Experimental study of phlogopite-forming reactions in the system orthopyroxene + garnet in presence of the H_2O -KCl fluids.



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Phlogopite

is accepted as a major mineral indicator of the modal metasomatism in the upper mantle within a very wide P-T range and fluid/melt compositions. It extensively forms in mantle peridotites transforming initial harzburgites and lherzolites to phlogopite wehrlites both in

Garnet

and spinel-facies.

As a rule, alkaline components are in the mantle in the salts form. Their high reactivity contributes to the effective manifestation of mantle metasomatism (Harlov & Aranovich, 2018).

The main source of salt components in mantle fluids are subducted serpentinites and volcanics of the oceanic crust (Scambelluri et al., 1997; Sharp & Barnes, 2004; Weiss et al., 2015; Barnes et al., 2018).

The addition of small amounts of F and Cl significantly increases stability of phlogopite coexisting with a melt during mantle melting (Condamine & Médard. 2014).

A reaction

$5En + Grt + [K_2O + 2H_2O in fluid] = Phl + Di$ (1)

is considered as the major mechanism for phlogopite formation in garnet-facies peridotites. It is a combination of two end-member reactions:

 $\frac{1}{2} Prp + \frac{3}{2} En + \frac{1}{2} K_2 O + H_2 O = Phl$ (2) $\frac{1}{2} Grs + \frac{9}{2} En + \frac{1}{2} K_2 O + H_2 O = Phl + \frac{3}{2} Di$ (3)

The presence of a knorringite component in garnet allows to add another one

 $1/2Knr + 3/2En + [1/2K_2O + H_2O] = Cr-Phl$ (4).

These reactions are commonly accompanied by regular compositional variations of primary garnet and pyroxenes.

In order to illustrate these regularities, we report results of the experimental study of the phlogopite-forming reactions in the model systems pyrope-enstatite (PEH), grossular-pyrope-enstatite (GPEH) and knorringite-pyrope-enstatite (KPEH) systems in presence of a H_2O -KCl fluid.

The experiments were performed at pressures 3 and 5 GPa and temperatures of 900 and 1000°C using a toroidal Bridgmen-type "anvil-with-hole" high-pressure apparatuses NL-13T and NL-40.







The experiments were aimed at the tracing of variations of grossular and knorringite contents in garnet, as well as Al content of pyroxenes, with variations of the KCl content in the fluid.

The increase of X_{KCI} in the fluid is accompanied by gradual decomposition of garnet and Al-bearing enstatite in all systems.



The formation of phlogopite occurred at $X_{KCI} = 0.1$.

Let's consider in more detail the PEH system.

The <u>sequential</u> disappearance of garnet and Al-containing orthopyroxene occured as a result of the following reactions:

En + $1/3Prp + [2/3KCl + 1/3H_2O] =$ 1/3Phl + 1/3Cl-Phl (5) En + $1/5MgTs + [2/5KCl + 1/5H_2O] =$ 1/5Phl + 1/5Cl-Phl (6)

The later one leads to a decrease in the Al_2O_3 content of orthopyroxene. The slight increase at $X_{KCI} = 0.2$ at 1000°C and 5 GPa could be due to both a complete decomposition of garnet and a presence of a small proportion of a melt in the system. Probable absence of the melt at 900°C results in a decrease of the Al_2O_3 content of orthopyroxene.



GPEH

The decrease of the aluminum content of Opx is characteristic for the GPEH system, as well.

The experiment showed that in the presence of even a small amount of salt in the fluid, composition of orthopyroxene began to change.



$1/2Prp + 3/2En + [1/2K_2O + H_2O] = Phl (2)$

Reaction

GPEH

predominates in the system with low concetration of KCl in the fluid resulting in a removal of the pyrope component from garnet and, thus, an increase of the grossular content. However, a further increase of a salt concentration results in the predominant effect of the reaction

$1/2Grs + 9/2En + [1/2K_2O + H_2O] = Phl + 3/2Di$ (3)

in the system, which leads to formation of clinopyroxene and, thus, a decrease of the grossular content in garnet.



