Tourmaline Isotopes: No Element Left Behind

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Tourmaline typically forms where crustal rocks interact with migrating hydrous fluids or silicate melts, and its isotopic composition provides a reliable record of the isotopic composition of the fluids and melts from which it crystallized. Minerals of the tourmaline supergroup are exceptional in their physical robustness and chemical variability, and they allow us to extract a uniquely broad range of isotopic information from a single mineral. The chemical variability of tourmaline confronts us with the difficulty of deciphering an extremely complex mineral system, but it also presents us with a geochemical recorder of half the periodic table, a breadth of representation that is unparalleled among minerals. Plate tectonic–scale geochemical cycles, local and regional fluid–rock interactions, magmatic–hydrothermal systems, ore-forming processes, and ages of tourmaline formation have all been reconstructed using this unique isotopic broadband recorder.

Thin section photomicrograph (crossed-polarizers) of zoned hexagonal tourmaline (grain diameter ~0.4 mm) with chlorite (dark blue), phengite (orange and pink), and epidote (inclusions in tourmaline). The measurement spots produced by SIMS are visible as white dots.

INTRODUCTION

The chemical differentiation of our planet is largely achieved by fluids and melts that transport material from sources typically deep in the crust or upper mantle to the shallow crust or surface. These migration processes are keys to the long-term evolution of the Earth's outer layers and the enrichment of the upper continental crust in melt- and fluid-soluble elements. The mobile phases involved in these processes are rarely preserved in the geologic record, hampering reconstruction of their sources and chemical evolution. Consequently, research focuses on minerals, as these can potentially preserve the chemical and isotopic compositions of the fluids and melts from which they grew. Minerals of the tourmaline supergroup are ideally suited as recorders of fluid and melt compositions. Tourmaline is a borosilicate mineral with significant chemical variability (Hawthorne and Dirlam 2011 this issue). Once formed, tourmaline is highly stable in a variety of rock types over an exceptionally large *P–T* range, extending from surface conditions to the diamond stability field at pressures prevailing in the upper mantle (Marschall et al. 2009; Dutrow and Henry 2011 this issue). The chemical and isotopic information is commonly preserved because volume diffusion of major and trace elements in tourmaline is insignificant up to temperatures of at least 600°C (van Hinsberg et al. 2011a this issue). Tourmaline is also exceptionally robust in sediments during transport, diagenesis, and metamorphism, and together with zircon and rutile has been referred to as an "ultrastable mineral" in sedimentary geology (van Hinsberg et al. 2011a). Detrital grains can be readily identified in sediments and metasedimentary rocks by their distinct optical, chemical, and isotopic zoning patterns (FIG. 1; Henry and Dutrow 1996; Marschall et al. 2008). With the development of in situ analytical techniques, we can now investigate the chemical and isotopic composition of multiply zoned tourmaline at a spatial resolution of less than 50 µm and, in some cases, as small as 5 µm (FIG. 1).

The chemical complexity of tourmaline provides a geochemical recorder of unparalleled breadth, and a large number of major and trace elements in tourmaline are important tools in isotope geochemistry. The isotope systems of B, O, H, Si, Mg, Li, Sr, Nd, Pb, K(Ar), and Cu have already been applied to tourmaline, providing valuable information on the physicochemical conditions associated with fluid–rock interaction, fluid origin and evolution, the sources and genesis of ore deposits, and the timing of the magmatic, metamorphic, and hydrothermal events that produce tourmaline, including the highly valued gem tourmalines.

BORON ISOTOPES, SUBDUCTION ZONES, SEAWATER, AND THE CONTINENTAL CRUST

Subduction zones are areas of intense interest to geoscientists. In addition to being the sites of widespread volcanism, earthquakes, and ore deposit formation, subduction zones are also where crust and mantle interact extensively, such that material exchange takes place between the two reservoirs. Oceanic crust is subducted into the mantle and releases fluids rich in solutes into the overriding plate. Such fluids make their way back to the surface as metasomatizing agents altering rocks of the overriding mantle and crust, and they trigger subduction-related volcanism. However, our understanding of the detailed nature of the geochemical cycling in subduction zones and the sources and pathways of fluids and melts is incomplete.

