

Effect of Carbonates on Crystallization and Composition of Potassium-Bearing Clinopyroxene at High Pressures

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In paper [1] devoted to the distribution of potassium between Cpx and carbonate melt, it was stated for the first time that clinopyroxene containing >1 wt % K_2O may crystallize at 1300–1700°C and 5–11 GPa from carbonate liquid containing 14–33 wt % K_2O . KCpx with as much as 5.75 wt % K_2O was obtained in experiments [2–4] as a product of melt crystallization in the Di–Grs– K_2CO_3 and Di–Grs– $K_2Mg(CO_3)_2$ systems at 7 GPa and 1500–1600°C.* Such high K_2O concentrations in Cpx in carbonate–silicate systems suggest a substantial influence of carbonates on incorporation of potassium into clinopyroxenes at high pressures [5]. However, a similar ultrapotassic clinopyroxene (up to 5.6 wt % K_2O) was synthesized later [6] in the Di–Lc system at the same pressure, and this result stimulated a special experimental study focused on the influence of carbonates on crystallization of high-K clinopyroxene. With this fact in mind, we have conducted a series of runs in the $Di_{40}Lc_{60}$ – $Dol_{40}Lc_{60}$ join at 7 GPa. The choice of the system and experimental conditions were dictated by the experimental results in the basic $CaMgSi_2O_6$ – $KAlSi_2O_6$ join at the same pressure [6].

The $CaMgSi_2O_6$ and $KAlSi_2O_6$ gels and crystalline $MgCO_3$ and $CaCO_3$ in stoichiometric proportions of dolomite were used as starting materials. The runs were carried out at 1480–1200°C during 300–150 min

* *Accepted abbreviations:* (Ca-Esk) Eskola Ca-molecule, (Ca-Ts) Tschermak Ca-molecule, (CEn) clinoenstatite, (Cpx) clinopyroxene, (Di) diopside, (Dol) dolomite, (Grs) grossular, (Grt) garnet, (Jd) jadeite, (Kc) K_2CO_3 , (KCC) $K_2Ca(CO_3)_2$, (KMC) $K_2Mg(CO_3)_2$, (KCpx) K-bearing clinopyroxene, (KJd) potassium jadeite, (Lc) leucite, (L_{CS}) carbonate–silicate melt, (NC) Na_2CO_3 , (Phl) phlogopite, (Prp) pyrope, and (SWd) Si-wadeite.

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(table) on an apparatus of anvil-with-hole type with toroidal sealing of a lithographic stone cell [7]. The starting mixtures were placed into $Pt_{60}Rh_{40}$ ampules. The pressure in runs calibrated by standard phase transitions in Bi was set with an accuracy of ± 0.2 GPa [7]. The temperature was controlled with an accuracy of $\pm 20^\circ C$ by calibration (temperature versus current power) curve plotted with a $Pt_{70}Rh_{30}/Pt_{94}Rh_6$ thermocouple. After the runs, the samples were studied with a CamScan MV2300 (VEGA TS 5130MM) electron microscope, and the phase compositions were analyzed with a Link INCA energy-dispersive microprobe at the Laboratory of Electron Microscopy and Microprobe of the Institute of Experimental Mineralogy, Russian Academy of Sciences. SiO_2 , MgO , Al_2O_3 , wollastonite, and microcline were used as standards for the determination of Si, Mg, Al, Ca, and K, respectively.

The results of experiments with participation of dolomite were compared with the results obtained previously in the $Di_{40}Lc_{60}$ join at 1500–1300°C [6]. In products of the previous experiments, the clinopyroxene crystals containing 2.5–4.5 wt % K_2O coexisted with Grt (pyrope–grossular), SWd, and aluminosilicate melt. The (Grt + Cpx) phase assemblage is also typical of most runs with participation of dolomite (table). Phlogopite crystallized in some samples due to the presence of a small amount of water in hygroscopic starting mixtures. A single crystal of high-Al clinopyroxene was detected among numerous garnet grains in products of run 1058 with $Di/Dol = 0.7$ (table). Only very small garnet crystals were found in the homogeneous carbonate–silicate quenched matrix (Fig. 1a) in products of the run performed at $Di/Dol > 0.7$ and $T > 1400^\circ C$. Cpx joins Grt at lower temperatures (Fig. 1b). Figure 2 demonstrates relationships between Cpx and Grt liquidus temperatures in the $Di_{40}Lc_{60}$ – $Dol_{40}Lc_{60}$ join. The diagram was plotted taking into account the crystallization sequence in the $Di_{40}Lc_{60}$ join [6]. As can be seen from this figure, the addition of dolomite expands the garnet stability field and reduces the Cpx field.

