Stable and radiogenic isotope studies of tourmaline: An overview

Studium stabilních a radiogenních izotopů v turmalínu: přehled (Czech summary)

(3 text-figs.)

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This paper presents an overview on stable isotope studies of O, H, B, and Si, and radiogenic isotope studies of Rb-Sr, Sm-Nd, Pb, and K-Ar in tourmaline from various geological settings. Tourmaline O-H isotopic compositions are good indicators of the sources of hydrothermal fluids and origin of the rocks and ore deposits, and can provide information regarding temperatures of tourmaline formation. Based on $\delta^{18}O$ and δD values of tourmaline, modified seawater has been distinguished from several massive sulfide deposits, and metamorphic fluids were responsible for the formation of many hydrothermal gold deposits. There are some problems in the previously published, empirical calibrated oxygen and hydrogen isotope fractionation equations of quartz-tourmaline and tourmaline-water. Hence, new empirically calibrated O-H isotope fractionation equations with high correlation coefficients are presented in this paper. In addition, an experimentally determined hydrogen isotope fractionation factor between tourmaline and water at temperatures > 350 °C has recently been published (Guo - Qian 1997).

Wide variations in $\delta^{11}B$ values of tourmaline exist from various environments. Controls over the boron isotopic compositions of tourmaline are principally compositions of the source rocks, water/rock ratios, seawater entrainment, formational temperatures, and regional metamorphism. Tourmaline $\delta^{11}B$ values are useful for distinguishing between marine and non-marine evaporitic boron sources. Using $\delta^{30}Si$ values, it is possible to distinguish between detrital and hydrothermal sources for Si in tourmalinite; silicon isotopes could be used as effective paleo-environmental indicators.

The Sr-Nd isotopic compositions of tourmaline have major implications for source reservoirs and the nature of hydrothermal fluids, and can yield tourmaline formation ages in some cases. Pb isotope studies of tourmaline obtained by stepwise Pb leaching techniques have been proven to be a good geochronometer. Tourmaline K-Ar ages may represent cooling ages with very high closure temperatures. However, only the $^{40}Ar/^{39}Ar$ dating of tourmaline provides unambiguous ages for tourmaline with a complex metamorphic history.

Overall, results show that isotopic studies of tourmaline are powerful geochemical tools for tracing the source of hydrothermal fluids and their solutes, for constraining the origin of tourmaline-bearing rocks and ore deposits, and for dating tourmalinisation and associated hydrothermal alteration, mineralisation, or metamorphism.

Key words: tourmaline, isotopes, hydrogen, oxygen, boron, silicon, strontium, neodymium, lead, argon

Introduction

Tourmaline is a structurally and chemically complex borosilicate mineral having the general formula $XY_3Z_6Si_6O_{18}(BO_3)_3W_4$, where X = Na, Ca, K, or vacancy; Y = Mg, Fe, Mn, Al, and Li; Z = Al, Mg, Fe, Cr, and V; and W = O, OH, F, and Cl. Other elements such as REE, Sr, and Pb are also reported as minor or trace constituents (Taylor - Slack 1984, Dietrich 1985, King et al. 1988, Jiang - Palmer 1995, Griffin et al. 1996). Tourmaline is widespread in many igneous, metamorphic, and sedimentary rocks, and in a variety of hydrothermal ores, especially massive sulfide, mesothermal Au-Ag, Sn-W, and U deposits (Slack et al. 1984, Kerrich 1987, Beaty et al. 1988, Hellingwerf et al. 1994, Jiang et al. 1995a, b; Slack 1996). This mineral thus can provide valuable information regarding the physico-chemical conditions of its formation, fluid-rock interactions, fluid origin and evolution, sources of contained elements (B, Sr, Nd, Pb, and other associated metals), as well as the origin and timing of tourmalinisation and related mineralisation. Many papers have reported data on the chemical composition of tourmaline (e.g., Ethier - Campbell 1977, Dietrich 1985, Henry - Guidotti 1985, London - Manning 1995, Henry - Dutrow 1996, Slack 1996). However, only a limited number of isotopic studies, both on stable (e.g. H, O, B, and Si) and radiogenic (e.g. Sr, Nd, Pb, and Ar) isotopes, have been published. Slack (1996) briefly reviewed isotopic data on tourmaline, mainly in the context of hydrothermal ore-forming systems. Henry and Dutrow (1996) also summarised some isotopic data and geochronology involving tourmaline. This paper provides a more detailed summary of tourmaline isotopic studies and discusses how to use stable and radiogenic isotopes to better understand geological and geochemical processes involved in tourmaline formation.

Oxygen and hydrogen isotopes

Fractionation between tourmaline and water

Oxygen and hydrogen isotope fractionation fators between tourmaline and water have been determined by experimental measurements, empirical estimates, and theoretical calculations. The published fractionation equations are listed in Table 1.

Blamart et al. (1988, 1989) conducted a reconnaissance experimental calibration study of D/H isotope fractionation between tourmaline and water at 500 °C to 700 °C. The calculated fractionation factors ($\alpha_{Tur\text{-}Water}$) at 700 °C, 600 °C, and 500 °C are 1.007, 1.002, and 0.980, respectively. No experimental studies of oxygen isotope fractionation between tourmaline and water have been reported.

An empirical estimate for oxygen isotope fractionation between quartz and tourmaline is 2.2 ‰ at 560 °C (Blamart et al. 1992). A more extensive empirical study was carried out by Kotzer et al. (1993) for both D/H and $^{18}O/^{16}O$ fractionations between tourmaline and water from 200 to 600 °C, based on isotopic compositions of contemporaneous quartz, tourmaline, chlorite, biotite, muscovite, and illite from several hydrothermal ore deposits and pegmatites. Their results show that tourmaline and muscovite have similar D/H and $^{18}O/^{16}O$ fractionation characteristics, implying that the dominant controls on the isotopic properties of the minerals are imposed by vibrational energies of the Al-Si-O and Si-O bonds. However, there are small differences in the $\delta^{18}O$ values of tourmaline and muscovite that may be due to the effect of BO_3 bonds in tourmaline.

Theoretical calculations of the oxygen isotope fractionation factors of tourmaline-water, quartz-tourmaline, and calcite-tourmaline were reported by Zheng (1993) (Table 1). He also calculated the oxygen isotope fractionation factor between tourmaline and its OH- component for potential single-mineral thermometry, if we can experimentally determine the $\delta^{18}O$ values of tourmaline and its hydroxyl. Calculations for different hydroxyl silicates show that tourmaline is ^{18}O-enriched relative to muscovite and illite (Zheng 1993).

The hydrogen isotope fractionation factors of tourmaline-water approximates those of muscovite-water at temperatures of 300-600 °C (Kotzer et al. 1993). Kotzer et al. (1993) found a discontinuity in the variation of tourmaline-water D/H fractionation factors at lower temperatures of 200-300 °C, and suggested that the hydrogen isotope exchange systematics of tourmaline are similar to those of many other hydroxyl minerals such as kaolinite and boehmite. The latter minerals also commonly display a reversal in hydrogen isotope fractionation at approximately 200 to 250 °C due to changes in the relative energies of hydrogen bonding within the mineral and in water near its critical point (Suzuoki - Epstein 1976, Graham et al. 1980, Kyser 1987). However, the assumptions of Kotzer et al. (1993) were based only on two analyses of low-temperature tourmalines from unconformity-type uranium deposits in the Athabasca Basin. The calculations for the two low-temperature tourmalines are considered unreliable because they used the illite-water D/H fractionation equation of Yeh (1980), which is only valid at temperature < 120 °C; no illite-water D/H fractionation equations are available at higher temperatures. Since illite is compositionally and structurally similar to muscovite and sericite, they have similar hydrogen isotope fractionation characteristics. Hence, it is reasonable to use muscovite-water or sericite-water D/H fractionation equations. For the temperature range of 150-250 °C, the only available D/H fractionation was estimated between sericite and water (Marumo et al. 1980). Recalculations using the sericite-water D/H fractionation data show a different tourmaline-water D/H fractionation trend from that proposed by Kotzer et al. (1993) at low temperatures of 150-250 °C (Fig. 1). Another major problem regarding the empirically estimated fractionation equations of Kotzer et al. (1993) is that the authors may have underestimated the true temperatures for the pegmatitic tourmalines using the quartz-muscovite oxygen isotope geothermometer of Eslinger et al. (1979). The temperature range of the pegmatitic tourmalines calculated by Kotzer et al. (1993) is mostly 350-470 °C, which is lower than the temperatures determined for pegmatite emplacement (730-700 °C) and for pocket mineral crystallisation (565-525 °C) based on fluid inclusion data and multiple mineral-pair oxygen isotope geothermometers (Taylor et al. 1979). Recalculations using the quartz-muscovite isotope fractionation factors calculated by Zheng (1993) give a reasonable temperature range of 615-505 °C for the pegmatitic tourmalines. Therefore, I have recalculated the data from Kotzer et al. (1993), together with many other available data from the literature (Table 2). These results show better correlation coefficients both for the quartz-tourmaline oxygen isotope fractionation equation and for the tourmaline-water hydrogen isotope fractionation equation (Fig. 1, Table 1):

Oxygen: $1000\ln a\alpha_{Q\text{-}Tur} = 1.05\ (10^6/T^2) + 0.49$ (200-600 °C)

Hydrogen: $1000\ln a\alpha_{Tur\text{-}Water} = -14.2\ (10^6/T^2) + 4.7$ (300-600 °C)

The newly calculated oxygen isotope fractionation equation is similar to that of Kotzer et al. (1993), but a large difference exists for the tourmaline-water hydrogen isotope fractionation equation. Recently, Guo and Qian (1997) studied experimentally hydrogen isotope exchange between tourmaline and water at temperatures > 350 to 800 °C (Table 1). However, at 350 °C, exchange between tourmaline and water is so slow that the equilibrium fractionation may not be reliably interpolated. Therefore, hydrogen isotope data are still lacking for low-temperature

Table 1. Oxygen and hydrogen isotope fractionation equations of quartz-tourmaline, tourmaline-water, and tourmaline-OH^-