The isotopic signatures of fluids and melts can be recorded in minerals such as tourmaline and provide important evidence for understanding subduction zone processes. The
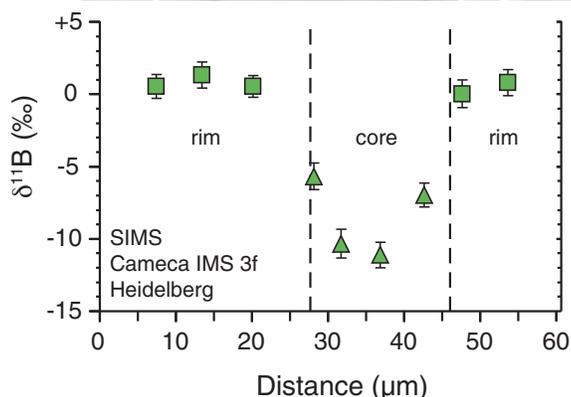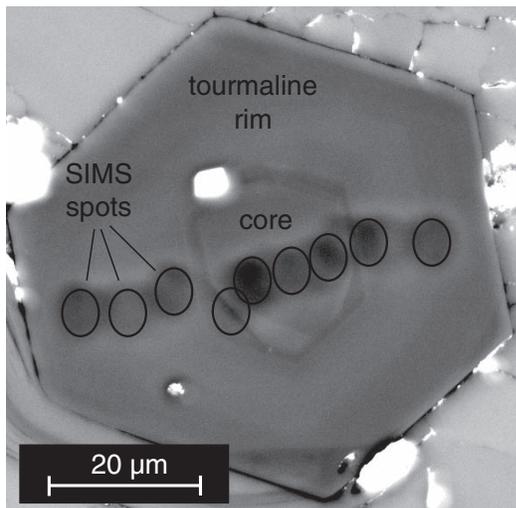
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FIGURE 1 Backscattered electron image of a tourmaline grain in a siliceous marble from Syros (Greece) displaying a detrital core that is distinct from its metamorphic rim (Marschall et al. 2008). The B isotope composition of different parts of the grain was determined by SIMS (secondary-ion mass spectrometry) with a spatial resolution of 5–10 µm. The delta notation for isotope ratios describes the deviation of a sample from a standard in parts per thousand. The standard for B has been chosen arbitrarily, and 0 ‰ has no geologic meaning. Note the distinct texture and B isotope composition of the preserved detrital core compared to the metamorphic rim.

chemical feature that sets tourmaline apart from other common silicate minerals is the presence of ~3 wt% boron (B), an element essential to its crystal structure (Dutrow and Henry 2011; Hawthorne and Dirlam 2011). Boron is a quintessentially crustal element. Its abundance in the mantle is very low, whereas seawater and rocks of the continental crust show relatively high abundances, containing a large fraction of Earth's B budget (Dutrow and Henry 2011). At the surface, ambient temperatures and extensive interaction of the lithosphere and hydrosphere lead to a large fractionation of the two stable isotopes of B, ^{10}B and ^{11}B. Rocks of the oceanic crust incorporate isotopically heavy B (i.e. they have a higher proportion of ^{11}B) from seawater during seafloor alteration, whereas rocks of the continental crust become depleted in the heavy isotope during subaerial weathering. Consequently, B in continental crustal rocks is isotopically lighter than B in the mantle, and rocks with marine affinity are enriched in ^{11}B relative to the mantle and continental crust (FIG. 2; Leeman and Sisson 1996). During subduction, altered oceanic crust releases fluids that carry isotopically heavy B inherited from the oceanic crust's interaction with seawater, and some of these fluids contribute to subduction-related magmatism. Consequently, magmas produced in subduction zones are generally enriched in ^{11}B (Leeman and Sisson

1996). However, a large amount of B-rich fluid is released from the subducting slab in the shallow fore-arc region where magmatism is not developed, and methods for detecting and deciphering the geochemical cycle of subduction zones in this region are needed.

High-pressure metamorphic rocks are important sources of geochemical information from subduction zones. These rocks are fragments of oceanic crust or of a continental margin that were subducted to depths of at least 50 kilometers and returned to the surface. Importantly, much of the exhumation of such rocks typically occurs while the subduction zone is active. The exhuming rocks travel in a narrow channel on top of the subducting slab and are metasomatized by fluids released from the slab (e.g. Marschall et al. 2006). Hence, metasomatic minerals crystallized in high-pressure rocks during exhumation typically carry geochemical signatures of subduction zone fluids sampled at various depths. High-pressure metamorphic rocks provide information on multiple stages of subduction zone processes: the solid products of dehydration inform us about the dehydration stage of the rocks, while rocks overprinted during the rehydration stage bear witness to fluids released from the slab in shallower regions. Tourmaline has been discovered in both dehydrated and rehydrated rocks, and, in some cases, even retains relics of the presubduction protolith.

