

XAS STUDY OF CL AND K IN THE DIAMOND-FORMING MANTLE ALKALIC MELTS AND RELATED CRYSTALLINE PHASES

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INTRODUCTION AND SCIENTIFIC BACKGROUND

The study addressed some important problems related to compositional and structural properties of diamond-forming alkaline Cl-rich silicate and carbonate-silicate melts. Being discovered as inclusions in kimberlitic diamonds worldwide, these substances are considered as potential media for formation of diamonds and precursors of a kimberlitic magmatism in the Earth's mantle. The main purpose of the project was to investigate the Cl and K speciation and local environments in the melt inclusions trapped in natural diamonds and in their synthetic proxies produced in high-pressure high-temperature (HPHT) experiments. Pronounced phase heterogeneity of many of the samples necessitates use of X-ray beams with diameters less than 20 microns.

PERFORMED EXPERIMENTS

The X-ray absorption spectra in a wide energy range (i.e., XANES+EXAFS) were collected at K and Cl K-edges for the following samples:

1) Synthetic glasses quenched from the aluminosilicate melts equilibrated with the immiscible K-Na-chloride melt in the system $\text{NaAlSi}_2\text{O}_6$ -KCl at 5 GPa;

2) Synthetic glasses quenched from the chlorine-bearing carbonate-silicate melts equilibrated with the immiscible chloride-carbonate melt in the system $\text{CaMgSi}_2\text{O}_6$ -($\text{CaCO}_3 \pm \text{Na}_2\text{CO}_3$)-KCl at 5 GPa;

3) Selected growth zones of well-characterised natural fibrous diamonds from Brazil bearing microinclusions of the K-Cl-rich melts (Shiryaev et al., 2005).

Many of these samples were also studied using Raman spectroscopy.

RESULTS

K and Cl in aluminosilicate glasses in the system $\text{NaAlSi}_2\text{O}_6$ -KCl

Experimental study of the melting relations in the system $\text{NaAlSi}_2\text{O}_6$ -KCl (Safonov et al., 2007a) revealed a very strong shift of the equation (all compounds are in the melt): $\text{NaAlSi}_2\text{O}_6 + \text{KCl} = \text{KAlSi}_2\text{O}_6 + \text{NaCl}$ to the right. This results in formation of the K-rich (up to 16 wt. % of K_2O) aluminosilicate melt with 1.6-1.8 wt.% of Cl coexisting with the immiscible (K,Na)Cl melt. This process indicates active separation of K and Cl, which implies differences in structural positions of these ions in the aluminosilicate melts. This assumption was tested in the present study. K XAS spectra of all the studied glasses showed similarity to the spectra of glasses in the system KAlSi_3O_8 - $\text{NaAlSi}_3\text{O}_8$ (Jackson et al., 1987), suggesting that K is mostly (or exclusively) bound to the silicate units in the melts (predominantly SiO_3^{2-} chain units, according to the Raman spectra). The K spectra could be represented by mixture of crystalline leucite (KAlSi_2O_6) and orthoclase. Thus, the potassium coordination number in the studied glasses likely lies between 6 and 9. In contrast to relatively simple interpretation of the K spectra, the interpretation of Cl spectra is less certain. Many of the spectra resemble crystalline KCl, though deviations from the standard KCl are rather obvious. Presumably, the main fraction of Cl in the quenched melt is indeed present as KCl-like clusters of different sizes. Contribution of NaCl units also can not be excluded.

The current XAS study of glasses in the system $\text{NaAlSi}_2\text{O}_6$ -KCl supports a hypothesis about fundamentally different structural positions of K and Cl ions in the glasses and corresponding melts: K is strongly bound to silicate network, while Cl is mostly surrounded by K (and, probably, Na) containing clusters, whose bonding to the network is, presumably, rather weak.

K and Cl in carbonate-silicate glasses in the system $\text{CaMgSi}_2\text{O}_6$ -($\text{CaCO}_3 \pm \text{Na}_2\text{CO}_3$)-KCl

Experiments in this system at 5 GPa showed an existence of a wide miscibility gap between Cl-bearing carbonate-silicate and Si-saturated chloride-carbonate melts (Safonov et al., 2007b). Carbonate-silicate and chloride-carbonate branches of the miscibility gap converge with an increase of carbonate content (decrease of the SiO_2 /carbonate ratio) in both coexisting melts. The K/Cl ratio in the carbonate-silicate melts exceeds unity, suggesting that dissolution of KCl in these melts results in significant K and Cl separation. These observations suggest fundamentally different mechanisms of the KCl solubility and K-Cl speciation in the melts with various concentration of the carbonate component. This conclusion is supported by present XAS study.

Potassium and chlorine XAS spectra show regular dependence on the silica content (SiO_2 /carbonate ratio) of the quenched carbonate-silicate melts. Potassium spectra of the carbonate-rich melts resemble the spectra of the glass of the $\text{K}_2\text{Si}_4\text{O}_9$ composition (Kamijo et al., 1996), likely mixed with small amount of crystalline KCl. The contribution of the KCl becomes more important with increase of the melt SiO_2 /carbonate ratio. It implies that the increase of the silicate content in the melts lead to segregation of potassium ions to KCl-like clusters. This suggestion is supported by evolution of the Cl spectra of the glasses with increasing SiO_2 /carbonate ratio: With the increase of the silicate content the environment of Cl ions becomes closer to that in crystalline KCl. The gradual assemblage of individual K-Cl units into the clusters 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.

K and Cl in inclusions in fibrous diamonds

Fibrous diamonds often contain myriads of micron-sized inclusions filled with chemically and physically complex mixtures of minerals and fluids. However, number density of inclusions is low and the absolute amount of the non-diamond material remains small, especially keeping in mind low penetration depth of soft X-rays. Not surprisingly, the XAS spectra from diamonds are rather noisy. The studied diamonds are known to be zoned in respect to the chemical composition of the inclusions. Preliminary examination of the experimental data suggests that K environment is similar to that in KAlSi-glass.

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References

1. Jackson W.E., Brown G.E., Ponader C.W. X-ray absorption study of the potassium coordination environment in glasses from the $\text{NaAlSi}_3\text{O}_8$ - KAlSi_3O_8 binary // J. Non-Cryst. Solids. 1987. 93. P. 311-322.
2. Kamijo N., Handa K., Umesaki N. Soft X-ray XAFS studies on the local structure of K_2O - SiO_2 glasses. Materials Trans. // JIM. 1996. 37. P. 927-931.
3. Safonov O.G., Perchuk L.L., Litvin Yu.A. Interaction of diopside and jadeite with potassium chloride at pressure 5 GPa // Doklady Earth Sciences. 2007a. 415. P. 789-793.
4. Safonov O.G., Perchuk L.L., Litvin, Yu.A. Melting relations in the chloride-carbonate-silicate systems at high-pressure and the model for formation of alkalic diamond-forming liquids in the upper mantle // Earth and Planetary Science Letters. 2007b. 253. P. 112-128.
5. Shiryaev A.A., Izraeli E.S., Hauri E.H., Zakharchenko O.D., Navon O. Chemical, optical and isotopic investigation of fibrous diamonds from Brazil // Russian Geology and Geophysics. 2005. 46. P. 1185-1201.

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