	Fractionation equations	Temperatures	r*	References
Oxygen	$1000\ln\alpha_{Q\text{-}Tur} = 1.0\ (10^6/T^2) + 0.39$	200-600 °C	0.75	Kotzer et al. (1993)
	$1000\ln\alpha_{Q\text{-}Tur} = 1.05\ (10^6/T^2) + 0.49$	200-600 °C	0.96	This study
	$1000\ln\alpha_{Q\text{-}Tur} = 0.27\ (10^6/T^2) + 2.22\ (10^3/T) - 0.92$	0-1200 °C		Zheng (1993)
	$1000\ln\alpha_{Tur\text{-}OH} = 0.92\ (10^6/T^2) + 6.28\ (10^3/T) - 2.62$	0-1200 °C		Zheng (1993)
Hydrogen	$1000\ln\alpha_{Tur\text{-}water} = -27.2\ (10^6/T^2) + 28.1$	300-600 °C	0.74	Kotzer et al. (1993)
	$1000\ln\alpha_{Tur\text{-}water} = -14.2\ (10^6/T^2) + 4.7$	300-600 °C	0.81	This study
	$1000\ln\alpha_{Tur\text{-}water} = -44.9\ (10^6/T^2) + 56.8$	500-700 °C	0.97	Blamart et al. (1988, 1989)
	$1000\ln\alpha_{Tur\text{-}water} = -27.9\ (10^6/T^2) + 2.3$	350-800 °C	0.999	Guo - Qian (1997)

* r = correlation coefficient of linear regression of the data

(< 300 °C) tourmalines. More work clearly needs to be done in order to better constrain the low-temperature D/H fractionation between tourmaline and water.

Variations in the Fe, Mg, and Al contents of hydroxyl minerals (micas, amphibole, and chlorite) can affect hydrogen isotope fractionation between the mineral and water (Suzuoki - Epstein 1976, Marumo et al. 1980, Graham 1984). However, contradictory results were obtained for tourmaline. Taylor and Slack (1984) and Kotzer et al. (1993) found no correlation between δD values and Fe/(Fe + Mg) ratios of tourmaline from hydrothermal ore deposits. Taylor et al. (1998) also found no chemical effect on the tourmaline-water hydrogen isotope fractionation factor from a detailed H-O isotopic studies of tourmaline from the giant Kidd Creek massive sulfide deposits, Ontario, but they observed an apparent positive correlation between $\delta^{18}O$ values and Fe/(Fe + Mg) ratios for footwall tourmalines. However, Taylor et al. (1992) found a negative correlation for hydrothermal tourmalines near the contact of granites in northwest Tanzania. They suggested that the relative proportions of Mg^{2+} and Fe^{2+} in the octahedral Y-site may control the incorporation of hydrogen isotopes into the tourmaline of dravite-schorl series, with the mole fraction of Fe^{2+} having the dominant effect. Al^{3+} in the octahedral Y-site of tourmaline may also affect D/H isotope fractionation, but the effect is likely to be minor because of its low atomic mass/charge ratio (Taylor et al. 1992, Suzuoki - Epstein 1976). Recently, Guo and Qian (1997) revealed correlation between the hydrogen isotope fractionation and concentrations of the octahedrally coordinated cations (Fe, Mg, Al), and suggested that this compositional dependence of hydrogen isotope fractionation is generally true for all nonhydrogen-bonded hydroxyl minerals such as mica, amphibole, tourmaline, brucite, and kaolinite. In a detailed chemical and stable isotopic studies of tourmaline from stratiform tourmaline-rich rocks from the Palaeozoic Cinco Villas massif (Spain), Pesquera and Velasco (1997) also observed a decrease in δD with increasing Fe content in tourmaline.

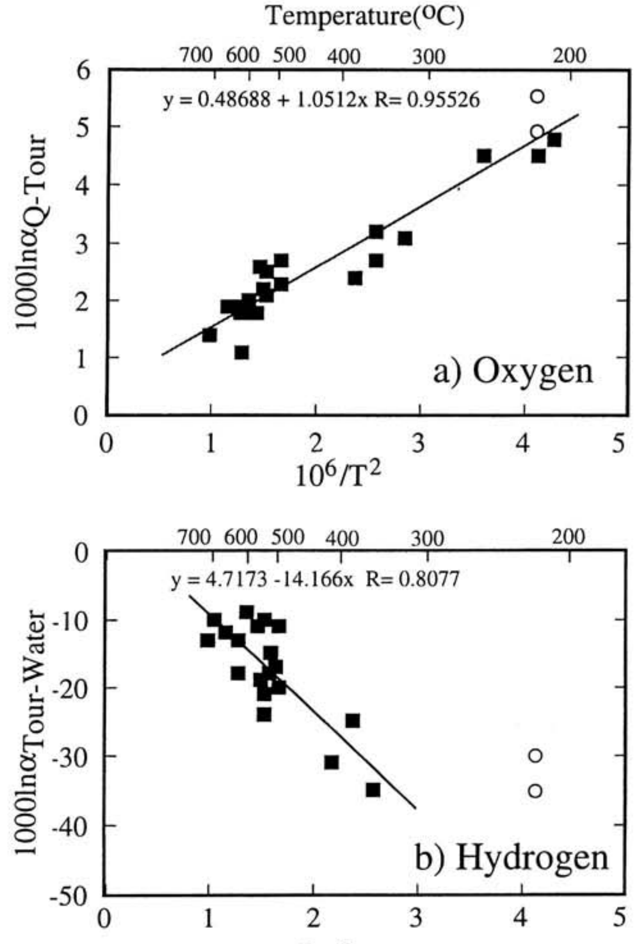

Fig. 1. Empirical oxygen (a) and hydrogen (b) isotope fractionation factors of quartz-tourmaline and tourmaline-water calculated from the data in Table 2. The two circles represent low-temperature tourmalines from Athabasca Basin uranium deposits. All other data are presented as squares

Geological applications

Oxygen and hydrogen isotope studies of tourmaline have largely focused on tourmalines from hydrothermal ore deposits and tourmalinites, and from granites and pegmatites, which have provided valuable information on the temperatures of tourmalinisation and associated ore formation, source of the hydrothermal fluids, and origin of the deposits.

Massive sulfide deposits and tourmalinites

Oxygen and hydrogen isotopic compositions of tourmaline are well documented from a number of massive sulfide deposits worldwide. Taylor and Slack (1984) showed that tourmalines from Appalachian-Caledonian massive sulfide deposits typically have high $\delta^{18}O$ (9.5 to 15.5‰) and less variable and high δD (-60 to -45‰) values, which are different from those of granitic and pegmatitic tourmalines. They suggested that large variations in the $\delta^{18}O$ data reflect controls from different formational temperatures, water/rock ratios, and isotopic compositions of the host lithologies. The higher $\delta^{18}O$ values of tourmaline from Bleikvassli (Norway) and Ely (Vermont) may reflect fluid reaction with high-^{18}O clastic metasedimentary country rocks, whereas the low δD values of Blackhawk (Maine) tourmalines may indicate involvement of low-D magmatic or metamorphic fluids during their recrystallisation. Calculations of oxygen and hydrogen isotopic compositions for the parent fluid imply its origin from modified seawater. Slack (1996) suggested that hydrogen isotopes are more easily exchanged with later metamorphic fluids than oxygen isotopes due to the different structural positions of these two elements in tourmaline. The hydrogen is weakly bound in brucite-type layers, whereas most oxygen is strongly bound in SiO_4 tetrahedra and BO_3 triangles.

Taylor et al. (1991) conducted a primary O-H isotopic studies of tourmaline from the Kidd Creek massive sulfi-

Table 2. $\delta^{18}O$ and δD values of tourmaline and coexisting minerals from various geological settings, with calculated oxygen isotope quartz-mineral pair temperatures, quartz-tourmaline oxygen isotope fractionations, and tourmaline-water hydrogen isotope fractionations

Sample No.		$\delta^{18}O$ (‰)								δD (‰)						T(°C)	$\Delta^{18}O$	$\Delta D/H$	
		Q(*)	Mus.	Lep.	Bio.	Chl.	Ill.	Ab.	Tur.	Mus.	Lep.	Bio.	Chl.	Ill.	Tur.	(***)	(Q-Tur)	(Tur-Water)	Data source
U deposits	Athal1	14.4					9.6		8.8					-87	-91	219	5.6		Kotzer - Kyser (1990)
	Athal2	14.1					9.3		9.6					-72	-81	219	4.5		
lode Au deposits	RK2	13.5	11.5						12.1	-51					-52	737	1.4	-13	King (1990)
	RK7	13.6	11.5							-51					-45	711		-10	
	RK3	14.6	10.9						11.5							319	3.1		
	RK4	13.1	10.3						10.5							555	2.6		
	HT2	11.3			5.7				8.4							500	2.9		
	85E	12				4.8			8.8							350	3.2		
	TL-141	10.6	7.5						7.9	-93					-90	350	2.7	-35	
	FR87025	12.3				6.7			9.9				-80		-69	377	2.4	-25	
Massive sulfide deposits	SULL	14.6							9.8							210	4.8		Beaty et al. (1988)
	T.C.	14.2							9.3							220	4.9		
Metapelites	Zone III	13	10.7		7.9				10.8			-76			-60	545	2.2	-19	Blamart et al. (1992)
	Zone II											-70			-60	525		-18	
	Zone I											-81			-61	510		-17	
Granites and Pegmatites	SD-14-2	10.4	7.5							-58					-68	538		-24	Taylor et al. (1979)
	SD-26-1A	10.6	7.7							-61					-68	538		-21	
	SD-38-2	10.3	7.6						8.5	-65						575	1.8		
	SD-42-1	10.9	7.8						8.2	-58					-61	505	2.7	-20	
	SD-28-2	11	8.1						8.5	-76						538	2.5		
	SD-37	10.5	8						8.7	-65					-74	615	1.8	-18	
	P-36	10.5	8.2						8.6	-72					-78	660	1.9	-12	
	SD-8-4	10.9	7.9							-60					-59	521		-15	
	SD-37-2	10.6	8.1						8.7	-65					-69	615	1.9	-13	
	S-3	10.7		8.2					9.6	-76						610	1.1		
	T.Q.A.-4	8.7	5.6						6.4	-99					-93	505	2.3	-11	
	T.Q.-3	10.7		8.1					8.7	-94					-74	590	2.0	-9	
	48-B-4	11.4						7.9	6.9						-80	254	4.5		Taylor-Friedrichsen (1983)
	T-7	11						8.9		-68					-70	405		-31	
	X77	13.7	10.8						11.6	-80					-75	538	2.1	-10	France-Lanordet et al. (1988)
	U464	13.7	10.9							-79					-77	555		-11	
	DK256	13.4			9.4				11.6							565	1.8		

* Abbreviations used are: Q-quartz, Mus.-muscovite, Lep. - lepidolite, Bio. - biotite, Chl. - chlorite, Ill. - illite, Ab. - albite, Tur. - tourmaline.