The resistant nature of tourmaline and its capacity to grow in a variety of environments make it a unique tracer of the B geochemical cycle within subduction zones. Subduction zone tourmaline has been subdivided into three genetic types (Marschall et al. 2009): (1) premetamorphic, relict grains derived from the protolith; (2) grains formed during subduction and dehydration under increasing pressure and temperature; and (3) grains formed during exhumation and influx of metasomatic fluids. Each tourmaline type contains information on the B isotope system in subduction zones: premetamorphic grains record information about the rock composition prior to subduction; prograde and peak-metamorphic grains record isotopic fractionation during dehydration; and retrograde metasomatic tourmaline reflects fluids released from the slab at shallower depths. Using experimentally determined tourmaline–fluid B isotope fractionation factors (Meyer et al. 2008), the B isotope composition of the fluid can be derived from the B isotope composition of tourmaline. However, experimental data are limited to simple Ca–Fe-free tourmaline compositions. In detail, B isotope fractionation may depend on the major element composition of tourmaline and on the amount of tetrahedrally coordinated B present in the crystal structure (cf. Hawthorne and Dirlam 2011). Boron isotope fractionation between crystallographic sectors with contrasting compositions has been detected, and may indicate a control related to major elements and tetrahedral B on tourmaline–fluid B isotope fractionation (van Hinsberg and Marschall 2007; Trumbull et al. 2009).

Several in situ B isotope studies have demonstrated that the ^{11}B/^{10}B ratio of prograde metamorphic tourmaline decreases from core to rim, consistent with preferential loss of ^{11}B during dehydration (e.g. Nakano and Nakamura 2001). In low-grade metamorphic rocks, B is primarily hosted in clay minerals and white mica. Upon heating and decomposition of these hydrous minerals, B-bearing fluids are released, and strong isotopic fractionation between sheet silicates (enriched in ^{10}B) and hydrous fluids (enriched in ^{11}B) drives the progressively dehydrating rock to successively lower ^{11}B/^{10}B ratios. Growing tourmaline captures part of the B released along the prograde metamorphic path and can be used to estimate the B isotope composition of released fluids (Nakano and Nakamura 2001). In contrast to B sourced directly from local rocks, during retrograde
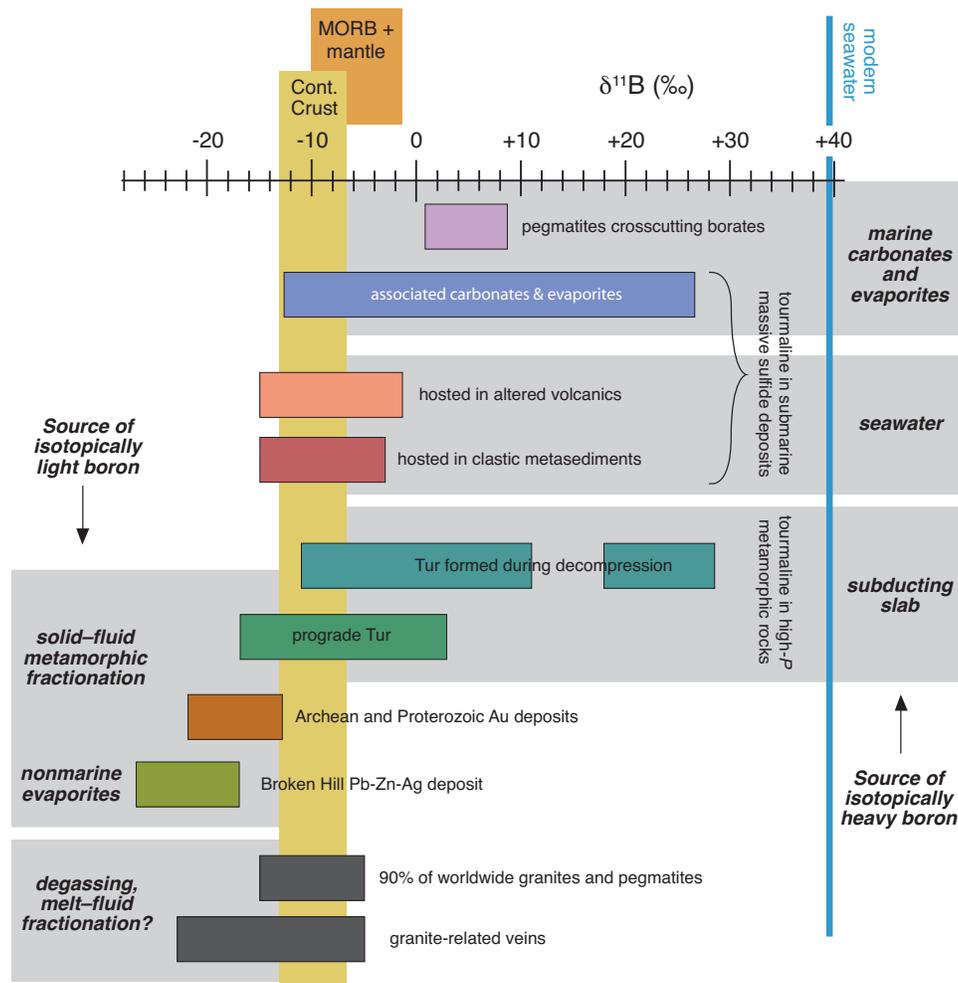
FIGURE 2 Measured B isotope composition as a function of host rock type (colored boxes) and inferred B sources (grey bands). Isotopically heavy B (= high $\delta^{11}B$ value) is ultimately sourced from seawater and may enter a rock via fluids or melts derived from a subducting slab or from carbonate or evaporite sequences in the crust, or directly from seawater circulating through the rocks. Isotopically light B (= low $\delta^{11}B$ value) is typically sourced from nonmarine evaporites or produced by isotopic fractionation between solids and fluids during metamorphic dehydration. Tourmaline in most granites and pegmatites shows $\delta^{11}B$ values close to average continental crust (–10 ± 3‰). Tur = tourmaline; MORB = mid-ocean ridge basalt. MODIFIED FROM VAN HINSBERG ET AL. 2011B

