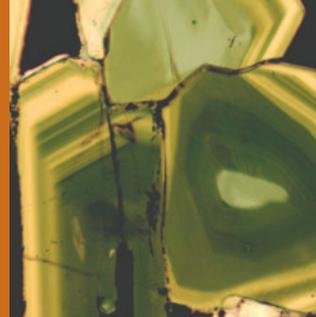


Tourmaline as a Recorder of Ore-Forming Processes



Zoned tourmaline from the Ore Knob VMS deposit, North Carolina, USA. The matrix (black) is chalcopyrite.

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Tourmaline occurs in diverse types of hydrothermal mineral deposits and can be used to constrain the nature and evolution of ore-forming fluids. Because of its broad range in composition and retention of chemical and isotopic signatures, tourmaline may be the only robust recorder of original mineralizing processes in some deposits. Microtextures and in situ analysis of compositional and isotopic variations in ore-related tourmaline provide valuable insights into hydrothermal systems in seafloor, sedimentary, magmatic, and metamorphic environments. Deciphering the hydrothermal record in tourmaline also holds promise for aiding exploration programs in the search for new ore deposits.

KEYWORDS: tourmaline, ore deposits, hydrothermal, compositions, isotopes

TOURMALINE IN HYDROTHERMAL ORE DEPOSITS

Tourmaline is a common mineral in many types of hydrothermal ore deposits from diverse tectonic settings (FIG. 1). Two broad categories of hydrothermal deposits are recognized: (1) those that formed by “epigenetic” processes in which mineralization was superimposed on preexisting rocks in veins, breccias, or replacements (FIGS. 2, 3, 4); and (2) “syngenetic” deposits in which ore minerals formed during the deposition of sedimentary or volcanic host rocks. Within the epigenetic category are porphyry Cu ± Mo deposits, Cu–Au breccia pipes, and Sn–W veins in or near granitoid intrusions; orogenic Au–quartz veins in greenschist and amphibolite facies metamorphic rocks and Au–quartz–sulfide veins in these rocks near granitoid intrusions; and iron oxide–copper–gold (IOCG) deposits in a variety of continental settings. The syngenetic category mainly comprises sedimentary-exhalative (SEDEX) Zn–Pb–Ag deposits and volcanogenic massive sulfide (VMS) Cu–Zn–Pb–Ag–Au deposits, both of which form in seafloor settings (FIG. 1). These diverse deposit types cover a broad spectrum of chemical environments and pressure–temperature conditions, from oceanic to deep crustal (Hedenquist et al. 2005), and the fact that tourmaline occurs in each is testament to its wide stability range (Dutrow and Henry 2011 this issue). As we explore in this article, tourmaline has the ability to preserve textural, chemical, and isotopic features that reveal considerable detail about the hydrothermal system in which it formed. Not discussed here are tourmalines in magmatic rare-metal deposits (Li, Cs, Ta) and gem varieties in pegmatites (see van Hinsberg et al. 2011 this issue; Pezzotta and Laurs 2011 this issue).

The formation of hydrothermal tourmaline requires the fortuitous convergence of complex processes: derivation of boron and other essential elements from one or more sources; transport in fluids of diverse provenance (magmatic-derived, metamorphic, basinal or evaporitic brines, heated meteoric water, evolved seawater); and finally precipitation in settings and conditions that may coincide with the deposition of economically valuable metals. In favorable cases, constraints on P – T – X conditions (where P , T , and X are pressure, temperature, and fluid

composition, respectively) of hydrothermal fluids can be obtained by measurements of primary fluid inclusions in mineral hosts, such as quartz, or estimated from isotope fractionation data or chemical equilibria among the associated minerals. However, many deposits have a polyphase history, and for these, primary fluid inclusions, mineral parageneses, and isotope compositions commonly are masked or destroyed by post-ore hydrothermal, tectonic, or metamorphic events. If not recrystallized, tourmaline may be the only robust recorder of original hydrothermal processes in such ore deposits. Documenting the hydrothermal record in tourmaline is important for furthering our understanding of mineralizing processes and can potentially aid in the exploration for new ore deposits.

