>–Mg<sub>2</sub>Si<sub>2</sub>O<sub>6</sub> join. *Tschermak's Mineralogische und Petrographische Mitteilungen*, 29, 223–240.
- Cameron, M., Sueno, S., Prewitt, C.T., and Papike, J.J. (1973) High-Temperature crystal chemistry of acmite, diopside, hedenbergite, jadeite, spodumene, and ureyite. *American Mineralogist*, 58, 594–618.
- Cameron, M. and Papike, J.J. (1981) Structural and chemical variations in pyroxenes. *American Mineralogist*, 66, 1–50.
- Cellai, D., Conticelli, S., and Menchetti, S. (1994) Crystal-chemistry of clinopyroxenes from potassic and ultrapotassic rocks in Central Italy: implications on their genesis. *Contribution to Mineralogy and Petrology*, 116, 301–315.
- Chudinovskikh, L.T., Zharikov, V.A., Ishbulatov, R.A., and Matveev, Yu.A. (2001) On the mechanism of incorporation of ultra-high amounts of potassium into clinopyroxene at high pressure. *Doklady Rossiiskoi Akademii Nauk, Earth Sciences*, 380, 1–4.
- Clark, J.R., Appleman, D.E., and Papike, J.J. (1969) Crystal-chemical characterization of clinopyroxenes based on eight new structure refinements. *Mineralogical Society of America Special Paper*, 2, 31–50.
- Dal Negro, A., Carbonin, S., Molin, G., Cundari, A., and Piccirillo, E.M. (1982) Intracrystalline cation distribution in natural clinopyroxenes of tholeiitic, transitional and alkaline basaltic rocks. In S.K. Saxena, Ed., *Advances in Physical Geochemistry*, vol. 2, 117–150. Springer, Berlin.
- Dobretsov, N.I., Shatsky V.S., and Sobolev, N.V. (1995) Comparison of the Kokchetav and Dabie Shan metamorphic complexes: coesite- and diamond-bearing rocks and UHP-HP accretional-collisional events. *International Geology Review*, 37, 636–656.
- Dobrozhineckaya, L.F., Braun, N.V., and Sheshkel, G.G. (1994) Geology and structure of diamond-bearing rocks of the Kokchetav massif (Kazakhstan). *Tectonophysics*, 233, 293–313.
- Ghorbani, M.R. and Middlemost, E.A.K. (2000) Geochemistry of pyroxene inclusions from the Warrumbungle Volcano, New South Wales, Australia. *American Mineralogist*, 85, 1349–1367.
- Harlow, G.E. and Veblen, D.R. (1991) Potassium in clinopyroxene inclusions from diamonds. *Science*, 251, 652–655.
- Harlow, G.E. (1996) Structure refinement of a natural K-rich diopside: the effect of K on the average structure. *American Mineralogist*, 81, 632–638.
- (1997) K in clinopyroxene at high pressure and temperature: an experimental study. *American Mineralogist*, 82, 259–269.
- (1999) Interpretation of Kcpx and CaEs in clinopyroxene from diamond inclusions and mantle samples. *Proceedings of Seventh International Kimberlite Conference*, Cape Town, 1, 321–331.
- Ibers, J.A. and Hamilton, W.C. Eds. (1974) *International Tables for X-ray Crystallography*, vol. IV, 366 p. Kynock, Dordrecht, the Netherlands.
- Jaques, A.L., O'Neill, H.St.C., Smith, C.B., Moon, J., and Chappell, B.W. (1990) Diamondiferous peridotite xenoliths from the Argyle (AK1) lamproite pipe, Western Australia. *Contribution to Mineralogy and Petrology*, 104, 255–276.
- Lavrova, L.D., Pechnikov, V.A., Pleshakov, A.M., Nadezhdina, E.D., and Shukolyukov, Yu.A. (1999) New genetic type of diamond-bearing deposits. *Moscow, Nauchnyi Mir*, 221 p.