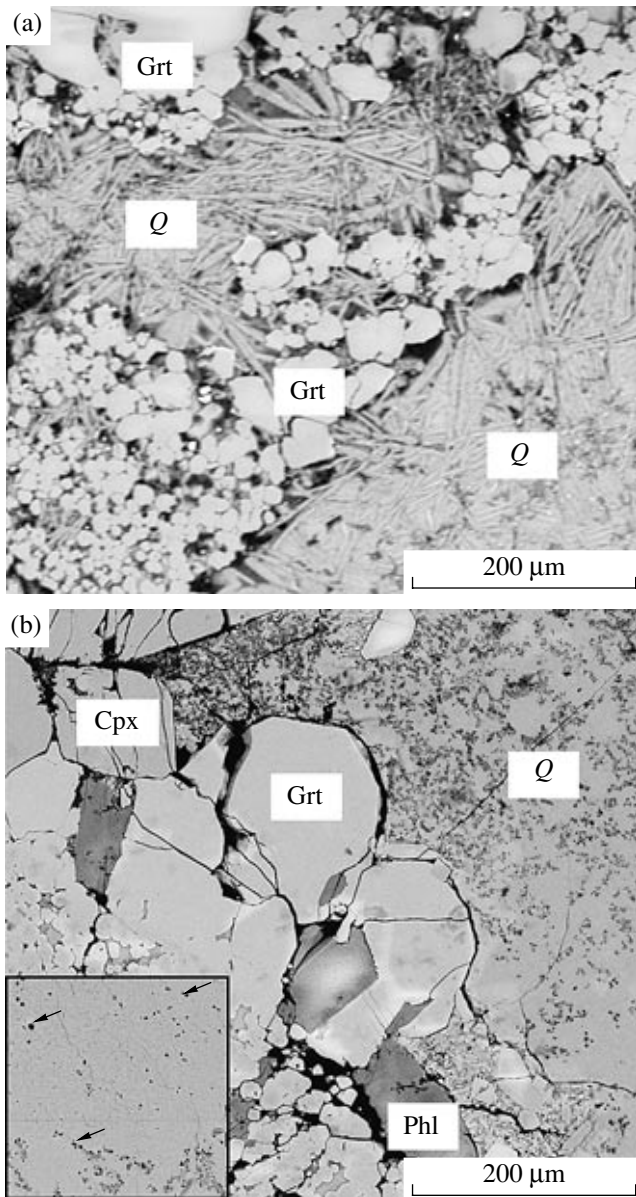
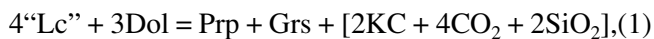


Fig. 1. Structural relationships of phases in products of runs in the $\text{Di}_{40}\text{Lc}_{60}$ - $\text{Dol}_{40}\text{Lc}_{60}$ join at 7 GPa. (a) Grains of pyrope-grossular garnet in products of the carbonate-silicate melt (Q) quenching near the liquidus join (run 1058, $\text{Di}_{28}\text{Dol}_{12}\text{Lc}_{60}$ join, $T = 1480^\circ\text{C}$); (b) (Grt + Cpx) assemblage that coexists with phlogopite and potassic carbonate-silicate melt (Q) (run 1378, $\text{Dol}_{40}\text{Lc}_{60}$, $T = 1200^\circ\text{C}$). Inset demonstrates pores (indicated by arrows) in quenched carbonate-silicate melt that testify to the release of dissolved CO_2 .