** Temperatures calculated using oxygen isotope fractionation equations of quartz-muscovite, quartz-biotite, and quartz-lepidolite (Zheng 1993), quartz-albite (Bottinga - Javoy 1973), quartz-illite (Eslinger - Savin 1973), and quartz-chlorite (Wenner - Taylor 1971, Matsuhisa et al. 1979).

*** δD_{water} values calculated using hydrogen isotope fractionation equations of muscovite-water and biotite-water (Suzuoki - Epstein 1976), chlorite-water (Savin - Lee 1988), and sericite-water (Marumo et al. 1980).

de deposit, Ontario, and suggested a modified seawater origin for the hydrothermal ore-forming fluids. Recently, their comprehensive O-H isotopic results (Taylor et al. 1998) revealed three fluids involved in the ore formation: 1) slightly modified seawater (SW), with $\delta^{18}O$ = 0‰, δD = 0‰, and an assumed normal salinity of ca. 3.2 wt% NaCl; 2) extensively modified seawater (MSW), possibly evolved from SW by boiling and water/rock reaction, with an estimated maximum salinity of 6.4 to 16 wt% NaCl, $\delta^{18}O$ = 4.0‰, and δD = 20‰; and 3) a high-temperature fluid (HT), evolved from MSW by high-temperature water/rock reaction, with a similarly estimated maximum salinity of 6.4 to 16 wt% NaCl, $\delta^{18}O$ = 6.0‰, and δD = 0‰. The $\delta^{18}O$ values of Kidd Creek tourmalines varies from 8.2 to 11.2‰, and δD values from -48 to -13‰. The massive sulfide-associated tourmalines from the hanging wall have generally lower δD values (-48 to -34‰) than the footwall ones (-35 to -13‰) from the stringer zone and stringer fringe. Taylor et al (1998) calculated quartz-tourmaline oxygen isotope equilibration temperatures from 183 to 429 °C. Their calculations also imply that cooler fluids (e.g., < 183 °C) were involved in precipitation of massive and bedded sulfide, and in mineralisation and alteration along the northern margin of the ore body; whereas hotter fluids (e.g., 373-429 °C) were responsible for formation of the copper stringer zone. In addition, they found that quartz-tourmaline isotopic temperatures strongly correlate with average Fe/(Fe + Mg) ratios for tourmaline in footwall stringer-zone samples, suggesting that tourmalines richer in Fe are products of hotter fluids (cf. Slack - Coad 1989).

Tourmaline is abundant in the Sullivan Pb-Zn-Ag massive sulfide deposit, British Columbia (Ethier - Campbell 1977, Hamilton et al. 1982). Previously, $\delta^{18}O$ and δD values were only reported for whole-rock tourmalinites due to the extremely fine-grained (< 10 μm) nature of most Sullivan tourmaline that makes it difficult to separate from coexisting quartz. Nesbitt et al. (1984) found that these tourmalinites have $\delta^{18}O$ values (10.7 to 13.1‰) similar to those of unaltered clastic metasedimentary rocks in the region (9.9 to 13.1‰), and suggested that the tourmalinites formed from low-temperature (< 100 °C) fluids. However, it should be noted that these whole-rock analyses included substantial amounts of detrital quartz, and hence may have underestimated the real temperature of formation (see Slack 1996). Beaty et al. (1988) used these data and calculated a series of hydrothermal models for the formation of Sullivan tourmalinites, assuming a high water/rock ratio and a moderate to very high degree of oxygen isotope exchange. Their results suggested that Sullivan tourmalinites formed from a highly evolved and deeply circulated fluid of marine origin at temperatures of 200-250 °C. This is further supported by recent H-O isotopic studies of the Sullivan deposit (Taylor et al. 1995). Taylor et al. (1995) reported a $\delta^{18}O$ of 12.0‰ and δD of -55‰ for the Sullivan tourmalinite, and a large range of $\delta^{18}O$ and δD (3.5 to 14‰ and -100 to -50‰, respectively) for the other rock types such as chlorite-pyrite, albite-chlorite, and quartz-muscovite-calcite. Beaty et al. (1988) reported $\delta^{18}O$ and δD values of tourmaline separates from a number of unmineralised settings in the Belt-Purcell Supergroup. These tourmalines have $\delta^{18}O$ values of 8.2 to 10.7‰, which are lower than the $\delta^{18}O$ values of the Sullivan tourmalinites. The tourmalines from barren hydrothermally altered rocks at Trestle Creek, Idaho, have $\delta^{18}O$ and δD values of 9.0 to 9.9‰ and -65 to -42‰, respectively, whereas vein tourmalines in, or adjacent to, gabbroic intrusions have slightly higher $\delta^{18}O$ values of 9.7 to 10.9‰ and δD values of -42 to -39‰. Two tourmalines in fracture fillings and disseminations in siltites have $\delta^{18}O$ values of 10.6 and 10.7‰ and δD values of -58 and -53‰. Beaty et al. (1988) suggested that all of these tourmalines were deposited from fluids of marine origin under varying temperature conditions.

Pesquera and Velasco (1997) measured O-H isotopic compositions of tourmaline from tourmaline-rich rocks (tourmalinites) in the Paleozoic Cinco Villas massif (Spain). They recognised three types of tourmaline-rich rocks. The first type is fine-grained stratiform tourmaline-rich rocks, which are associated with carbonaceous metapelites, tourmalines in this type of rocks show very high $\delta^{18}O$ values (17.7 to 19.0‰), whereas their δD values vary from -35 to -42‰. The extremely high $\delta^{18}O$ values probably reflect the quartz impurities present in these tourmaline samples. Pesquera and Velasco (1997) suggested that this type of tourmaline formed by several processes, including direct precipitation from B-rich hydrothermal fluids or colloids, early diagenetic reactions of carbonaceous pelitic sediments with these fluids, and subsequent recrystallisation during regional metamorphism. The second type is stratabound tourmaline-rich rocks that associated with metapelites in the contact aureole of the Aya granitoid pluton. This type of tourmaline mainly developed by metamorphic recrystallisation of the type 1 tourmalines, and shows slightly lower values of $\delta^{18}O$ (11.3 to 14.6‰) and δD (-40 to -55‰) than the type 1 tourmalines. The third type is stratabound to massive tourmaline-rich rocks that associated with psammopelites in contact with granites and pegmatites. Tourmalines in this type of rocks have relatively low $\delta^{18}O$ and δD values (11 to 13‰ and -47 to -76‰, respectively), possibly due to boron metasomatism by boron-rich fluids derived from assimilated stratiform tourmalinites (Pesquera - Velasco 1997).

Hydrothermal Au-Ag deposits

Oxygen and hydrogen isotopic compositions of tourmaline have been studied in a number of hydrothermal Au-Ag deposits in Precambrian metamorphic rocks. Ibrahim and

Kyser (1991) reported $\delta^{18}O$ and δD values of quartz, tourmaline, and coexisting silicate minerals from Au-quartz veins of the Proterozoic Star Lake Au deposit, northern Saskatchewan. They found that quartz from auriferous veins has $\delta^{18}O$ values of 10 to 11.6‰ that are lower than those of quartz from barren veins (12.9 to 13.4‰), indicating that the quartz was precipitated from distinct fluid sources. Tourmalines from various auriferous veins in the deposit have $\delta^{18}O$ values of 8.4 to 8.9‰, but tourmaline from the Rush Lake veins has much higher δD values (-50 to -52‰) than tourmaline (-108‰) and associated biotite and amphibole (-86 to -111‰) from other veins. Hence, it is believed that the Rush Lake veins may have precipitated from a fluid richer in D (Ibrahim - Kyser 1991). Calculations of the fluid $\delta^{18}O$ and δD values (6 to 8‰ and -80 to -40‰, respectively) in the Star Lake Au deposit suggest its derivation from metamorphic sources and show that the hydrothermal systems had low water/rock ratios.

Tourmaline and quartz from auriferous veins in the Proterozoic Tartan Lake Au deposit, Manitoba, have $\delta^{18}O$ values of 7.9 to 8.8‰ and 10.6 to 12.0‰, respectively, whereas quartz from unmineralised veins shows a larger range of $\delta^{18}O$ values from 10.3 to 15.5‰, similar to that of the Star Lake Au deposit (Fedorowich et al. 1991). One tourmaline from the Tartan Lake deposit has a δD value of -90‰, which is nearly identical to the δD value of coexisting muscovite (-93‰). Fedorowich et al. (1991) suggested that the Au-bearing hydrothermal fluids at Tartan Lake were derived by metamorphic dehydration at a pressure of 1.2 to 2.4 kbars.

