Experimental model for alkalic chloride-rich mantle liquids

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INTRODUCTION

Potassium and chlorine-rich inclusions in diamonds were firstly recognized in Chinese kimberlites (Chen et al., 1992), while positive correlation between K and Cl was reported for Yakutian, Botswanian, and Canadian diamonds (e.g. Johnson et al., 2000). Izraeli et al. (2001) firstly published data on individual chloride-rich inclusions in cloudy diamonds from the Koffiefontein pipe, S. Africa. They interpreted these inclusions as relics of quenched liquids, whose composition correspond to mixtures of alkali chlorides (predominately, KCl) and carbonates with varying contents of H_2O and silicates. Similar chloride-carbonate inclusions were recently described in diamonds from Canada (Diavik: Klein-BenDavid et al., 2004, 2006, 2007; Panda: Tomlinson et al., 2006). The chloride-carbonate relics in diamonds are closely associated with both eclogitic and peridotitic minerals, as well as with the phases produced from mineral-liquid reactions (Izraeli et al., 2004; Klein-BenDavid et al., 2006; Tomlinson et al., 2006, 2007). These data indicate an active interaction of the liquids with the upper mantle mineral assemblages. Data by Zedgenizov et al. (2007*a*) on chloride-carbonate inclusions in diamonds from the eclogite xenolith of the Udachnaya kimberlite, Siberia, clearly showed that the chloride-carbonate liquids interacted with the mantle rocks before the production of the kimeberlite melt and were closely related to kimberlite evolution. This conclusion perfectly agrees with the data on chloride-carbonate inclusions in groundmass olivines of these kimberlites (Kamenetsky et al., 2004, 2007).

The chloride-carbonate liquids are compositionally linked to alkalic silicate, carbonate-silicate, and carbonate Cl-bearing liquids trapped in diamonds worldwide (Navon et al., 1988, 2003; Schrauder, Navon, 1994; Shiryaev et al., 2005; Zedgenizov et al., 2007*b*). This link between the above types of liquids is illustrated in Figure 1 (Safonov et al., 2007*a*). Continuous trends between silicate and carbonate inclusions, from one side, and between chloride-rich and carbonate inclusions, from another side, suggest a complete miscibility of the corresponding liquids at the upper mantle conditions. A lack of links between carbonate-silicate and carbonate-chloride liquids suggests an existence of a wide miscibility gap between these liquids at the upper mantle P-T (Fig. 1).

In order to substantiate the "immiscibility" model following from the above data, we performed experiments on chloride-carbonate-silicate systems at pressures about 5 GPa, i.e. a mean pressure deduced

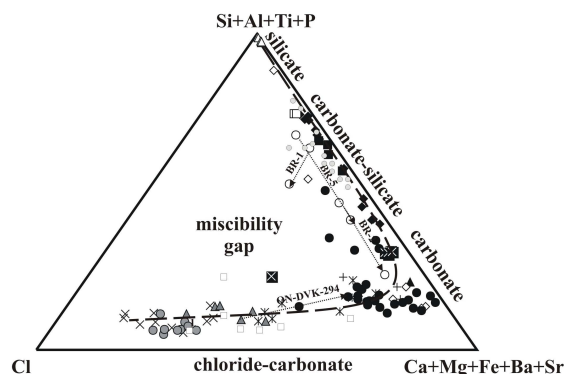for the inclusions (Izraeli et al., 2004; Zedgenizov et al., 2004; Tomlinson et al., 2006).

