Eclogite partial melting with participation of the H_2O-CO_2(+KCl) fluid: experimental data at 5 GPa and 1200-1300^{0}C

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INTRODUCTION.

Partial melting is the spectacular feature of eclogite xenoliths from kimberlites worldwide. It was described for eclogites from South African kimberlites (e.g. Taylor, Neal, 1985 and references therein), while the most detailed study of this phenomenon was performed for eclogites from Yakutian kimberlites (Spetsius, Taylor, 2002, 2003; Misra et al., 2004; Shatsky et al., 2005). In addition to the hypothesis considering kimberlite magma as an agent of partial melting of xenoliths (Spetsius, 1999), there is a basis to suggest that the partial melting is related to penetration of deep-seated fluids into mantle eclogites prior their capture by kimberlite magma (Spetsius, Taylor, 2002, 2003). There are petrological and geochemical evidences for relation of the partial melting of eclogites with crystallization of microdiamonds or formation of «fibrous coats» (Spetsius, Taylor, 2002, 2003; Shatsky et al., 2005). Thus, the eclogite partial melting could proceed within the diamond stability field, i.e. above 4.0-4.5 GPa.

In some cases, the products of partial melting in the eclogite xenoliths preserved glasses or mineral associations, which are products of subsequent re-crystallization of these glasses. These quenched melts show unique, but widely varying, composition (Fig. 1). The SiO_2 content varies from 40 to 70 wt. %, while alkali content is above 5 wt. % and, in some cases, reaches 15-17 wt. % (Fig. 1). In many cases, potassium notably dominates over sodium. Alumosilicate melts of similar composition (Fig. 1) are known as inclusions in diamonds associated with eclogitic minerals, (Bulanova et al., 1993; Novgorodov et al., 1990; O. Navon, pers. comm.). It gives additional evidence for possible relation of such melts to the diamond formation. Similarity of compositions of partial melts in eclogite xenoliths and that of the melt inclusions in diamonds shows that both types of melts could be closely related to each other.

Following to the above compositional characteristics, we can conclude that such melts can not be produced during the isochemical melting of eclogites, rather than related to the interaction with highly alkalic fluids. Data on mineral assemblages in the products of partial melting of some xenoliths (especially, from the Yakutian kimberlites) allow suggest a possible composition of a fluid participated in the process. In some cases, the products of partial melting involve unique phases: sanidine, djerfisherite, phlogopite, sodalite, various carbonates
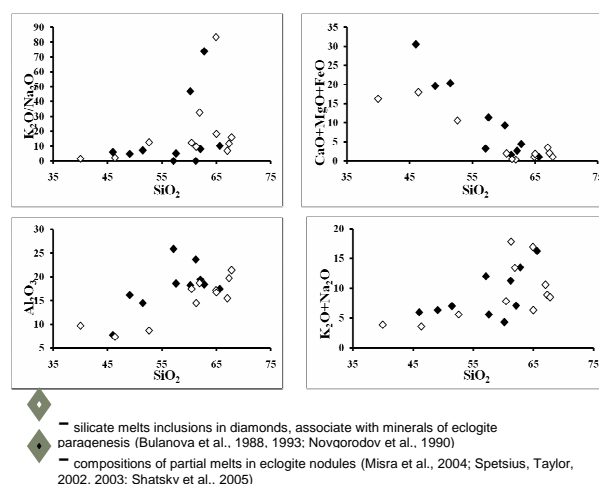
Fig. 1 *Compositional characteristics of silicate melts in partially molten eclogite nodules and inclusions in diamonds.*

and sulfates (e.g. Misra et al., 2004; Shatsky et al., 2005). Most of these phases are mostly related to the low-pressure re-crystallization of the products of the partial melting. Nevertheless, their presence provides an evidence for an active role of carbonate (or CO_2) and alkali-chloride compounds in the fluids. Chlorine, from 0.1 to 1-2 wt. %, is usually present in some aluminosilicate melt inclusions in diamonds, as well (Bulanova et al., 1993; O. Navon, pers. comm.). Inclusions of alkalic chloride-carbonate quenched liquids were recently discovered in diamonds from partially molten eclogite xenolith from the Udachnaya pipe (Zedgenizov et al., 2007). These data support an idea on activity of chlorides in the fluids participated in the partial melting of the eclogite xenoliths.

A participation of alkali chlorides in transformation of eclogites is very attractive hypothesis. Chloride melts are immiscible with silicate melts at the mantle conditions (Safonov et al., 2005, 2007a, b). However, strong exchange of components (mostly, K-Na) between chloride and silicate melts results in formation of low-temperature silicate melts with K/Na > 1.

