



XAS study of Cl and K speciation in glasses quenched from alkalic silicate and carbonate-silicate melts at high-pressure

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Data on microinclusions in kimberlitic diamonds and experimental results indicate that potassic Cl-bearing silicate and carbonate-silicate melts could be potential media for diamond nucleation and precursors of carbonatite-kimberlite magmatism in the Earth's mantle. These HP melts were presumably formed in equilibrium immiscible chloride or chloride-carbonate liquids [1, 2]. The immiscibility results from structural properties of the melts, in particular, from K and Cl speciation in them. We report preliminary results on X-ray absorption study of K and Cl local environments in the glasses quenched from melts in the systems $\text{NaAlSi}_2\text{O}_6$ -KCl and $\text{CaMgSi}_2\text{O}_6$ - CaCO_3 - Na_2CO_3 -KCl at pressure 5 GPa.

Experimental study of the system $\text{NaAlSi}_2\text{O}_6$ -KCl [3] revealed a very strong shift of equilibrium between immiscible aluminosilicate and (K,Na)Cl melts $\text{NaAlSi}_2\text{O}_6 + \text{KCl} \rightleftharpoons \text{KAISi}_2\text{O}_6 + \text{NaCl}$ to the right, resulting in formation of the K-rich (up to 16 wt. % of K_2O) aluminosilicate melt with 1.6-1.8 wt.% of Cl. It indicates active separation of K and Cl, which implies different structural positions of these ions in the aluminosilicate melt. Cl XAS spectra in most cases are fairly similar to the spectra of crystalline KCl with minor contribution of NaCl. Thus, chlorine is totally segregated into K(Na)Cl-like clusters of different sizes. K XAS spectra of the glasses could be represented as superposition of contributions from KCl and KAISi_3O_8 - $\text{NaAlSi}_3\text{O}_8$ glass [4]; the second component is dominant. Thus, in the glasses (and, presumably, in corresponding melts) K is predominantly bound to silicate units, represented by 4-membered rings as follows from Raman spectroscopy. Its CN is higher, than in crystalline leucite (>6). In contrast, Cl is coordinated exclusively by alkali ions in chloride clusters.

System $\text{CaMgSi}_2\text{O}_6$ - CaCO_3 - Na_2CO_3 -KCl at 5 GPa shows a wide miscibility gap between Cl-bearing carbonate-silicate and Si-saturated chloride-carbonate melts [1], which converge with a decrease of the SiO_2 /carbonate ratio. The K/Cl ratio in the carbonate-silicate melts is > 1, suggesting different K and Cl speciation in the melts with various carbonate content. Both K and Cl XAS spectra of glasses show regular variations with the SiO_2 . The potassium spectra of the carbonate-rich glass resemble the spectra of the $\text{K}_4\text{Si}_4\text{O}_9$ glass [5] mixed with crystalline KCl. The KCl contribution increases with the SiO_2 /carbonate ratio in the glasses. Thus, an increase of the silicate content in the melts results in segregation of potassium ions to KCl-like clusters. The environment of Cl ions becomes closer to KCl with increase of the silicate content, as well. The clustering of the individual K-Cl units with the increase of the silica content in the melts could be considered as a structural manifestation of the immiscibility processes in the studied system.

XAS spectra obtained for microinclusions in Brazilian fibrous diamonds [6] shows that local environment of K and Cl included contributions both from KCl and K-Al-Si glass. This fair similarity supports the applicability of experimental approach by Safonov et al. [1, 2, 3].

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