

Interaction of model peridotite with (Ca, Na₂)CO₃–KCl melts and H₂O–KCl fluids at 1.0–2.5 GPa

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Introduction

Petrological and geochemical data obtained during last 20–30 years show that KCl and NaCl are important constituents of aqueous brine fluids and carbonatite melts circulating in the upper mantle and, possibly, in the transition zone of the Earth's mantle. Inclusions of Cl-bearing melts in kimberlitic diamonds [Israeli *et al.*, 2001; Klein-BenDavid *et al.*, 2004, 2007; Tomlinson *et al.*, 2006; Wirth *et al.*, 2009], in phenocrysts and xenocrysts from kimberlites [Kamenetsky *et al.*, 2004, 2009], in minerals from xenoliths in kimberlites [Zedgenizov *et al.*, 2007; Golovin *et al.*, 2008] point to a presence of chlorides in the zones of production of the kimberlitic magmas at depths more than 100 km. Findings of Cl-rich apatites and amphiboles, as well as brine inclusions in minerals of peridotite nodules in basaltoids [Smith *et al.*, 1981; Exley and Smith, 1982; Ionov *et al.*, 1997; O'Reilly and Griffin, 2000; Frezzotti *et al.*, 2002, 2010] give implications that chlorides are active in the processes of mantle modification at depths 30–60 km. All these data inspire for experimental study of a role of chloride components in the upper mantle processes.

Present short paper shows results of two experimental series. Experiments on interaction of the model garnet lherzolite $Fo_{63}En_{30}Prp_5Di_2$ with the $[CaCO_3]_{25}[Na_2CO_3]_{25}[KCl]_{50}$ melt at 1.0 and 2.0 GPa were aimed to study the mutual role of chloride and carbonate components during transformation and partial melting of the peridotite. The purpose of the experiments on interaction of the model pyrolite $Fo_{57}En_{17}Prp_{14}Di_{12}$ (+0.3 wt. % of Na₂O) with the H₂O–KCl fluid at 2.5 GPa was to investigate an influence of KCl on phase transformations in the Al₂O₃, CaO, Na₂O-rich water-bearing peridotite, in particular, on stability of garnet, pyroxenes, and amphibole in presence of KCl.

Experimental and analytical procedures

The starting silicate charges for the experiments were prepared from synthetic forsterite (Mg₂SiO₄), enstatite gel (MgSiO₃), pyrope glass (Mg₃Al₂Si₃O₁₂), and synthetic diopside (CaMgSi₂O₆) mixed in the above ratios. In the first experimental series, 20 wt. % of a mixture composed of Na₂CO₃ (25 wt. %), CaCO₃ (25 wt. %), and KCl (50 wt. %) was added to the silicate portion. In the experiments with the model pyrolite, 14 wt. % of Mg(OH)₂ accounting for 4.4 wt. % of H₂O in the system and KCl (2.4, 3.7 and 5.0 wt. %) were added to silicates. Experiments were performed with the piston-cylinder apparatus using ½-inch talc high-pressure cells equipped with graphite heaters and ceramic pressure-transmitting holders. Pressure in the cells at high temperatures was calibrated via brucite = periclase + H₂O and albite = jadeite + quartz reaction curves. Temperature was controlled with an accuracy of ±1°C with the W₉₅Re₅/W₈₀Re₂₀ thermocouple. Spherical and tube platinum capsules with 0.2 mm of wall thickness were used in the experiments. Run products were studied with electron microscope CamScan MV2300 (VEGA TS 5130MM) with EDS INCA-Energy-250.

Experimental results

Reactions of the garnet lherzolite with the $[CaCO_3]_{25}[Na_2CO_3]_{25}[KCl]_{50}$ melt at 2.0 and 1.0 GPa result in disappearance of the garnet and orthopyroxene constituents of the starting peridotite. At 2.0 GPa and <1200°C, homogeneous carbonate-chloride melt (L_{CC}) coexists with forsterite (Fo), merwinite (Mrw) and/or monticellite (Mtc), which form via reactions of the pyroxene component of the peridotite with Ca-carbonate component of L_{CC} : $3En + \{3CaCO_3\} = Mrw + Fo + \{3CO_2\}$. At 1200°C, the assemblage $Fo + Cpx + Kfs$ (fig. 1a) forms via reaction: $Prp + 2En + \{2KCl + Na_2CO_3 + 1/3CaCO_3\} = 2Kfs + 7/3Fo + 1/3Di + \{2NaCl + 4/3CO_2\}$. The assemblage coexisting with L_{CC} at 1 GPa and 1050°C includes forsterite, melilite (containing up to 0.5 wt. % of K₂O and 2.0 wt. % of Na₂O), and monticellite. These phases form at expense of the

enstatite and pyrope constituents of the starting lherzolite: $Prp + 3En + \{5CaCO_3\} = Ak + Geh + Mtc + 2Fo + \{5CO_2\}$.