metamorphism the B necessary to form tourmaline is typically introduced by external fluids, and these have distinctly higher $^{11}B/^{10}B$ ratios (FIG. 2).

The isotopically heavy B found in tourmaline formed from subduction-related fluids implies that ^{11}B enrichment could be used to identify subduction-related tourmaline. This hypothesis is important for studies of ancient crust, where most of the evidence of active continental margins has been lost to erosion and detrital grains in sediments may remain the sole geologic witnesses. Tourmaline is a stable detrital mineral and is relatively abundant in mature clastic sediments, forming an important source of information in provenance studies. Unfortunately, subduction-related fluids are not the sole carriers of isotopically heavy B. Tourmaline from two other geologic settings may also be enriched in ^{11}B (FIG. 2; Palmer and Slack 1989): (1) tourmaline in marine evaporites and carbonates or tourmaline formed from fluids or melts that interacted with such rocks (up to +26.5‰) and (2), less pronounced, tourmaline that formed in submarine massive sulfide deposits (up to –1.5‰). Ultimately, all these sources of isotopically heavy B are derived from seawater. In contrast, continental lithologies constitute the isotopically light part of the natural B cycle, and tourmaline formed in and around granite intrusions is typically enriched in ^{10}B, corresponding to the B isotope range of typical continental crust (FIG. 2).

The formation of tourmaline requires a local concentration of B. Tourmaline is commonly developed in sedimentary and metasedimentary rocks and in granites produced by melting of deeply buried sediments. In addition, tourmaline readily forms in crustal rocks as a result of the introduction of B-bearing hydrous metasomatic fluids derived from granitic intrusions, dehydrating metasediments, or subducting slabs. The physical and chemical robustness of tourmaline is indicative of its potential as a geochemical recorder of highly evolved continental crust. This feature may be particularly useful in the investigation of tectonic processes based strictly on the sedimentary and metamorphic record. In studies of Archean and Proterozoic crustal evolution, reliable and robust mineral recorders are of particular importance, as the rock record is very incomplete for the early eras of Earth history. While important insight has been gained from zircon and rutile, the unique advantage of tourmaline is that it contains a large number of isotope systems that can be related to highly differentiated crust, intracrustal recycling, and recycling at active plate margins.

Tourmaline tends to strongly influence our estimates of the B isotope composition of the continental crust because it is typically the dominant reservoir of B in a rock. It is a highly stable mineral, and no change in the bulk-rock B isotope composition can occur during metamorphism when no B enters or leaves the system. In tourmaline from

metamorphic rocks of increasing metamorphic grade, B isotope compositions do not vary, and partial melting in these rocks does not significantly fractionate B isotopes, as demonstrated by Kasemann et al. (2000). These authors also showed that tourmaline from metamorphic rocks and granites in the same crustal section have overlapping B isotope compositions, consistent with their estimate for the average continental crust of $\delta^{11}B = -10 \pm 3$‰ (FIG. 2).

Secular change of the B isotope composition of seawater is still largely enigmatic, but attempts to define such a change have used tourmaline. The oldest tourmaline-bearing rocks described in the literature are 3.6–3.8 Ga metasediments from Isua, West Greenland, and 3.44–3.23 Ga metasediments from the Barberton greenstone belt, South Africa (Hazen et al. 2011). Tourmaline from both localities formed on or near the seafloor during the alteration of submarine lava flows by seawater-derived hydrothermal fluids. The isotopic composition of this tourmaline was controlled by the two interacting reservoirs, i.e. the volcanic rocks and entrained seawater that fed the hydrothermal circulation. However, the B isotope composition of the tourmaline-forming fluids was likely not identical to that of seawater; rather, B was derived from and fractionated by the seafloor sedimentary and meta-igneous rocks that dominated the B budget and isotopic composition of the fluids (Byerly and Palmer 1991). Hence, fluid–rock isotopic fractionation prior to tourmaline formation hinders attempts to define the B isotope composition of Archean seawater. Still, the Isua tourmaline samples suggest that seawater has been enriched in the heavy isotope ^{11}B for at least the last 3.6 billion years.