Tourmalines from other Proterozoic mesothermal Au deposits, such as Rio and Frontier in Saskatchewan, also have similar ranges of $\delta^{18}O$ and δD values of 7.4 to 9.9‰ and -84 to -69‰, respectively (Ansdell - Kyser 1992, Kotzer et al. 1993). Analogous values of $\delta^{18}O$ (9.6 to 10.5‰) and δD (-67 to -60‰) have been reported for tourmalines from the Beaumont Mine and Maclcenzie lode Au deposits in the Archean Abitibi belt, Canada (King 1990, Kotzer et al. 1993). It is suggested that all of these Proterozoic and Archean Au deposits may have similar fluid compositions and origins (Fedorowich et al. 1991, Ansdell - Kyser 1992). However, tourmalines from the Deep Dome and Coniaurum lode Au deposits in the Abitibi belt have higher $\delta^{18}O$ values of 11.5 to 12.1‰ and higher δD values of -52 to -45‰ (King 1990, Kotzer et al. 1993). Tourmalines from the Proterozoic Laurel Lake Au-Ag deposit in the Flin Flon greenstone belt of northern Saskatchewan and Manitoba also have high $\delta^{18}O$ (9.7 to 9.9‰) and δD (-60 to -36‰) values, and have been suggested as recording precipitation from modified seawater that circulated deeply through volcanic rocks of the area (Ansdell - Kyser 1991). A seawater origin for hydrothermal fluids has also been proposed for the Loulo Au deposit in Mali, West Africa, on the basis of high $\delta^{18}O$ (13.9-16.6‰) and δD (-41 to -32‰) values of tourmaline and quartz associated with the Au mineralization (Fouillac et al. 1993).

U deposits

Tourmaline occurs in the altered wall rocks of many unconformity-type uranium deposits in the Athabasca Basin in Saskatchewan (Hoeve - Sibbald 1978, Kotzer - Kyser 1990). Two stages of tourmaline formation were recognised, an early dravite stage associated with euhedral quartz in quartz-tourmaline breccias has $\delta^{18}O$ and δD values similar to those of illite in the alteration rocks, and may have formed in equilibrium with the oxidizing basinal brine responsible for the formation of the diagenetic illite. The later stage of dravite associated with kaolinite and remobilized uranium in reactivated fault zones has low $\delta^{18}O$ and δD values similar to those of kaolinite, and may have formed from low-temperature (< 50 °C) meteoric water (Kotzer - Kyser1990).

Granites and pegmatites

France-Lanord et al. (1988) reported $\delta^{18}O$ and δD values of magmatic tourmaline from the Manaslu leucogranite in the Himalayas. The variations of δD values are relatively small (-64 to -89‰) compared to those of coexisting biotite and muscovite (-89 to -143‰ and -64 to -127‰, respectively). It is suggested that tourmaline is particularly resistant to post-crystallisation hydrogen isotope exchange, and therefore retains its magmatic hydrogen isotope composition. Several low-δD biotites and muscovites may have experienced hydrogen isotope exchange with a D-poor fluid, with the biotite being more easily affected than the muscovite. Most coexisting muscovite, biotite, and tourmaline have relatively uniform δD values (δD_{mus} = -77 ± 7‰, δD_{bi} = -98 ± 10‰, and δD_{tur} = -74 ± 4‰), indicating that they crystallised at isotope equilibrium. Only two samples of tourmaline in the Manaslu leucogranite and pegmatite were analysed and both had identical $\delta^{18}O$ values of 11.6‰ (France-Lanord et al. 1988).

Tourmalines from granitic pegmatite and aplite dikes in San Diego Co., California, have lower $\delta^{18}O$ (9.8 to 6.4‰) and larger δD (-59 to -98‰) values than those of tourmalines from the Manaslu leucogranite (Taylor et al. 1979). However, δD ranges for the tourmaline are relatively small within each individual dike, i.e., -59 to -80‰ for the Himalaya Dike, -85‰ for the Stewart Dike, -71‰ for the Spessartine Dike, and -74 to -98‰ for the Tourmaline Queen Dike. Taylor et al. (1979) suggested that the $\delta^{18}O$ and δD values of tourmaline and other minerals in the pegmatite-aplite dikes of this region are compatible with a magmatic rather than metamorphic or metasomatic origin, having been derived from an ^{18}O-depleted magma. Similar $\delta^{18}O$ and δD values of tourmaline from several other granitic pegmatites in North America and Norway were reported by Taylor and Friedrichsen (1983).

In a more detailed study of oxygen and hydrogen isotopic compositions of tourmaline from granites and related hydrothermal rocks in the Karagwe-Ankolean belt of northwest Tanzania, Taylor et al. (1992) found that magmatic tourmalines have higher $\delta^{18}O$ and δD values (12.2 to 11.6‰ and -79 to -65‰, respectively) than hydrothermal tourmalines ($\delta^{18}O$ = 10.8 to 9.8‰; δD = -99 to -8‰). They observed systematic variations in both chemical [i.e., Fe/(Fe + Mg) ratios] and O-H isotopic compositions of the magmatic and hydrothermal tourmalines. Taylor et al. (1992) suggested that igneous differentiation produces larger oxygen isotope fractionation between coexisting quartz and tourmaline than hydrothermal processes, i.e., with higher $\delta^{18}O$ in quartz and lower $\delta^{18}O$ in tourmaline, and this fractionation may reflect a combination of decreasing temperature of crystallisation and increasing Fe/(Fe + Mg) ratios in the residual melt. The $\delta^{18}O$ values of magmatic tourmalines from the Karagwe-Ankolean granites (12.2 to 11.6‰) are the highest so far reported and are indicative of a sedimentary protolith for the granitic magma in the source area. Dyar et al. (1997) reported O-H isotopic compositions of tourmaline from two pegmatites in southwestern Maine, U.S.A., which display contrasting styles of emplacement. The Black Mountain pegmatite, which may have formed *in situ* as a result of the coincidence of hydrothermal solutions and boron-rich sediments, displays limited $\delta^{18}O$ (13.6 to 12.9‰) and large δD (-76 to -96‰) variations in tourmaline. The systematic decrease in tourmaline δD from the pegmatite core (-76‰) and wall (-81‰), to the country rocks (-80 to -96‰) implies a high degree of interaction between the pegmatitic fluids and surrounding rocks at Black Mountain. At Mount Mica, tourmalines show lower $\delta^{18}O$ values (13.2‰) within the pegmatite and higer values (15.5‰) in the country rocks. Tourmaline δD values at Mount Mica are -109‰ at the core, -116‰ at the wall, and -74 to -91‰ in the surrounding rocks. These data suggest little interaction between the pegmatite and fluids from the country rocks, and the pegmatitic tourmalines crystallised directly from pegmatitic magma, whereas tourmalines in the country rocks were products of water/rock interaction as a result of fluids emanating from the pegmatite (Dyar et al. 1997).

Sedimentary and metamorphic rocks

Studies on $\delta^{18}O$ and δD values of tourmaline from sedimentary and metamorphic rocks (except tourmalinites) are relatively rare. Blamart et al. (1992) studied oxygen and hydrogen isotopic compositions of tourmaline and associated quartz, biotite, and muscovite in metapelites. Three tourmalines have essentially identical δD values (-61 to -60‰), and one has an $\delta^{18}O$ value of 10.8‰. Similar $\delta^{18}O$ values (10.5 to 10.8‰) were reported for tourmaline from tourmalinites in the same area, but the tourmalinites have slightly lower δD values (-63 to -73‰). Oxygen isotopic compositions were also reported for tourmalines in pelitic schists from the central Alps by Gieré and Rumble (1994), who found differences in oxygen isotopic compositions of tourmaline between inner and outer growth zones that they suggested are due to growth of the two zones under distinctly different conditions.

Fluid sources for tourmaline from various geological settings

Taylor and Slack (1984) found that the $\delta^{18}O$ and δD values of tourmalines from granites and pegmatites are systematically different from those of tourmaline associated with massive sulfide deposits. However, because of the strong temperature dependence of O and H isotope fractionation in tourmaline, it is difficult to evaluate the fluid origin directly from the oxygen and hydrogen isotopic

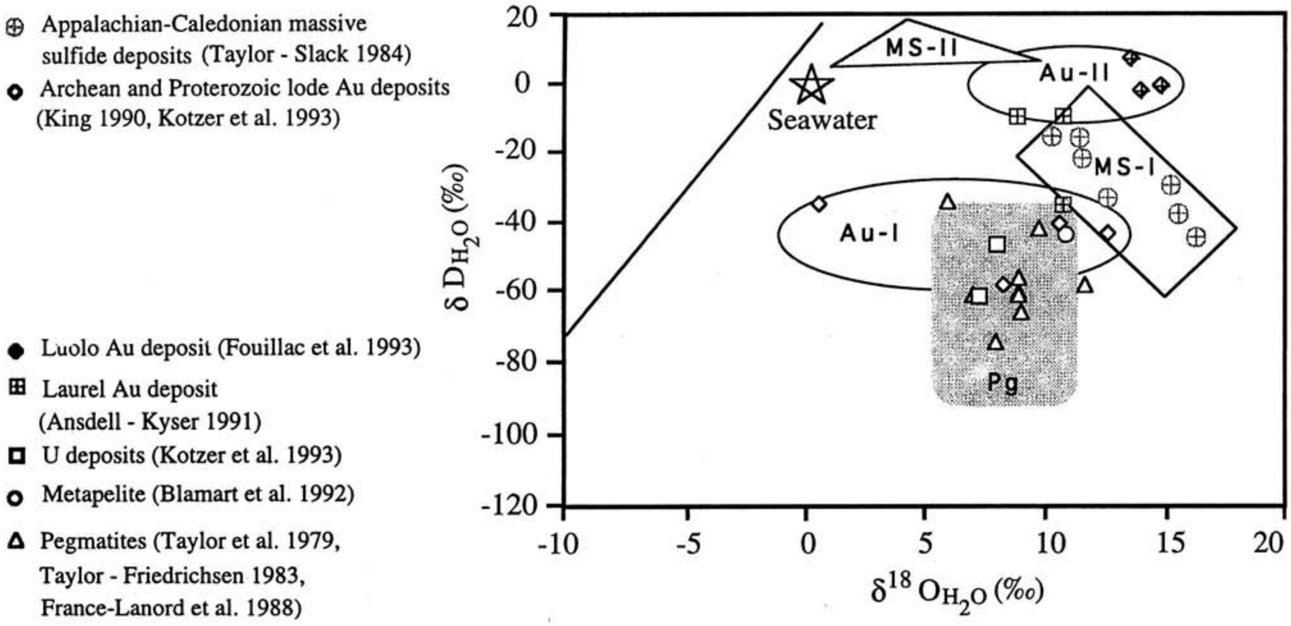

Fig. 2. A comparison of calculated $\delta^{18}O$ and δD values of the hydrothermal fluids responsible for tourmaline formation. The fields outlined are: MS-I = Appalachian-Caledonian massive sulfide deposits; MS-II = Kidd Creek massive sulfide deposit; Au-I = Archean and Proterozoic lode Au deposits; Au-II = Laurel and Luolo Au deposits; Pg = pegmatites

