Assemblages with titanite (CaTiOSiO₄), 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 P2₁/a ↔ 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 (P2₁/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 (CaTiOSiO₄), 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-Fe₂O₃-TiO₂-SiO₂, suggest that the reactions:

augite + ilmenite = titanite + spinel phase + quartz

and

augite + ilmenite + quartz = titanite + orthopyroxene

impose well defined fO₂, aSiO₂, and XFeOpx restrictions to the assemblages (1) titanite + spinel phase + quartz, (2) titanite + orthopyroxene, (3) augite + ilmenite, and consequently titanite stability. The absence of quartz (aSiO₂ < 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 XFeOpx values, regardless of fO₂ conditions, whereas the assemblage titanite + orthopyroxene + spinel phase requires high fO₂, relative Mg-enrichment (from high to moderate XFeOpx), 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 fO₂ condition close to FMQ and relative Fe-enrichment (from moderate to high XFeOpx), and temperatures ≤650 °C.

INTRODUCTION

Titanite can participate in reactions among silicates, oxides, and carbonates. Moreover, it has been shown that such reactions can constrain intensive parameters and place limits on the stability of major rock-forming phases (e.g., Hunt and Kerrick 1977; Wones 1989; Manning and Bohlen 1991). In this paper, we discuss the petrological significance of reactions among end-member titanite, Ca-Fe-Mg pyroxenes and olivine, and Fe-Mg-Ti ilmenite and spinel, and quartz.

Titanite-bearing, oxide-silicate equilibria have been long considered to indicate relatively oxidizing conditions (Verhooegen 1962; Carmichael and Nichols 1967). More important, the assemblage titanite + magnetite + quartz is also generally thought to mark a fundamental boundary between relatively reducing and oxidizing conditions (Wones 1989). The Wones (1989) predictions were confirmed experimentally in the system CaO-FeO-Fe₂O₃-TiO₂-SiO₂ (Xirouchakis 1997; Xirouchakis and Lindsley 1998). The phase relations, however, are more complex than originally proposed (Wones 1989), with the presence of titanite placing tight limits on the stability of hendenbergite, fayalite, ilmenite, magnetite, and quartz (Xirouchakis and Lindsley 1998).

We expand upon these results by considering the stability of the assemblage titanite + spinel phase + quartz in the model.