**Introduction**

Geikielite (Gk) and baddeleyite (Bd) are common trace minerals in contact metamorphosed siliceous dolomitic limestones that develop during prograde metamorphism at the expense of detrital rutile (Rt) and zircon (Zrn) by the reactions:

\[ \text{TiO}_2 + \text{CaMg(CO}_3\text{)}_2 = \text{MgTiO}_3 + \text{CaCO}_3 + \text{CO}_2 \]  

(1) rutile dolomite geikielite calcite fluid

and

\[ \text{ZrSiO}_4 + 2 \text{CaMg(CO}_3\text{)}_2 = \text{ZrO}_2 + \text{Mg}_2\text{SiO}_4 + 2 \text{CaCO}_3 + 2 \text{CO}_2 \]  

(2) zircon dolomite baddeleyite forsterite calcite fluid

[these and all other abbreviations for minerals follow Kretz (1983)]. Isograds can be mapped in contact aureoles based on reactions 1 and 2, and they lie at grades above that of the forsterite (Fo) isograd but below that of the periclase (Per) isograd (e.g., Ferry 1996a) where the major minerals in marbles are dolomite (Dol), calcite (Cal), and Fo. Equilibria involving Gk and Bd based on reactions 1 and 2 therefore offer the potential to constrain pressure (P) and the activity of CO₂ (aCO₂) over a range of metamorphic conditions at which the major minerals in siliceous dolomitic marbles are uninformative. Furthermore, because Bd can be dated radiometrically, equilibria among Bd, Zrn, Dol, Cal, and Fo in principle can help define quantitatively the P-aCO₂-temperature (T)-age conditions of a specific mineral reaction during metamorphism. In order for the potential to be realized fully, however, accurate thermodynamic data are required for Gk and Zrn, and this was the motivation for the phase equilibrium experiments. The reactions:

\[ \text{TiO}_2 + \text{MgCO}_3 = \text{MgTiO}_3 + \text{CO}_2 \]  

(3) rutile magnesite geikielite fluid

and

\[ \text{ZrSiO}_4 + 2 \text{MgCO}_3 = \text{ZrO}_2 + \text{Mg}_2\text{SiO}_4 + 2 \text{CO}_2 \]  

(4) zircon magnesite baddeleyite forsterite fluid

were investigated rather than reactions 1 and 2 because thermodynamic analysis of equilibria based on reactions 3 and 4 is uncomplicated by the effects of solid solution between Cal and Dol. Current thermodynamic databases (Berman 1988, updated 1992; Holland and Powell 1998, updated 2001) predict that reactions 1 and 3 and reactions 2 and 4 are almost parallel in P-T space separated by only 40–60 °C at constant P. Reactions 3 and 4 therefore are good analogs to reactions 1 and 2 and, furthermore, have direct application to coesite- and diamond-bear-