compositions. Using the oxygen and hydrogen isotope fractionation equations given in this study, temperatures for tourmaline formation can be estimated and the $\delta^{18}O$ and δD values of the parental fluids calculated. The hydrothermal fluids responsible for most of the Archean and Proterozoic mesothermal Au vein deposits have a metamorphic origin, except for the Luolo and Laurel Au deposits that show a modified seawater origin (Fig. 2). Tourmaline from the Kidd Creek massive sulfide deposit also may have precipitated from seawater-dominant fluids, which include three distinct fluids such as slightly modified seawater, extensively modified seawater, and a high-temperature fluid (Taylor et al. 1998). A negative correlation exists among the $\delta^{18}O$ and δD values of the hydrothermal fluids for the Appalachian-Caledonian massive sulfide deposits (Fig. 2), which may indicate mixing of the original tourmaline-forming fluids with later D-poor and ^{18}O-rich metamorphic fluids. The pegmatitic tourmalines formed from magmatic hydrothermal fluids as they share similar isotopic compositions (cf. Sheppard 1986).

Boron isotopes

Fractionation between tourmaline and aqueous vapor

Palmer et al. (1992) determined experimental $^{11}B/^{10}B$ fractionation factors between tourmaline and aqueous vapor at temperatures of 350-750 °C and pressures of 50-200 MPa. The fractionation equations are as follows:

$1000\ln\alpha_{tur\text{-}fluid} = 2.289\ (10^6/T^2) + 0.273$ (350-750 °C and 200 MPa)

$1000\ln\alpha_{tur\text{-}fluid} = 3.083\ (10^6/T^2) - 0.263$ (350-750 °C and 100 MPa)

Unlike oxygen and hydrogen isotope fractionations, the boron isotope fractionation is dependent not only on temperature but also on pressure. The boron isotope fractionation is smaller at higher pressure at an equivalent temperature, possibly due to bonding of the dissolved trigonal species of $B(OH)_3$ to form a pseudo-trigonally coordinated species that is adsorbed onto mineral surface at higher pressure, instead of the normal pseudo-tetrahedral species (Palmer et al. 1992). Palmer and Swihart (1996) suggested that the results of this experiment are applicable to other high-temperature fluid-solid interactions involving exchange of boron, due to the similar mechanism of boron incorporation into tourmaline and other aluminosilicate minerals. However, Hervig et al. (1997) found a much larger boron isotope fractionation (5-7‰) between hydrous vapor and peraluminous high-silica granitic melt at 650-750 °C and 200 MPa, relative to the fractionation of 2.2-2.8‰ determined by Palmer et al. (1992).

Boron isotope fractionation between mineral and water is also pH-dependent (Oi et al. 1989, 1991, Palmer et al. 1987, Palmer 1991). Boron has two bonding forms of trigonal complex $[B(OH)_3]$ and tetrahedral complex $[B(OH)_4^-]$. ^{11}B is concentrated in the trigonal species, whereas ^{10}B is concentrated in the tetrahedral species. The proportion of both species varies as a function of pH, and this controls the $\delta^{11}B$ values of the minerals precipitated from solution (Hemming - Hanson 1992, Hemming et al. 1995). This phenomenon is seen in most borate minerals (Oi et al. 1989, 1991, Palmer - Swihart 1996), but not in tourmaline because it is only stable at low pH conditions, for which $B(OH)_3$ is the only boron species present in solution (Morgan - London 1989, Palmer et al. 1992).

Boron isotopic compositions of tourmaline from various geological settings

Boron isotope studies of tourmaline from hydrothermal ore deposits have largely focused on massive sulfide deposits and tourmalinites. Other studied ore deposits include granite-related hydrothermal Sn-W, mesothermal Au, and metamorphosed borate deposits. Variations in $\delta^{11}B$ values of tourmaline from these deposits are illustrated in Fig. 3.

Massive sulfide deposits

Palmer and Slack (1989) conducted a pioneering boron isotope study of tourmaline in massive sulfide deposits and tourmalinites worldwide. The tourmalines display a wide range of $\delta^{11}B$ values from -23 to 18‰, which was interpreted to mainly reflect source compositions. Other possible controls include formational temperature, regional metamorphism, water/rock ratios, and seawater entrainment. No correlations exist between the tourmaline $\delta^{11}B$ values and the age, size, mineralogy, or metamorphic grade of the massive sulfide deposits and tourmalinites (Palmer - Slack 1989). Tourmalines from dominantly clastic metasedimentary terranes have $\delta^{11}B$ values from -15.4 to -1.7‰, which are nearly identical to those of tourmalines from dominantly felsic metavolcanic terranes (-15.7 to -1.5‰). Tourmalines in massive sulfide deposits and tourmalinites associated with marine evaporites and carbonates have generally high $\delta^{11}B$ values (mostly > 0‰), indicating a marine evaporitic (or carbonate) boron source. Tourmaline from the Broken Hill Pb-Zn-Ag deposit (Australia) has low $\delta^{11}B$ values (-17 to -27‰) that suggest a source from non-marine evaporitic borates (Palmer - Slack 1989; Slack et al. 1989, 1993).

In the Kidd Creek massive sulfide deposit, Ontario, tourmaline has $\delta^{11}B$ values of -13.6 to -7.8‰; hanging wall tourmalines comprise a narrower range (-10.1 to -9.6‰) than the footwall ones (-13.3 to -8.5‰), whereas tourmalines from the postore quartz-tourmaline vein, and from altered mafic and ultramafic rocks, have the highest values of -8.2 to -7.8‰ (Taylor et al. 1991, 1998). Calculated $\delta^{11}B$ values of the hydrothermal fluids vary from -8.7 to +6.6‰, and the estimated $\delta^{11}B$ values for the high-temperature fluid (HT), extensively and slightly modified seawater (MSW and SW) are -3.0, 0, and +3‰, respectively. The boron is thought to be leached from the fo-

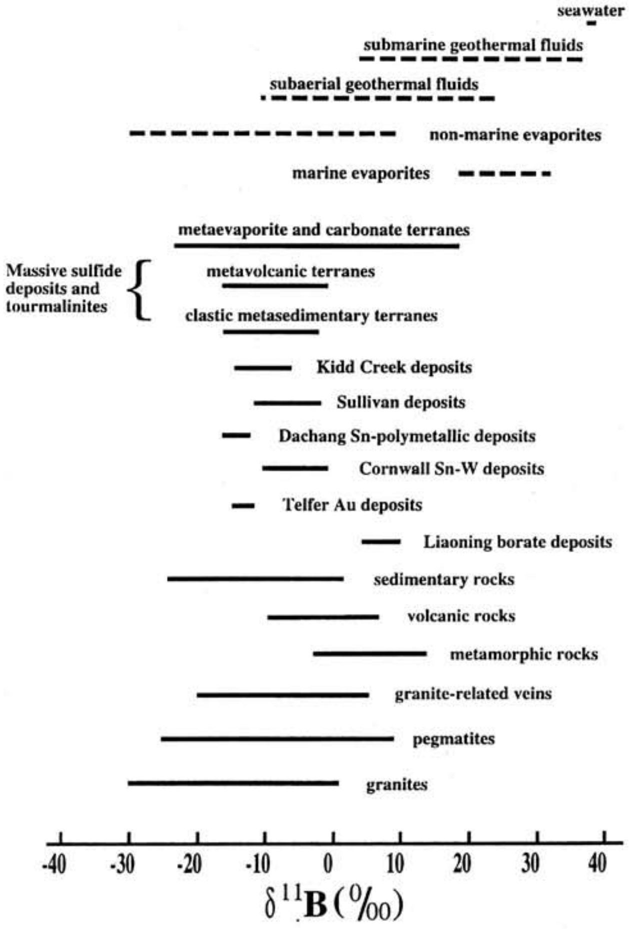

Fig. 3. Variations of $\delta^{11}B$ values in tourmaline from various environments (*solid lines*), in comparison with the $\delta^{11}B$ values of significant boron reservoirs (*dashed lines*). Data are from Byerly and Palmer (1991), Chaussidon and Albarčde (1992), Chaussidon and Appel (1997), Deb et al. (1997), Jiang (1997), Jiang et al. (1995a, 1997), Palmer (1991), Palmer and Slack (1989), Rowins et al. (1997), Slack et al. (1989, 1993), Smith and Yardley (1996), Swihart et al. (1986), and Taylor et al. (1998

otwall lithologies of abundant mafic/ultramafic rocks and minor clastic sediments, especially if previously altered at low temperatures (Taylor et al. 1998).

Jiang et al. (1995a) undertook a detailed boron isotope study of tourmaline from the giant Sullivan Pb-Zn-Ag massive sulfide deposit, British Columbia. Tourmalines from the deposit have $\delta^{11}B$ values of -11.1 to -2.9‰, compared to values of -15.4 to -1.9‰ in tourmalines from regional tourmalinites within the Belt-Purcell Supergroup. It is suggested that the $\delta^{11}B$ variations at Sullivan reflect several factors, including formational temperatures, water/rock ratios, entrainment of seawater into the hydrothermal system at the site of tourmaline formation, and multiple stages of tourmaline formation. The boron may have been leached from footwall clastic rocks by deeply circulating hydrothermal fluids, with a significant contribution likely from non-marine evaporites that may occur deeper in the unexposed sequence of the Aldridge basin (Jiang et al. 1995a).

