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Trace Element Analyses of Tourmalines
From Appalachian-Caledonian Massive Sulfide Deposits

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INTRODUCTION

This report is a contribution to the geochemical data base for tourmalines associated with massive sulfide deposits. It represents part of a much larger investigation (Taylor and Slack, 1983; unpub. data) of the textural, chemical, and isotopic characteristics of the tourmalines, and the implications of these characteristics for mineral exploration and ore genesis. The present study is limited to data on tourmalines from deposits in the Appalachian-Caledonian orogen. Future work is planned on the trace-element chemistry of tourmalines from massive sulfide deposits in other regions, including Finland, Australia, and South Africa.

Tourmalines used for the trace-element analyses were obtained from 6 different deposits. Most of the deposits are in the U.S. Appalachians, including Elizabeth and Ely, Vermont; Croydon, New Hampshire; Black Hawk, Maine; and Ore Knob, North Carolina. Two deposits from the Scandinavian part of the orogen were also sampled, Bleikvassli from Nordland, Norway, and Vassfjell from near Trondheim, Norway. The geologic settings of these deposits vary considerably, but all are of late Proterozoic or early Paleozoic age and metamorphosed to the greenschist or amphibolite facies (see Slack, 1982).

ANALYTICAL METHODS

The geochemical data reported here (Table 1) are based on analyses of pure tourmaline separates. These separates were prepared by the standard laboratory procedures of crushing, sieving, and use of heavy liquids and a Franz isodynamic separator. Removal of extraneous minerals (i.e., sulfides) was carried out by careful hand picking under a binocular microscope. Nearly all of the tourmalines are transparent, and purity of selected grains was insured by using only small (<1 mm) perfectly clear, inclusion-free fragments. Unfortunately, insufficient pure material was available for complete quantitative analyses for all samples from every deposit. In several cases (i.e., Vassfjell), mineral separates were rejected for spectrographic analysis because of the presence of intimate (microscopic) intergrowths of tourmaline and base-metal sulfides. Only the purest separates were used for the quantitative analyses, made on 15 separates for 14 elements including Co, Cr, Cu, Ga, Li, Mn, Ni, Pb, Sc, Sn, Sr, V, Zn, and Zr. Semiquantitative analyses are reported also for Ag, Ba, Be, Ce, La, Mo, Rb, Y, and Yb.

Concentrations of trace elements were determined using spectrographic D-C arc techniques. Reconnaissance semiquantitative analyses were made for 44 elements initially using a six-step spectrographic method modified from the procedure developed by Myers et al. (1961). Ten milligrams of each finely ground tourmaline separate was mixed with 20 milligrams of pure graphite powder, packed into a shallow crater electrode, and burned in a D-C arc for 120 seconds using a Jarrell-Ash 3.4-meter Wadsworth-mounted grating spectrograph. Spectra were recorded on Kodak photographic plates. The observed spectra of each separate was compared visually to reference spectra. The results are reported as midpoints of geometric brackets whose boundaries are 1.2, 0.83, 0.56, 0.38, 0.26, 0.18, 0.12, etc; the midpoints are 1, 0.7, 0.5, 0.3, 0.2, 0.15, 0.1, etc. The precision of a reported value is approximately plus or minus one bracket at 68 percent confidence, or two brackets at 95 percent confidence (Motooka and Grimes, 1976).

The quantitative spectrographic method used is similar to the semi-quantitative method described above, except that each separate was diluted with a mixture of pure quartz and high-purity sodium carbonate, the components ground together in an agate mortar. The resulting diluted separate was mixed with one-fourth weight of graphite powder and burned in a D-C arc. Standards containing known amounts of the analyzed elements were prepared and burned under the same conditions. The spectra of the separates and standards were recorded on the same photographic plate. The density of the various spectral lines of each element was then measured using a Jarrell-Ash densitometer. The concentration of individual elements in each separate was determined from working curves drawn from the standard spectra. The overall precision is approximately plus or minus 15 percent of the amount present. This method follows closely that described in detail by Bastron and others (1960).

RESULTS AND DISCUSSION

Trace elements consistently detected in the tourmalines include Cr, Cu, Ga, Mn, Pb, Sc, Sr, V, and Zn. For the base-metals, Cu contents range from 1.5 to 350 ppm, Pb from <10 to 500 ppm, and Zn to as much as 1200 ppm. Gallium varies from a low of 10 to 70 ppm, and Mn from 85 to a high of 850 ppm. Additional trace elements detected in the tourmalines are Sc (10 to 1700 ppm), Sr (20 to 300 ppm), and V (20 to 590 ppm). Concentrations of other transition metals generally are low, including Ag (<7 ppm), Co (<10 ppm), Mo (<15 ppm), and Ni (<10 ppm); wider ranges of values were found for Cr (1.5 to 560 ppm) and Sn (<7 to 50). Notably, the light elements are systematically depleted in all samples, with Be <1.5 ppm and Li <16 ppm.

