The Canadian Mineralogist
Vol. 32, pp. 599-605 (1994)

EPIGENETIC TOURMALINE IN SEDIMENTARY RED-BEDS: AN EXAMPLE FROM THE SILURIAN ROSE HILL FORMATION, VIRGINIA

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ABSTRACT

Acicular epigenetic tourmaline is developed hemimorphically on the *c* pole of detrital tourmaline in a Silurian red-bed sandstone of the Rose Hill Formation from western Virginia. Rounded quartz with minor detrital tourmaline and clay-mineral ooids are cemented by berthierine and hematite that formed epigenetically during a late Paleozoic influx of fluid associated with the Alleghenian orogeny. Detrital grains of tourmaline are very Fe- and Ti-rich but Al-poor. Compositional signatures of the detrital tourmaline suggest a provenance from a highly oxidized granitic rock or a quartz–tourmaline vein. Relative to the detrital substrates, the composition of the epigenetic overgrowths is distinctly different, consisting of Al-rich schorl–dravite with a Fe/(Mg+Fe) value of 0.66 and a significant *X*-site vacancy. Al-enrichment and the *X*-site vacancy reflect operation of the exchange vector: $\square\mathrm{AlNa}_{-1}\mathrm{Mg}_{-1}$, a consequence of growth in an Al-rich but Na- and Ca-poor environment. A high proportion of *X*-site vacancies is commonly observed in epigenetic tourmaline from sandstones, but the epigenetic tourmaline in this red-bed sequence is the most Fe-rich reported. Epigenetic tourmaline is a sensitive recorder of the chemical environment during early stages of metamorphism of the red-bed sequence.

Keywords: tourmaline, epigenetic, red-bed, sandstone, hemimorphic, detrital, vacancy, hematite, berthierine, exchange vectors, Rose Hill Formation, Virginia.

SOMMAIRE

Un surcroissance hémimorphique de tourmaline aciculaire authigène s'est développée sur le pole *c* de grains détritiques de tourmaline dans une séquence de grès rouges de la Formation de Rose Hill, dans l'ouest de la Virginie. Des grains arrondis de quartz, avec une faible concentration de tourmaline détritique et de nodules de minéraux du groupe des argiles, ont été cimentés par un assemblage de berthierine et d'hématite, dont la formation épigénétique serait due à une incursion de fluide vers la fin du Paléozoïque, lors de l'orogenèse alléghenienne. La tourmaline détritique est très riche en Fe et Ti, et appauvrie en Al. Une telle composition indiquerait une provenance d'un socle granitique fortement oxydé ou bien d'une association hydrothermale de quartz + tourmaline en fissures. Par rapport au substrat, la tourmaline en surcroissance épigénétique est chimiquement distincte; elle est faite de schorl–dravite alumineuse ayant un rapport Fe/(Fe + Mg) de 0.66 et une proportion importante de lacunes dans le site *X*. L'enrichissement en Al et les lacunes résultent du vecteur d'échange $\square\mathrm{AlNa}_{-1}\mathrm{Mg}_{-1}$, conséquence d'une croissance dans un milieu riche en Al mais pauvre en Na et Ca. Une teneur élevée de lacunes dans le site *X* est courante dans la tourmaline épigénétique des grès; par contre, celle de cette séquence de grès rouges montre le plus fort enrichissement en fer qui soit. La tourmaline épigénétique s'avère être un indicateur sensible du milieu chimique au cours des stades précoces du métamorphisme des grès rouges.

(Traduit par la Rédaction)

Mots-clés: tourmaline, épigénétique, grès rouge, hémimorphique, détritique, lacune, hématite, berthierine, vecteurs d'échange, Formation de Rose Hill, Virginie.

