# Breakdown of Phlogopite in Presence of Carbonate: Metasomatic Agents in the Sub-Continental Lithospheric Mantle

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## Summary

First results in the phlogopite + magnesite (KMASH-$CO_2$) system demonstrate that a potassium-bearing fluid will be the metasomatic agent at sub-continental-lithospheric-mantle conditions with a continental geotherm of 40 $mWm^{-2}$. In this case, phlogopite can be stable to a depth of 200 km in the presence of carbonate, and will coexist with potassic fluids. Assuming a hotter geotherm of 44 $mWm^{-2}$, these fluids can be present to a depth of about 180 km. Beyond this depth, at the base of a thick sub-continental lithospheric mantle, a hydrous, potassium- and $CO_2$-rich silicate melt would be the metasomatic agent. In this system, garnet is present above solidus as a residual phase, which implies that a K-$CO_2$-$H_2O$-enriched metasomatic fluid or melt could react with garnet peridotite to form phlogopite.

## Introduction

Phlogopite is (a) found as a main constituent in mantle derived magmas such as kimberlites and (b) brought up in mantle xenoliths by such magmas from the sub-continental lithospheric mantle (Erlank et al. 1987; Edwards et al., 1992). It is clearly a common phase in the uppermost portion of the mantle and the breakdown of this water-bearing, alkali-rich mineral will considerably affect mantle processes: water released could lower the mantle solidus and induce partial melting, or it could give rise to fluids. Both, melts and fluids, could infiltrate and metasomatise mantle rocks (e.g. Thompson, 1992).

Many experimental studies have been carried out already to constrain the stability of phlogopite in simple and more complex mantle systems as summarized by Frost (2006). Phase relations of phlogopite in carbonated systems, however, still need to be determined. Melting reactions of *phlogopite + magnesite + enstatite = forsterite + pyrope + melt* at pressures of ≥ 5 GPa (≈ 160 km in depth; Wendlandt and Eggler, 1980) and *phlogopite + magnesite = forsterite + enstatite + pyrope + melt* at ≥ 4 GPa (≈ 130 km in depth; Ulmer and Sweeney, 2002) have been proposed and need to be tested.

We intend to constrain the stability of phlogopite with carbonate in the sub-continental lithospheric mantle to identify possible metasomatic agents. Here we present initial results in the phlogopite + magnesite (KMASH-$CO_2$) system from 4 to 6 GPa (≈ 130 to 200 km in depth).

## Experimental and Analytical Methods

Phlogopite was synthesized from a stoichiometric mix of high purity oxides and carbonate. The mixture, along with 7 wt. % $H_2O$, was loaded into a Pt-capsule and run in an end-loaded piston cylinder apparatus at 1.5 GPa and 1000°C. This phlogopite was then mixed with natural magnesite and experiments were performed at different pressure and temperature conditions using a USSA-2000 uniaxial split-sphere multi-anvil apparatus. 1.5 mm diameter Pt-capsules

were loaded with the starting material, sealed by arc-welding and assembled as described in Luth (1997).

Following the experiment, the capsules were mounted in epoxy, ground open, polished and carbon coated for microprobe analysis (JEOL 8900) at the University of Alberta.

