Experimental study of the Fe-Mg exchange between garnet and biotite: Constraints on the mixing behavior and analysis of the cation-exchange mechanisms

C.K. Gessmann,* B. Spiering, and M. Raith
Mineralogisch-Petrologisches Institut, Universität Bonn, 53115, Bonn, Germany

ABSTRACT

New experimental data are presented for the Fe-Mg exchange between garnet and biotite in the temperature range 600–800 °C at 0.2 GPa. The Fe-Mg-Al mixing properties of biotite were evaluated and the garnet-biotite geothermometer was recalibrated. SEM observations and comparative laser granulometry show that solution-precipitation largely controls the cation exchange mechanism, involving about 50% of the mineral volume. Mass balance calculations emphasize the effectiveness of the experimental design: A high Gt/Bio ratio ensures that the garnet composition remains approximately constant and close to equilibrium, even if the entire garnet volume is not involved in the cation exchange. Progressively decreasing partition coefficients with decreasing Fe content of garnet indicate nonideal thermodynamic mixing behavior. The application of various garnet activity models support nearly ideal Fe-Mg mixing in garnet. The remaining nonidealities were attributed to nonideal Fe, Mg, and Al mixing in biotite as the initially binary biotite samples changed toward more aluminous compositions during the experiments. Adopting the standard state properties and the garnet-mixing model of Berman (1988, 1990), least square regressions reveal nearly ideal mixing of Fe and Mg in biotite with $W_{FeMg} = 52.3 \pm 2.3$ kJ/mol, while the difference between Fe-Al and Mg-Al interactions yield $\Delta W_{Al} = 17.6 \pm 2.4$ kJ/mol (1 cation). This interaction parameter is strictly valid only for Tschermak-substituted $[^6]Al$ in biotite according to the operational substitution. Application of the suggested garnet-biotite geothermometer reproduces well the reference temperatures of experimental and natural garnet biotite assemblages.

INTRODUCTION

The Fe-Mg exchange between garnet and biotite is strongly temperature dependent and therefore is widely used as a geothermometer. The cation exchange reaction can be expressed as

$$
\text{Mg}_{Al, Si} O_{12} + \text{KFe}_{Al, Si} O_{12}(OH)_2 \leftrightarrow \text{Fe}_{Al, Si} O_{12} + \text{KMg}_{Al, Si} O_{12}(OH)_2.
$$

(1)

almandine

phlogopite

Early calibrations of this exchange reaction were based either on natural assemblages for which the $P$-$T$ conditions were constrained by independent methods (e.g., Thompson 1976; Goldman and Albee 1977) or on experimental data (Ferry and Spear 1978; Perchuk and Lavrent’eva 1983 and Perchuk et al. 1985). The two experimental studies differ in starting materials and experimental conditions employed: Ferry and Spear (1978) carried out exchange experiments with synthetic binary (Fe-Mg) phases at temperatures from 550 to 800 °C at 0.2 GPa; Perchuk and Lavrent’eva (1983) used predominantly natural minerals as reactants for their experimental data. (Perchuk 1972), Wones (1972), Schulien (1975), and Ganguly (1978) in experimental and empirical investigations, while ideal mixing of Fe and Mg in garnet has been inferred in consideration of a similarity of their ionic radii (Shannon and Prewitt 1969), omitting that thermodynamic ideality is not always simply a function of the sizes of the mixing cations (e.g., Geiger and Rossman 1994).

The application of these calibrations to natural assemblages is restricted, however, because the effects of additional cations, such as Ca and Mn in garnet or Ti, $[^6]Al$, and Fe$^{3+}$ in biotite, on the Fe-Mg partitioning between the two phases are not considered (e.g., Saxena 1969; Dallmeyer 1974).

To obtain reliable temperature estimates for a wide compositional range of natural assemblages, a knowledge of the mixing properties of both phases is required. The mixing behavior of quaternary Ca-Mn-Fe-Mg garnets has been extensively studied (e.g., Ganguly and Saxena 1984; Chatterjee 1987; Geiger et al. 1987; Berman 1988, 1990; Hackler and Wood 1989; Koziol and Bohlen 1992; Berman and Aranovich 1996; Ganguly et al. 1996). The at-