

Experimental Study of the Effect of Composition and Phase State of Chloride Fluid on Solubility of Chlorine in the Granodiorite Melt. On Structural Positions of Chlorine in the Melt

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Experiments have been conducted in the system NaCl-KCl-CaCl₂-AlCl₃-H₂O fluid –; Na₂O-K₂O-CaO-Al₂O₃-SiO₂ haplogranodiorite melt at P=1kbar and t=1000°C. Internally heated gas pressure vessels were used. The chlorine was introduced into the system only through starting fluid. Beforehand saturated by H₂O, 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 Figure 1. Areas of a lower salinity vapor phase (L1) and high-salinity liquid phase (L2), and two-phase (L1+L2) of the fluids also are shown here. It is found that the dependence between the content of chlorine in the granodiorite melt and the contents of chlorides (as CaCl₂, NaCl, KCl) in the fluids, coexisting in equilibrium with this melt, is non-linear. The appearance of second high-salinity fluid phase (L2) in the system in addition to vapor fluid phase (L1) (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 agree with the other studies (Malinin et al., 1995). The existence of maximum (extremum) on the curve of dependence of solubility of chlorine in the aluminosilicate melt from the contents of total chlorides in the fluid is shown. Probably, this maximum can be related to the acid-base fractionation between the L1 and L2 fluid phases and the concentration of HCl in the vapor fluid phase (L1) (Shmulovich et al., 1998). It is known that the solubility of chlorine as HCl in the aluminosilicate melt is higher than that as NaCl, KCl and CaCl₂. With increasing total chlorides concentration in the two-phase fluid the mass of L1 phase decreases and therefore the solubility of chlorine in the melt also begin 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 300-700cm⁻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)(Simakin et al., 1998). Our obtained data shown that the rise of the molar ratio Al₂O₃/(CaO+Na₂O+K₂O) in the quench glasses from 0.7 up to 1.1 is accompanied by rise of relative share of six membered rings. Thus, excess of alkali metals and Ca stabilizes

feldspar structural components. In accordance with the form of chlorine incorporation we expect different mechanisms of its dissolution. At the HCl dissolution it would leach cation - modifier 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 co-ordination with partial destruction of feldspar structural components. In this scheme there a two structural position of chlorine – one in the co-ordination sphere of free cations and second linked with Ca²⁺ 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 hydroxyls for the same structural positions at free cations not connected with aluminosilicate network while water content lose is mainly for the OH groups contribution.

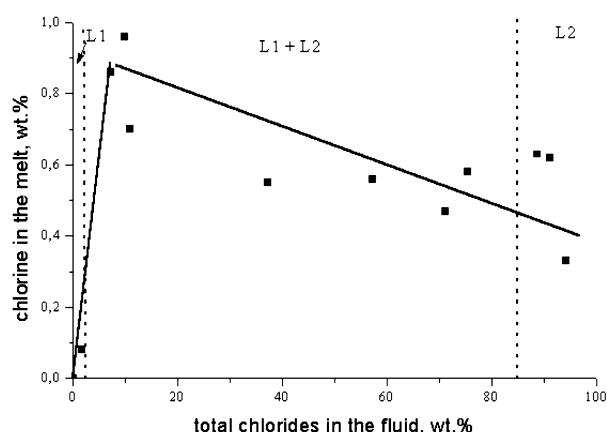


Figure 1. Our experimental data for the solubility of chlorine in the haplogranodiorite melt at the various contents of total chlorides in the fluid.

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