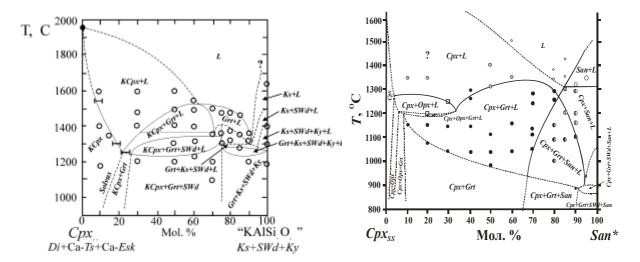
## PHASE EQUILIBRIA IN ULTRA-POTASSIC SYSTEMS AT HIGH PRESSURES

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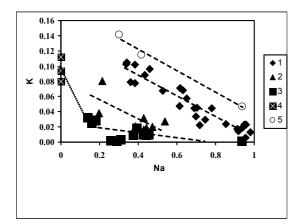
<u>Key words:</u> experimental study, ultra-potassic alumino-silicate, carbonate-silicate and chloride-silicate liquids, potassium-bearing clinopyroxene, liquid immiscibility, mantle

We present a review of recent experimental data on phase equilibria with participation of ultrapotassic (> 10 wt. % of  $K_2O$ ) alumino-silicate, carbonate-silicate, and chloride-silicate melts at P > 3GPa. These melts are three major constituents of liquids included in diamonds from kimberlites [1].



**Fig.1.** Preliminary phase diagrams for the pseudo-binary joins CaMgSi<sub>2</sub>O<sub>6</sub>-KAlSi<sub>2</sub>O<sub>6</sub> at 7 GPa [2] and CaMgSi<sub>2</sub>O<sub>6</sub>-KAlSi<sub>3</sub>O<sub>8</sub> at 6 GPa. Cpx – clinopyroxene (KCpx – potassium-bearing clinopyroxene); Grt – garnet, Ks – kalsilite, Ky – kyanite, Opx – orthopyroxene, San – sanidine, SWd – Si-wadeite.

The characteristic phase of the ultra-potassic systems is potassium-bearing clinopyroxene (*KCpx*). This mineral crystallizes at liquid of alumino-silicate and carbonate-silicate systems. The K<sub>2</sub>O content in Na-free *KCpx* reaches 5.0-5.6 wt. % (23-25 mol. % of KAlSi<sub>2</sub>O<sub>6</sub> or *KJd*) at 7 GPa [2, 3] (Fig. 1a). Presumably, it is the maximal *KJd* content in Na-Fe-free *KCpx* at least for 7 GPa, since at higher *KJd* content the *KCpx* solid solution is unstable being replaced by garnet+K<sub>2</sub>Si<sub>4</sub>O<sub>9</sub> [2]. Concentration of K clinopyroxenes irregularly decreases with decompression (Fig. 2). However, the K<sub>2</sub>O content of 0.5-1.5 wt. %, known for eclogitic clinopyroxenes, can be reached at pressures about 5-6 GPa in equilibrium with the ultra-potassic melts. Cooling assists to accumulation of K in clinopyroxene. Jadeite (*Jd*) and Ca-Tschermak (Ca-*Ts*) components strongly limit the *KJd* content in *KCpx* (Fig. 2).



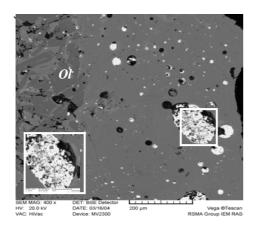
**Fig.2.** The influence of pressure and the limiting influence of the jadeite component on the K substitution into omphacites at 7 GPa (1), 6 GPa (2), 5 GPa (3) [see 4 for details]. Data for 10 GPa (5) are for the carbonate-bearing system [5]. Dashed lines illustrate the limiting influence of *Jd* on solubility of *KJd*. Dotted line shows a relative abrupt increase of the *KJd* solubility in Na-free *KCpx* at 5 GPa (4). Similar leap is observed at 7 GPa as well [2]. Deviation of some data points from the isobar 5 GPa reflects a limiting effect of Ca-*Ts* component on the K substitution into clinopyroxene.

The contents of Ca-Ts and Ca-Eskola (Ca-Esk) molecules in KCpx produced in the ultra-potassic aluminosilicate systems are very similar to those in natural KCpx. Their concentrations in KCpx de-

pend on *P* and the composition of the coexisting melts. «Dilution» of the alumino-silicate melts by carbonates or chlorides, as well as decompression, result in the decrease of the Ca-*Esk* content, which is accompanied by the increase of the Ca-*Ts* concentration. Decompression produces a specific zoning in *KCpx*: the increase of the Ca-*Ts* component from cores of crystals toward their rims at expense of the *KJd* and Ca-*Esk* end-members.