There are many experimental studies on the partial melting of eclogites and garnet pyroxenites at pressures 2-20 GPa, including anhydrous melting (Pertermann, Hirschmann, 2003; Hirschmann et al., 2003; Kogiso, Hirschmann, 2006; Spandler et al., 2008), H_2O-bearing melting (Stern, Wyllie, 1978; Ryabchikov et al., 1996; Kessel et al., 2005), and carbonate-bearing melting (Hammouda, 2003; Yaxley, Brey, 2004; Dasgupta et al., 2006). According to these studies, near-solidus anhydrous or water-saturated melting of eclogites

produces Na-enriched melts (2-5 wt. % of Na_2O), whose SiO_2 and Al_2O_3 contents are very comparable to those in the products of partial melting of eclogite xenoliths. However, K/Na << 1.0 in these melts. Only in melts from some specific "tonalite-like" systems, K/Na is close to 1.0 (Stern, Wyllie, 1978; Ryabchikov et al., 1996; Spandler et al., 2007). Partial melting of carbonated eclogite produces carbonate-rich melts (Hammouda, 2003; Yaxley, Brey, 2004; Dasgupta et al., 2006), which are not relevant to the eclogite xenoliths. The composition of the natural melts could be roughly produced by exchange Na for K in the partially molten eclogite. It could be possible with participation of chloride-bearing liquids (Safonov et al., 2005, 2007a, b).
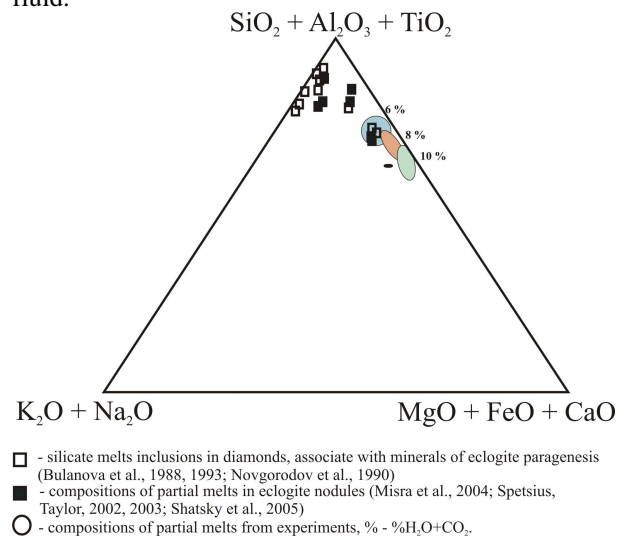
Present paper demonstrates preliminary results of experimental study on melting of bimineral eclogite at 5 GPa and 1200-1300°C with participation of H_2O-CO_2 and H_2O-CO_2–KCl fluids. Two types of starting materials were used: (1) model Fe-free eclogite $(Prp_{80}Grs_{20})_{50}(Di_{60}Jd_{40})_{50}$ (gel mixture) and (2) mixture of garnets and omphacites from the natural bimineral eclogite from the Udachnaya pipe, Yakutia. Silicate mixtures were placed into PtRh capsules with oxalic acid and crystalline KCl on the bottom, pressurized and heated to desired P and T using the toroidal anvil-with-hole Bridgmen-type apparatus.

EXPERIMENTAL RESULTS

Firstly, KCl-free systems were investigated. Quantity of melt regularly increased with the increase of the H_2O-CO_2 fluid content in the system $(Prp_{80}Grs_{20})_{50}(Di_{60}Jd_{40})_{50}$ at constant temperature (1300°C). At 6 wt. % of H_2O+CO_2, this melt coexist with Cpx and Grt, while only Grt is associated with the melt at 8 wt. % of the fluid. Nearly complete melting occurred at 18 wt. % of fluid in the system. Corundum-like phase and coesite were found in these runs. At similar temperature and run duration, much higher content of the fluid is necessary to produce the same quantity of the melt in the natural eclogite. Up to 8 wt. % of the fluid just boundary thin films of fluidized melt occurred in the run samples. At higher fluid content, the melt portion rapidly increased. Evidently, the difference between two run sets is related to the kinetics of the fluid penetration into the starting charges, since the gel mixture much easier accommodates fluid in comparison to pressurized Grt-Cpx crystalline aggregate. Nevertheless, regularities in changing of the melt composition are similar for the both run sets. Similar to results of other studies on eclogite melting, near-solidus melting produces the SiO_2 and Na_2O–enriched melts. With melting progress (in our case related to the increase of the fluid content) and consummation of garnet, the Al_2O_3, CaO, and MgO contents in the melt increase (Fig. 2). According to the trend in Fig. 2, composition of melts from products of eclogite melting can be produced by much lower degree of melting, which corresponds to either low fluid content or lower temperature. Nevertheless, eclogite melting under H_2O-CO_2 fluid only can not explain high alkali content and domination of K over

Na in the melts formed during partial melting of eclogite xenoliths.