The past decade has witnessed major progress in the use of tourmaline in ore research on two fronts. The first is the assembly of a growing geochemical database on tourmaline from diverse hydrothermal settings (Slack 2002). This database includes major elements determined by electron microprobe (EMP) analysis and, for some deposits, trace elements and stable isotopes (B, O, H, Si) measured on tourmaline separates. The second is the increased use of secondary ion mass spectrometry (SIMS) for in situ boron isotope analysis of hydrothermal tourmaline (following the early work of Smith and Yardley 1996), and a much-improved understanding of boron isotope systematics in geologic systems (Marschall and Jiang 2011 this issue). These advances have opened a new window on provenance and fluid evolution in ore deposits (e.g. Jiang et al. 2008; Trumbull et al. 2011).

The potential of in situ techniques for determining element and isotope compositions in tourmaline has by no means been fully exploited. For example, there are surprisingly few studies of ore-metal concentrations in tourmaline, although trace element analysis for Cu, Zn, Pb, Sn, etc. can be made with high precision at very low detection limits (<10 ppm) by laser ablation–inductively coupled plasma–mass spectrometry (LA–ICP–MS). Moreover, because

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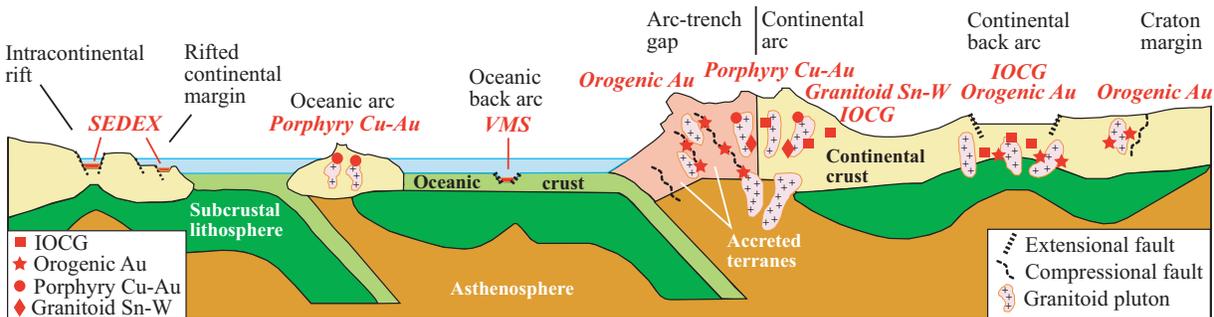


FIGURE 1 Schematic diagram showing tectonic settings of tourmaline-bearing hydrothermal ore deposits.

Abbreviations: SEDEX, sedimentary-exhalative; VMS, volcanogenic massive sulfide; IOCG, iron oxide–copper–gold. MODIFIED FROM GROVES ET AL. (2005)

tourmaline is a hydrous mineral, it would be valuable to expand SIMS studies to include oxygen and hydrogen as well as boron isotope ratios (Trumbull et al. 2010).

GENETIC LINKS TO ORE DEPOSITION

An important precondition for the use of tourmaline as an aid in understanding ore formation is a clear temporal link between the deposition of tourmaline and ore minerals. Close spatial associations, even on the scale of a thin section, can be misleading because many ore deposits form by multistage processes involving different paragenetic stages and different fluids. Tourmaline may form in one or more stages that predate or postdate ore deposition. For example, tourmaline in diverse types of granitoid-related hydrothermal deposits commonly formed prior to the ore minerals, as shown by textural analysis (e.g. Frikken et al. 2005). However, detailed paragenetic studies have demonstrated contemporaneous tourmaline deposition and ore mineralization in many orebodies, such as the Batu Hijau porphyry Cu–Au deposit in Indonesia (Garwin 2002), the San Rafael Sn–Cu vein deposit in Peru (Mlynarczyk and Williams-Jones 2006), the Sigma, Big Bell, and Mount Gibson orogenic Au–quartz vein deposits in Québec and Western Australia (Garofalo et al. 2002; Jiang et al. 2002), the Kidd Creek Cu–Zn–Pb–Ag VMS deposit in Ontario (Slack and Coad 1989), the Broken Hill Pb–Zn–Ag SEDEX deposit in Australia (Slack et al. 1993), and the Igarapé Bahia Au–Cu–REE–U IOCG deposit in Brazil (Dreher et al. 2008). Some VMS and SEDEX deposits also have associated stratabound tourmaline-rich rocks (tourmalinites; >30 vol% tourmaline) that occur in the hangingwall and/or footwall of the orebodies, or along strike at the same stratigraphic level (FIG. 5).