The garnet crystallization at the liquidus of the $\text{Dol}_{40}\text{Lc}_{60}$ mixture may schematically be presented as



where the components in brackets denote a K_2O -rich carbonate-silicate melt. The reaction is shifted to the right, because the potassium aluminosilicate (“Lc”)

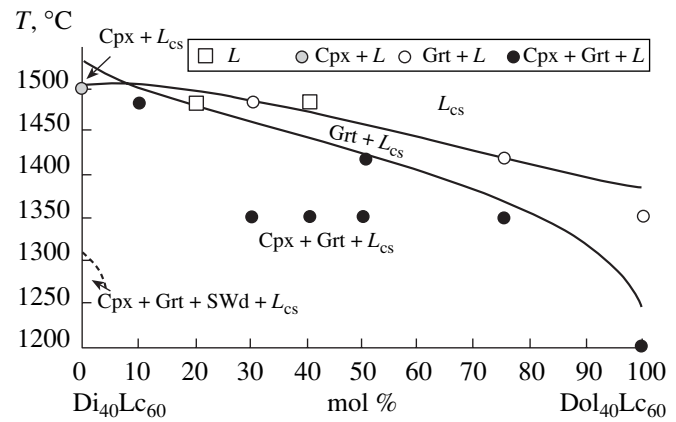
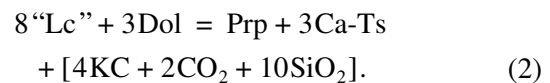


Fig. 2. Cpx and Grt liquidus lines in the $\text{Di}_{40}\text{Lc}_{60}$ - $\text{Dol}_{40}\text{Lc}_{60}$ join at 7 GPa.

molecule becomes unstable in the presence of dolomite and enriches the carbonate-silicate melt with K_2O . The K_2O concentration varies from 19 to 34 wt % (table). The K_2O content in melt markedly increases with bulk dolomite content in the starting mixture (Fig. 3a). The average grossular content in garnet amounts to 50 mol % and increases to 65–75 mol % in garnets that crystallize from a $\text{Dol}_{40}\text{Lc}_{60}$ mixture (table). The presence of CO_2 dissolved in melt is identified by the occurrence of numerous rounded pores in carbonate-silicate melt produced in the course of gas release during the quenching (see inset in Fig. 1b).

The relationships between the KJd and Ca-Ts contents in Cpx and the dolomite content in the starting mixtures are shown in Figs. 3b and 3c. The clinopyroxenes that crystallize from dolomite-rich mixtures are markedly enriched in Ca-Ts and depleted in KJd. Clinopyroxenes contain Ca-Esk in both carbonate-free and carbonate-bearing runs. However, no Ca-Esk was detected in clinopyroxenes in the runs with admixtures containing more than 20 mol % of dolomite. The growth of Ca-Ts content in clinopyroxenes situated in the equilibrium with carbonate-silicate melt as a function of the initial dolomite content in the system may be described by the reaction similar to (1):



This effect probably depends strongly on the composition of the carbonate component. Like in reaction (1), the concentration of Ca-Ts in clinopyroxene provokes the enrichment of the equilibrium melt in alkaline components. In other words, the direct correlation must exist between the Ca-Ts content in clinopyroxene and the potassium content in melts. Such a correlation is actually revealed from comparison of Figs. 3a and 3c. The positive correlation between Na_2CO_3 content in the melt and Ca-Ts content in the coexisting omphacite was established in the experiments on melting carbon-

