INTRODUCTION

Tourmaline is the most common B mineral in the Earth’s crust. Its formation has been documented in several geological processes, from diagenesis to metamorphism (Grew and Sandiford 1984; Cotkin 1987; Henry et al. 1994). Pegmatites, hydrothermally altered rocks around granitic plutons, active geothermal fields, and ore deposits in various geological settings commonly contain tourmaline (Cavarretta and Puxeddu 1990; London and Manning 1995; Henry and Dutrow 1996; Slack 1996; Audétat et al. 1998; Federico et al. 1998).

The presence of tourmaline-bearing rocks in different geological environments shows that B is a mobile element in many crustal processes, and an understanding of the mechanisms of tourmaline precipitation provides insights into the hydrothermal transport of B and associated ore-forming elements. To date, these processes cannot be quantified because of insufficient thermodynamic data on tourmaline (Anovitz and Hemingway 1996).

The purpose of this study is the determination of the standard molar properties of some tourmaline end-members using established estimation methods in conjunction with the limited experimental data on natural B silicates (Kuyunko et al. 1984; Hemingway et al. 1990). Following the so-called “polyhedral model” (Robinson and Haas 1983; Chermak and Rimsidt 1989; Holland 1989), standard enthalpy and entropy of the fictive \( \text{III} \text{B}_2\text{O}_3 \) polyhedron have been derived from standard entropy and enthalpy of formation of the natural tourmaline sample studied by Kuyunko et al. (1984). Using these values, standard entropy and enthalpy were estimated for five tourmaline end-members. The method shown by Helgeson et al. (1978) has allowed heat-capacity functions to be derived for several tourmaline end-members. Appropriate reactions have been formulated that involve a natural dumortierite, a B silicate structurally analogous to tourmaline, for which the heat capacities have been measured over a large temperature interval. Use of these reactions has proven to be the most successful method for estimating heat-capacity functions for the tourmaline end-members considered.

Tourmaline stability calculated from these data has allowed reliable estimates to be made of B solubility in a tourmaline-saturated, magmatic-hydrothermal system (Mole Granite, Australia).

CRYSTAL CHEMISTRY OF TOURMALINE AND DUMORTIERITE

The generalized structural formula of tourmaline is \( \text{XY}_3\text{Z}_6(\text{BO}_3)_3\text{T}_6\text{O}_{18}(\text{W})_4 \) (Henry and Dutrow 1996). The structure is built from planar, six-membered rings of \( \text{T}_6\text{O}_{18} \) tetrahedra \( (\text{T}_6\text{O}_{18}) \) linked by two types of octahedra, \( \text{Z} \) and \( \text{Y} \). These octahedra share their edges to form brucite-like subunits. The \( \text{Z} \) site is relatively small and slightly distorted, whereas the \( \text{Y} \) site is relatively large and regular. Triangular \( \text{BO}_3 \) groups are located at the height of the apical oxygen atoms of the \( \text{T}_6\text{O}_{18} \) rings and lie parallel to the \( (0001) \) plane. These groups are linked to the \( \text{Y} \) and \( \text{Z} \) octahedral sites and to the ninefold coordinated \( \text{X} \) site. Thirty-one anions are present in the tourmaline structural formula, and occupy the apices of coordination polyhedra. Their position is identified by eight distinct sites (01-08), four of which can accommodate \( \text{OH}^- \) and \( \text{F}^- \) (Henry and Dutrow