

Investigating a possible relationship between color, chemical composition, and unit cell size in tourmalines

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INTRODUCTION AND GOALS

The varied colors exhibited in tourmaline are attributed to the many chemical combinations possible in the crystalline structure of this mineral. With three possible site substitutions in the crystal structure it is generally assumed that a complete chemical analysis is required to classify tourmalines. The goal of this project was to ascertain if unit cell parameters in tourmaline could be correlated with both chemical composition and color. Dr. Carl Francis of the Harvard Mineralogical Museum proposed this investigation to see if a simpler method of determining tourmaline composition would be possible. He suggested that an XRD study of unit cell size vs. color in tourmalines might permit estimates of chemical composition, facilitating the classification of this mineral without a detailed chemical analysis.

METHODOLOGY

We began our study with a data collection on fifty-four tourmalines that had been studied in detail from a variety of worldwide locations (Dyar et al. 1994). To this we added data on twenty-two tourmalines donated by Dr. W.B. Simmons, three zoned crystals from Dr. C. Francis, and five samples collected during our Maine fieldwork.

We prepared our tourmaline crystals for analysis using standard laboratory methods. We ran XRD analysis on a Scintag XDS 2000 under the following operating conditions : 45 kV, 40 ma, and 1 degree 20 per minute. This data was corrected to plus/minus .008 to determine unit cell dimensions. We ran SEM-EDS analysis on the KeveX 8000 under standard operating conditions and also sent prepared samples to Rutgers University for more precise electron probe analysis.

All results were entered into a master data base which then contained information on over eighty samples, forty-five of these exhibiting colors other than black. We felt this data set contained enough variation to give us meaningful results.

DISCUSSION AND INTERPRETATION

We began our analysis with some widely recognized theories; the foremost one acknowledging the main controlling factor for color in tourmaline as the presence or absence of Iron, (Deer, Howie, and Zussman et al., 1986). This is corroborated by our findings as demonstrated by Fig. 1 (total Fe versus volume). Dunn (1977) established a relationship between a decrease in Fe content and a decrease in color intensity, which is also depicted in Fig. 1. The obvious first step was to compare the established Fe content : color intensity data to the XRD data on unit cell size and see if a correlation could be established. Our findings are plotted in Fig.2. A general trend was displayed, but no definitive boundaries were seen between colors and specific unit cell sizes. Further study would be necessary to determine what, if any, correlations could be found between chemical composition, color and cell size.

We began to survey each tourmaline by type, starting with elbaite because it showed the most separation and range of size on Fig. 2. As established by Dunn (1977) the elbaites clearly exhibit the decreasing color intensity: Fe content effect, with dark blue elbaite grading to green to pink elbaite

following the decreasing iron content curve. Most texts agree that the typical pink or rubellite color of many tourmalines is related to the Mn content -- with either a very small amount of Mn³⁺ or a larger amount of Mn²⁺ responsible for this color. This was also verified in our study. Nassau (1975) states that yellows appear as a variation of pink, possibly as a result of irradiation. Our yellow sample showed chemistry very similar to most pinks. Green colors range from a colorless, pale green to a very dark green which appears almost black, with total Fe content directly linked to intensity of color. Some greens, lacking iron, may take their color from the presence of tiny amounts of Cr or V. The same iron trend is seen in the blue colors, without the extremely light colors present. It is suggested by Dietrich (1985) that the blue spectra is strongly influenced by the Fe²⁺ to Fe³⁺ charge-transfer process. The darker blues also appear black in hand samples and only show blue under the microscope; indeed it is sometimes hard to make a distinction between the very dark greens and blues, and black. The extremely dark colors are all probably caused by the above described charge-transfer process or the Fe³⁺ to O²⁻ charge transfer. These processes are very intense and will take precedence over other color causing phenomenon.

The schorls are fairly straightforward as they display only extremely dark or black colors. These high intensity colors are probably produced from the above described charge transfer processes. The dravites, Mg-rich tourmalines, follow the same trend as the other tourmalines, but appear to be larger than the elbaïtes and schorls with respect to corresponding colors. Fe content again controls the color intensity, with hues ranging from dark brown down to oranges and then to golden yellows. Now that we have established some basis for the causes of color it is time to examine our data and see if we can determine a corresponding change in unit cell size and a change in color.

As noted previously, we began to relate chemical composition to color by comparing unit cell volume to color and charting our results (Fig. 2). A definite trend becomes apparent with the lighter colors occupying the smaller cell volumes and the darker colors becoming increasingly larger in volume. By comparing changing chemical compositions and size of the substituting ions it appears Al³⁺ (ionic radius 0.61) replacing Fe²⁺ (ionic radius 0.86) or Mg²⁺ (ionic radius 0.80) in *x* and/or *y* sites is the major controlling factor in unit cell size (ionic radii from Faure, 1985). Many other chemical combinations are possible, but the most common ion substitutions are between ions with very similar ionic radii.