Fig. 1. *Compositions of alkalic chloride-bearing liquids trapped in diamonds. Trends for diamonds BR-1, BR-2, BR-5 (Shiryaev et al., 2005) and ON-DVK-294 (Klein-BenDavid et al., 2004) are discussed in the text. References for used data sets see in Safonov et al. (2007).*

EXPERIMENTAL STUDY OF THE CHLORIDE-CARBONATE-SILICATE SYSTEMS

$CaMgSi_2O_6$-(Na_2CO_3, $CaCO_3$)-KCl. Experiments in this model system at 5 GPa fully supported the above model (Safonov et al., 2007*a*). They revealed a wide miscibility gap between Cl-bearing carbonate-silicate (L_{CS}) and Si-bearing chloride-carbonate (L_{CC}) melts. Crystallization of silicates within broad compositional range shifts the L_{CS} and L_{CC} compositions along the gap boundaries toward the low-temperature carbonate region. Cooling at constant pressure results in displacement of the $L_{CS}+L_{CC}$ interval toward the more silica-rich portion of the system, while the interval of homogeneous L_{CC} coexisting with silicates expands. Schematic cross section of the ternary system (Fig. 2) indicates three petrologically significant temperature intervals: $L_{CC}+S$, $L_{CC}+L_{CS}+S$, and $L_{CC}+L_{CS}$.

Contrast compositions of silicates and L_{CC} inevitably would result in active reactions between them within the fist T-X interval. Before the appearance of the immiscible L_{CC} and L_{CS} at higher temperature, these reactions would modify both the resulting mineral assemblages and the composition of the melts. It is evident that progress of the reactions would be greatly dependent both on silicate composition and carbonate/chloride ratio in the melt. In order to investigate an interaction of silicates with the chloride-carbonate melts and a mutual role of chlorides and carbonates in these reactions, additional runs

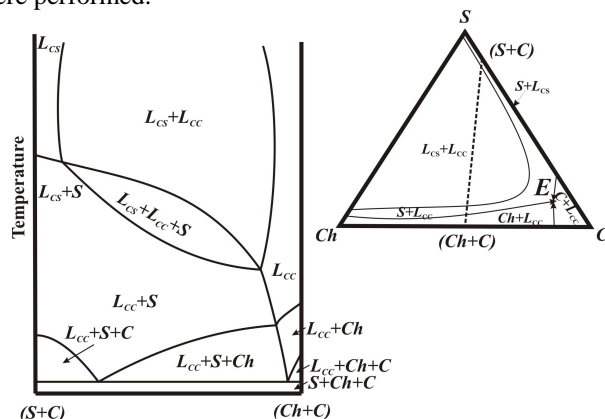involving model end-members and natural minerals were performed.

Fig. 2. *Schematic T-X section of the pseudo-ternary system chloride(Ch)-carbonate(C)-silicate(S) with the wide miscibility gap along an arbitrary join (silicate+carbonate)-(chloride+carbonate) (dashed line) at constant pressure.*

Mg_2SiO_4-(Na_2CO_3, $CaCO_3$)-KCl. Fig. 3 shows phase relations during the interaction of forsterite (*Fo*) with the L_{CC}, whose composition corresponds to the mix. 7. The sequence of phase assemblages perfectly matches the scheme in fig. 2. Immiscible $L_{CS}^{(1)}$ and $L_{CC}^{(1)}$ coexist at 1510^OC (Fig. 4). As crystallization of *Fo* begins (1450^OC), compositions of $L_{CS}^{(2)}$ and $L_{CC}^{(2)}$ are displaced toward the carbonate-rich (Na+Ca+Mg) apex. At lower temperatures, *Fo* (±*Mrw*) coexists with the single L_{CC} (Fig. 4). It is evident that the Ca-carbonate component is a leading factor in reactions of *Fo*, i.e. *Fo* + [$CaCO_3$] = [2MgO + $CaSiO_3$ + CO_2] or $2Fo$ + $3[CaCO_3]$ = *Mrw* + [3MgO + $3CO_2$]. Chloride does not participate in the reactions, but creates a possibility for the liquid immiscibility between L_{CC} and L_{CS} at higher temperature.
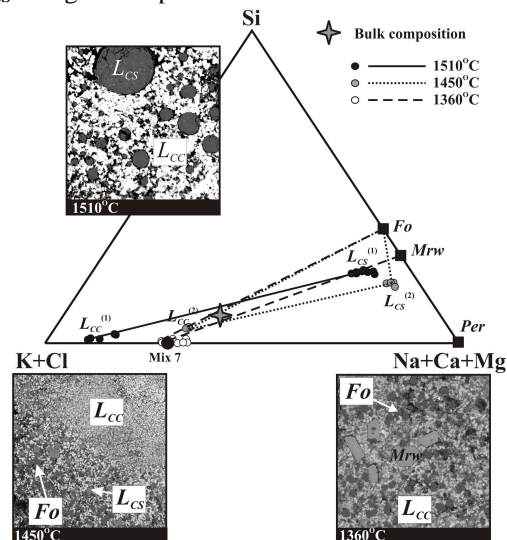