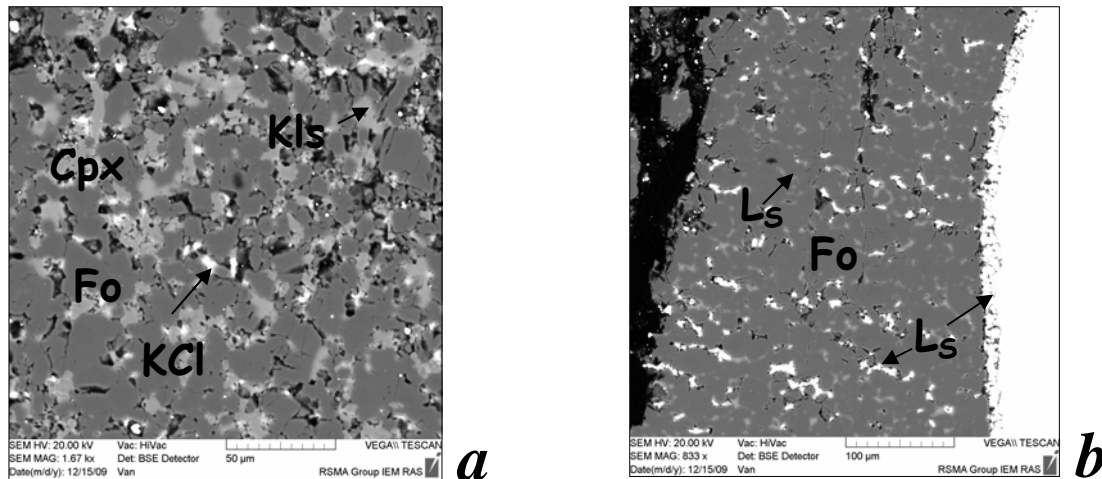


Fig. 1. Assemblages formed by interaction of the model garnet lherzolite with the $[CaCO_3]_{25}[Na_2CO_3]_{25}[KCl]_{50}$ melt at 2.0 GPa. (a) Assemblage $Fo+Cpx+Kfs$ coexisting with the quenched chloride melt in the products of the run at $1200^{\circ}C$; (b) Immiscible silicate (L_s) and chloride (L_c) melts coexisting with Fo in the products of the run at $1300^{\circ}C$. Pores in a glass indicate active degassing (CO_2) of the melts in the experiment.

It is evident that reactions of the lherzolite with the chloride–carbonate liquid is controlled mainly by activities of the carbonate components, whereas the role of the chloride components in these reaction is subordinate. Just in some cases, presence of chlorides results in formation of new silicate phase, such as kalsilite and K-bearing melilite. Nevertheless, chlorides make wider a temperature interval where carbonatitic melt coexists with silicates. It is related to a strong lowering of temperatures of the carbonate–chloride eutectics with respect to the melting of pure carbonates and chlorides. The strongest influence of chlorides is observed within $1200\text{--}1300^{\circ}C$, where carbonate and/or larnite-normative silicate melts form (Table 1). These melts coexist with CO_2 fluid and chloride liquids (fig. 1b). Partitioning of K and Cl between immiscible silicate and chloride melts results in enrichment of the silicate melts in K_2O [Safonov *et al.*, 2009], making their composition close to the kamafugite melts (Table 1).

Table 1. Compositions of the melts produced during interaction of the model garnet lherzolite with the $[CaCO_3]_{25}[Na_2CO_3]_{25}[KCl]_{50}$ melt at 2.0 and 1.0 GPa.

P, GPa	T, $^{\circ}C$	SiO ₂	Al ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	Cl	Total
1	1200	44.84	9.98	8.84	18.57	6.00	10.22	1.19	99.63
2	1200	38.24	10.97	8.44	11.63	8.66	11.74	1.37	91.04
2	1300	38.94	10.47	5.44	14.66	8.79	12.48	1.60	92.38

The subsolidus of the model pyrolite ($< 1025^{\circ}C$) containing 4.4 wt. % of H_2O at 2.5 GPa includes forsterite, clinopyroxene (Cpx), orthopyroxene (Opx), pargasite-tschermackite amphibole (Amp) and some amount of pyrope-grossular garnet (Grt) and spinel. Beginning of melting is, probably, coincides with the reaction $3/2Opx + 1/2Fo + 1/2Amp = Grt + Cpx + 1/2H_2O + (L)$ in accordance with the results of the experiments in amphibole-bearing lherzolites [Niida and Green, 1999]. In general, these relations are also observed in the system containing 2.4 wt. % of KCl (fig. 2a). However, the reaction $6Opx + Fo + Amp + KCl = [Cl-Phl + Phl] + Grt + 2Cpx + (L)$ in this case results in formation of Cl-bearing phlogopite (up to 1 wt. % of Cl) (fig. 2a). At the KCl content of 3.7 wt. %, interaction of the pyrolite with the H_2O -KCl fluid is marked by disappearance of garnet, orthopyroxene, and amphibole with formation of Cl-bearing phlogopite in assemblage with clinopyroxene and olivine (fig. 2b).