Boron isotopic compositions of tourmaline have also been reported for massive sulfide deposits in the Nagpur district (India) with $\delta^{11}B$ values of -13.8 to -13.0‰ (Bandyopadhyay et al. 1993), for the Yindongzi-Tongmugou Pb-Zn-Ag deposits, northwestern China, with $\delta^{11}B$ values of -8.8 to -7.6‰ (Jiang et al. 1995b), and for the Rampura-Agucla and Deri Zn-Pb deposits, western India, with $\delta^{11}B$ values of -16.4 to -15.5% (Deb et al. 1997). The boron of these deposits is believed to have been leached from footwall clastic sediments by seawater-derived hydrothermal fluids.

Jiang (1997) reported $\delta^{11}B$ values of tourmaline from the giant Dachang Sn-polymetallic ore deposit, China. The $\delta^{11}B$ values of tourmaline from bedded tourmalinites and sulfide ores are between -17.5 and -14.9‰. Small tourmaline-sulfide veinlets in the orebodies have tourmaline $\delta^{11}B$ values of -15.0 to -13.8‰; tourmalines from quartz-tourmaline veins in granites display a $\delta^{11}B$ range of -16.5 to -14.2‰. Although the $\delta^{11}B$ values of the bedded tourmalinites and granitic hydrothermal tourmalines overlap, the calculated $\delta^{11}B$ values of the parental hydrothermal fluids are different since the two types of tourmaline formed at different temperatures (250-350 °C and 450-600 °C, respectively). Jiang (1997) suggested that the bedded tourmalinites and associated Sn-Pb-Zn mineralisation have no genetic relationship to the granite.

Granite-related hydrothermal Sn-W deposits

Clarke et al. (1989) reported $\delta^{11}B$ values of -18.5 to 3.5‰ in tourmaline from a number of granite-related Sn-W veins, polymetallic deposits, and barren rocks in Nova Scotia. However, their data were obtained by ICP-MS methods with a low analytical precision (± 7‰). Smith and Yardley (1996) conducted a detailed ion microprobe analysis of $\delta^{11}B$ values for tourmaline from the granite-related Cornwall Sn deposits, southwest England. Tourmalines from the hydrothermal veins and altered rocks have $\delta^{11}B$ values of -10.8 to -2.8‰, which are higher than those of the granitic tourmalines (-12.7 to -5.9‰) but similar to those of tourmaline from tourmalinites and quartz-topaz-tourmaline rocks (-10.5 to 0.7‰). Smith and Yardley (1996) suggested that the boron for the hydrothermal veins was derived from the granites, with the $\delta^{11}B$ variations in the granites and hydrothermal veins reflecting boron isotope fractionations between aqueous fluids and melt.

Mesothermal Au deposits

Only limited boron isotope data are available for hydrothermal Au deposits. Rowins et al. (1997) reported $\delta^{11}B$ values of tourmaline from the giant Telfer Au deposit, Western Australia. Tourmalines from the auriferous veins have identical $\delta^{11}B$ values of -14.0 to -12.6‰; the calculated fluid $\delta^{11}B$ values are between -9.0 and -0.6‰. In contrast, tourmaline from the Minyari granites has lower $\delta^{11}B$ values of -16.2 to -15.2‰, with calculated fluid $\delta^{11}B$ values of -14.2 to -13.2‰. Rowins et al. (1997) suggested that the boron source for the hydrothermal veins was the clastic sedimentary host rocks rather than the granites.

Metamorphosed borate deposits

Peng and Palmer (1995) and Jiang et al. (1997) conducted comprehensive boron isotopic studies of tourmaline and borates from the Proterozoic Liaoning borate deposits, China. Tourmaline from a footwall granite has a $\delta^{11}B$ value of 0.8‰, which is different from tourmaline in footwall host rocks ($\delta^{11}B$ = 3.9 to 4.5‰) and from the borate orebodies and hanging wall tourmalinites ($\delta^{11}B$ = 6.7 to 9.7‰). The borate minerals have relatively high $\delta^{11}B$ values of 9.6 to 11.1‰. Jiang et al. (1997) suggested that the boron source for the borate orebody was not the granite, but non-marine evaporites.

Granites and pegmatites

Swihart and Moore (1989) reported reconnaissance results for tourmaline from granitic pegmatites ($\delta^{11}B$ = -12 to -5‰). Three samples of tourmaline within a single pegmatite gem pocket from the Dunton Quary, Maine, have different chemical compositions (elbaite or schorl) but identical $\delta^{11}B$ values of -9 to -7‰, which suggests a lack of correlation between tourmaline $\delta^{11}B$ values and major element compositions. However, Chaussidon and Albarède (1992) found that Li-rich tourmalines have generally higher $\delta^{11}B$ values than Li-poor ones. A correlation between Li contents and $\delta^{11}B$ values was also observed on tourmaline from southwest England granites and associated hydrothermal veins (Smith - Yardley 1996). Tonarini et al. (1997) reported boron isotopic compositions of tourmaline from LCT miarolitic pegmatites, Elba, Italy. The analysed samples were collected from a complex and a simple zoned, and a unzoned aplite-pegmatite dike, respectively, which show a wide range of composition (schorl-elbaite) and formational temperatures (650-300 °C) but a limited $\delta^{11}B$ variations (-9.6 to -8.5‰), indicating that the boron isotopic compositions are decoupled from chemical composition of tourmaline. Tonarini et al. (1997) suggested that the tourmalines crystallised in a closed system, and their boron isotopic compositions were not affected significantly by late-stage development of open-system fluid circulation.

Chaussidon and Albarède (1992) found a negative correlation between the age and $\delta^{11}B$ values of Li-rich granitic tourmalines. They explained this relationship by a model of constant boron isotope fractionation between seawater and continental crust, in which the average $\delta^{11}B$ values of the crust increased from -25‰ at 4 Ga to a present-day average of -5‰, with the $\delta^{11}B$ value of seawater showing a concomitant increase from 15‰ to its present-day value of 40‰. However, the assumptions made in this model are unproven and the correlation between the age and the $\delta^{11}B$ values, which is the basis for the model, is not readily apparent when data from other studies are considered (Palmer - Swihart 1996).

Sedimentary, volcanic, and metamorphic rocks

Byerly and Palmer (1991) studied the boron isotopic compositions of tourmaline from altered basalts, evaporites, stromatolites, and quartz-tourmaline veins in the Archean Barberton greenstone belt, South Africa. Tourmalines from the evaporite-bearing sediments have $\delta^{11}B$ values of -0.3 to -0.2‰, similar to tourmalines from basalts and komatiites (2.2 to -1.9‰). Tourmalines from cross-cutting quartz veins have lower $\delta^{11}B$ values of -3.7 to -5.7‰; the lowest $\delta^{11}B$ values are in tourmalines from the stromatolitic cherts (-9.8 to -10.5‰). Byerly and Palmer (1991) suggested that the boron source for the tourmalines in the sedimentary and volcanic rocks was marine evaporites and that the formational temperatures were low (< 100 °C). The quartz-tourmaline veins were precipitated at higher temperatures (350-600 °C) by remobilisation of the evaporitic boron. Formation of low-$\delta^{11}B$ tourmaline-rich stromatolitic cherts involved a two-stage boron enrichment, in which earlier marine evaporitic boron was hydrothermally remobilised and vented in shallow marine or subaerial sites, mineralising algal stromatolites.

Preliminary results of a boron isotope study of tourmaline from Miocene sediments (10 Ma) eroded from the Himalaya in the Bengal Fan (ODP Leg 116) were reported by Chaussidon et al. (1991) with a $\delta^{11}B$ range from -10.2 to 4‰ (most values -6 to 4‰). Although the $\delta^{11}B$ values of these detrital tourmalines overlap those of tourmaline both from High Himalaya crystalline rocks (-16.1 to -9.0‰) and from the metasedimentary Lesser Himalaya Formation (-14.4 to 3.5‰), it is likely that most of the detrital tourmalines came from the Lesser Himalaya Formation.

Tourmalines from mafic volcaniclastic rocks in the 3.8 Ga Isua supracrustal rocks of West Greenland have $\delta^{11}B$ values between -12.6 and 5.8‰, with a mean at -3.2 ± 5.1‰, which are close to the $\delta^{11}B$ values of -6.7 ± 1.4‰ found in tourmalines from Isua felsic volcanic tuffs (Chaussidon - Albarède 1992, Chaussidon - Appel 1997). Chaussidon and Appel (1997) suggested that there is no difference in $\delta^{11}B$ values of the mantle or the continental crust between Early Archean times and the present. In contrast, tourmalines from a marine conglomerate in the Isua supracrustal rocks have lower $\delta^{11}B$ values of -25.0 to -17.4 ‰. The source of the boron for the tourmalines in conglomerates is thought to be marine sediments, and a $\delta^{11}B$ value of 27 ± 11‰ was estimated by Chaussidon and Appel (1997) for Archean seawater at 3.8 Ga, which is considerably lower than the present-day $\delta^{11}B$ value of 40‰.

Only preliminary results of $\delta^{11}B$ values of tourmaline from high-grade metamorphic rocks have been reported. Tourmalines from upper amphibolite-facies rocks in the Adirondack Lowlands, New York, display $\delta^{11}B$ values of 7 to 13 ‰, whereas tourmaline and serendibite from granulite-facies rocks of the Adirondack Highlands have lower $\delta^{11}B$ values of -2 to 2‰ (Bohlen et al. 1985, Swihart

1987, Grew et al. 1991). These data suggest that large boron isotope fractionation may occur during progress metamorphism.

Silicon isotopes

Silicon isotope variations in nature have been studied since the 1950s (Reynolds - Verhoogen 1953, Epstein - Taylor 1970, Douthitt 1982, Clayton 1986). However, most analyses have been made of meteorites and lunar rocks because of the limited range of silicon isotope ratios in terrestrial rocks and minerals ($\delta^{30}Si$ = -4 to +4‰) and the relatively poor analytical precision of > 0.3-0.6 ‰ (Douthitt 1982). Fortunately, the analytical method has recently been improved and it is now possible to obtain high-precision $\delta^{30}Si$ data with an analytical error of better than ± 0.1‰ (Ding et al. 1988, 1996). Since this improvement, silicon isotopes have been shown to be useful in addressing diverse geological problems (Ding et al. 1988, 1996, Jiang et al. 1992, 1993, 1994, 1997).

