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Equilibria among titanite, hedenbergite, fayalite, quartz, ilmenite, and magnetite: Experiments and internally consistent thermodynamic data for titanite

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ABSTRACT

For iron-rich compositions, reactions among titanite, clinopyroxene, olivine, quartz, magnetite, and ilmenite can constrain the conditions under which common rocks form. Phase equilibrium experiments in the system CaO-FeO-Fe_2O_3-TiO_2-SiO_2 constrain two of these reactions:

$$\text{clinopyroxene} + \text{ilmenite} = \text{titanite} + \text{olivine} \quad (1)$$

$$\text{clinopyroxene} + \text{ilmenite} = \text{titanite} + \text{magnetite} + \text{quartz} \quad (2)$$

in the range 600–1100 °C and <1 bar −3.8 kbar, and under controlled f_{O_2} conditions. The experimental results indicate that the assemblage clinopyroxene-ilmenite represents reducing conditions relative to titanite-magnetite-quartz. However, the latter is not necessarily indicative of oxygen fugacity conditions higher than that of the FMQ buffer. The data also strongly suggest that the equilibrium positions of reaction 1 and 2 reflect changes in pressure, temperature, f_{O_2}, a_{SiO_2}, $\mu Fe^{2+}Ti^{4+}Fe^{3+}_{-2}$, and $\mu CaFe_{-1}$ in the coexisting Fe-Ti oxides and silicates. Standard state thermodynamic data and solution models for Ca-Fe olivine and clinopyroxene solid solutions, Fe-Ti ilmenite and magnetite solid solutions, and quartz (QUILF database) allow refinement of standard state thermochemical data for end-member titanite (*A*2/*a* space group):

$$\Delta H^0 = -2607.41 \text{ kJ/mol}$$

$$S^0 = 106.00 \text{ J/(mol·K)}$$

$$\Delta G^0 = -2458.95 \text{ kJ/mol}$$

and require modification of published heat capacity equations to:

$$C_p = \frac{591\,460\,608}{T^3} - \frac{5\,118\,324}{T^2} - \frac{1038.4}{\sqrt{T}} + 247.47.$$

The derived data for titanite are internally consistent with an enthalpy of formation of −2610.13 ± 2.90 (2 std. error) kJ/mol, established by drop solution calorimetry, and are specific to the QUILF database. However, analysis of the experimental results using different internally consistent databases suggest that the revision proposed in this study of the currently accepted entropy value of 129.20 J/(mol·K) is largely independent of the databases used. The new entropy is required by the enthalpy of formation for titanite adopted here, which may also require revision of the heat capacity.