MULTIPLE-ISOTOPE SYSTEMATICS AND FLUID SOURCES OF HYDROTHERMAL ORE DEPOSITS

Differentiation of the crust through fluid and melt migration leads to a strong enrichment of certain elements. Ore deposits are domains in the crust where enrichment of societally important elements reach a sufficient concentration to make mining operations economically viable. Because mining operations and exploration benefit from geologic guidance, knowledge of the genesis, internal structure, and spatial extent of these deposits is of direct economic importance. Tourmaline is widespread in a variety of hydrothermal ore deposits, especially massive sulfide, mesothermal gold, granite-related tin–tungsten, and uranium deposits (Slack and Trumbull 2011 this issue). Multiple-isotope systematics, extending from major (e.g. O, H, B, Si) to trace elements (e.g. Sr, Nd, Pb), have been successfully applied to the tourmaline supergroup minerals to identify likely fluid sources for, and to constrain, ore genesis.

The oxygen and hydrogen isotope compositions of tourmaline from several types of deposits, including lead–zinc massive sulfides, hydrothermal gold, and deposits in granites and pegmatites, have provided critical insights into the temperatures of tourmalinization and associated ore formation, sources of hydrothermal fluids, and genetic evolution of the deposits. Based on H–O isotope systematics of tourmaline, several different fluid sources have been identified:

1. Modified seawater for several massive sulfide deposits (e.g. Kidd Creek, Ontario; Taylor et al. 1999)

2. Metamorphic fluids for Archean and Proterozoic gold deposits (e.g. Star Lake, Rio, and Frontier, Saskatchewan; Tartan Lake, Manitoba; Big Bell, Western Australia; e.g. Ansdell and Kyser 1992; Jiang et al. 2002)

3. Granite-derived magmatic fluids for tin-rich hydrothermal veins (e.g. northwestern Tanzania; Taylor et al. 1992)

Boron isotopes also play a central role in the investigation of ore deposits. A global B isotope study conducted on tourmaline from over 40 massive sulfide deposits and associated tourmalinites (i.e. rocks with >30% tourmaline) revealed a wide range of B isotope compositions, largely indicative of the nature of the footwall lithologies (Palmer and Slack 1989). Tourmaline associated with rocks formed from marine evaporites and carbonates reflects the ^{11}B-enriched characteristic of seawater, whereas tourmaline from deposits hosted in clastic metasedimentary rocks shows relatively low $\delta^{11}B$ values, typical of continental crust (FIG. 2). Tourmaline from the Broken Hill, Australia, lead–zinc–silver ore deposit, interpreted to have been originally associated with nonmarine evaporites, has very low $\delta^{11}B$ values (FIG. 2).

Based on the silicon isotopes in tourmaline from tourmalinites of the Sullivan lead–zinc–silver deposit, British Columbia, Jiang et al. (2000) established the origin of two distinct ore-forming processes: (1) subseafloor replacement of clastic sediments by silicon from a local source (detrital clays), and (2) hydrothermal–exhalative processes with a significant hydrothermal silicon source. Tourmaline Si isotopes have also been used as an effective paleoenvironmental indicator and to define a stratigraphic horizon prospective for mineral exploration (Jiang et al. 2000). Silicon isotope ratios of rocks and minerals are not easily reset during regional metamorphism because the high Si abundance in most rocks would require massive silica exchange to significantly alter the initial isotopic composition.

Other isotopic systems and trace elements in tourmaline have been used to gather geological information. Initial Sr isotope compositions of hydrothermal fluids are recorded in tourmaline because of its strong preference for the daughter element Sr over the parent element Rb in the Rb–Sr decay system. Strontium isotope systematics have been used to trace sources of the fluids and to quantify fluid mixing in ore-forming systems (e.g. Ansdell and Kyser 1992). Tourmaline shows considerable variability in rare earth element (REE) concentrations and REE patterns, which can be used as an indicator of petrogenesis and ore genesis. The Sm–Nd isotope system and the initial Nd isotope composition of tourmaline reveal sources of REEs in the mineralizing fluids and track fluid–rock interaction (Anglin et al. 1996).