Cooling of the ultra-potassic alumino-silicate and carbonate-silicate liquids at P > 4 GPa results in crystallization of Ca-rich garnet (20-50 mol. % of grossular) along with KCpx (Fig. 1a, b). Sanidine appears at P < 6.5 GPa only from «dry» alumino-silicate melts, containing above 70 mol. % KAlSi<sub>3</sub>O<sub>8</sub> (Fig. 1b). At lower KAlSi<sub>3</sub>O<sub>8</sub> content in the system, sanidine is unstable, while potassium accumulates in KCpx. Cooling at constant pressure (for example 6 GPa; Fig. 1b) results in partial decomposition of sanidine to form KCpx via the pseudo-peritectic reaction sanidine + melt = KJd (in KCpx) [6].

Ultra-potassic alumino-silicate melts are immiscible with the KCl-rich liquids at 4-6 GPa (Fig. 3). The Cl content in ultra-potassic alumino-silicate melts equilibrated with the KCl-rich liquid reaches 3 wt. % at  $1300^{\circ}$ C, but significantly decreases with pressure within 4-6 GPa (Fig. 4). The *P-T* dependence of the Cl wt. % in the KCl-saturated alumino-silicate melt is approximated by equation: Cl (wt. %) =-40.064(±15.34)-0.757(±0.42) $P^2$ +6.809(±4.24)P+0.022(±0.005) T ( $r^2$ =0.95) for the range 4-6 GPa and 1150- $1300^{\circ}$ C. Carbonate-silicate melts do not show liquid immiscibility at these parameters [7].



Pressure, kbar  $L_{si}+Cpx+Ol+Grt+Phl+KCl$   $L_{si}+L_{ch}+Ol+KCl$ 55 L si +L ch +Ol+KCl 45 2.66 40  $L_{si}+L_{ch}+Cpx+Phl+KCl$  $L_{si} + L_{ch}$ 35 30 1100 1150 1200 1250 1300 1350 1400 1450 1500 Temperature, <sup>O</sup>C

**Fig.3.** Liquid immiscibility between the potassic alumino-silicate melt (gray matrix) and the KCl-rich liquid (light globes) at 4 GPa; the inset shows a texture "globe-in-globe" clearly indicating liquid immiscibility.

**Fig.4.** Preliminary data on the Cl content in the aluminosilicate melt equilibrated with the KCl-rich liquid at 4-6 GPa (see Fig. 3). Isopleths present the least square approximation of the experimental data indicated with figures (Cl, wt. %).  $L_{\rm Si}$  – silicate melt,  $L_{\rm Ch}$  – KCl-rich liquid, Ol – olivine, Phl –phlogopite, Cpx – clinopyroxene, Grt – garnet.

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## References

- 1. Navon O., Izraeli E.S., Klein-Ben David O. (2003) Fluid inclusions in diamonds the carbonatitic connection. 8<sup>th</sup> International Kimberlite Conference Long Abstracts, FLA\_0107.
- 2. Safonov O.G., Litvin Y.A., Perchuk L.L., Bindi L., Menchetti L. (2003) Phase relations of potassium-bearing clinopyroxene in the system CaMgSi<sub>2</sub>O<sub>6</sub>-KAlSi<sub>2</sub>O<sub>6</sub> at 7 GPa // Contrib. Mineral. Petrol., V. 146. PP. 120-133.
- 3. *Chudinovskikh L.T., Zharikov V.A., Ishbulatov R.A., Matveev Y.A.* (2001). On the mechanism of incorporation of ultra-high amounts of potassium into clinopyroxene at high pressure // Doklady Rossikoi Akademii Nauk, Earth Sciences, V. 380. PP. 1-4.
  - 4. Safonov O.G., Litvin Y.A., Perchuk L.L. (2004). Synthesis of omphacites and isomorphic features

of clinopyroxenes in the system CaMgSi<sub>2</sub>O<sub>6</sub>-NaAlSi<sub>2</sub>O<sub>6</sub>-KAlSi<sub>2</sub>O<sub>6</sub> // Petrology, V. 12. PP. 84-97.

- 5. *Harlow G.E.* (1997). K in clinopyroxene at high pressure and temperature: an experimental study // Am. Mineral. V. 82. PP. 259-269.
- 6. Perchuk L.L., Safonov O.G., Yapaskurt V.O., Barton J.M. (2002). Crystal-melt equilibria involving potassium-bearing clinopyroxene as indicators of mantle-derived ultrahigh-potassic liquids: an analytical review. Lithos, V. 60 (3-4). PP. 89-111.
- 7. Safonov O.G., Matveev Y.A., Litvin Y.A., Perchuk L.L. (2002). Experimental study of some joins of the system CaMgSi<sub>2</sub>O<sub>6</sub>-(Ca,Mg)<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>-KAlSi<sub>2</sub>O<sub>6</sub>-K<sub>2</sub>(Ca,Mg)(CO<sub>3</sub>)<sub>2</sub> at 5-7 GPa in relation to the genesis of garnet-clinopyroxene-carbonate rocks of the Kokchetav Complex (Northern Kazakhstan) // Petrology, V. 10. PP. 519-539.

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