Quaternary (Ca-Fe-Mg-Mn) garnet: Displaced equilibrium experiments and implications for current garnet mixing models*

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Abstract: The mixing properties of a spessartine-rich garnet composition (Alm$_{64.5}$Prp$_{10.5}$Sp$_{25}$) with grossular garnet have been determined by phase-equilibrium experiments at 1000 and 900 °C and 8 to 13 kilobars (kb) in the assemblage garnet-plagioclase-kyanite-quartz. The addition of 2 to 4 wt.% Li$_2$MoO$_4$ promoted equilibration. The results indicate that the addition of up to 21 mol.% spessartine to almandine-rich Ca-Mg-Fe garnets does not significantly perturb the activity coefficient of grossular relative to Ca-Mg-Fe garnet and therefore does not affect pressures calculated with the GASP (garnet-alumino-silicate-quartz-plagioclase) geobarometer. Limited data do not allow retrieval of Margules parameters for pyrope-spessartine mixing.

Key-words: garnet, spessartine, experimental petrology, phase equilibria, geobarometry.

Introduction

Great strides have been made in recent years in understanding more of the metamorphic histories of rocks through application of geothermometry and geobarometry. Improved calibrations of the geothermometers and geobarometers have been obtained by experimental studies of the end-member equilibria and consideration of the thermodynamic mixing properties of the minerals exhibiting solid solution. In particular, important work has been done on garnet, a mineral that participates in many metamorphic reactions. Various researchers have recently determined some of the mixing properties of almandine (alm)-grossular (grs)-pyrope (prp)-spessartine (sps) garnets with phase equilibrium experiments, including data on binary alm-grs (Koziol, 1990), prp-grs (Wood, 1988), sps-grs (Koziol, 1990), alm-prp (Koziol & Bohlen, 1992), and on ternary grs-alm-prp mixing (Koziol & Newton, 1989). This has enabled Berman (1990) to formulate a comprehensive garnet mixing model and Berman & Koziol (1991) to constrain the ternary interaction constant ($C_{123}$) to be effectively zero.

However, many low- to medium-grade pelitic rocks contain garnet which has significant amounts of spessartine (manganese) garnet component, or show significant zoning in spessartine component. For this reason, these garnets must be considered as quaternary solutions. To date there has been little experimental work on the mixing of spessartine in garnet. Koziol (1990) showed by phase equilibrium experiments that grs-sps mixing is nearly ideal. Cation exchange experiments on garnet-ilmenite pairs by Pownceby et al. (1987) suggested nearly ideal mixing between iron and manganese (Fe-Mn) garnet. These results were confirmed by O'Neill et al. (1989) with experiments constraining the Fe-Mn mixing properties of ilmenite-pyrophanite. Additional constraints on spessartine mixing in garnet were suggested by Williams & Grambling (1990). Their statistical analysis of garnet-biotite pairs showed that the extent of non-ideal mixing on the prp-alm and prp-sps joins were strongly correlated and could not be individually determined. Instead a range of paired values were allowed. Berman (1990) used all available data to constrain his quaternary (grs-