Jiang et al. (1994) reported $\delta^{30}Si$ values (-0.5 to 0.0‰) of tourmalinites from the Sullivan Pb-Zn-Ag deposit, British Columbia. The isotopically lighter tourmalinites are from a fine-grained cherty tourmalinite in the immediate footwall of the Sullivan orebody ($\delta^{30}Si$ = -0.3 ‰), a garnet-rich tourmalinite near the projected horizon of the nearby North Star orebody ($\delta^{30}Si$ = -0.5 ‰), and a stratiform fine-grained tourmalinite at the Neg regional prospect ($\delta^{30}Si$ = -0.3 ‰). Other tourmalinites in the Sullivan deep footwall below the orebody have identical high $\delta^{30}Si$ values of 0.0 ‰. Jiang et al. (1994) suggested that these $\delta^{30}Si$ data support the genetic model of Slack (1993) for tourmalinite formation at Sullivan, whereby tourmalinites deep in the footwall formed by subseafloor replacement of clastic sediments with an *in-situ* silicon source (e.g., detrital clays), with the stratiform and garnet-rich tourmalinites near the sulfide orebody having formed mainly by hydrothermal exhalative processes with a significant hydrothermal silicon source. Silicon isotope ratios do not appear to be reset during the regional metamorphic overprint because the high abundance of silicon in most rocks requires massive silica exchange to fractionate the original isotopic compositions significantly. It is suggested that silicon isotopes could be used as an effective paleo-environmental indicator and as an aiding in defining stratigraphic horizons prospective for mineral exploration (Jiang et al. 1993, 1994, 1997).

Rubidium and strontium isotopes

Tourmaline has very low Rb and high Sr contents (Taylor - Slack 1984, King - Kerrich 1989, Griffin et al. 1996, Jiang et al. 1997), which makes it an ideal indicator of the initial strontium isotope composition of the hydrothermal fluid and source of the strontium. Although Sr contents of tourmaline have been reported from various rocks and ore deposits, strontium isotope studies of tourmaline have mainly focused on Archean and Proterozoic mesothermal Au deposits. The most comprehensive study was conducted by King and Kerrich (1989) who obtained $^{87}Sr/^{86}Sr$ ratios of tourmaline from 21 gold deposits in the Archean Abitibi belt of Ontario and Quèbec. The total range of $(^{87}Sr/^{86}Sr)_{2670\ Ma}$ initial ratios was determined to be 0.7009 - 0.7174, with the majority of data falling in a narrow range from 0.7012 to 0.7032. King and Kerrich (1989) found that the $^{87}Sr/^{86}Sr$ ratios of tourmaline are unrelated to the Sr contents and the Rb/Sr ratios of their host rocks and suggested that the ratios were largely controlled by the chemistry of the hydrothermal fluids that leached Sr (and possibly Au) from lithologically complex source regions.

Ansdell and Kyser (1991) reported $^{87}Sr/^{86}Sr$ ratios of two tourmaline samples from auriferous quartz-tourmaline veins in the Proterozoic Laurel Lake Au-Ag deposit, Saskatchewan. The tourmalines have $^{87}Sr/^{86}Sr$ ratios of 0.7021 and 0.7026, similar to initial ratios for rocks of the regional Amisk Group and the syntectonic Annabel Lake granitoid. Although oxygen and hydrogen isotope data for tourmaline from the deposit indicate a modified seawater source of the hydrothermal fluids, the strontium isotope compositions do not support the derivation of Sr directly from seawater. Instead, the Sr may have come from the same sources as the Amisk Group magmas, or by leaching volcanic rocks of the Amisk Group. At the Rio Au deposit in the same region, a tourmaline sample has a $^{87}Sr/^{86}Sr$ ratio of 0.7028, like the values of the Laurel Lake tourmalines, implying derivation of the Sr by leaching of Proterozoic island-arc volcanic rocks and granitoids in the region (Ansdell - Kyser 1992). Ansdell and Kyser (1992) obtained a Rb-Sr isochron age of 1760 ± 9 Ma on coexisting tourmaline and muscovite from the Rio deposit, which is close to the $^{40}Ar/^{39}Ar$ plateau ages determined for muscovites from the Laurel Lake deposit.

$^{87}Sr/^{86}Sr$ ratios of tourmaline were also reported from auriferous quartz-tourmaline veins in the Proterozoic Star Lake lode Au deposit, northern Saskatchewan (Ibrahim - Kyser 1991). Tourmalines from the Rush Lake veins have $^{87}Sr/^{86}Sr$ ratios of 0.7022-0.7923, whereas tourmaline from the Hill Top vein has an ratio of 0.7026. Considering also their different δD values, Ibrahim and Kyser (1991) suggested that the parent hydrothermal fluids were slightly different in each vein. Using Rb-Sr data for three tourmalines and two feldspars from the auriferous veins, Ibrahim and Kyser (1991) obtained an age of 1742 ± 87 Ma and an initial $^{87}Sr/^{86}Sr$ ratio of 0.7022 ± 0.0005, indicating that the auriferous veins were deposited at 5 to 100 Ma after crystallisation of the Star Lake pluton and contemporaneous with the waning stages of Hudsonian metamorphism.

Mueller et al. (1991) conducted a strontium isotope study of 23 scheelites and one tourmaline from epigenetic Archean Au deposits in the Yilgarn Block, Western Australia. The tourmaline has an initial $(^{87}Sr/^{86}Sr)_{2650\ Ma}$ ratio of 0.7014, which is compatible with ratios reported by King and Kerrich (1989) for tourmalines from Archean gold deposits in the Abitibi belt, Canada. Mueller et al. (1991) suggested that the variations in $^{87}Sr/^{86}Sr$ ratios of the Rb-poor scheelite and tourmaline in the deposits reflect mixing between radiogenic Sr introduced by the hydrothermal fluid and nonradiogenic Sr released from the wallrocks during interaction with this fluid.

A detailed isotopic study of Paleozoic vein Au deposits in the Meguma Terrane of Nova Scotia by Kontak and Kerrich (1997) obtained $^{87}Sr/^{86}Sr$ ratios for several vein tourmalines. The tourmalines display $^{87}Sr/^{86}Sr$ ratios ranging from 0.7131 to 0.7228, in contrast to those of the associated vein carbonates (0.7012-0.7185). Kontak and Kerrich (1997) suggested that the isotopic heterogeneity between tourmaline and carbonate reflects variable contamination of a primary fluid with radiogenic Sr derived from Meguma Group lithologies during its ascent or at the site of vein formation.

Jiang (1997) reported $^{87}Sr/^{86}Sr$ ratios of tourmaline from the giant Dachang Sn-polymetallic ore deposit, China. Tourmalines from bedded tourmalinites have $^{87}Sr/^{86}Sr$ ratios of 0.713-0.718, whereas tourmalines from local granites have more variable $^{87}Sr/^{86}Sr$ ratios of 0.712-0.721. Tourmalines from the bedded tourmalinites and from the granites form two separate mixing lines in plots of $^{87}Sr/^{86}Sr$ versus reciprocals of the strontium content (1/Sr), probably indicating a complex origin involving different hydrothermal systems (Jiang 1997).

Samarium and neodymium isotopes

Rare earth elements have been analysed in tourmalines from diverse rocks and ore deposits, and show considerable variations both in concentrations and distribution patterns that are useful as indicators for petrogenesis and ore genesis (Jolliff et al. 1987, King et al. 1988; Hellingwerf et al. 1994, Jiang and Palmer 1995; Jiang et al. 1997). King et al. (1988) suggested that precise age determinations might be possible based on Sm-Nd isochrons of tourmaline. However, only limited Sm-Nd isotopic data of tourmaline are available in the literature. King (1990) conducted a Sm-Nd isotope study of tourmaline from 11 Archean lode Au deposits in Canada. The tourmalines have initial $(^{143}Nd/^{144}Nd)_{2670\ Ma}$ ratios of 0.5078 to 0.5109, which are decoupled from those of the host rocks probably due to a hydrothermal input of non-radiogenic Nd (King 1990).

Anglin et al. (1996) reported Sm-Nd isotopic data on scheelite and tourmaline from Au-quartz veins from the Sigma, Pascalis North, and Siscoe Extension deposits in the Val d'Or gold camp of the Abitibi greenstone belt, western Quèbec. One tourmaline from the Sigma mine has a present-day $^{147}Sm/^{144}Nd$ ratio of 0.331 and a $^{143}Nd/^{144}Nd$ ratio of 0.5151. Tourmalines from the Pascalis North mine display large variations in $^{147}Sm/^{144}Nd$ (0.147 to 0.491) and $^{143}Nd/^{144}Nd$ (0.5119 to 0.5166) ratios. Data for scheelite and tourmaline form an Sm-Nd isochron with an age of 2593 ± 26 Ma and εNd value of 2.6, which were interpreted to represent the age of vein-hosted gold mineralisation in the area. The high εNd value indicates derivation of the REE in the mineralising fluids from a relatively homogeneous reservoir similar to depleted mantle or material recently derived from a depleted mantle, i.e., komatiites and/or basalts, and no significant interaction of the fluids with more enriched older crustal material (Anglin et al. 1996).

Jiang (1997) reported $^{143}Nd/^{144}Nd$ ratios of tourmaline from the giant Dachang Sn-polymetallic ore deposit, China. Tourmalines from bedded tourmalinites and sulfide ores have $^{143}Nd/^{144}Nd$ ratios ranging from 0.51197 to 0.51217, whereas tourmalines from nearby granite have higher ratios of 0.51210 to 0.51224. The two types of tourmaline form two separate mixing lines in plots of $^{143}Nd/^{144}Nd$ ratios versus 1/Nd that suggest the tourmalines formed from different hydrothermal systems, in agreement with evidence from their chemical, boron, and strontium isotopic compositions (Jiang 1997).