COMPOSITIONAL AND ISOTOPIC ZONING

An overview of within-grain compositional variations in tourmaline from hydrothermal ore deposits and their implications deserves its own richly illustrated monograph. For lack of space, we focus here on a few examples where compositional zoning combined with in situ chemical and/or stable isotope data provide information with which to decipher ore-forming processes.

Concentric growth zoning is only one of several distinct patterns of internal variations reported in tourmaline. Meaningful interpretation of compositional differences can depend critically on recognizing what the “zoning” represents. The principal types of tourmaline zoning that may be found in hydrothermal ore deposits are:

1. Concentric growth zoning resulting from compositional changes in the growth medium, not uncommonly rhythmic (FIG. 6A)

2. Hourglass (sector) zoning, a variety of growth zoning, where the polar properties of the tourmaline lattice cause selective partitioning of elements—and isotopes—into opposite poles
3. Irregular, patchy variations in composite grains or clusters of anhedral tourmaline subgrains; common in recrystallized (“healed”) brecciated tourmaline
4. Overgrowth or replacement zoning that can occur in stratabound deposits, in which hydrothermal tourmaline encloses older detrital grains. In cases of discontinuous or multistage tourmaline growth, late material may be deposited on (or cut) preexisting crystal faces or fill cracks within fractured grains (FIG. 6A, 6B).

One example of chemical and isotopic zoning of tourmaline is in the shear zone–hosted Jaduguda U–Cu deposit in India (Pal et al. 2010). In this deposit, two-stage tourmaline

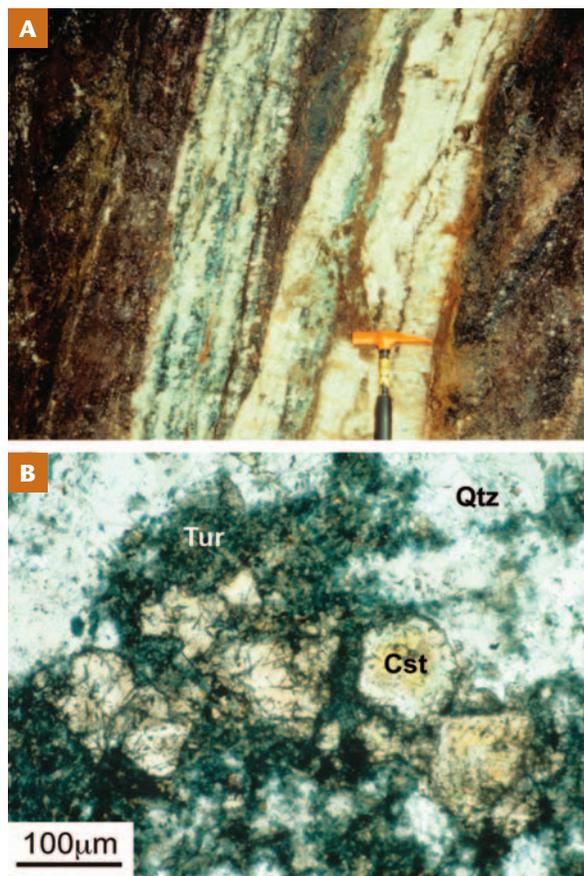


FIGURE 2 (A) Cassiterite-bearing quartz–tourmaline vein (left-center), Geevor tin mine, Cornwall, England. (B) Fine-grained tourmaline intergrown with zoned cassiterite and quartz, South Crofty tin mine, Cornwall. Abbreviations: Cst, cassiterite; Qtz, quartz; Tur, tourmaline. PHOTOS BY D. A. C. MANNING

