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**EXPERIMENTAL STUDY OF THE REACTION ENSTATITE + PYROPE = PHLOGOPITE IN THE PRESENCE OF A H2O-KCl FLUID AT 5 GPa AND ITS APPLICATION TO THE MODAL MANTLE METASOMATISM.**

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The concept of mantle metasomatism has been developed in the 1970 - 1980s on the basis of studies of upper mantle xenoliths in kimberlites and alkali basalts (Harte, 1983; O'Reilly, Griffin, 2013; Sobolev, 1974; Dawson, 1983). According to this concept, modifications of the mantle rocks via their interaction with external fluids and melts (regardless of their composition and origin), which leads to the formation of minerals that are not characteristic of typical peridotites (amphiboles, phlogopite, apatite, carbonates, sulfides, titanite, ilmenite etc.), was collectively classified as the process of modal mantle metasomatism. The H2O and/or CO2 activities are considered to be the most important factors of the modal mantle metasomatism (O'Reilly, Griffin, 2013 and references therein). However, mineralogical and geochemical data also indicate an active role of alkalis, essentially K and Na, in this process. These components are dissolved in the mantle fluids as various salts, among which chlorides are of special interest (e.g. Safonov, Butvina, 2016).

A typical mineral indicator of the modal mantle metasomatism is phlogopite. Appearance of this mineral in the mantle rocks as a result of their interaction with potassium-bearing aqueous fluids is explained by the reaction (Kushiro, Aoki, 1968; Safonov, Butvina, 2013, 2016):

5MgSiO3 + CaMg2Al2Si3O12 + [K2O + 2H2O] = K2Mg6Al2Si6O20(OH)4 + CaMgSi2O6 (1)

or 5En + Grt + [K2O + 2H2O] = Phl + Di, which is a combination of two end-member reactions

1/2Prp + 3/2En + [1/2K2O + H2O] = Phl (2)

1/2Grs + 9/2En + [1/2K2O + H2O] = Phl + 3/2Di (3)

In the above reactions, the alkaline component is K2O for clarity. However, in real fluids potassium exists in the forms of chlorides, carbonates, etc.

Present study shows preliminary results of the experiments at 5 GPa and 900-1250°С on the reaction (2) in presence of the H2O-KCl fluid with starting XKCl = KCl / (KCl + H2O) from 0.05 to 0.4. The experiments were performed using a high-pressure toroidal “anvil-with-hole” apparatus (Litvin, 1991) in the Korzhinskii Institute of Experimental Mineralogy RAS. As a starting material, a mixture of pyrope gel, brucite and quartz with the following bulk composition (wt. %) was used: 47.82 SiO2, 32.18 MgO, 11.76 Al2O3, 8.23 ​​H2O. KCl was added to produce the required XKCl.

The products of the KCl-free experiments contain pyrope and Al-bearing enstatite. In the presence of KCl in the starting fluid, phlogopite appears in the products of the experiments at 1000 and 900°C, but is absent at 1250°C. An increase in KCl is accompanied by a decrease of the amount of pyrope and enstatite in the products of the experiments, so that in experiments with fluids with XKCl = 0.4 they are rare or absent, and phlogopite is the dominant phase. The phase relationships demonstrate that the phlogopite-forming reactions have a positive slope in terms of T-XKCl (an increase in the salt concentration increases the phlogopite stability to higher temperatures). Experiments at 1000°C show that pyrope is the first phase to disappear as the concentration of KCl in the fluid increases, and subsequently Al-bearing enstatite gives up. These relations indicate the consequent operation of the reactions:

En + 1/3Prp + [2/3KCl + 1/3H2O] = 1/3Phl + 1/3Cl-Phl (4)

En + 1/5MgTs + [2/5KCl + 1/5H2O] = 1/5Phl + 1/5Cl-Phl, (5)

where MgTs is the Mg-Tschermack molecule (MgAl2SiO6) in the orthopyroxene solid solution and Cl-Phl is the KMg3AlSi3O10Cl2 end-member in the phlogopite solid solution. Reaction (5) is manifested in a decrease of the Al content in orthopyroxene with the increase in XKCl in the starting fluid. With the increase of XKCl in the starting fluid, the Cl content in mica also increases reaching 0.6-0.8 wt. % at XKCl = 0.2-0.4. Such Cl content in the synthetic phlogopite is consistent with the Cl content in phlogopites of metasomatized peridotites and inclusions in diamonds (see Figure 3 in Safonov, Butvina, 2013). In the products of some experiments at XKCl > 0.1, kyanite (Ky) appears. Its formation, possibly, is also provoked by the decomposition of pyrope in the presence of the H2O-KCl fluid by a reaction

Prp + [KCl + 1/2H2O + 1/2SiO2] = 1/2Phl + 1/2Cl-Phl + 1/2Ky. (6)

The presence of SiO2 in the fluid can be due to both the initial slight excess of this component in the starting mixtures and the sufficiently high solubility of SiO2 in the fluid in equilibrium with the Phl + En assemblage (e.g. Schneider, Eggler, 1986). High activity of SiO2 in the fluid is indirectly indicated by the absence of forsterite in the run products (it was observed only in one experiment), which is a typical product of phlogopite dissolution in aqueous fluids (e.g. Schneider, Eggler, 1986).

Thus, the experiments showed that the Al content of orthopyroxene and Cl in phlogopite according to reaction (5) are good indicators of KCl activity in the fluid. These effects can be used to quantify this activity, and hence the concentration of KCl in saline fluids in the processes of the modal mantle metasomatism.

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