Crystal-chemical characterization of tourmalines from the English Lake District: Electron-microprobe analyses and Mössbauer spectroscopy

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ABSTRACT

Electron-microprobe analyses (EMPA) and Mössbauer spectra (MS) have been acquired for natural tourmalines sampled near Crummock Water and Haweswater, English Lake District. In the former, the dravite-schorl series is prevalent, whereas in the latter, the dravite species is dominant. All tourmaline samples presently studied are chemically disordered. The compositional and MS data give an insight into the thermal and fluid evolution experienced by the tourmalinite rocks. The tourmalines from Crummock Water crystallized in a closed, low \( f_{O_2} \), environment, under the influence of a magmatic fluid. The tourmalines from Haweswater are of hydrothermal origin and were formed under low, variable \( T \) and low \( f_{O_2} \) conditions, from a fluid of constant composition.

INTRODUCTION

Tourmaline is a group of structurally and chemically complex borosilicate minerals that can incorporate by total or partial substitution a great variety of elements. Its composition provides important information about the intensive parameters such as pressure, temperature, and oxygen fugacity under which it is formed. Hence, tourmaline is as an important petrogenetic indicator (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). This mineral group can be represented by the general formula \( XY_3Z_6(T_6O_{18})(BO_3)_3V_3W \) (Hawthorne and Henry 1999), where \( X = Na^+, Ca^{2+}, K^+, or \) vacancy; \( Y = Mg^{2+}, Fe^{2+}, Al^{3+}, Fe^{3+}, Mn^{2+}, Cr^{3+}, V^{3+}, Cu^{2+}, Li^+, Ti^{4+}; \) and \( Z = Al^{3+}, Mg^{2+}, Fe^{3+}, Cr^{3+}, V^{4+}. \) 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 focuses on the composition and cation distribution of tourmalines from tourmalinites collected near Crummock Water and Haweswater, English Lake District, in an effort to decipher the genesis of these rocks. The techniques used are electron-microprobe analysis (EMPA) and Mössbauer spectroscopy (MS). The latter was chosen because it allows measuring the site occupancies of \( Fe \) among structurally different sites and to determine and quantify the oxidation state. The number of non-equivalent \( Fe \) sites can serve as a characteristic for the degree of ordering in the structure and the amount of \( Fe^{3+} \) vs. \( Fe^{2+} \) is an indicator of the oxygen fugacity conditions prevailing during the crystallization of tourmaline or during subsequent transformations (Dyar et al. 1998; Fuchs et al. 1998).

GEOLGICAL SETTING AND TOURMALINITE PETROGRAPHY

Tourmalinites have been reported at three locations in the English Lake District (Fig. 1). In the Black Combe inlier and near Crummock Water, they occur in metapelites of the Skiddaw Group (Cooper et al. 2004). Near Haweswater, they are mainly hosted by ignimbrites and tuffs of the Borrowdale Volcanic Group (Nutt 1970).

The Crummock Water tourmalinites

The Crummock Water tourmalinites are situated within the Crummock Water aureole (Jeans 1973), an elongated zone 24 km long and up to 3 km wide in which the dark slates of the Kirkstile Formation have been bleached. The aureole was generated by retrogressive metasomatism following contact metamorphism (Cooper et al. 1988). The tourmalinization occurred in association with the retrogressive metasomatism. The extent of the Crummock Water aureole suggests that it originated from an underlying intrusion, and geophysical modeling (Lee 1986) revealed a granite pluton beneath the aureole. This intrusion, the Grasmoor granite, might form part of the Ordovician Lake District batholith, although it is not physically connected with any other nearby Ordovician intrusive such as the Ennerdale granophyre (Lee 1986). Cooper et al. (1988) argued that the age of the Grasmoor granite must be similar to that of the metasomatism and tourmalinization (400 Ma) it induced.

Because of the inferred relationship between the Crummock Water aureole and the presumed Grasmoor granite, the tourmalinizing fluids, including B, might have originated from this intrusion. Because there is no direct evidence for the latter, Fortey and Cooper (1986) stated that the Skiddaw Group metapelites might also have served as a source of B.

Tourmalinization took place in wall rocks enclosing a series of faults and joints, transforming the original metapelites into tourmaline-rich rocks by metasomatic alteration (Fortey and Cooper 1986). The tourmalinites form veins, which consist almost ex-