Lead isotopes

Studies of Pb isotopes of tourmaline are few, although this mineral may contain significant amounts of U, Th, and Pb (e.g., Taylor - Slack 1984, Jiang - Palmer 1995, Griffin et al. 1996, Jiang et al. 1997), and its refractory nature likely makes it resistant to isotope resetting by later hydrothermal or metamorphic events. Recently, Frei and Pettke (1996) successfully obtained Pb-Pb ages of tourmaline from a shear zone-hosted Au deposit within Archean cratons in Zimbabwe by stepwise Pb leaching techniques. Stepwise leaching of a zoned fibrous dravitic tourmaline produced a Pb-Pb isochron age of 2647 ± 9 Ma, which is significantly older than the step-leaching Pb-Pb age of associated pyrrhotite (1926 ± 49 Ma). Frei and Pettke (1996) suggested that this Archean age represents an initial mineralising event recorded by the tourmaline that remained unaffected by the Proterozoic hydrothermal activity. Frei and Pettke (1996) also obtained a Pb-Pb age of 2021 ± 17 Ma for a schorlitic tourmaline associated with sulfides and quartz, which is close to a Pb-Pb age of 1936 ± 26 obtained from the sulfides and quartz in the same sample. Frei and Pettke (1996) noted that the sulfides and quartz occur as crack fillings and cementations within and around the tourmaline, and therefore suggested that the tourmaline and sulfides were not part of a progressive mineralisation but rather were deposited during at least two separate Proterozoic events, from a hydrothermal fluid having a common source. Frei and Pettke (1996, 1997) suggested that the combined pyrrhotite-arsenopyrite-quartz isochron age of 1936 ± 26 Ma represents the age of gold mineralisation in the deposit.

Potassium and argon isotopes

Tourmaline K-Ar ages are reported from a number of geological environments. Due to the low content of K in most tourmalines, the tourmaline K-Ar system is sensitive to any incorporation of excess radiogenic Ar. Altherr et al. (1982) found that K-Ar ages of tourmaline from granites and pegmatites in the Greek Cyclades are older than the muscovite K-Ar and Rb-Sr ages, but close to the whole-rock Rb-Sr ages. It is believed that the older tourmaline K-Ar ages reflect excess radiogenic Ar in tourmaline, which can be easily trapped in the crystal structure of ring silicates (Damon - Kulp 1958, Dalrymple - Lanphere 1969). Similar K-Ar ages of tourmaline and muscovite from several aplitic-pegmatitic dikes in Naxos, Greece, were also reported by Andriessen et al. (1991). However, they suggested that the older tourmaline ages and younger muscovite ages record a succession of cooling ages, with tourmaline being closed with respect to the K-Ar system at high temperatures.

Excess radiogenic Ar may exist in tourmalines from granites and gneisses that have undergone multiphase metamorphism. For instance, in Palaeozoic suites of the Mulhacen Complex, tourmalines yield various K-Ar ages, some of which are even older than the host-rock ages (Andriessen et al. 1991). Hence, Andriessen et al. (1991) suggested that conventional K-Ar dating is inadequate for providing unambigious, geologically meaningful tourmaline ages. Success has been achieved using the $^{40}Ar/^{39}Ar$ systematics of tourmaline to provide ages of metamorphism and tourmalinisation, as small amounts of excess Ar are released at relatively low temperatures during heating steps (Fitch - Miller 1972, de Jong 1991). Using this technique, it is also possible, in some instances, to separate isotopic signatures and ages of polymetamorphic growth zones in tourmaline (Andriessen et al. 1991, de Jong 1991).

Conclusions

Tourmaline is an important structurally and chemically complex borosilicate mineral that occurs in many rock types and ore deposits. It is stable over a wide range of magmatic, metamorphic, and hydrothermal conditions. Stable and radiogenic isotopic studies of tourmaline have yielded valuable information regarding the physico-chemical conditions of its formation, fluid-rock interaction, fluid origin and evolution, sources of contained elements (B, Sr, Nd, Pb, and other associated metals), as well as the genesis and timing of tourmalinisation and related mineralisation.

1. Oxygen and hydrogen isotope studies of tourmaline have focused on the calibration of isotope fractionation between tourmaline and water, as well as applications of these isotopes on solving various geological problems.

Calibration of H-O isotope fractionation between tourmaline and water has been carried out by experimental measurements, empirical estimates, and theoretical calculations. There are some problems with the previously published empirical calibrated H-O isotope fractionation equations. Hence, new empirical calibrated fractionation equations with high correlation coefficients are presented in this paper as follows:

Oxygen: $1000\ln\alpha_{\text{Q-Tur}} = 1.05\ (10^6/T^2) + 0.49$ (200-600 °C)

Hydrogen: $1000\ln\alpha_{\text{Tur-Water}} = -14.2\ (10^6/T^2) + 4.7$ (300-600 °C)

Studies of tourmaline H-O isotopes have largely applied to hydrothermal ore deposits, granites, and pegmatites, to trace the origin of hydrothermal fluids and to provide the formational temperatures. For example, H-O isotopes have shown that modified seawater was involved in several hydrothermal gold and massive sulfide ore deposits.

2. Boron isotope fractionation between tourmaline and aqueous vapor has been experimentally determinated, and is both temperature- and pressure-dependent (Palmer et al. 1992):

$1000\ln\alpha_{\text{tur-fluid}} = 2.289\ (10^6/T^2) + 0.273$ (350-750 °C and 200 MPa)

$1000\ln\alpha_{\text{tur-fluid}} = 3.083\ (10^6/T^2) - 0.263$ (350-750 °C and 100MPa)

There are wide variations in $\delta^{11}B$ values of tourmaline from various environments, which make it a sensitive tool to trace the boron source and can provide information concerning petrogenesis and ore genesis. Controls over the boron isotopic compositions of tourmaline are principally the compositions of the source rocks, water/rock ratios, seawater entrainment, formational temperatures, and regional metamorphism.

3. Silicon isotopes are recently developed, robust geochemical tracers which have shown to be useful in solving various geological problems. Studies of silicon isotopic compositions of tourmalinite from massive sulfide deposit revealed a hydrothermal silica component in the formation of these tourmalinites. Silicon isotopes could be used to distinguish replacive from exhalative tourmalinites, and as effective paleo-environmental indicators.

4. Tourmaline has high Sr but negligible Rb concentrations. Hence, it is an ideal mineral to record the initial $^{87}Sr/^{86}Sr$ ratios of the parental fluid. Studies of Sr isotopes in tourmaline from hydrothermal gold and massive sulfide ore deposits revealed diverse sources of Sr in the deposits. A combination of Rb-Sr determinations in tourmaline and coexisting minerals can yield valuable age information for crystallisation and mineralisation.

5. Tourmaline has variable REE concentrations and distribution patterns that are useful as indicators for petrogenesis and ore genesis. Sm-Nd isotope systematics of tourmaline can be used to trace the source of REE in the hydrothermal fluids, and to yield precise formation ages in some cases.

6. Tourmaline contains significant amounts of U, Th, and Pb. Success has been achieved to produce precise Pb-Pb ages of tourmaline formation and associated mineralisation.

7. Tourmaline K-Ar isotopic system is sensitive to any incorporation of excess radiogenic Ar due to its low K concentrations. Hence, conventional K-Ar dating may be inadequate for providing unambigious, geologically meaningful tourmaline ages, but the $^{40}Ar/^{39}Ar$ systematics of

tourmaline can be used to distinguish isotopic signatures and ages of polymetamorphic growth zones in tourmaline.

Acknowledgments. The author would like to thank the Alexander von Humboldt Foundation for financial support. The manuscript has benefited from comments by John Slack, Vojtěch Janoušek, Milan Novák, and Martin Palmer.

Submitted November 20, 1997

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Studium stabilních a radiogenních izotopů v turmalínu: přehled

Tato práce podává přehled studia stabilních izotopů O, H, B a Si, a radiogenních izotopů Rb-Sr, Sm-Nd, Pb a K-Ar v turmalínu z různých geologických prostředí. Izotopická složení O a H jsou dobrým indikátorem zdrojů hydrotermálních fluid, vzniku hornin a rudních ložisek a mohou také poskytnout informace týkající se teploty vzniku turmalínu. Na základě $\delta^{18}O$ a δD hodnot v turmalínu byly rozpoznány modifikované mořské vody ve zdroji několika ložisek masivních sulfidů, a fakt, že metamorfní fluida jsou odpovědná za vznik mnoha hydrotermálních ložisek zlata. Ve dříve publikovaných pracích jsou určité problémy s empiricky kalibrovanými rovnicemi křemen-turmalín a turmalín-voda. Proto jsou zde uvedeny nové empiricky kalibrované rovnice frakcionace izotopů O a H s vysokými koeficienty korelace. Navíc byl publikován (Guo - Qian 1997) experimentálně stanovený faktor frakcionace izotopů H mezi turmalínem a vodou za teplot nižších než 350 °C.

Existují široké variace hodnot $\delta^{11}B$ v turmalínu z různých prostředí. Izotopické složení $\delta^{11}B$ v turmalínu je v zásadě ovlivňováno zdrojovou horninou, poměrem voda/hornina, účastí mořské vody, teplotou vzniku a regionální metamorfózou. Hodnoty $\delta^{11}B$ v turmalínu jsou využitelné pro rozlišení mořských a jezerních evaporitických zdrojů B. Pomocí $\delta^{30}Si$ hodnot lze rozlišit detritické a hydrotermální zdroje Si v turmalínu, izotopy Si by mohly být využívány jako účinné indikátory paleoprotředí.

Izotopické Sr-Nd složení turmalínu má zásadní význam pro rozeznání zdroje a původu hydrotermálních fluid, a v některých případech může poskytnout stáří vzniku turmalínu. Izotopy Pb v turmalínu, získané technikou stepwise Pb leaching, byly prokázány jako dobrý geochronometr. K-Ar stáří turmalínu může reprezentovat teploty chladnutí s velmi vysokou uzavírací teplotou, ale pouze datování $^{40}Ar/^{39}Ar$ může poskytnout jednoznačná data pro turmalín s komplikovaným metamorfním vývojem.

Výsledky izotopického studia turmalínu ukazují, že mohou sloužit jako účinný nástroj hledání zdrojů hydrotermálních fluid.