EXPERIMENTAL STUDY OF THE EFFECT OF COMPOSITION AND PHASE STATE OF CHLORIDE FLUID ON SOLUBILITY OF CHLORINE IN THE HAPLOGRANODIORITE MELT AT T =1000°C AND P =1 Kbar

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Experiments have been conducted in the system NaCl-KCl-$CaCl_2$-$AlCl_3$-H_2O fluid – Na_2O-K_2O-CaO-Al_2O_3-SiO_2 haplogranodiorite melt at P=1 kbar and t=1000^{o}C. Internally heated gas pressure vessels were used. The chlorine was introduced into the system only through starting fluid. Beforehand saturated by H_2O, one-pieces of haplogranodiorite glass were used as starting materials. We have varied the contents and the ratios of different chlorides in starting fluid, so that the composition of quench granodiorite melt remained close to constant.

Our experimental data for the solubility of chlorine in the haplogranodiorite melt at the various contents of total chlorides in the fluid are shown in fig.1. Areas of a lower salinity vapor phase (L_1) and high-salinity liquid phase (L_2), and two-phase (L_1+L_2) of the fluids also are shown here.

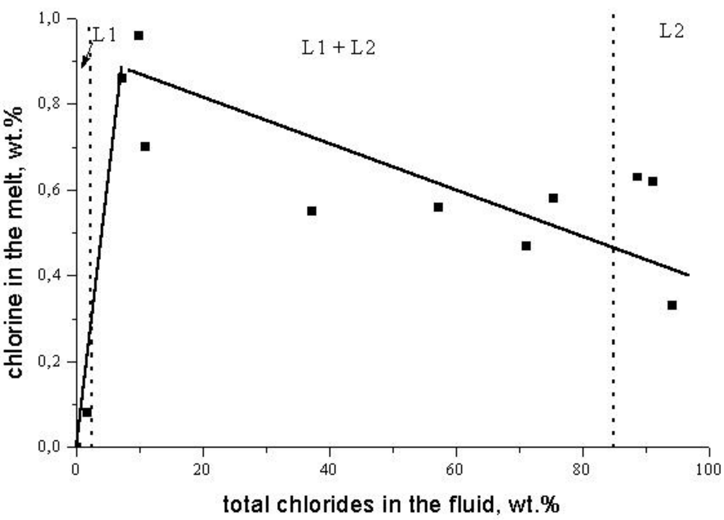

Fig. 1

It is found that the correlation between the content of chlorine in the granodiorite melt and the contents of chlorides (as $CaCl_2$, NaCl, KCl) in the fluids, coexisting in equilibrium with this melt, is nonlinear. The appearance of second high-salinity fluid phase (L_2) in the system in addition to vapor fluid phase (L_1) (phase separation in fluid) lead to an abrupt increase of solubility of chlorine in the melt. This increase of chlorine solubility, probably, was determined by significant increase of activity of chlorine in the total fluid and it well agrees with the other studies [1, 2]. The existence of maximum (extremum) on the curve of correlation between solubility of chlorine in the aluminosilicate melt and the contents of total chlorides in the fluid is shown. Probably, this maximum can be related to the acid-base fractionation between the L_1 and L_2 fluid phases and the concentration of HCl in the vapor fluid phase (L_1) [3]. It is known that the solubility of chlorine as HCl in the aluminosilicate melt is higher than that as NaCl, KCl and $CaCl_2$. With increasing total chlorides concentration in the two-phase fluid the mass of L_1 phase decreases and therefore the solubility of chlorine in the melt also begins to decrease.

By the IR data on the quench glasses the internal structure of the granodiorite melts with various contents of chlorine, water and alkali and earth-alkali metals have been characterized. The complex infrared absorption bands in the range of frequencies 300-700 cm^{-1} have been approximated by two contours, those are related to oscillations of three, four and six membered aluminosilicate and silicate rings (with GRAMS program) [4].

Our obtained data have shown that the rise of the molar ratio Al_2O_3/(CaO+Na_2O+K_2O) in the quench glasses from 0.7 up to 1.1 is accompanied by rise of relative share of six membered rings (fig.2). Thus, excess of alkali metals and Ca stabilizes feldspar structural components.

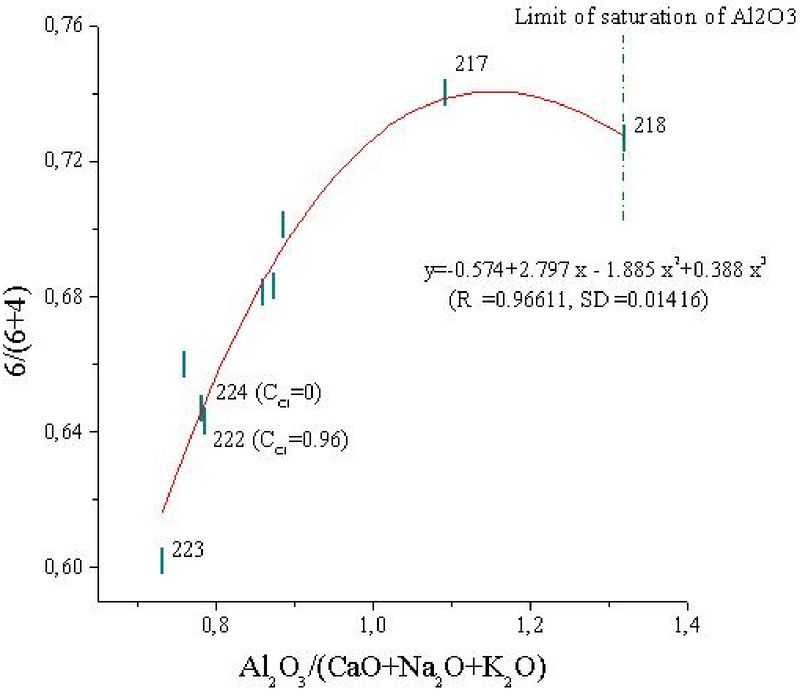

Fig. 2

In accordance with the form of chlorine incorporation we expect different mechanisms of its dissolution. At the HCl dissolution it would leach cation - modificator from the feldspar components (into free form) in the melt. At the chlorides dissolution we can expect exchange reactions with complete or partial transition of Ca to the chlorine coordination with partial destruction of feldspar structural components. In this scheme there are a two structural positions of chlorine – the first in the coordination sphere of free cations and the second linked with Ca^{2+} still connected with aluminosilicate network. This model is in agreement with experimental data available. Preliminary data on the water content demonstrate presumably negative correlation with chlorine content. It can be connected with competition of chlorine and hydroxyles for the same structural positions at free cations not connected with aluminosilicate network while water content lose is mainly for the OH groups contribution.

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