INTRODUCTION

Tourmalines are important as petrogenetic indicators because they can incorporate by total or partial substitution a great variety of chemical elements depending on the mineralogical and metalogenetic history of the rock (e.g., Clarke et al. 1989; Cleland et al. 1996; Griffin et al. 1996; Henry and Dutrow 1996; Henry and Guidotti 1985; Koval et al. 1991; Slack 1996).

The chemical composition of the tourmaline group minerals can be represented by the general formula \( XY_3Z_6(T_6O_{18})(BO_3)_3V_3W \) (Hawthorne and Henry 1999), where \( X = Na^+, Ca^{2+}, K^+ \), and vacancy (\( \square \)); \( Y = Mg^{2+}, Fe^{2+}, Mn^{2+}, Al^{3+}, Fe^{3+}, Mn^{3+}, Cr^{3+}, and Li^+ \); \( Z = Al^{3+}, Mg^{2+}, Fe^{3+}, Mn^{3+}, Cr^{3+}, and Li^+ \); \( Z = Al^{3+}, Mg^{2+}, Fe^{3+}, Cr^{3+}, and V^{3+} \). The T site is occupied by Si or Al in fourfold coordination with oxygen and in threefold coordination with boron. The Y and Z octahedral sites share edges to form brucite-like fragments. The Z octahedra also share edges with other Z octahedra in a helical linkage parallel to the \( c \) axis (Burns et al. 1994; Donnay and Barton 1972; Grice and Erceit 1993; Hawthorne 1996). OH groups can occupy two structurally distinct positions: the center of the hexagonal rings (OH\(_1\)), and the corner of brucite-like fragments of three edge-sharing octahedra (OH\(_2\)) (e.g., Fig. 1 from Castañeda et al. 2000). These structurally distinct positions have been assigned to the W site, which is dominated by OH\(_1\) O1, F\(^-\), or O\(^2-\), and the V site, which is dominated by OH\(_1\) [O3], or, more rarely, O\(^2-\) (Hawthorne and Henry 1999). Although extensive solid solution is possible, the main compositional varieties are Na- and Mg-rich dravite, Na- and Fe-rich schorl, Ca- and Mg-rich uvite, and Na- and Li-rich elbaite (Dietrich 1985).

Alkali-deficient tourmalines in which a vacancy is dominant in the X site have been synthesized in the laboratory, but they have only been reported for a limited number of natural occurrences (Rosenberg and Foit 1979; Foit 1989; McDonald et al. 1993). Furthermore, the tourmaline group minerals can be divided into three principal groups based on the dominant species at the X site: alkali tourmaline (Na), calcic tourmaline (Ca), and X site vacant tourmalines (Hawthorne and Henry 1999).

The present work reports for the first time the results of a systematic study of Brazilian tourmalines from different geological environments using infrared spectroscopy (IR) complemented with Mössbauer spectroscopy (MS). The objective of the study was to extend the earlier results of Castañeda et al. (2000) to more compositions and to more geological environments. The different behaviors observed in the IR spectra are discussed in order to provide a basis for petrogenetic studies and to place further constraints on substitutions in tourmalines. Only the OH stretching bands were examined because they are very sensitive to crystal-chemical features, which are partly controlled by the bulk chemical environment, water content available in the system, rock/fluid ratio, and temperature-pressure conditions. MS was used to examine site occupancies and valence states of Fe, and, hence, to estimate the Fe\(^{3+}/Fe^{2+}\) ratio. The number of non-equivalent Fe sites can be used to determine the degree of ordering in the structure and the amount of ferric against ferrous iron is a good indicator for the oxygen fugacity conditions prevailing during the crystallization of tourmaline or during subsequent transformations (Dyar et al. 1998; Fuchs et al. 1998).