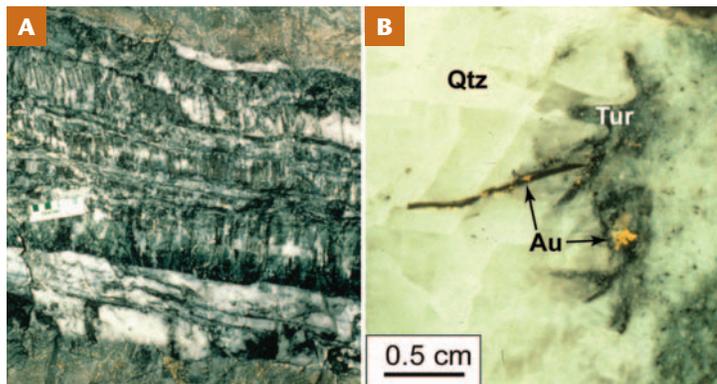


FIGURE 3 (A) Multistage gold-bearing quartz-tourmaline extension vein, Sigma gold mine, Québec (scale is in centimeters). (B) Gold grains (yellow) intergrown with tourmaline (black) in quartz gangue, Sigma mine. Abbreviations: Au, gold; Qtz, quartz; Tur, tourmaline. PHOTOS BY F. ROBERT

growth records a shift from host-rock to fluid control (FIG. 7). Paragenetically early tourmaline from different sample types shows distinctive chemical differences that reflect the local host-rock composition. In contrast, second-stage tourmaline, which is related to the main ore-forming event in shear zones, displays a narrow compositional range due to a high fluid flux within the shear zones. The early and late tourmalines in this case also have contrasting boron isotope compositions (FIG. 7C), which is consistent with the shift from a dominance of locally derived (host-rock sourced), isotopically heavy boron to a distally sourced, isotopically lighter boron as mineralizing fluids were channeled along the shear zone.

INSIGHTS INTO HYDROTHERMAL PROCESSES

Compositional and stable isotope data from ore-related tourmaline can reveal valuable details of hydrothermal ore-forming processes, including fluid mixing and boiling, redox states, temperature and pressure conditions, and fluid provenance. The use of such data is limited if assumptions of equilibrium between the hydrothermal fluid and tourmaline, or between tourmaline and coexisting phases, cannot be justified. Other limitations involve recrystallization of tourmaline by hydrothermal or metamorphic events, which may erase any preexisting growth zoning, resulting in compositions that are appropriate for the new P - T - X conditions but differ from those during mineralization. Deformation can also produce compositional modification by causing chemical diffusion between and among growth zones (Büttner and Kasemann 2007). Stable isotope systematics of B, O, and H in tourmaline are commonly preserved through deformation and recrystallization, but not during high-fluid-flux events (Marschall and Jiang 2011). Despite these caveats, geochemical and isotopic studies of tourmaline using well-characterized samples that contain primary tourmaline crystals have proven valuable in constraining several key parameters, as outlined below.

Fluid Properties

The precipitation of ore metals and the paragenesis and composition of ore and gangue mineral assemblages in many ore deposits are controlled by diverse features of the hydrothermal system, including fluid flux, fluid composition, fluid mixing, and boiling. Tourmaline is an excellent monitor of such features as its composition is governed largely by those of the fluid and/or wall rocks and by chemical equilibria with coexisting phases. In low fluid/rock systems, represented by stratabound tourmaline-rich rocks (tourmalinites) like those in the Broken Hill district

of Australia (FIG. 5), tourmaline chemistry is mainly controlled by the bulk composition of argillaceous sedimentary protoliths (Slack 2002). Protolith controls are strong in cases where ferromagnesian minerals are selectively replaced by tourmaline. In high-fluid-flux systems, such as those in breccia pipes, shear zones, veins, and feeder zones of seafloor-hydrothermal deposits, tourmaline chemistry is generally buffered by the fluid phase. A good example of the latter is shown by the Kidd Creek VMS deposit, where tourmaline displays a range of compositions, from schorl (Na-Fe²⁺-rich) to near dravite (Na-Mg-rich) (FIG. 8); this range of composition is interpreted to mainly record subsurface mixing of Fe-rich hydrothermal fluid and Mg-rich seawater (Slack and Coad 1989). This fluid-mixing model is further supported by oxygen, hydrogen, and boron isotope systematics in Kidd Creek tourmaline (Taylor et al. 1999). Modeling of isotope variations in that study also suggests that boiling occurred in the hydrothermal system prior to ore deposition. Boiling is an important mechanism for metal precipitation in many ore deposits, and in some cases it can also lead to tourmaline formation by increasing the concentration of B(OH)₃—the major B species in hydrothermal fluids—within the residual liquid (Lynch and Ortega 1997).