GEOCHRONOLOGY USING TOURMALINE

Knowledge of the absolute time of formation or cooling to a threshold temperature is essential to deciphering the temporal evolution of geological terranes. Dating tourmaline provides a way to link various recorded geochemical signatures to a distinct time frame. Tourmaline has a number of advantages in geochronology, such as relatively large grain size and growth zones recognizable at the microscopic or macroscopic scale. The color changes associated with differences in major and trace elements in tourmaline can be related to changing conditions, thus facilitating geochronological analytical procedures and geologic interpretations (van Hinsberg et al. 2011a). Of particular importance, tourmaline is characterized by very slow intracrystalline diffusion. This is evident from the preservation of sharp intragrain zoning in high-grade metamorphic grains (e.g. Henry and Dutrow 1996) and from experimental diffusion studies (e.g. Desbois and Ingrin 2007). Slow volume diffusion translates to a high retention of parent and daughter isotopes such that the isotopic clocks are not easily reset by subsequent thermal events. Tourmaline, therefore, can record its time of crystallization from a magmatic liquid, metasomatic fluid, and/ or metamorphic event. High closure temperatures in

various isotope systems, the chemical and physical robustness of tourmaline, and its large *P–T* stability range make tourmaline a unique chronometer. Despite its apparent utility, there are a limited number of studies on tourmaline geochronology. These utilize a variety of radiogenic isotope systems, primarily K–Ar, ^{40}Ar/^{39}Ar, Rb–Sr, Sm–Nd, and U–Th–Pb. Tourmaline samples as old as the Archean and Proterozoic and as young as the Miocene have been used in geochronology.

The most widely applied geochronologic method is ^{40}Ar/^{39}Ar, which is based on the decay of ^{40}K to radiogenic ^{40}Ar. The challenges of this method include low K contents (typically <500 µg/g) in most common tourmalines and the possibility of incorporation of excess ^{40}Ar during tourmaline growth, which would yield erroneously old apparent ages. However, tourmaline samples with excess Ar can be recognized by disturbed Ar signals, and careful petrographic examination can eliminate tourmaline samples that have inclusions or show domains of recrystallization or dissolution–reprecipitation (see van Hinsberg et al. 2011a). Following this approach, several recent studies have obtained high-quality ^{40}Ar/^{39}Ar geochronologic results using tourmaline (e.g. Martínez-Martínez et al. 2010). Closure temperatures for Ar in tourmaline appear to be higher than in amphibole, based on investigations from Naxos Island (Greece), where K–Ar ages of tourmaline are indistinguishable from U–Pb crystallization ages of zircon, while K–Ar ages of amphibole and mica are ~5 and ~8 million years younger, respectively (Andriessen et al. 1991). This pattern has been interpreted in terms of cooling of the metamorphic complex, with zircon and tourmaline recording the time of peak-metamorphic temperatures of ~700°C, whereas amphibole and mica record subsequent cooling (FIG. 3). Closure temperatures for other radiogenic isotope systems in tourmaline are also considered to be high, with estimates of 580–630°C for the U–Th–Pb system and >600°C for Sr (e.g. Duncan et al. 2006).

Geochronological studies using tourmaline have been carried out on other isotopic systems. Tourmaline alone cannot be used for Rb–Sr isotope geochronology due to its generally low Rb and high Sr abundances. However, in combination with cogenetic minerals, it has been used successfully in multimineral Rb–Sr isochron geochronological studies of some ore deposits (e.g. Ansdell and Kyser 1992). The Sm–Nd isotopic system has been successfully applied to tourmaline and tourmalinites. For example, the inert nature of REEs in tourmaline preserves age information of a primary ore-related hydrothermal event and the Sm–Nd isotope system was unaffected by later metamorphic overprints (Anglin et al. 1996). Single-mineral dating of tourmaline using the Pb–Pb stepwise leaching method yielded precise ages (±0.5–3%) for Archean and Proterozoic tourmaline samples from mono- and even polygenetic hydrothermal veins (e.g. Duncan et al. 2006). The high-precision analytical facilities currently available (e.g. laser ablation multicollector ICP–MS, ion microprobe) provide the tools needed to date individual growth zones in tourmaline grains and to use contemporaneous sector zones in tourmaline for isochron dating of single grains.