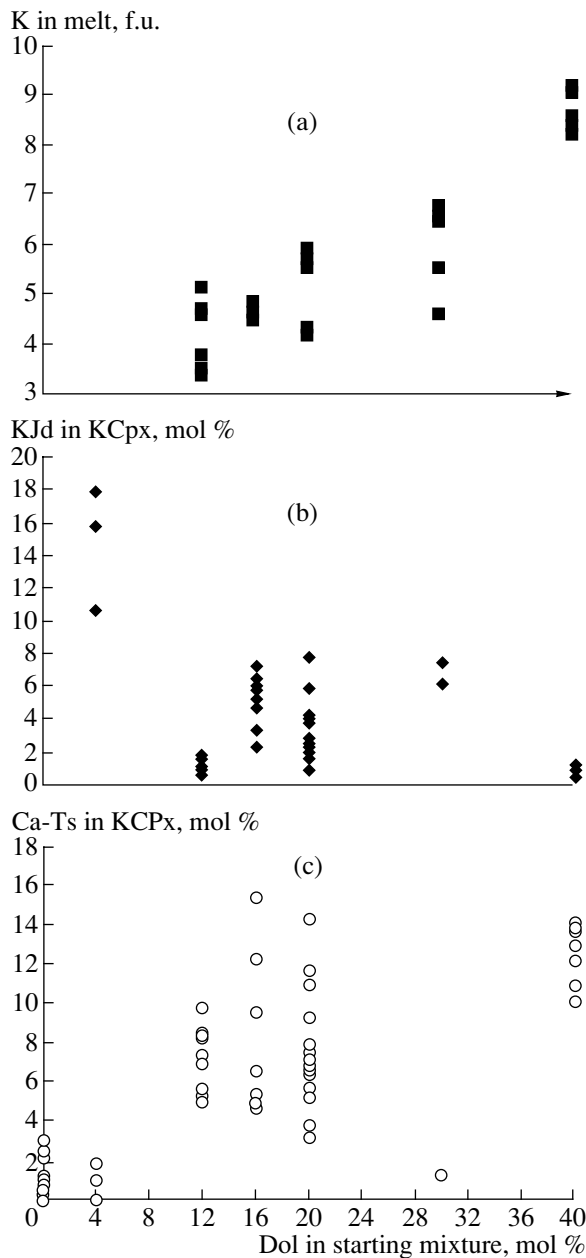
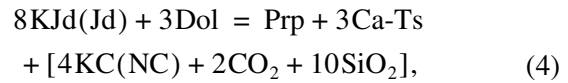
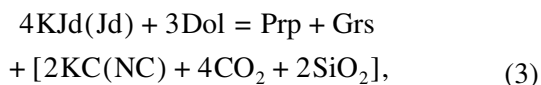


Fig. 3. (a) Positive correlation of K content in the carbonate–silicate melt (f.u. based on 24 oxygen atoms), (b) negative correlation of KJd, mol. % in coexisting clinopyroxene, and (c) positive correlation of Ca-Ts content, mol. % in clinopyroxene with the bulk dolomite content.

ated eclogite at 2.5–5.5 GPa [8] as a result of interaction of jadeite with dolomite components of the melt.

However, the predominance of alkali carbonates in melt shifts equilibrium (2) to the left, i.e., toward the clinopyroxenes with a lower Ca-Ts content. Eqs. (1) and (2) rewritten as



should be shifted to the left, thus leading to the enrichment of clinopyroxene in KJd or Jd. Indeed, the clinopyroxenes that contain less than 4 mol % Ca-Ts crystallize in the systems with an excess of alkali carbonates (KC, KCC, and KMC). However, KCpx containing more than 2 wt % K_2O was obtained in most of these systems [1–4]. Hence, crystallization of KCpx in carbonate–silicate systems requires either an excess of potassium carbonates or the presence of K-rich aluminosilicate melt along with a small amount of alkali-earth carbonates. Thus, crystallization of KCpx is apparently controlled by a degree of saturation of carbonate–silicate melt with potassium. The degree of saturation, in turn, depends on the concentration of carbonate component in the melt. When the carbonate content is relatively low, this melt is saturated with potassium rapidly, leaving an opportunity for buildup of the KJd component in clinopyroxene. If the carbonate content is high, the whole potassium is extracted into the melt, preventing crystallization of KCpx. The saturation of carbonate–silicate melts with potassium depending on dolomite content in the system is clearly seen in Fig. 3a.

The experiments in the $\text{Di}_{40}\text{Lc}_{60}\text{--Dol}_{40}\text{Lc}_{60}$ join confirmed the expansion of the field of garnet stability as a result of dilution of aluminosilicate components with alkali-earth carbonates (Fig. 2). The reactions of garnet crystallization from melt have also been described in other carbonate–silicate systems (see, for example, [9]), where the residual liquid is enriched in alkali metals. Thus, we come to the simple logical conclusion: the crystallization of garnet on the carbonate–silicate melt liquidus fosters the enrichment of residual liquids in alkali metals and shifts their composition toward the alkali carbonates.

