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Assemblages with titanite ($CaTiOSiO_4$), Ca-Mg-Fe olivine and pyroxenes, Fe-Mg-Ti oxides, and quartz: Part I. Theory

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ABSTRACT

Critical evaluation of the thermodynamic data for titanite, in conjunction with a heat capacity equation that takes into account the $P2_1/a \leftrightarrow A2/a$ transition and a more complete *P-V-T* data set for titanite, indicates that: (1) enthalpy of formation values greater than –2600 kJ/mol are not supported by calorimetry; (2) calculated internally consistent feasible solutions converge to enthalpy of formation from the elements values between –2608 and –2600 kJ/mol and 113 to 121 J/mol·K for the entropy; (3) the practice of adjusting the enthalpy of formation to fit phase equilibrium experiments may be erroneous, in contrast, it is the currently accepted entropy of 129.20 ± 0.84 J/mol·K that may need revision to a smaller value. Consequently, we optimize standard-state properties for end-member titanite ($P2_1/a$ structure) consistent with the thermodynamic data in the program QUILF. In addition, we use a modified version of the program to calibrate equilibria among titanite ($CaTiOSiO_4$), Fe-Mg-Ti ilmenite and spinel, Ca-Mg-Fe pyroxenes and olivine, and quartz. Calculations at 1 and 3 kbar, and 650, 850, and 1100 °C, in the system CaO-MgO-FeO-Fe_2O_3-TiO_2-SiO_2, suggest that the reactions:

augite + ilmenite = titanite + spinel phase + quartz

and

augite + ilmenite + quartz = titanite + orthopyroxene

impose well defined f_{O_2}, a_{SiO_2}, and X_{Fe}^{Opx} restrictions to the assemblages (1) titanite + spinel phase + quartz, (2) titanite + orthopyroxene, (3) augite + ilmenite, and consequently titanite stability. The absence of quartz ($a_{SiO_2} < 1$ with respect to Qz) favors the sub-assemblage Fe-Mg-Ti spinel + titanite over augite + ilmenite, and the latter over titanite + orthopyroxene. Nonetheless, in the absence of quartz, no titanite-bearing assemblage is stable relative to olivine + orthopyroxene + augite + ilmenite + Fe-Mg-Ti spinel. From the phase relations, we can also infer that in quartz-saturated rocks: (1) titanite can coexist with orthopyroxene only at low X_{Fe}^{Opx} values, regardless of f_{O_2} conditions, whereas the assemblage titanite + orthopyroxene + spinel phase requires high f_{O_2}, relative Mg-enrichment (from high to moderate X_{Fe}^{Opx}), and temperatures ≤650 °C. (2) The association of titanite with a spinel phase is generally indicative of relatively oxidizing conditions. (3) The assemblage titanite + olivine requires f_{O_2} condition close to FMQ and relative Fe-enrichment (from moderate to high X_{Fe}^{Opx}), and temperatures ≤650 °C.