

Safonov O.G.¹, Litvin Yu.A.¹, Perchuk L.L.². Potassium-bearing clinopyroxene in the systems diopside-leucite and diopside-leucite-K₂Ca(CO₃)₂ at P=7 GPa.

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Clinopyroxene containing up to 1.5 wt. % K₂O (*KCpx*) is known as a diamond satellite mineral from kimberlites and limproites [e.g. 6, 10, 12], as well as in ultra-high pressure rocks of the Kokchetav Complex (N. Kazakhstan) [2, 11]. According to natural and experimental data *KCpx* is an indicator both high pressure and high potassium activity in mantle melts or fluids [3, 5, 9].

Cation K, whose radius at normal pressure is 1.51Å, becomes commensurable to Ca (1.12Å) and Na (1.18Å) cations at P>5 GPa. That is a reason for its incorporation into clinopyroxene only at ultra-high pressure. Replacement of Ca by K in the M2 site occurs by the scheme (Mg, Fe)^{M1}Ca^{M2}⇌(Al, Cr)^{M1}K^{M2} [2, 4, 5, 7]. Thus, the system CaMgSi₂O₆-KAlSi₂O₆ is a simplest model for *KCpx*, whose study is necessary for descrip-

tion of thermodynamic properties of the potassium clinopyroxene solid solution.

A purpose of the experimental study of the system CaMgSi₂O₆-KAlSi₂O₆±K₂Ca(CO₃)₂ was to identify phase equilibria with participation of *KCpx*, to determine a maximal solubility of KAlSi₂O₆ component in diopside, and to estimate an influence of carbonate on it. The experiments were carried out at P=7 GPa and T=980–1650°C using an “anvil-with-hole” assembly [1].

The phase diagram for the pseudo-binary system CaMgSi₂O₆-KAlSi₂O₆ was constructed on the basis of the experiments. According to the diagram, *KCpx* (CaMgSi₂O₆-KAlSi₂O₆ solid solution) is a liquidus phase at the KAlSi₂O₆ content in the system below 70 mol. %. The K₂O content in clinopyroxene at liquidus (~1600°C) is up to 2.5 wt. % (see Table). At higher KAlSi₂O₆ content, clinopyroxene disappears and gives place to pyrope-grossular garnet. At solidus (~1300°C), *KCpx* coexisting with garnet (*Grt*), kalsilite and Siwadeite (*SWd*) contains up to 5.5 wt. % K₂O (Fig. 1a, Table). This is the maximal K₂O content in clinopyroxene ever produced experimentally, including carbonate-silicate systems [5, 8]. At T, P, and Di/Lc ratio being equal, K₂O concentration in *KCpx* from the system with 15 mol. % K₂Ca(CO₃)₂ is found to be higher by ~1 wt. % (Fig. 1b, Table) in comparison to the carbonate-free system.

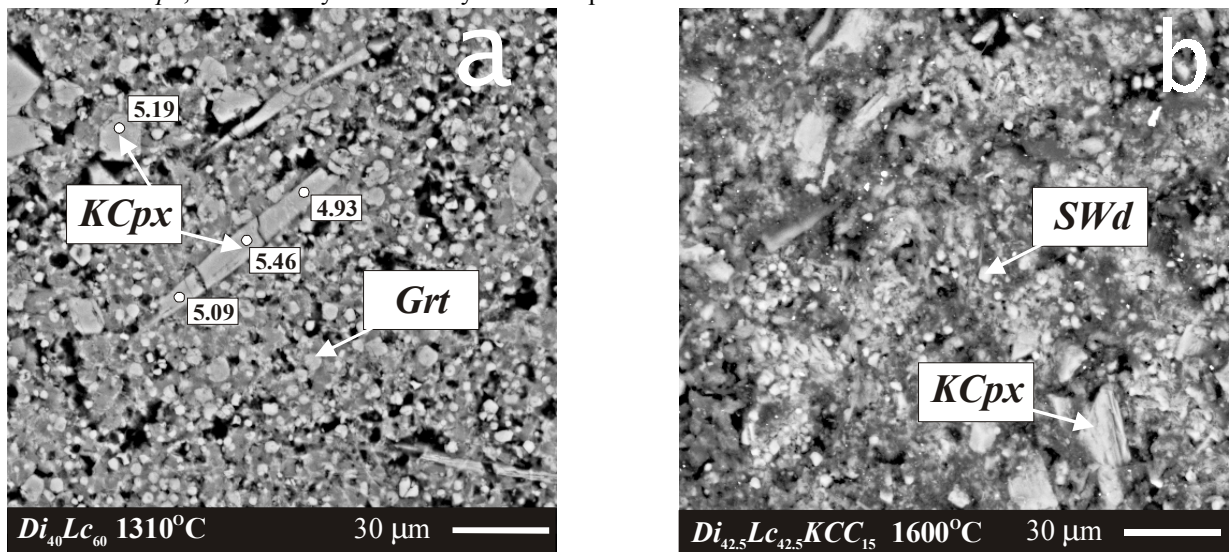


Fig. 1. Potassium-bearing clinopyroxene in the run products in the systems CaMgSi₂O₆-KAlSi₂O₆ and CaMgSi₂O₆-KAlSi₂O₆-K₂Ca(CO₃)₂ at P = 7 GPa. a) Ultra-potassic *KCpx* coexisting with *Grt* in the solidus of the system CaMgSi₂O₆-KAlSi₂O₆. b) *KCpx* coexisting with *SWd* in carbonate matrix in the sub-liquidus of the system CaMgSi₂O₆-KAlSi₂O₆-K₂Ca(CO₃)₂.