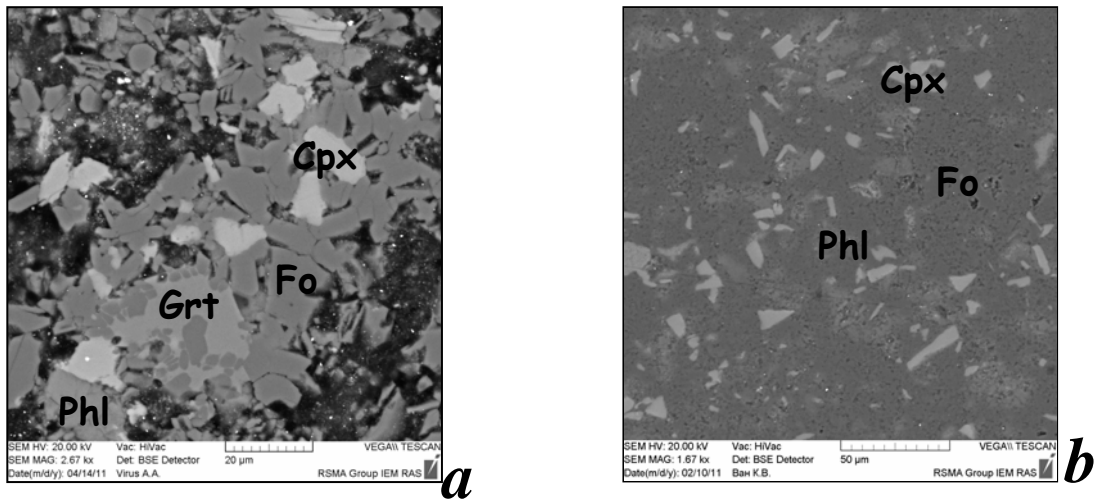


Fig. 2. Assemblages formed by interaction of the model pyrolite with the H₂O-KCl fluid at 2.0 GPa. (a) Assemblage *Fo+Grt+Cpx+Phl* coexisting with the quenched silicate melt in products of the run at 1000°C and the KCl content in the system 2.4 wt. %; reaction relations of *Grt* with other phases are analogous to those in the KCl-free system; (b) The final stage of pyrolite transformation: assemblage *Fo+Cpx+Phl* coexisting with the quenched silicate melt in products of the run at 1000°C and the KCl content in the system 5.0 wt. % .

Phlogopite is found to be stable at higher temperatures (probably, >1200°C) with respect to amphibole. This result is qualitatively consistent with the experimental data on melting of phlogopite and amphibole-bearing peridotites at pressures >1.5 GPa [Modreski and Boettcher, 1973; Mysen and Boettcher, 1975; Mengel and Green, 1989]. Nevertheless, the solidus temperature of the water-bearing pyrolite drops below 900°C with addition of KCl. It is more than by 100°C lower than the solidus temperature of the H₂O-bearing pyrolite without KCl. Apparently, lowering of temperature is related to formation of phlogopite, which forms low-temperature eutectics with other silicates, as well as to solubility of Cl in the melts. Unfortunately, composition of the melts is hard to identify correctly. On the basis of composition of the quenching products, it is evident that “phlogopite constituent” mainly contributes to the composition of the melts. Immiscible chloride melt seems to form at 3.7–5.0 wt. % of KCl in the system. This melt extracts chlorine from the coexisting silicate melt, which, in turn, becomes K₂O-rich.

Conclusions

The present experiments allow conclusions about a role of chloride components in modification of peridotite assemblages via chloride-carbonate melts and brine fluids. It is evident, that influence of KCl on phase relations in diverse peridotites is appears only in presence of carbonates or H₂O. Chlorides themselves are mostly inert with respects to silicates.

1. At 1.0–2.5 GPa, reactions governed mainly by carbonate components in the chloride-carbonate melts of H₂O in brines result in decomposition of orthopyroxene, garnet, and amphibole. In presence of KCl, the formation of new phases, such as kalsilite, Cl-bearing phlogopite, is possible. Alkali exchange between silicates and chlorides results in an enrichment of some phase in potassium.

2. Chlorides cause a decrease of the solidus temperatures of both carbonate-bearing and water-bearing peridotites. In respect to the carbonatized peridotite, this conclusion is consistent with the experiments at higher pressures [Litasov and Ohtani, 2009; Safonov *et al.*, 2010]. In respect to hydrous peridotite, this conclusion contradicts to the experiments on melting of the *Fo+En* assemblage in presence of H₂O+KCl at 5 GPa [Chu, 2010], which showed that the solidus temperature of this assemblage increases with addition of KCl to the system because of decreases of the water activity in a fluid. However *Chu's* (2010) experiments did not account for a presence of Al₂O₃ in peridotite. Results of the present experiments indicate an important role of alumina, which forms phlogopite, which, in turn, leads to the decrease of the solidus temperature.

3. During melting, liquid immiscibility conditioned by chlorides assists to the enrichment of the silicate (carbonate-silicate) melts in potassium, while chlorine is predominantly stored in the coexisting chloride (chloride-carbonate) melt or in the brine fluid.

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