The concentrations of trace elements reported here are of particular interest in relation to the associated sulfide deposits, and as chemical discriminators of tourmalines related to a sulfide source, from tourmalines derived from other sources such as granites, pegmatites, and aplites. The most important elements in this respect are Cr, Cu, Li, Mn, Pb, Sr, and V. In granitic environments, tourmalines typically have greater amounts of Li and Mn, relative to those from massive sulfide deposits. The massive-sulfide tourmalines are noteworthy also in containing more Cr, Cu, Pb, Sr, and V, chiefly as a function of the associated sulfide and carbonate assemblages (Taylor and Slack, unpub. data). Discovery of abundant tourmaline (and tourmalinites) with high concentrations of these elements suggests a relationship to mineralizing processes, and the potential for nearby stratabound sulfide deposits (Slack, 1982).

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Table 1.-- Spectrographic analyses of tourmaline mineral separates, in parts per million (ppm).
[Semiquantitative values* in parentheses; all others quantitative (see text)]

Element**	Elizabeth Mine			Ely Mine		Croydon Mine		Bleikvassli Mine			Black Hawk Mine				Ore Knob Mine	
	Vt-105-57	EZ-272	AM-2	CP-16	JS-79-15	JS-79-15	JS-79-24f	BH-D-2	BH-D-3	BH-D-4	BH-D-9	BH-D-15	65-M	111199/29		
Ag (0.5)	--	--	--	--	(1.5)	--	--	(0.7)	--	(2)	--	--	--	--	--	--
Ba (2)	--	(2)	(7)	(15)	(7)	(15)	(2)	(15)	--	--	--	--	--	--	(7)	--
Be (1.5)	--	--	--	--	--	(1.5)	--	--	--	(1.5)	--	--	--	--	--	--
Ce (100)	--	--	--	--	--	--	--	(150)	--	--	--	--	--	--	--	--
Co (3)	(3)	9	8	10	--	--	--	--	--	--	--	--	--	--	8	--
Cr (1)	20	270	160	560	5	(1.5)	(7)	7	6	(3)	10	10	5	100	100	--
Cu (1)	120	50	110	40	20	20	230	15	4	80	110	(1.5)	(1.5)	350	350	--
Ga (5)	70	60	70	50	70	50	50	10	50	50	60	50	60	70	70	--
La (50)	--	--	--	--	--	--	--	(70)	--	--	--	--	--	--	--	--
Li (1)	13	8	8	6	5	10	1	3	7	5	3	4	7	16	16	--
Mn (1)	100	190	85	170	310	400	660	300	550	730	510	430	850	180	180	--
Mo (3)	--	--	--	--	--	--	(15)	--	--	--	--	--	--	--	--	--
Ni (1)	(3)	(3)	--	10	(2)	--	--	3	5	(2)	(3)	5	(2)	(5)	(5)	--
Pb (10)	20	20	20	(10)	170	290	70	500	40	230	50	120	30	--	--	--
Rb (2)	--	--	--	--	--	--	(3)	(2)	--	--	--	--	--	--	--	--
Sc (5)	90	90	60	60	40	20	20	15	10	30	14	20	170	40	40	--
Sn (7)	--	--	(7)	20	50	30	30	10	20	20	30	20	20	--	--	--
Sr (5)	40	40	40	300	60	250	30	300	20	100	30	70	20	90	90	--
V (7)	590	380	470	410	120	30	130	30	20	20	30	70	40	480	480	--
Y (10)	--	--	--	--	--	(15)	(15)	--	--	--	(15)	(30)	--	--	--	--
Yb (1)	--	--	--	--	--	(1.5)	(1.5)	--	--	--	(1.5)	(3)	--	--	--	--
Zn (300)	400	500	400	(300)	1200	700	500	--	300	300	--	--	300	300	300	--
Zr (10)	--	--	--	40	--	340	50	150	--	--	60	150	--	--	--	--

* Semiquantitative data are reported as midpoints of geometric brackets (1, 1.5, 2, 3, 5, 7, 10, etc.), and include the quantitative value at least 60 percent of the time. Precision of a reported value is approximately plus or minus one bracket at 68 percent, or two brackets at 95 percent confidence (Motooka and Grimes, 1976).

** Elements looked for but not found and their approximate lower limits of detection (in parentheses): As(1000), Au(20), Bi(10), Cd(50), Cs(10), Ge(10), Hf(100), In(10), K(2000), Nb(10), P(2000), Pd(2), Pt(50), Re(50), Sb(200), Ta(500), Te(2000), Th(200), Tl(50), U(500), W(100). -- = not detected.