The next stage of experiments involved the eclogite melting with participation of the KCl-bearing H_2O-CO_2 fluid.

$SiO_2 + Al_2O_3 + TiO_2$

$K_2O + Na_2O$ $MgO + FeO + CaO$

□ - silicate melts inclusions in diamonds, associate with minerals of eclogite paragenesis (Bulanova et al., 1988, 1993; Novgorodov et al., 1990)

■ - compositions of partial melts in eclogite nodules (Misra et al., 2004; Spetsius, Taylor, 2002, 2003; Shatsky et al., 2005)

○ - compositions of partial melts from experiments, % - %H_2O+CO_2.

Fig. 2. *Comparison of synthetic melts in the KCl-free experiments with composition of melts in partially molten eclogite nodules and inclusions in diamonds.*

Phase assemblages in the products of experiments with $(Prp_{80}Grs_{20})_{50}(Di_{60}Jd_{40})_{50}$ depends both on temperature and the KCl/(H_2O+CO_2+KCl) (i.e. KCl/fluid) ratio in the starting fluid. Complete melting is observed both at 1300 and 1200°C and KCl/fluid < 0.75. Immiscible KCl-rich liquid is found at KCl/fluid > 0.5. Garnet appears at 1200°C and KCl/fluid > 0.75. Produced melts are highly alkaline (5-14 wt. % of K_2O+Na_2O) with K notably predominating over Na. The Cl content in the melts varies from 3 to 5.5 wt. % and shows negative dependence on the KCl content in the starting fluid. In contrast K_2O shows clear positive correlation with the KCl content in the system (Fig. 3). The K_2O/Cl ratio in the melts increases with the KCl content in the system, but show unclear dependence on the KCl/fluid ratio (Fig. 3).
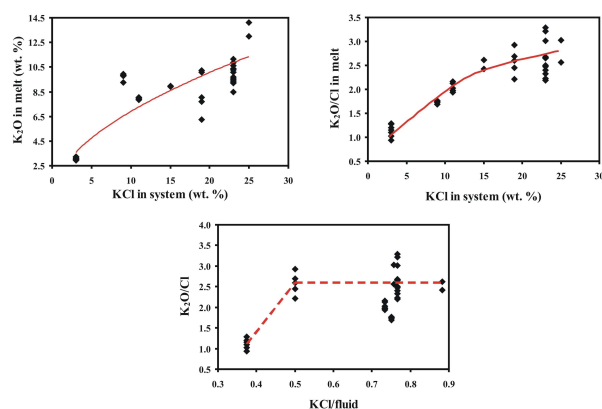
Fig 3. *Compositional characteristics of synthetic melts in the KCl-bearing experiments.*

Thus, solubility of KCl in the aluminosilicate melt equilibrated with the immiscible chloride liquid,

apparently, does not depend on presence of the H_2O-CO_2 fluid. The K_2O/Cl ratio close to 1.3 (i.e. as in KCl) in the silicate melts, which are not equilibrated with the immiscible chloride liquid (at KCl/fluid < 0.5) Thus, domination K over Na results from the K-Na exchange between chloride and silicate liquids (Safonov et al., 2007*b*). An increase of the KCl activity in fluid results in enrichment of the silicate melts in potassium and in a decrease of the K_2O/Cl ratio in it.

Addition of KCl into the H_2O-CO_2 fluid causes more active melting of the natural eclogite, as well, with formation of melts enriched in K and Cl. However, the K_2O/Cl ratio in these melts is close to 1.3, while no immiscible chloride liquid is observed.

MAJOR CONCLUSIONS

1. Addition of KCl into the fluid assists to more active melting of eclogite. It is, probably, an effect both of notable solubility of chlorine (up to 4.5-5.0 wt. % of Cl) in the silicate melt and K-Na exchange between silicate and chloride liquids.
2. Increase of the KCl content in the system and appearance of the immiscible chloride liquid assists to enrichment of the silicate melt in K and its separation from Cl owing to the strong K-Na exchange between two liquids.
3. The experiments imply that the immiscible chloride liquid is a possible factor assisting to formation of the K-rich Cl-bearing silicate melts during the eclogite melting.

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