Redox State

Ferric/ferrous ratios in ore-related tourmaline serve as a monitor for changes in the redox state of hydrothermal fluids, which in turn can be a trigger for ore deposition. Fluid oxidation related to ore deposition is recorded by variations in Fe³⁺/Fe²⁺, such as in tourmaline from Sn-Cu veins at San Rafael, Peru (Mlynarczyk and Williams-Jones 2006). Textural and analytical work in that study underpinned a model in which influx of meteoric waters into the vein system produced late oxidation of hydrothermal fluids, precipitation of Fe³⁺-rich tourmaline, and initiation of cassiterite deposition (see also Williamson et al. 2000). Tourmaline in some porphyry Cu ± Mo deposits also likely formed from oxidized fluids, based on EMP data documenting Al-poor compositions and inverse Al-Fe correlations that imply significant Fe³⁺ in the tourmaline (Slack 2002). More detailed studies, including Mössbauer determinations of Fe³⁺/Fe²⁺, are needed for evaluating redox changes

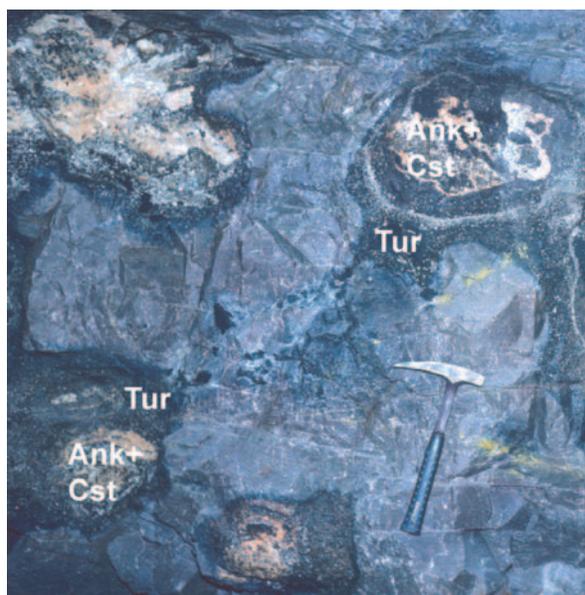


FIGURE 4 Zoned tourmaline-ankerite-cassiterite orbicules (replacements) in dark arkose, Rooiberg tin mine, South Africa. Abbreviations: Ank, ankerite; Cst, cassiterite; Tur, tourmaline. PHOTO BY F. PIRAJNO



FIGURE 5 Layered quartz-tourmaline tourmalinite in the Broken Hill district, Australia, from the same stratigraphic level as the main Pb-Zn-Ag lodes

during the formation of tourmaline-bearing ore deposits and the influence of such changes on metal concentration.

Temperature Conditions

Tourmaline has been used in several ways to constrain mineralizing temperatures. Fluid inclusion microthermometry, the most obvious method, has seen limited application because primary inclusions in hydrothermal tourmaline appear to be uncommon and, where present, are generally small (<5 μm ; Skewes et al. 2003; Frikken et al. 2005) and difficult to study. Some deposits, however, contain abundant large primary fluid inclusions in tourmaline that provide useful microthermometric data (Ootes et al. 2010). Other workers have used oxygen isotope fractionations in coexisting tourmaline-quartz pairs for geothermometry, an approach that has proven fruitful even for moderately deformed and metamorphosed deposits such as Kidd Creek (Taylor et al. 1999). Data from fluid inclusions, stable isotopes, and mineral assemblages indicate a temperature range for tourmaline precipitation in hydrothermal ore deposits, from ~150–300°C in seafloor base metal deposits (VMS and SEDEX) to at least 450°C in granitoid-related Cu \pm Mo deposits. Tourmaline also forms from higher-*T* (350–550°C) and high-*P* metamorphic fluids in orogenic Au-quartz vein deposits, under greenschist to amphibolite facies conditions (see Jiang et al. 2002).

