Surkov N.V.[1], Darmenko O.L.[2] Experimental investigation of clinopyroxene stability in the section Di-CaTs-CaEs at pressure 30 kbar

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Investigation of stability of clinopyroxene solid solutions is very important for the solution of the problems connected with geothermobarometry of eclogites. Two-phase association is not mandatory for eclogites. This paragenesis contains often also several additional phases, e.g., coesite, quartz, kyanite. The experimental investigations have shown, that at high pressure and temperature the stoichiometric composition of clinopyroxene is violated forming the solid solutions with silica. This type of clinopyroxene solid solutions is connected with a particular calcium end-member phase with composition $Ca_{0.5}AlSi_2O_6$. This high-silica phase was named the "calcium molecule Eskola". The first experimental evidence that the nonstoichiometric clinopyroxens exist was obtained by I. Kushiro [1]. Systematic investigations of the stability of such clinopyroxens were started for the first time under administration of V.A. Zharikov since 1974 [2-7]. On the base of thermodynamic evaluations and experimental data, T. Gasparik [8] has estimated the regions of composition of nonstoichiometric clinopyroxene solid solutions in association with anortite, garnets, kyanite, and quartz, however, partially, these evaluations were conducted for the phase associations impossible in the system $CaO-Al_2O_3-SiO_2$ [9].

A lot of experimental investigations on these solid solutions were carried out but neither the phase relations, nor the limits in nonstoichiometric clinopyroxene composition for these solid solutions have been established so far. In this connection, the experimental study of the stability of clinopyroxene solid solutions in silica-rich part of the system $CaO-MgO-Al_2O_3-SiO_2$ at pressure 30 kbar was conducted.

The experimental part of the work was executed using the high-pressure apparatus "piston - cylinder" according to a conventional technique. The temperature was measured using a thermocouple PtRh6-PtRh30. The starting materials for the synthesis were prepared by mixing the oxides, preliminary heated, of super high-purity mark and melting them into a transparent glass. The obtained samples were used to produce two-sided polished petrography plates, which were studied with usual petrographic methods using the polarizing microscope. Polished petrography plates were prepared according to their orientation, after transversal shear of a specimen. The products were analyzed with X-ray diffraction methods, the composition of phases was determined with the electron microanalyzer.

Join calcium-tschermakite - "calcium molecule Eskola". The experiments were conducted in a range of the temperatures 1200-1525 °C (fig.1). On the base of obtained results, the binary phase diagram of the join at pressure 30 kbar was constructed. At the interval of temperatures 1380-1410 °C, anorthite is stable. At temperature 1400°C, the association An+Q melts according to the peritectic reaction An+Q=L+Ky, and at temperature 1410 °C anortite melts according to the reaction An=Gross+Ky+L. The clinopyroxens in this join are stable in the interval of temperatures 1410-1650 °C and represented by solid solutions with the "calcium molecule Eskola" content about 10-15 percents.

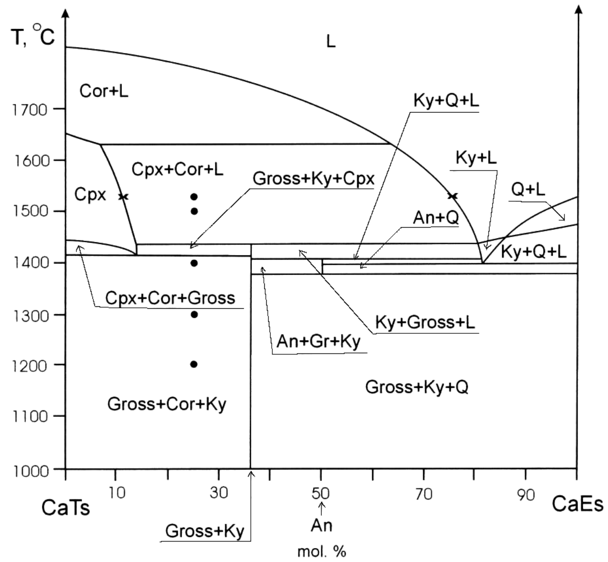

Fig.1. The phase diagram of the join CaTs-CaEs at pressure 30 kbar The melting of calcium-tschermakite, the reactions CaTs=Gross+Cor, An+Q=Ky+L, An=Gross+Ky+ Q, An=Gross+Ky and Cor+L=Gross+Ky are shown according to the work [9]. Points indicate the experimental conditions, oblique crosses - composition of the clinopyroxene solid solutions and liquid.

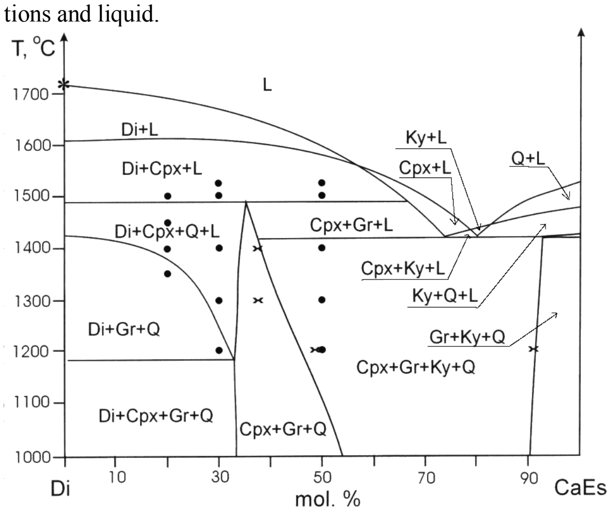

Fig. 2. The phase diagram of the join Di-CaEs at pressure 30 kbar. The dark circles indicate the experimental conditions, oblique crosses shown the points of intersection of the join diopside - "calcium molecule Eskola" with tie-line Cpx-Q and plane Gr-Ky-Q. The melting of the diopside is shown according to the data of Boyd and England [10].

Join diopside - "calcium molecule Eskola". The experiments were conducted in the interval of temperatures 1200-1525 °C (fig 2). The experimental results allow us to establish that nonstoichiometric clinopyroxenes form the solid solutions limited with the content of "calcium molecule Eskola" component up to 14 mol. %. These clinopyroxene solid solutions are outside the investigated join. The content of the $Ca_{0.5}AlSi_2O_6$, component in clinopyroxenes increases with decreasing temperature. In the diopside-rich side of the join the coexistence of two clinopyroxenes was established: 1) nonstoichiometric clinopyroxene, and 2) diopside. It should be noted that diopside always contains the excess in the magnesium content with respect to the calcium content. In the calcium-rich part of the section, the nonstoichiometric clinopyroxene solid solutions coexist with garnets of essentially grossular composition, kyanite and quartz. The melting in this association occurs according to the eutectic reaction Cpx+Gr+Ky+Q=L at the temperature above 1400 °C. The composition of the liquid in this reaction does not comply the plane $CaMgSi_2O_6$-$CaAl_2SiO_6$-$Ca_{0.5}AlSi_2O_6$, and is considerably enriched with calcium and silicon, coming nearer to a side system CaO-Al_2O_3-SiO_2.

Thus, nonstoichiometric solid solutions of the clinopyroxenes are stable at high pressure. Their limiting composition depends on temperatures and, according to the data of other authors, on pressure. The experimental data on the composition of nonstoichiometric clinopyroxenes make it possible to develop geothermobarometric relationship, suitable for the determination of the temperature and pressure of deep rocks formation, such as quartz eclogites, kyanite eclogites and grospydites.

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