Fig. 3 *Phase relations in the system [mix 7]$_{71}Fo_{29}$ at 5 GPa.*

Similar sequence is observed for the system **$MgSiO_3$-(Na_2CO_3, $CaCO_3$)-KCl** In this first system, the assemblage *Fo+Di±Mrw* (3*En* + $CaCO_3$ = *Fo* + *Di* + CO_2) coexisting with a single L_{CC} in this system below 1450^OC suggests that chloride again does not participate in "dissolution" of enstatite (*En*).

Another situation is deduced for the systems involving pyrope and jadeite. Pyrope have not been observed in any run product in the system **$Mg_3Al_2Si_3O_{12}$-($CaCO_3$, Na_2CO_3)-KCl**. In the case of starting L_{CC} corresponding to mix.6 (Fig. 4), liquidus spinel (*Spl*) coexists with two melts at 1500^OC. At 1400-1300^OC, it gives place to *Fo* (±Cl-bearing *Phl*) via reaction of *Spl* with highly-K chloride-rich liquid, because of a strong affinity of Al to K in the melt (the trend $L_{CS}^{(1)} \rightarrow L_{CS}^{(3)}$ in fig. 5 is directed toward the enrichment of L_{CS} in K and Cl). In the case of starting L_{CC} corresponding to mix.7 (Fig. 4), no *Spl* is observed at high temperature, while *Fo* is still present. At 1360^OC, it coexists with homogeneous chloride-rich melt, enriched also in Si and Al (reflected in mice-like phase in the products of melt quenching).
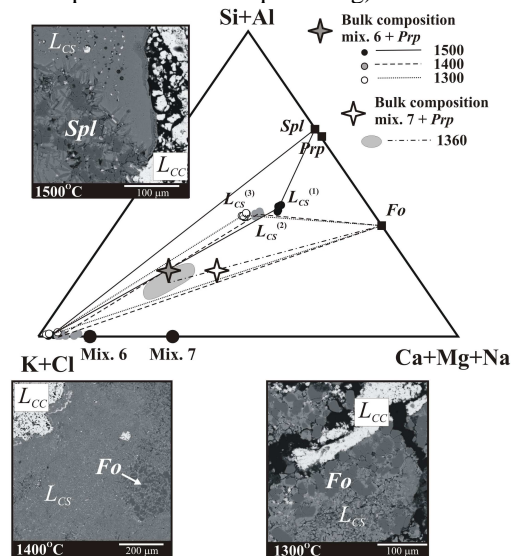

Fig. 4 *Phase relations in the systems [mix 6]$_{71}Fo_{29}$ and [mix 7]$_{71}Fo_{29}$ at 5 GPa.*

Close trends are characteristic for the system **$CaMgSi_2O_6$-$NaAlSi_2O_6$-($CaCO_3$, Na_2CO_3)-KCl**: two liquids coexist at temperatures > 1500^OC, while appearance of *Cpx* and *Mrw* at lower temperatures results in accumulation of Si and Al simultaneously with K and Cl in the residual L_{CS}. At ~1350^OC, an assemblage *Cpx+Mrw*+Ca-*Grt* coexists with homogeneous L_{CC}. Similar to the system with pyrope, this low-temperature homogeneous L_{CC} is characterized by elevated concentrations of Si and Al.