ABSTRACT

Infrared (IR) spectra in the OH stretching region and Mössbauer spectra (MS) have been acquired for natural tourmalines from magmatic and hydrothermal deposits in the state of Minas Gerais, Brazil. In the magmatic environment, samples of tourmaline were collected from granitic pegmatites and granitoids. In the former, the elbaite-schorl series is prevalent, while in the latter the schorl species is dominant. Tourmalines from hydrothermal gold deposits are typically intermediate members of the dravite-schorl series, whereas the uvite and Fe-bearing uvite species are present in tourmaline samples from a magnesite deposit. Different behaviors are discussed in terms of local lattice environment, geological history, fluid/rock interaction or magma evolution, and degree of crystallinity.

INTRODUCTION

Tourmalines are important as petrogenetic indicators because they can incorporate by total or partial substitution a great variety of chemical elements depending on the mineralogical and metallogenetic history of the rock (e.g., Clarke et al. 1989; Cleland et al. 1996; Griffin et al. 1996; Henry and Dutrow 1996; Henry and Guidotti 1985; Koval et al. 1991; Slack 1996).

The chemical composition of the tourmaline group minerals can be represented by the general formula \( XY_3Z_6(T_6O_{18})(BO_3)_3V_3W \) (Hawthorne and Henry 1999), where \( X = Na^+, Ca^{2+}, K^+ \), and vacancy (\( \square \)); \( Y = Mg^{2+}, Fe^{2+}, Mn^{2+}, Al^{3+}, Fe^{3+}, Mn^{3+}, Cr^{3+}, and Li^+ \); \( Z = Al^{3+}, Mg^{2+}, Fe^{3+}, Mn^{3+}, Cr^{3+}, and V^{3+} \). The T site is occupied by Si or Al in fourfold coordination with oxygen and in threefold coordination with boron. The Y and Z octahedral sites share edges to form brucite-like fragments. The Z octahedra also share edges with other Z octahedra in a helical linkage parallel to the \( c \) axis (Burns et al. 1994; Donnay and Barton 1972; Grice and Erceit 1993; Hawthorne 1996). OH groups can occupy two structurally distinct positions: the center of the hexagonal rings (OH\(_1\)), and the corner of brucite-like fragments of three edge-sharing octahedra (OH\(_2\)) (e.g., Fig. 1 from Castañeda et al. 2000). These structurally distinct positions have been assigned to the W site, which is dominated by OH\(_1\) O1, F\(^-\), or O\(^2-\), and the V site, which is dominated by OH\(_1\) [O3], or, more rarely, O\(^2-\) (Hawthorne and Henry 1999). Although extensive solid solution is possible, the main compositional varieties are Na- and Mg-rich dravite, Na- and Fe-rich schorl, Ca- and Mg-rich uvite, and Na- and Li-rich elbaite (Dietrich 1985).

Alkali-deficient tourmalines in which a vacancy is dominant in the X site have been synthesized in the laboratory, but they have only been reported for a limited number of natural occurrences (Rosenberg and Foit 1979; Foit 1989; McDonald et al. 1993). Furthermore, the tourmaline group minerals can be divided into three principal groups based on the dominant species at the X site: alkali tourmaline (Na), calcic tourmaline (Ca), and X site vacant tourmalines (Hawthorne and Henry 1999).

The present work reports for the first time the results of a systematic study of Brazilian tourmalines from different geological environments using infrared spectroscopy (IR) complemented with Mössbauer spectroscopy (MS). The objective of the study was to extend the earlier results of Castañeda et al. (2000) to more compositions and to more geological environments. The different behaviors observed in the IR spectra are discussed in order to provide a basis for petrogenetic studies and to place further constraints on substitutions in tourmalines. Only the OH stretching bands were examined because they are very sensitive to crystal-chemical features, which are partly controlled by the bulk chemical environment, water content available in the system, rock/fluid ratio, and temperature-pressure conditions. MS was used to examine site occupancies and valence states of Fe, and, hence, to estimate the Fe\(^{3+}/Fe^{2+}\) ratio. The number of non-equivalent Fe sites can be used to determine the degree of ordering in the structure and the amount of ferric against ferrous iron is a good indicator for the oxygen fugacity conditions prevailing during the crystallization of tourmaline or during subsequent transformations (Dyar et al. 1998; Fuchs et al. 1998).