## First Results

Figure 1 shows the melting relations of phlogopite with magnesite from 4 to 6 GPa. Synthetic phlogopite breaks down to phlogopite plus pyrope and fluid at a pressure of 4 GPa and 1150°C and is found with magnesite to 1250 and 1270°C at 6 and 4 GPa, respectively. Breakdown of synthetic phlogopite to *phl + py + fluid* at sub-solidus conditions is not due to the presence of carbonate but rather caused by the slightly non-stoichiometric nature of the synthetic phlogopite. A similar reaction was observed in experiments by Sato et al. (1997) using a natural phlogopite as starting material. This phlogopite in equilibrium with pyrope, magnesite and fluid is referred to as "primary phlogopite" in this text.
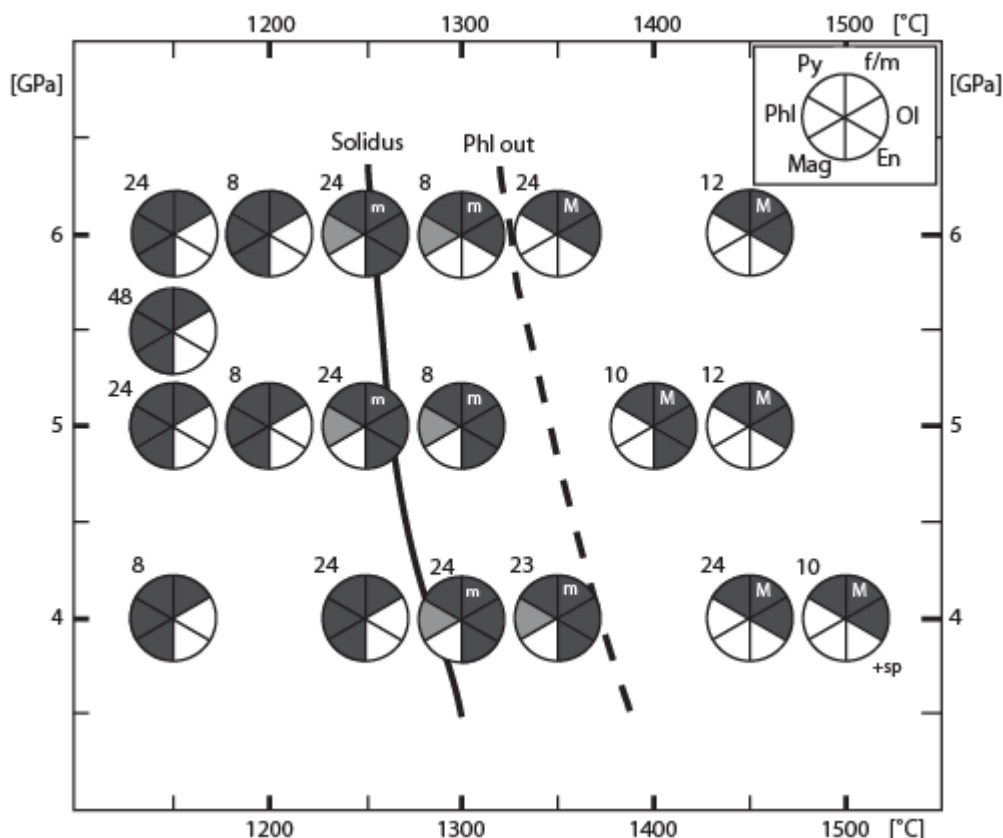


**Figure 1.** Phase relations of phlogopite with magnesite from 4 to 6 GPa. A dark gray quadrant means that the corresponding phase is present; the key is given in the upper right of the diagram. A light gray quadrant means the phase is not in equilibrium anymore and is reacting out. The numbers on the upper left of each pie chart give the duration of the experiment in hours. Abbr.: phl: phlogopite, mag: magnesite, py: pyrope garnet, ol: olivine, en: enstatite, f: fluid, m: melt, sp: spinel. The bigger the letter "m", the more melt (quench phlogopite) is present. No "m" in a dark gray f/m quadrant means there is fluid present.

To date, the fluid phase has not been analyzed quantitatively. Because there is no other crystalline phase present, potassium, extra silica and magnesium might be dissolved in the fluid.

Above 1250 and 1270°C at 6 and 4 GPa, respectively, a change in texture becomes obvious; which, thanks to further experiments, extends to lower temperatures than we previously reported in Enggist et al. (2009). Over a range of 50 and 100°C at 6 and 4 GPa, respectively, the amount of primary phlogopite decreases and elongated, skeletal phlogopite crystals become more common. This skeletal phlogopite is interpreted to have grown upon quench of the experiment from a hydrous melt that, in this system, quenches to phlogopite plus a hydrous solution. At this point, magnesite has reacted out and the new stable phases are olivine and enstatite; pyrope is present still and its amount increases to higher pressures and temperatures. When a Pt-capsule run at those transitional conditions, resulting in small amount of quench phlogopite with primary phlogopite present still, is breached during the mounting and polishing procedure, the hydrous solution exits the capsule and a gas phase, most probably $CO_2$, escapes from the solution inducing precipitation of solutes that were identified as being K-rich.

After quench of experiments run above 1300 and 1350°C at 6 and 4 GPa, respectively, the only phlogopite phase occurring is quench phlogopite, coexisting with olivine ± enstatite, pyrope, plus a hydrous solution. At low pressures and high temperatures, spinel can be found in the run products. No, or only minor precipitation of solutes was observed from the hydrous solution escaping the capsules that were run at conditions where primary phlogopite reacted out completely.