In theory, geothermometry using boron isotope fractionation between tourmaline and coexisting B-bearing hydrothermal minerals, such as white mica, biotite, or amphibole, should be feasible but remains untested. Mineral-exchange geothermometry of tourmaline and coexisting phases is complicated by intersite partitioning within the tourmaline, but there is promise for a new method that utilizes partitioning of Ca and Ti between opposing sectors of hourglass-zoned crystals to yield temperatures of tourmaline formation (van Hinsberg and Schumacher 2011). This method has two possible limitations for studies of ore deposits: (1) the required hourglass zoning may be uncommon in hydrothermal tourmaline, and (2) the method has not been calibrated for temperatures less than ~350°C, meaning that it may be relevant only for higher-*T* ores such as those in porphyry Cu \pm Mo deposits, orogenic Au-quartz veins, and IOCG deposits.

Fluid Provenance

Isotopic data from tourmaline yield an important record of fluid sources in hydrothermal ore deposits. Less useful in this regard is major element chemistry, which commonly reflects compositions of the local hydrothermal fluid, precursor minerals, or wall rocks. Thus, fluid provenance

generally is poorly indicated by data for major cations, although trace element contents can be useful (Griffin et al. 1996). Insights are best provided by stable isotope data, especially from boron isotopes, which in many cases can discriminate among diverse B reservoirs, including crustal, granitic, sedimentary, volcanic, seawater, basinal brine, marine evaporitic, and nonmarine evaporitic reservoirs (Marschall and Jiang 2011). Boron isotope studies of ore-related tourmaline have been crucial in identifying major fluid components that were derived from evaporite-bearing sequences, including nonmarine evaporites at the giant Broken Hill Pb-Zn-Ag deposit (Slack et al. 1993) and marine evaporites at the giant Carajás IOCG deposits (Xavier et al. 2008). Tourmaline B isotope compositions can also readily distinguish between B sources from continental versus marine protoliths. Granites, felsic gneisses, and schists have isotopically light compositions ($\delta^{11}\text{B} < -5\text{‰}$), whereas metabasites, MORB, altered oceanic crust, and marine sediments have higher $\delta^{11}\text{B}$ values (Marschall and Jiang 2011). This distinction is generally sufficient to demonstrate, or rule out, a granitic origin for associated ore deposits (e.g. Garda et al. 2009; Trumbull et al. 2011). However, it is rarely possible to identify more specific source lithotypes within these two broad categories, partly because a number of processes related to fluid evolution and tourmaline precipitation fractionate B isotopes