- North, A.C.T., Phillips, D.C., and Mathews, F.S. (1968) A semiempirical method of absorption correction. *Acta Crystallographica*, A24, 351–359.
- Perchuk, L.L. and Yapaskurt, V.O. (1998) Mantle-derived ultrapotassic liquids. *Russian Geology and Geophysics*, 39, 1746–1755.
- Perchuk, L.L., Yapaskurt, V.O., and Okay, A. (1995) Comparative petrology of diamond-bearing metamorphic complexes. *Petrology*, 3, 238–276.
- Perchuk, L.L., Sobolev, N.V., Yapaskurt, V.O., and Shatsky, V.S. (1996) Relics of potassium-bearing pyroxenes from diamond-free pyroxene-garnet rocks of the Kokchetav massif, northern Kazakhstan. *Doklady Rossiiskoi Akademii Nauk*, 348, 790–795.
- Perchuk, L.L., Safonov, O.G., Yapaskurt, V.O., and Barton, J.M. Jr. (2002) Crystal-melt equilibria involving potassium-bearing clinopyroxene as indicators of mantle-derived ultrahigh-potassic liquids: an analytical review. *Lithos*, 60(3–4), 89–111.
- Reid, A.M., Brown, R.W., Dawson, J.B., Whitfield, G.G., and Siebert, J.C. (1976) Garnet and pyroxene compositions in some diamondiferous eclogites. *Contributions to Mineralogy and Petrology*, 58, 203–220.
- Robinson, K., Gibbs, G.V., and Ribbe, P.H. (1971) Quadratic elongation: a quantitative measure of distortion in coordination polyhedra. *Science*, 172, 567–570.
- Rossi, G., Oberti, R., Dal Negro, A., Molin, G., and Mellini, M. (1987) Residual electron density at the M2 site in C2/c clinopyroxenes: relationships with bulk chemistry and sub-solidus evolution. *Physics and Chemistry of Minerals*, 14, 514–520.
- Safonov, O.G., Litvin, Yu.A., and Perchuk, L.L. (2001) Potassium-bearing clinopyroxene in the system diopside-leucite at 7 GPa: composition and phase relations. *Proceedings of the 3<sup>rd</sup> EMU Workshop. Solid Solutions in silicate and oxide systems of geological importance*. Ed: C.A. Geiger, Lubeck, 33.
- Safonov, O.G., Litvin, Yu.A., and Perchuk, L.L. (2002) Phase equilibria and composition of potassium-bearing clinopyroxene in the system CaMgSi<sub>2</sub>O<sub>6</sub>–KAlSi<sub>2</sub>O<sub>6</sub> at P = 7 GPa. *Doklady Rossiiskoi Akademii Nauk*, 382, 379–383.
- Shatsky, V.S., Jagoutz, E., Sobolev, N.V., Kozmenko, O.A., Parkhomenko, V.S., and Troesch, M. (1999) Geochemistry and age of ultrahigh pressure metamorphic rocks from the Kokchetav massif (Northern Kazakhstan). *Contributions to Mineralogy and Petrology*, 137, 185–205.
- Sheldrick, G.M. (1993) SHELXL-93: A new structure refinement program. *University of Göttingen, Germany*.
- Sobolev, N.V. and Shatsky, V.S. (1990) Diamond inclusions in garnets from metamorphic rocks: a new environment for diamond formation. *Nature*, 343, 742–746.
- Ungaretti, L., Smith, D.C., and Rossi, G. (1981) Crystal chemistry by X-ray structure refinement and electron microprobe analysis of a series of sodic-calcic to alkali-amphiboles from the Nybo eclogite pod, Norway. *Bulletin of Mineralogy*, 104, 400–412.

MANUSCRIPT RECEIVED JULY 3, 2002

MANUSCRIPT ACCEPTED NOVEMBER 26, 2002

MANUSCRIPT HANDLED BY ROBERT DYMEK