The above examples clearly indicate difference between reactions of the chloride-carbonate melts with peridotite-related silicates and eclogite-related silicates. The reason for it is peculiarities of the chloride-silicate boundary joins. The *Di* (*Fo*, *En*) - KCl joins are nearly binary systems with high-T (> 1700-1800^OC) liquid immiscibility and no reaction of silicates with KCl melt (e.g. Safonov et al., 2007*b*). In contrast, the join *Jd*-KCl is a pseudobinary system, where strong K-Na exchange between silicate and chloride results in formation of K-rich aluminosilicate melt, coexisting with K-Na chloride melt at 1250-1300^OC at 5 GPa (Safonov et al., 2007b). The join *Prp*-KCl at 5 GPa is also pseudobinary, where *Spl* and *Fo* form in

equilibrium with Si-Al-rich silicate melt and Mg-enriched chloride liquid.

APPLICATION OF THE EXPERIMENTAL RESULTS TO THE EVOLUTION OF MELTS INCLUDED IN DIAMONDS.

Schrauder, Navon (1994), Shiryaev et al. (2005), Zedgenizov et al. (2007b) showed that compositions of the carbonate-silicate liquids included in some diamonds varies from the SiO_2-enriched melts to the SiO_2-depleted CaO-rich melts. For example, an evolution of inclusions in the Brazilian diamonds BR-5 and BR-2 (Shiryaev et al., 2005) (Fig. 1) resembles the trend of the evolution of the synthetic melts $L_{CS}^{(1)}$-$L_{CS}^{(2)}$ in Fig. 3 and the trends of L_{CS} evolution in the system $CaMgSi_2O_6$-($CaCO_3$, Na_2CO_3)-KCl (Safonov et al., 2007). Another type of the evolutionary trend in the diamond BR-1 (Fig. 1) it could be resulted from an intensive fractionation of olivine (Shiryaev et al., 2005). This suggestion is remarkably supported with the experiments in the system Prp-($CaCO_3$, Na_2CO_3)-KCl (Fig. 4): the decrease of temperature is accompanied by Fo precipitation, while the melt becomes richer in K and Cl. Thus, both trends reflect silicate crystallization from the Cl-bearing carbonate-silicate melt during cooling. Following to the experiments, it can be assumed that two types of trends for liquids in the Brazilian diamonds are resulted from different mineral environments of their growth, i.e. peridotitic for BR-5 and BR-2, and eclogitic for BR-1.

An evolution of inclusions in diamond ON-DVK-294 from the Diavik pipe, Canada (Klein-BenDavid et al., 2004) proceeds from the chloride-carbonate liquid the inner zone to the carbonatitic liquid in the outer zone (Fig. 1). Taking to account compositions of the chloride-carbonate liquids in other diamonds of the Diavik pipe (Klein-BenDavid et al., 2006, 2007), a single trend appears. This trend is consistent with the evolution of the chloride-carbonate liquids in the systems $CaMgSi_2O_6$-($CaCO_3$, Na_2CO_3)-KCl and Mg_2SiO_4-($CaCO_3$, Na_2CO_3)-KCl ($L_{CC}^{(1)}$-$L_{CC}^{(2)}$ in fig. 3) and corresponds to the diamond growth during cooling.

Following to the experimental results, K and Cl-rich carbonate liquids in diamonds of the Udachnaya pipe (Zedgenizov et al., 2007b) can be considered as low-temperature liquids. Nevertheless, they could evolve from the primary carbonate-silicate melts equilibrated with the immiscible chloride-carbonate liquids, whose relics were found in diamonds of the eclogite xenolith (Zedgenizov et al., 2007a) and in groundmass olivines (Kamenetsky et al., 2004) from this pipe.

Tomlinson et al. (2006) identified compositional differences in chloride-carbonate liquids coexisting with peridotitic and eclogites phases in diamonds from the Panda pipe (Canada). The compositions of the "peridotitic" liquids are located along the chloride-carbonate join of the ternary system, while "eclogitic" liquid is enriched in Al and Si. This difference is reproduced in our experiments, as well.

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