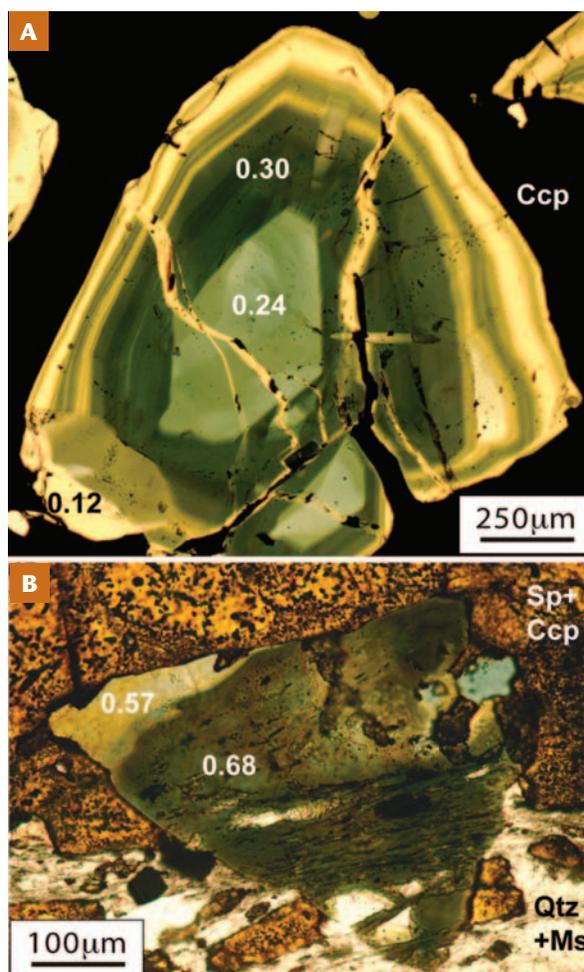


FIGURE 6 (A) Oscillatory growth zoning and discordant reaction rims in dravite, Ore Knob VMS deposit, North Carolina; note crosscutting dravite veinlets (yellow). (B) Pale discordant metamorphic reaction rims on schorl, Kidd Creek VMS deposit, Ontario. Values are Fe/(Fe+Mg) ratios determined by EMP (Taylor and Slack 1984; Slack and Coad 1989). Abbreviations: Ccp, talcopyrite; Qtz, quartz; Ms, muscovite; Sp, sphalerite (in B, the black inclusions in yellow sphalerite grains are chalcopyrite).

and thus modify the source signal. In principle, these processes can be recognized and their effects accounted for, but doing this requires independent constraints on temperature and fluid composition. Valuable as they are, boron isotope data work best when combined with data from other stable isotope systems. Additional insights into hydrothermal processes have come from Sr and Nd isotopes in ore-related tourmaline (Slack 2002) and from Si isotopes (Marschall and Jiang 2011).

Tourmaline Geochronology

Tourmaline can be dated directly by a variety of radiometric methods, including Rb–Sr, Sm–Nd, Pb–Pb, K–Ar, and $^{40}\text{Ar}/^{39}\text{Ar}$. Analyses of mineral separates by these methods yield meaningful results when the effects of mineral inclusions are carefully considered or eliminated. For example, robust Pb–Pb ages of metamorphic tourmaline in the Mount Isa Inlier of Australia were obtained by Duncan et al. (2006) using sequential step-leaching and LA–ICP–MS analyses. Especially promising is the application of high-precision $^{40}\text{Ar}/^{39}\text{Ar}$ dating (e.g. Martínez-Martínez et al. 2010), if potential problems of low K contents and excess ^{40}Ar in tourmaline can be addressed. The use of tourmaline geochronology in ore deposit studies is not yet fully explored but has the potential to provide critically needed ages of mineralization for orebodies that, otherwise, lack suitable minerals for dating.

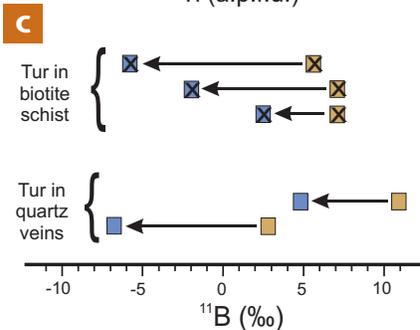
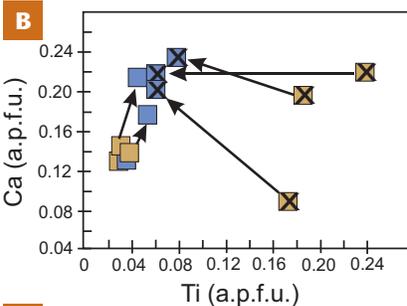
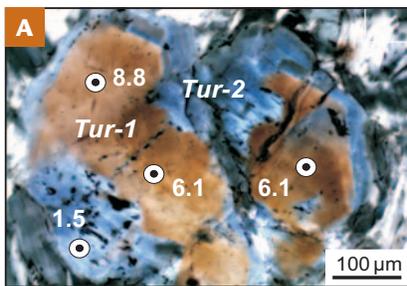


FIGURE 7 Two-stage tourmaline growth in the shear zone–hosted Jaduguda U–Cu deposit, India (Pal et al. 2010). (A) Cores of brown tourmaline (Tur-1) rimmed and partly replaced by blue tourmaline (Tur-2); dots locate SIMS analyses and numbers give $\delta^{11}\text{B}$ values. (B) Chemical zoning is interpreted to reflect a shift from host-rock control for Tur-1 (wide range of Ti, Ca) to fluid control for Tur-2 (narrow range). (C) Fluid-controlled Tur-2 is isotopically lighter than Tur-1; the isotopic shift is observed in both vein-hosted and schist-hosted tourmaline.

