



## Phase relations in the hydrous CMAS pyrolite in presence of KCl at 2 GPa

O. Safonov

Institute of Experimental Mineralogy, Laboratory of Lithosphere, Chernogolovka, Russian Federation (oleg@iem.ac.ru, +7(496)524-44-25)

In the upper mantle, chlorides are constituents of concentrated aqueous solutions (brines), as well as chloride-carbonate and carbonatite melts. Mineral assemblages coming from diverse depth levels show that mobile (K, Na)Cl-bearing fluids are able to provoke intensive metasomatism of the peridotitic mantle accompanied by melting. Scarce experimental studies on influence of brines on mineral equilibria in the peridotitic mantle (Stalder et al., 2008; Chu et al., 2011) indicate that influence of chlorides on water activity in a fluid equilibrated with forsterite enstatite at pressures above 2 GPa is very similar to their effect at lower “crustal” pressures (e.g. Aranovich, Newton, 1997): decrease of the H<sub>2</sub>O activity with an increase of the salt content results in an increase of the melting temperature of silicates. Nevertheless, these experiments were performed in the Al-free systems. Presence of Al would provoke an active interaction of alkali chlorides, namely KCl, with silicates with formation of new K-Al-bearing phases, such as phlogopite (in presence of H<sub>2</sub>O), which would influence on the melting of complex assemblages.

In order to investigate an effect of KCl on phase relations in the Al<sub>2</sub>O<sub>3</sub>, CaO, Na<sub>2</sub>O-rich hydrous peridotite and on stability of garnet, pyroxenes, and amphiboles, in particular, experiments on interaction of the model CMAS pyrolite Fo<sub>57</sub>En<sub>17</sub>Prp<sub>14</sub>Di<sub>12</sub> (+0.3 wt. % of Na<sub>2</sub>O) with the H<sub>2</sub>O-KCl fluid were performed at 2 GPa in the temperature interval 900-1200. Mixtures of synthetic forsterite, diopside, enstatite and pyrope in the above weight ratio were mixed with 14 wt. % of Mg(OH)<sub>2</sub> corresponding to 4.4 wt. % of H<sub>2</sub>O in the system. 2.4, 3.7, 5 and 10 wt. % of KCl were added to silicate-H<sub>2</sub>O mixture. Experiments were performed using a piston-cylinder apparatus with  $\frac{1}{2}$ -inch talc high-pressure cells calibrated via brucite = periclase + H<sub>2</sub>O and albite = jadeite + quartz equilibria curves. Temperature was controlled with accuracy [U+F0B1]1 with the W95Re5/W80Re20 thermocouple. Spherical and tube Pt capsules with 0.2 mm-thick walls were used in the experiments. Run products were analyzed using CamScan MV2300 (VEGA TS 5130MM) electron microscope equipped with EDS INCA-Energy-250.

The subsolidus assemblage of the model pyrolite (< 1025°C) containing 4.4 wt. % of H<sub>2</sub>O at 2.5 GPa includes forsterite (Fo), low-Al<sub>2</sub>O<sub>3</sub> (below 0.5 wt. %) clinopyroxene (Cpx), orthopyroxene (Opx) with up to 7 wt. % of Al<sub>2</sub>O<sub>3</sub>, pargasite-tschermackite amphibole (Amp), pyrope-grossular garnet (Grt), and minute spinel (Spl). It is consistent with the results of experiments with amphibole-bearing lherzolite (e.g. Niida, Green, 1999). Reaction relations  $3/2\text{Opx} + 1/2\text{Fo} + 1/2\text{Amp} = \text{Grt} + \text{Cpx} + 1/2\text{H}_2\text{O}$  are observed in the run samples. Melting apparently begins in the temperature interval 1025-1050 and results in gradual disappearance of amphibole. In general, similar relations are available in presence of 2.4 wt. % of KCl. However, reaction  $6\text{Opx} + \text{Fo} + \text{Amp} + \text{KCl} = [\text{Cl-Phl} + \text{Phl}] + \text{Grt} + 2\text{Cpx}$  results in formation of Cl-bearing phlogopite solid solution, Phl (up to 1 wt. % of Cl). It seems to be stable at higher temperatures (apparently, above 1200) with respect to amphibole, consistently with the experimental data on melting of phlogopite and amphibole-bearing peridotites at pressures >1.5 GPa (Modreski, Boettcher, 1973; Mysen, Boettcher, 1975; Mengel, Green, 1989). Garnet, orthopyroxene, and amphibole, i.e. all alumina-rich phases of the “starting” KCl-free peridotite, are totally disappear with addition of 3.7 wt. % and more of KCl, while the assemblage of Cl-bearing phlogopite with Al-poor clinopyroxene and olivine is stable. The solidus temperature of the H<sub>2</sub>O-bearing pyrolite with addition of KCl is about 900 at 2.4 wt.% of KCl and seems to be much lower at 10 wt. % of KCl. Anyway, these temperatures are more than by 100 lower of the melting temperature of the H<sub>2</sub>O-bearing pyrolite without KCl, as well as Cl-free Di+Phl assemblage (Modreski, Boettcher, 1973). Apparently, decrease of the temperature is related to solubility of Cl in the melts where the “phlogopite” component is predominant.

Thus, the preliminary experimental data show that KCl decreases the solidus temperature of the hydrous peridotite. This result contradicts with the experiments on melting of the Mg<sub>2</sub>SiO<sub>4</sub>+MgSiO<sub>3</sub> system in presence of H<sub>2</sub>O+KCl at 5 GPa (Chu et al., 2011) showing the increase of melting temperature with an increase of KCl content in the system. The present experimental results indicate an important role of alumina as a component regulating phase relations in H<sub>2</sub>O-bearing peridotite in presence of alkali chlorides.

The study is supported by Russian Foundation for Basic Research (project #10-05-00040) and RF President Grant for young scientists (project #MD-222.2012.5).

References:

- Aranovich L.Y., Newton R.C. H<sub>2</sub>O activity in concentrated KCl and KCl-NaCl solutions at high temperatures and pressures measured by the brucite-periclase equilibrium // *Contribution to Mineralogy and Petrology*. 1997. Vol. 127. P. 261-271.
- Chu L. Effect of chlorine on the melting of the subcratonic lithospheric mantle // *Contribution to Mineralogy and Petrology*. 2011. Vol. 162. P. 565-571.
- Mengel K., Green D.H. Stability of amphibole and phlogopite in metasomatized peridotite under water-saturated and water-undersaturated conditions // *Fourth International Kimberlite Conference, Geological Society of Australia Special Publications*. 1989. Vol. 14, P. 571– 581.
- Modreski P.J., Boettcher A.L. Phase relationships of phlogopite in the system K<sub>2</sub>O–MgO–CaO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–H<sub>2</sub>O to 35 kilobars: a better model for micas in the interior of the Earth // *American Journal of Science*. 1973. Vol. 273, P. 385–414
- Mysen B.O., Boettcher A.L. Melting of hydrous mantle. I. Phase relations of natural peridotite at high pressure and temperature with controlled activities of water, carbon dioxide, and hydrogen // *Journal of Petrology*. 1975. Vol. 16, P. 520-548
- Niida K., Green D.H. Stability and chemical composition of pargasitic amphibole in MORB pyrolite under upper mantle conditions // *Contribution to Mineralogy and Petrology*. 1999. Vol. 135, P. 18-40.
- Stalder R., Kronz A., Simon K. Hydrogen incorporation in enstatite in the system MgO–SiO<sub>2</sub>–H<sub>2</sub>O–NaCl // *Contribution to Mineralogy and Petrology*. 2008. Vol.156. P.653–659.