LITHIUM ISOTOPES, GRANITES, AND PEGMATITES

The interpretation of Li isotopes has undergone significant paradigm shifts in the last decade. Li isotope fractionation in rock–fluid–melt systems was previously assumed to be governed by equilibrium fractionation among coexisting minerals, melts, and fluids. Equilibrium stable isotope fractionation decreases with increasing temperature, and it was assumed that Li isotope fractionation would be negligible at high-grade metamorphic and magmatic tempera-
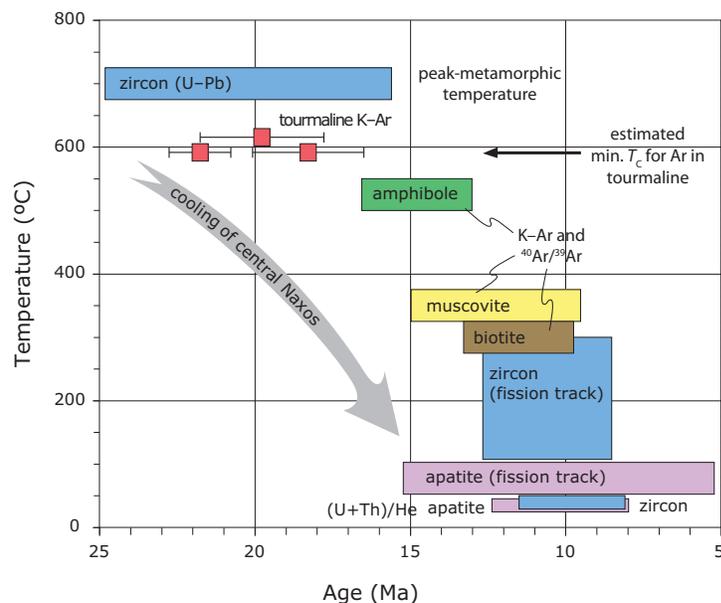

FIGURE 3 Temperature–time diagram for the high-grade metamorphic dome of central Naxos (Greece), displaying crystallization and cooling ages determined using different chronometers with accepted closure temperatures (data from Martin et al. 2006 and references therein). The tourmaline K–Ar ages (Andriessen et al. 1991) are in the same range as the zircon U–Pb ages and are significantly older than K–Ar and ^{40}Ar/^{39}Ar ages of amphibole and mica, arguing for a very high closure temperature (T_C) for Ar in tourmaline.

tures. Lithium isotope compositions of minerals and rocks were, therefore, interpreted to represent the source regions of melts and fluids. However, in the course of experimental fractionation studies and analysis of natural samples, it became evident that in many natural, high-temperature geologic processes, ^{6}Li and ^{7}Li are strongly fractionated kinetically due to their different diffusivities. The lighter isotope, ^{6}Li, diffuses faster than the heavy isotope, ^{7}Li, creating transient isotopic excursions in minerals and rocks with magnitudes that far exceed those produced by equilibrium fractionation (e.g. Teng et al. 2006; Richter et al. 2009).

The amount of Li isotope data on bulk rocks and minerals from granites and pegmatites is relatively small, and the quantity of Li isotope data on tourmaline is even smaller (e.g. Ludwig et al. 2011). However, Li–B-rich granite–pegmatite systems show the following general trends: (1) the main granite bodies, which have relatively low Li concentrations, have low δ^7Li values, in a range typical of continental crust (0 ± 2‰); (2) pegmatites show a general increase in Li concentrations with increasing magmatic differentiation, accompanied by a rise in δ^7Li values; and (3) pegmatites show strong Li isotope disequilibria among coexisting minerals, such as spodumene, tourmaline, feldspar, mica, and quartz. (e.g. Teng et al. 2006; Maloney et al. 2008; Ludwig et al. 2011). This Li isotope evolution has been explained by fluid–melt separation processes in the granite–pegmatite systems and by preferential diffusive loss of isotopically light Li from the pegmatite dikes into the country rocks (e.g. Teng et al. 2006; Maloney et al. 2008). Tourmaline Li isotopes (in contrast to B isotopes) are, therefore, not suitable for tracing sources of pegmatites. However, large tourmaline crystals in pegmatites are typically chemically zoned (e.g. from schorl to elbaite) and record the chemical and isotopic evolution of the dikes. These crystals are most suitable for monitoring the Li isotope evolution of pegmatite dikes, from emplacement,

through magmatic–hydrothermal transition, to solidification and cooling (Maloney et al. 2008).

ISOTOPES IN GEM TOURMALINE

Gem tourmaline is commonly close to elbaite in composition and occurs in pegmatite dikes as comb-like layers and as crystals in miarolitic cavities and veins (Pezzotta and Laurs 2011 this issue). Prices for gem tourmaline vary by several orders of magnitude, depending not only on quality, color, and clarity, but also on provenance. The highest-quality blue Paraíba tourmaline from the Batalha mine, Brazil (the original discovery site) may demand prices of more than twenty thousand dollars per carat (1 ct = 0.2 g), whereas similarly colored stones from Mozambique or Nigeria may sell for a fraction of that price, despite similar qualities. Hence, there is a potential for fraud, and gemologists are challenged to develop effective provenance tools.

Elbaite major element compositions are variable, and all three localities show compositional overlaps such that chemistry provides no provenance criteria. Trace element abundances (e.g. Ga, Bi, Pb) have been successfully employed to distinguish Paraíba tourmaline from Paraíba-type tourmaline from Mozambique and Nigeria, but the grains show significant zoning and some compositional overlap exists between localities (Rossman 2009). Thus additional provenance tools are required. The three localities can be distinguished using B and Li isotopes (Ludwig et al. 2011). Boron isotopes of Brazilian and Mozambican samples, in particular, differ by ≥ 10‰ in $\delta^{11}B$ (FIG. 4), a difference that is well outside analytical uncertainties of secondary-ion mass spectrometry (SIMS), used to analyze the Li and B isotopes. Because SIMS uses a minimum of sample material, with analysis spots significantly less than 1 μm deep and ~10 μm in diameter (FIG. 1), the critical criterion in gemology of an essentially nondestructive analytical method is fulfilled by this technique.