Both *y* and *z* sites are possible for most elemental substitutions, with the *y*-site favored by iron and the *z*-site favored by aluminum (Dietrich, 1985). These sites share an edge bond, with two *z*-site octahedra adjoining one *y*-site octahedra. With two Al (*z*-site) bonded to one Al³⁺ in the *y*-site the overall crystal structure appears to be in it's "smallest" configuration. As iron, initially Fe²⁺, replaces some Al³⁺ the *a*-axis appears to lengthen (Figs. 3&4). With continuing Fe (or Mg²⁺) replacement of Al³⁺ we see a lengthening of the *c*-axis (Fig.5), especially noted in dravites. When all Al³⁺ is replaced by Fe²⁺, Fe³⁺, or Mg the crystal takes on it's "largest" configuration. We looked at Li and Mg as possible ion substitutions affecting the length of the *a*-axis (Figs.1&2), but need further refinements in our data to make a statement regarding these. Since tourmaline has screw axis symmetry, multiple and identical site substitutions, coupled substitutions and other problems associated with charge balancing, it goes beyond the scope of this study to make definitive judgments on determining chemical composition based solely on cell parameters beyond the above observations.

CONCLUSIONS

We believe a strong correlation exists between the Al³⁺ and total Fe content of tourmaline and the unit cell size, with the lighter elbaïtes having the largest amount of aluminum and the smallest size, grading through the schorls containing more iron and an intermediate size, all the way up to the dravites with a high iron and magnesium content and the largest size. This is a very general comparison of color to content to size relationship which can possibly be refined further with more study. We still seem to need electron micro-probe data to determine the composition where elements with very similar ionic radii are substituting for each other. Further analysis could be possible, with this very extensive data set providing an excellent opportunity for more study.

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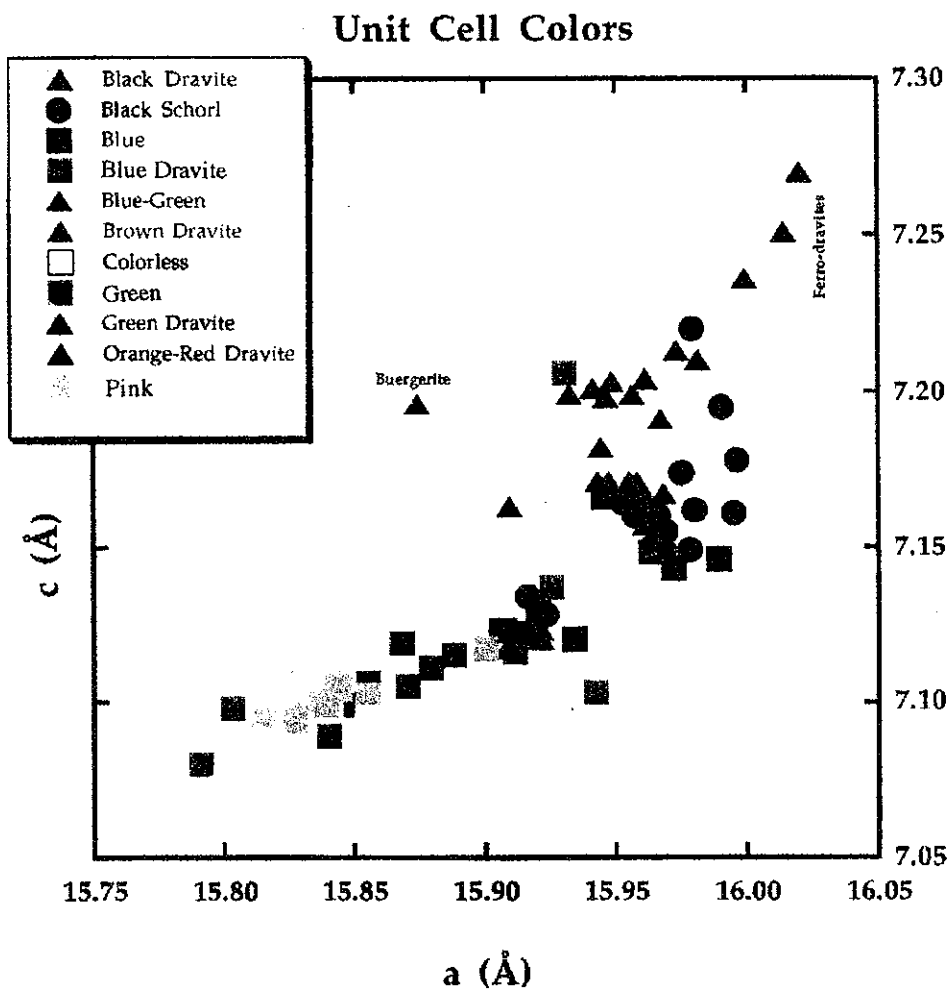


Figure 1.