The assemblage of clinopyroxene, containing as much as 1.5 wt % K_2O , with dolomite or calcite is known in the garnet–clinopyroxene–carbonate rocks of the Kokchetav Complex in northern Kazakhstan [10]. Therefore, many researchers engaged in genetic models of these rocks place emphasis on alkali carbonate–silicate melts. According to [3, 5, 11], these melts are of the primary mantle origin. However, according to [12], their origin is related to interaction of carbonate rocks with K-rich aluminosilicate melts formed by partial melting of metapelites, and KCpx is considered the mineralogical indicator of such interaction [13]. Our experiments make it possible to constrain the latter hypothesis. As follows from these results, at $P = 4.5\text{--}5.0$ GPa, which is typical of the formation of rocks in the Kokchetav Massif [12], KCpx is formed if the potassic aluminosilicate component prevails over dolomite. Therefore, mass assimilation of carbonate material by aluminosilicate melt is ruled out in the course of KCpx formation in the garnet–clinopyroxene–carbon-

Experimental conditions and average compositions of the phases synthesized in the $\text{Di}_{40}\text{Lc}_{60}\text{-Dol}_{40}\text{Lc}_{60}$ join at 7 GPa

Component	Run 1051, Di/Dol = 0.9, T = 1480°C, τ = 240 min		Run 1054, Di/Dol = 0.5, T = 1480°C, τ = 240 min		Run 1058, Di/Dol = 0.7, T = 1480°C, τ = 240 min		Run 1060, Di/Dol = 0.25, T = 1420°C, τ = 240 min		Run 1362, Di/Dol = 0.25, T = 1350°C, τ = 150 min			
	Grt (4)	Cpx (4)	Grt (3)	Cpx (10)	Q (4)	Grt (7)	Cpx ^a (1)	Q (4)	Grt (2)	Grt (5)	Cpx (2)	Q (5)
SiO ₂	42.12	54.89	42.23	53.69	46.16	42.23	48.07	51.56	40.58	41.83	55.00	43.69
Al ₂ O ₃	23.07	4.52	23.80	3.75	12.96	23.64	15.04	12.52	22.39	23.24	2.64	8.36
MgO	9.31	15.02	15.03	17.18	2.19	16.94	16.26	3.70	9.28	11.71	16.47	1.34
CaO	24.71	21.93	18.68	24.60	2.46	17.58	20.32	4.70	27.68	23.44	24.19	0.92
K ₂ O	0.56	3.64	0.00	0.47	18.48	0.09	0.16	16.67	0.00	0.25	1.47	25.67
Total	99.77	100.00	99.74	99.69	82.25	100.48	99.85	89.15	99.93	100.47	99.77	79.98
Formulas based on the numbers of oxygen atoms indicated below												
O	12	6	12	6	24	12	6	24	12	12	6	24
Si	3.050	1.985	3.000	1.938	8.334	2.975	1.709	8.451	2.966	2.998	1.988	8.631
Al	1.968	0.193	1.992	0.159	2.762	1.962	0.630	2.420	1.928	1.963	0.112	1.950
Mg	1.004	0.809	1.590	0.924	0.586	1.777	0.861	0.902	1.010	1.250	0.887	0.399
Ca	1.916	0.849	1.421	0.951	0.475	1.326	0.773	0.823	2.167	1.799	0.936	0.193
K	0.054	0.168	0.000	0.022	4.257	0.008	0.007	3.484	0.000	0.022	0.068	6.442
Total	7.992	4.004	8.003	3.994	16.414	8.048	3.980	16.080	8.071	8.032	3.991	17.615
End members of clinopyroxene and garnet solid solutions, mol %												
Di		81.7		88.9			48.3				92.0	
Ca-Ts		1.5		6.2			29.1				1.2	
KJd		16.8		2.2			0.7				6.8	
CEn		0.0		2.0			19.9				0.0	
Ca-Esk		0.0		0.7			2.0				0.0	
Grs	65.6		47.2			42.7			68.2	54.3		
Prp	34.4		52.8			57.3			31.8	45.7		

ate rocks. This fact is also supported by very low (<3 mol %) contents of Ca-Ts component in KCpx of the Kokchetav rocks. However, KCpx in rocks of the Kokchetav Complex might crystallize in the equilibrium with liquids initially enriched in alkali carbonates, the relicts of which were found as inclusions in diamonds contained in the same rocks [14, 15].

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