## Reversed phase equilibrium constraints on the stability of Mg-Fe-Al biotite

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## ABSTRACT

The stability of Mg-Fe-Al biotite has been investigated with reversed phase-equilibrium experiments on four equilibria. Experimental brackets in pure H<sub>2</sub>O and H<sub>2</sub>O-CO<sub>2</sub> mixtures for the equilibrium:

 $phlogopite + 3 quartz = enstatite + sanidine + H_2O$ (1)

are in good agreement with previous experiments in mixed-volatile fluids (Bohlen et al. 1983) and H<sub>2</sub>O-KCl solutions (Aranovich and Newton 1998), while indicating a reduced stability field for phlogopite compared to previous data in pure H<sub>2</sub>O (Wood 1976; Peterson and Newton 1989). Aluminum solubility in biotite has been determined in the Fe-, Mg-, and Fe-Mg systems from reversed phase-equilibrium data for the equilibria:

3 eastonite + 6 quartz = 2 phlogopite + 3 sillimanite + sanidine + 
$$H_2O$$
 (2)

 $3 \text{ siderophyllite } + 6 \text{ quartz} = 2 \text{ annite } + 3 \text{ sillimanite } + \text{ sanidine } + \text{H}_2\text{O}$  (3)

over the *P*-*T* range ~600–750 °C and 1.1–3.4 kbar. Over the investigated temperatures, the brackets define nominal Al saturation levels of  $1.60 \pm 0.04$  in Mg-biotite,  $2.08 \pm 0.05$  in Fe-biotite, and  $1.81 \pm 0.03$  in biotite with Fe/(Fe + Mg) = 0.43–0.44. The slight decrease in Al with increasing *T* and decreasing *P* suggested by the data is less than experimental uncertainties.

Compared to biotite on the Phl–Ann join, Al-saturated biotites have a markedly larger stability field, particularly in the Fe-system. This effect has been quantified in the Fe-system with one reversal between 691–709 °C at 2.4 kbar for the equilibrium:

biotite + sillimanite + quartz = almandine + sanidine + 
$$H_2O$$
 (4)

The combined experimental results place tight constraints on the thermodynamic properties of phlogopite, annite, eastonite, and siderophyllite. The resulting nonzero ( $\Delta H_{298} = -9.4 \text{ kJ/mol}$ , with  $\Delta S = \Delta V = 0$ ) energetics for the internal equilibrium:

Eastonite + 
$$2/3$$
 Annite =  $2/3$  Phlogopite + Siderophyllite (5)

reflect strong Fe-Al affinity in biotite, which has a marked effect on thermobarometers involving biotite.

**Keywords:** Biotite, phase equilibria, experimental petrology, mixing properties, annite, phlogopite, siderophyllite, eastonite