Figure 2.

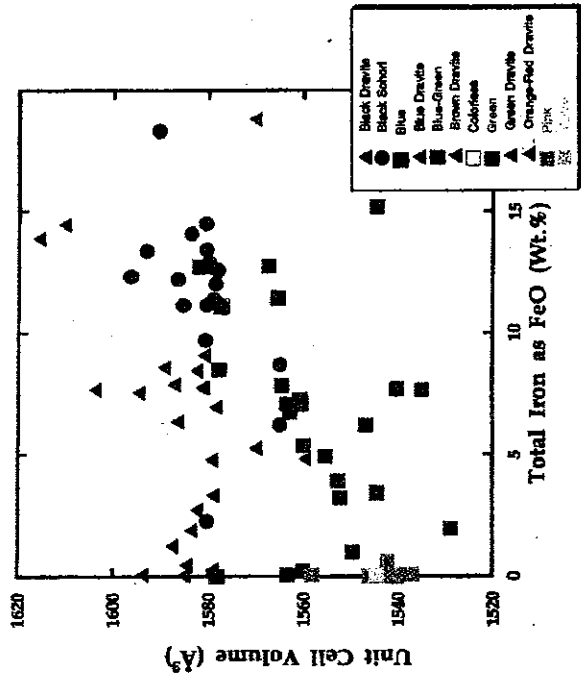


Figure 3.

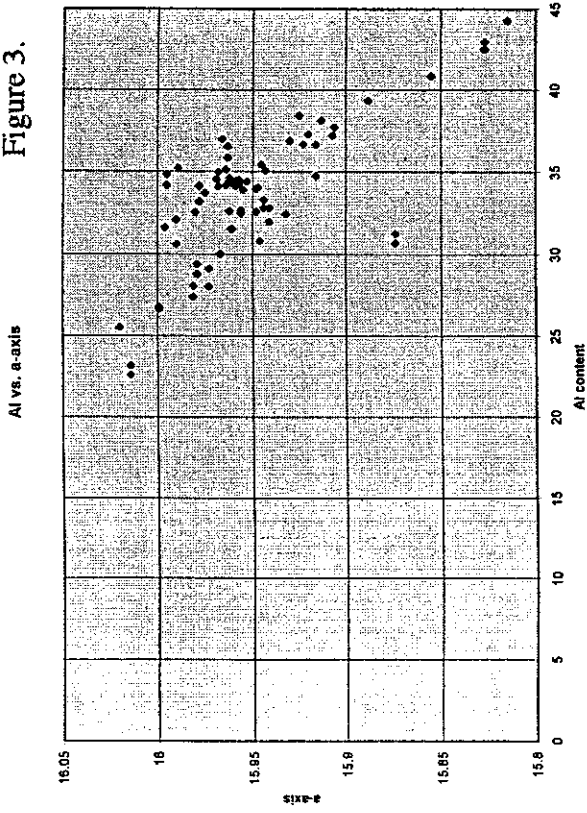


Figure 4.

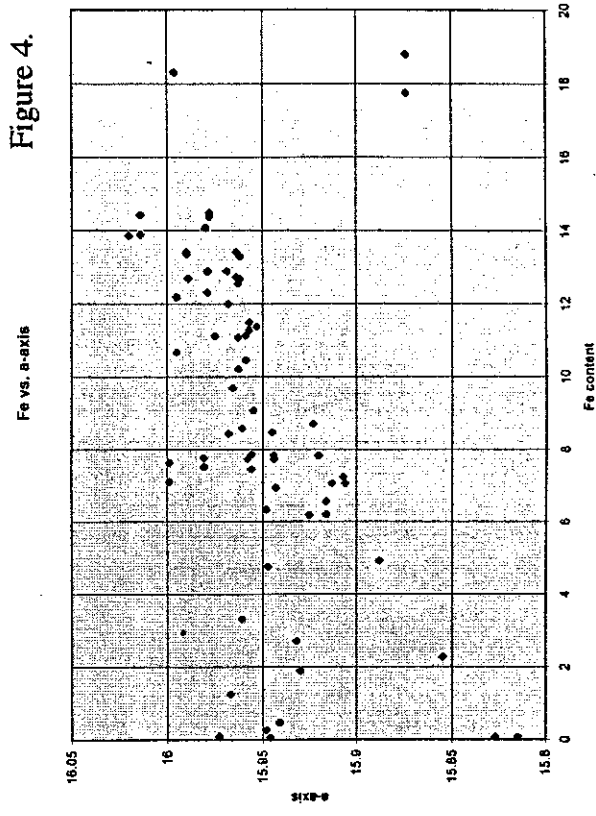


Figure 5.