## Conclusions

Phase relations seem to be controlled by three reactions: (1) synthetic phlogopite breaks down at sub-solidus conditions to *primary phl + py + K-bearing fluid* which most probably is due to a sub-stoichiometric composition of the synthetic phlogopite.

(2) The reaction *primary phl + mag + fluid = ol + en + py + K-$CO_2$-$H_2O$-rich melt* marks the location of the first occurrence of melt and thus the location of the solidus of the system at 1250 and 1270°C at 6 and 4 GPa, respectively. This reaction should be univariant in the six component system and its divariant appearance is probably caused by thermal gradients within the Pt-capsules.

(3) The increasing amount of garnet to higher temperatures and pressures indicates a divariant relation for garnet. The fact that garnet is present supra-solidus implies that a hydrous, K-$CO_2$-rich fluid or silicate melt could react with garnet peridotite to form phlogopite.

The melt close to solidus is highly enriched in K relative to other elements such as Si, Al, Mg since only minor quench phlogopite is present and thus K remains in the hydrous solution after quench. After all primary phlogopite reacted out, more abundant quench phlogopite incorporates most potassium but not all the water and thus a hydrous, $CO_2$-rich solution is left behind.

Figure 2 shows a compilation of phlogopite breakdown curves of previous studies and our study. The addition of $CO_2$ to the system shifts the solidus significantly to lower temperatures.

The cooler 40 mWm$^{-2}$ geotherm intersects the solidus above 6 GPa implying that phlogopite will be stable down to about 200 km in depth in presence of carbonate and will coexist with a fluid at sub-continental lithospheric mantle conditions. The metasomatic agent in this case would be a K-bearing fluid.

The hotter geotherm intersects the solidus at a depth of about 180 km. To this depth a fluid would be present. Beyond this depth, at the base of the sub-continental lithospheric mantle, a hydrous, $CO_2$-bearing silicate melt will be the possible metasomatic agent.
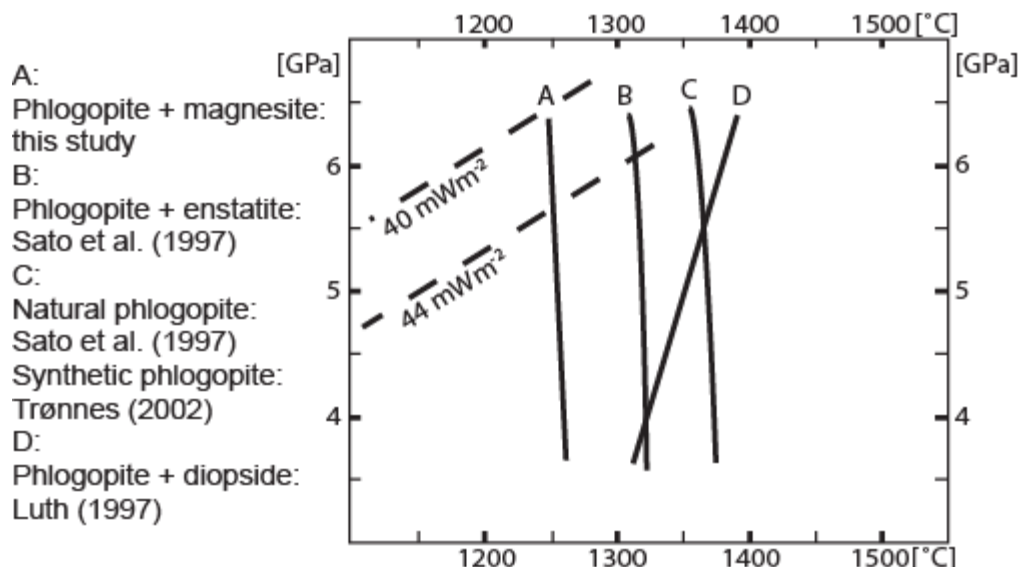
**Figure 2.** Phlogopite breakdown curves (solid lines). The dashed lines give two continental geotherms. The 40 mWm$^{-2}$ geotherm intersects the solidus above 6 GPa showing that a K-bearing hydrous fluid will be the potential metasomatic agent to a depth of 200 km. In a hotter environment, i.e. 44 mWm$^{-2}$, a melt is present at the base of the sub-continental lithospheric mantle.

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