In the KPEH system, at low X_{KCI} in the fluid (0 - 0.1), by analogy with the previous systems, the pyrope component of garnet decreases according to reaction (2), thus, leading to a slight increase of Cr_2O_3 content. Reaction (4)

$1/2Knr + 3/2En + [1/2K_2O + H_2O] = Cr-Phl$ (4).

begins to dominate in the system with an increase of the salt concentration leading to a decrease of the knorringite content in garnet, but a concomitant increase of the Cr_2O_3 content in orthopyroxene.

A decrease in the Cr_2O_3 content in <u>garnet</u> at $X_{KCI} = 0.2$ is also associated with an appearance of Cr-rich kyanite (~7 wt.%).





The amount of Cr_2O_3 in phlogopite decreases with an increase in the salt concentration.

However, in contrast to the PEH and GPEH systems, the Al content in orthopyroxene remains virtually unchanged.



The amount of CI in phlogopite gradually increases in all systems with an increase X_{KCI} . However, in the GPEH system at 900°C and 3GPa, and in the PEH system at 1000°C and 5 GPa, the chlorine content in phlogopite is much lower than in other systems, which can be caused by the presence of excess melt at these parameters, which includes most of the chlorine.



Applications to mantle assemblages

Reactions (1) - (4) closely reproduce the process of a gradual modification of garnet lherzolites and harzburgites (GP) through phlogopite-bearing garnet peridotites (GPP) into phlogopite peridotites (PP), which is well known in series of xenoliths from kimberlites worldwide (e.g., van Achterbergh et al., 2001; Luguet et al., 2015).

Further transformation results in a transition from PP to phlogopite K-Richterite peridotites (PKP) (Erlank et al., 1986; Waters and Erlank, 1988; Konzett et al., 2000). PKP peridotites are considered as the most metasomatized. Unfortunately, this stage is not reproduced in our experiments.

$\mathbf{GP} \longrightarrow \mathbf{GPP} \longrightarrow \mathbf{PP} \longrightarrow \mathbf{PKP}$

An increase of the alkali activity in a sequence GP-GPP-PP-PKP led to a decrease in the Al₂O₃ content in orthopyroxene (Waters & Erlank, 1988; Van Archterbergh et al., 2001), as well as a regular change in the composition of garnet, until the garnet complete disappearence. At the early stages of metasomatism, an increase in N_{grs} in garnet results in their modification from Ca-depleted "harzburgitic"-type to Ca-enriched "Iherzolitic"-type. Further the grossular content decreases with increasing fluid activity in accordance with reaction (3). Similar metasomatic changes lead to the formation of reaction coronas on garnet (Schulze 1995; Smith et al., 1991; Griffin et al., 1999).





In garnets from harzburgite xenoliths of the Wesselton pipe, South Africa (Griffin et al; 1999), an increase in the content of CaO, MgO, Cr_2O_3 from the center of grains to their rims was described, so that composition of garnet, in general, varies from "harzburgitic" to "lherzolitic" with formation of aggregated of phlogopite and Cr-Spl around them. The latest episode of metasomatism, which occurred shortly before kimberlite activity, led to the formation of new, low-Ca zones around garnet, which shifted their composition back to "harzburgitic".

Conclusions

- 1. Garnet and Al-bearing orthopyroxene are unstable in the presence of the H_2O -KCl fluid.
- 2. An increase in the salt concentration in the fluid results in change in composition of primary minerals as of phlogopite froms.
- 3. Al_2O_3 in orthopyroxene is decreasing.
- 4. Garnet composition is highly dependent on the degree of metasomatism. The CaO and Cr_2O_3 contrents in garnet decreases at the highest stages of metasomatism. 5. The amount of chlorine in phlogopite is increasing.

These effects can be applied for the quantitative and qualitative estimates of variations in K activity during the modal mantle metasomatism.



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