Apart from provenance certification, a second important challenge for gemologists is the identification of gems that have been modified. Most widely applied treatments to improve color involve the heating of stones to several hundred ºC and/or irradiation with gamma rays. Many of these methods are legal, but gems must be clearly labeled as "treated" and the method must be disclosed to the customer. Treatment methods, however, have become sophisticated, and gems that have been colored by diffusion techniques have recently entered the market. For example, specimens exhibiting colors that bring lower prices are packed with mixtures of oxides containing the necessary chromophores (e.g. Cu) to improve color and then pressurized and heated for several hours or days, during which time the chromophores diffuse into the gems. Tourmaline is less susceptible to this method because of its slow volume diffusion and its more limited temperature stability compared to other gems (e.g. varieties of corundum). However, small grains of tourmaline may still be treated in this way. Also, both irradiation prior to diffusion and the use of high oxygen fugacity in the diffusion setup increase the density of lattice defects, which significantly enhances diffusivities. Chemical zoning and compositional heterogeneity are common in tourmaline, and both hamper clear identification of diffusion-treated specimens. However, diffusion is a kinetic process that fractionates elements according to their relative diffusivities. Different elements diffuse at different velocities within a crystal structure, and the same is true for different isotopes of the same element, generating isotopic patterns that are distinct from those produced by equilibrium fractionation (Richter et al. 2009). For example, in situ analyses of Cu isotope ratios ($^{65}Cu/^{63}Cu$) in Cu-bearing gem tourmaline by laser ablation ICP–MS with a spatial resolution of ~200 μm revealed very large intragrain variations in $^{65}Cu/^{63}Cu$ ratios, thus allowing the stones to be identified as diffusion treated (Fontaine et al. 2010). In fact, an entire range of isotope systems could be employed to identify diffusion treatment in tourmaline and other gems, and different elements could be used to detect diffusion treatment at different temperatures and timescales.

CONCLUSIONS AND OUTLOOK

Tourmaline is typically formed from boron carried by hydrous fluids or silicate melts migrating through the continental crust in the course of tectonomagmatic processes. As tourmaline records the isotopic signature of these fluids and melts, it can be used to reconstruct sources, pathways, and interaction processes of the mobile agents. Significant progress has been made in applying tourmaline as a geochemical monitor of crustal systems, combined with precise geochronology and thermobarometry. Studies on the generation of ore deposits, on tectonic processes in orogens, on fluid and melt migration in fossil subduction zones, and on the provenance of clastic sediments have all been made possible by the unique isotopic characteristics of tourmaline supergroup minerals. However, the potential of this broadband geochemical recorder has yet to be fully exploited. Combining various isotope systems and trace element data derived from individual growth zones in tourmaline grains will provide a path forward for studies of processes in magmatic, metamorphic, and hydrothermal rocks and on detrital tourmaline in (meta)sediments.
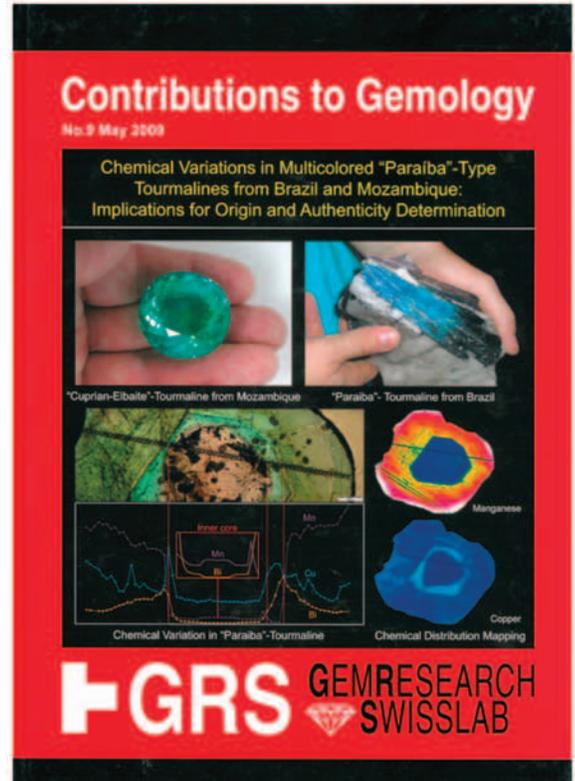
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