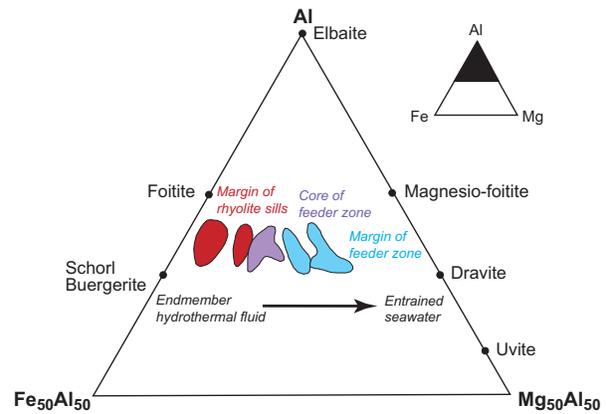


FIGURE 8 Large compositional range in ore-related tourmaline from the Kidd Creek VMS deposit, Ontario, due to mixing of Mg-rich seawater with Fe-rich hydrothermal fluid (modified from Slack and Coad 1989). Each field represents data for a single sample, based on ca 25 EMP analyses. The restricted compositional variation for each sample, together with the large overall range (for VMS deposits), indicate control on tourmaline composition by the hydrothermal fluids and not the host rocks. The trends in two samples toward dravitic compositions reflect post-ore overprints by sulfide–silicate reactions during metamorphism.

EXPLORATION APPLICATIONS

Early workers considered the empirical association of tourmaline with diverse types of ore deposits as a simple, first-order prospecting guide. Studies in the 1990s, and later, demonstrated that hydrothermal tourmaline has a large range of major element compositions and that a strong control was exerted in many deposits by the compositions of precursor minerals and wall rocks that were selectively tourmalinized during B metasomatism (Slack 2002). Thus, special care must be taken in using major element data on tourmaline in mineral exploration programs because such data do not necessarily record a hydrothermal signature. Nevertheless, some generalizations are warranted. In granitoid-related ore deposits, tourmaline compositions typically evolve from schorl in magmatic assemblages toward dravite (with or without a povondraite [Na–Fe³⁺-rich] component) in hydrothermal assemblages. Dravite predominates in VMS and most SEDEX systems, owing to the influence on tourmaline composition of Mg-rich seawater during subsurface fluid mixing and to later sulfide–silicate reactions between tourmaline and iron sulfide minerals (pyrite, pyrrhotite) during post-ore metamorphism (Slack 2002). Identifying an appreciable povondraite component may have exploration applications because this appears to form preferentially from highly saline fluids (van Hinsberg et al. 2011). Such fluids are critical in forming rich porphyry, SEDEX, and IOCG deposits because the high salinities permit greater concentrations of aqueous metal-chloride complexes to be carried in the hydrothermal fluids. Identification of such high-salinity fluids can also be done by modeling B and H isotope data from tourmaline, as shown by Taylor et al. (1999) for the Kidd Creek VMS deposit.

A promising approach for mineral exploration is the use of trace elements in tourmaline. Griffin et al. (1996) acquired in situ trace element data on tourmaline from VMS and SEDEX deposits and from stratabound tourmalinites using a proton microprobe (PIXE). They found broad Zn–Fe correlations that suggest chemical control on Zn contents by temperature or fluid–mineral equilibria, and Cu–Zn–Pb signatures in the tourmalines that broadly match those of the associated ore deposits. Furthermore, these signatures were not destroyed by post-ore metamorphism, enhancing utility of the trace element data for exploration. Development in the early 1990s of the LA–ICP–MS method for in situ analysis of a wider suite of trace

elements in minerals offers exciting potential for improved understanding of tourmaline formation in hydrothermal systems and its use as an exploration guide. This technique can provide rapid multielement analyses at low detection limits, yielding a wealth of trace element data that will likely further enhance tourmaline applications in the exploration for new ore deposits.

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