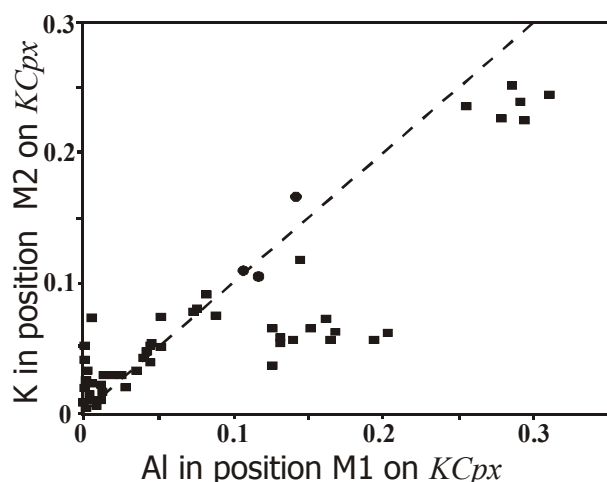


Fig. 2. Correlation between K^{M1} and Al^{M2} in $KCpx$ from the experiments in the systems $CaMgSi_2O_6$ - $KAlSi_2O_6$ (filled squares) и $CaMgSi_2O_6$ - $KAlSi_2O_6$ - $K_2Ca(CO_3)_2$ (filled circles) at $P = 7$ GPa.

Table. Representative analyses of potassium-bearing clinopyroxenes produced experimentally in the systems $CaMgSi_2O_6$ - $KAlSi_2O_6$ and $CaMgSi_2O_6$ - $KAlSi_2O_6$ - $K_2Ca(CO_3)_2$ at $P = 7$ GPa.

| Run N | 688 | | | 650 | | 611 | | 612 | | |
|--------------------------------|--------------------|-------------|-------------|--------------------|-------------|--------------------|-------------|-----------------------|-------------|------------|
| Conditions | $Di_{40}Lc_{60}$, | 1310°C | | $Di_{30}Lc_{70}$, | 1350°C | $Di_{50}Lc_{50}$, | 1600°C | $Di_{42.5}Lc_{42.5}K$ | 1600°C | |
| | | | | | | | | CC_{15} | | |
| SiO ₂ | 54.89 | 54.71 | 54.98 | 54.07 | 54.15 | 55.67 | 56.01 | 55.32 | 54.78 | 55.19 |
| Al ₂ O ₃ | 7.54 | 7.29 | 7.88 | 5.22 | 4.9 | 3.39 | 1.04 | 2.95 | 2.82 | 3.35 |
| MgO | 13.36 | 13.3 | 13.4 | 16.4 | 16.5 | 15.69 | 18.46 | 16.94 | 15.78 | 15.5 |
| CaO | 19.3 | 19.24 | 18.39 | 22.42 | 22.71 | 22.02 | 23.74 | 22.3 | 24.32 | 22.14 |
| K ₂ O | 4.96 | 5.46 | 5.34 | 1.57 | 1.42 | 2.53 | 1.05 | 2.29 | 2.34 | 3.6 |
| Total | 100 | 100 | 100 | 99.67 | 99.67 | 99.29 | 100.31 | 99.8 | 100 | 99.78 |
| Formulae per 6 O atoms | | | | | | | | | | |
| Si | 1.975 | 1.975 | 1.976 | 1.941 | 1.945 | 2.013 | 2.006 | 1.992 | 1.987 | 1.999 |
| Al | 0.319 | 0.31 | 0.334 | 0.221 | 0.207 | 0.144 | 0.044 | 0.125 | 0.121 | 0.143 |
| Mg | 0.716 | 0.715 | 0.717 | 0.877 | 0.883 | 0.845 | 0.985 | 0.908 | 0.841 | 0.836 |
| Ca | 0.746 | 0.744 | 0.708 | 0.862 | 0.873 | 0.853 | 0.911 | 0.86 | 0.945 | 0.859 |
| K | 0.225 | 0.251 | 0.245 | 0.072 | 0.065 | 0.117 | 0.048 | 0.105 | 0.108 | 0.166 |
| Total | 3.978 | 3.995 | 3.98 | 3.973 | 3.973 | 3.972 | 3.994 | 3.99 | 4.002 | 4.003 |
| Al ^{IV} | 0.025 | 0.025 | 0.024 | 0.059 | 0.055 | 0 | 0 | 0.008 | 0.013 | 0.001 |
| Al ^{VI} | 0.294 | 0.285 | 0.31 | 0.162 | 0.152 | 0.144 | 0.044 | 0.117 | 0.107 | 0.142 |
| Mg ^{M1} | 0.706 | 0.714 | 0.69 | 0.838 | 0.848 | 0.856 | 0.956 | 0.883 | 0.893 | 0.86 |
| Mg ^{M2} | 0.01 | 0.003 | 0.027 | 0.039 | 0.035 | 0 | 0.029 | 0.026 | 0 | 0 |

$KCpx$ from the both systems shows a direct correlation of Al^{M1} with K^{M2} (Fig. 2). That corresponds to multi-site isomorphism $Mg^{M1}Ca^{M2} \leftrightarrow Al^{M1}K^{M2}$. These results show, that, apparently, there is no difference between the *mechanisms* of potassium incorporation into $KCpx$ in aluminosilicate and carbonate-silicate systems. Difference in potassium concentrations in $KCpx$ in these systems is due to different properties of coexisting melts, that has been shown earlier [9].

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