INTRODUCTION

Tourmaline has long been known to be a diagenetic or epigenetic mineral in sedimentary rocks. For over 100 years, tourmaline has been reported as an overgrowth on cores of detrital tourmaline (Wichmann 1880, Van Hise 1885, Lory 1887). A diagenetic or epigenetic origin was inferred for these occurrences on the basis that tourmaline overgrowths typically develop as fragile, slender, syntactic needles, which could not have survived transport in a clastic sedimentary environment (Spencer 1925, Stow 1932, Alty 1933, Deverin 1934, Krynine 1946, Mader 1978, Ricketts 1978, Gautier 1979). An additional feature of diagenetic or epigenetic tourmaline is its tendency to nucleate hemimorphically on pre-existing detrital tourmaline *only* at the positive end of the *c* axis (antilogous pole) of the detrital grain (*e.g.*, Stow 1932, Alty 1933, Krynine 1946, Chatterjee *et al.* 1975, Dietrich 1985). Generally, overgrowths have been described as having pale colors and, on the basis of optical properties, have been postulated to be elbaite or intermediate schorl–dravite (*e.g.*, Alty 1933, Awasthi 1961, Govinda Rajulu & Nagaraja 1969, Mader 1978). However, owing to complex competing substitutions in tourmaline, an approach based on optical properties can lead to equivocal determinations of tourmaline composition (Henry & Dutrow 1992). Consequently, a microanalytical approach is warranted for these fine overgrowths.

The only microanalytical data available on epigenetic overgrowths on tourmaline were published by O'Connor (1990). He examined compositions of detrital cores and epigenetic rims of tourmaline from Ordovician arenites of the Tuscarora Formation, central Virginia. Dark green to opaque, rounded detrital cores of tourmaline feature overgrowths of clear, cockscomb-like epigenetic tourmaline. The analytical data of O'Connor (1990) revealed generally Fe- and F-rich detrital cores, with a relatively wide compositional variation (14–20% FeO, 0.2–6.2% MgO and 0.2–1.25% F). Epigenetic overgrowths are generally richer in Mg and contain more X-site vacancies (${}^{X}\square$), and are distinctly poorer in Fe, F, Na, Ca and Ti (<9–10.5% FeO, 3.5–4.5% MgO, 0–0.1% F, 0.8% Na_2O, <0.3% CaO and TiO_2). These overgrowths can be characterized as ${}^{X}\square$-rich, aluminous intermediate schorl–dravite. The core and rim compositions are believed to reflect growth in different geochemical environments (O'Connor 1990).

In this paper, we examine and report analytical data relevant to the development of epigenetic tourmaline in a red-bed sandstone from the Silurian Rose Hill Formation, western Virginia. Tourmaline in this geochemical setting has not been previously investigated. This paper provides insights into the development of epigenetic tourmaline in an Fe^{3+}-rich geological environment, the influence of local reactions on the chemistry of newly developed tourmaline, and the relative partitioning of elements among tourmaline and other epigenetic minerals.

GEOLOGICAL SETTING AND PETROGRAPHY

The sample of red-bed sandstone was drilled from the Rose Hill Formation of the Middle Silurian Clinton Group, Appalachian Valley and Ridge Province, western Virginia (Lu 1994). This sandstone was deposited about 420 Ma ago and subsequently deformed in late Carboniferous to early Permian time, *i.e.*, 300–270 Ma. Remagnetization by epigenetic chemical processes occurred during or after deformation, in the late Paleozoic (French & Van der Voo 1979). Tectonically driven fluid-flow associated with the Alleghenian orogeny probably gave rise to epigenetic reactions that resulted in hematite formation and attendant late Paleozoic chemical remanent magnetism (Hearn *et al.* 1987, Lu *et al.* 1991, Lu 1994). Based on studies of fluid inclusions, conodont color indices and data from vitrinite reflectance on proximal stratigraphic units, the maximum temperatures estimated for this red-bed unit are 200–250°C (Epstein *et al.* 1977, Harris 1979, Hearn *et al.* 1987, Dorobek 1989, Lewis & Hower 1990, Thorne 1992).

The sandstone is dominated by rounded to subrounded detrital quartz grains (Fig. 1) that exhibit minor pressure-solution, microfractures and features

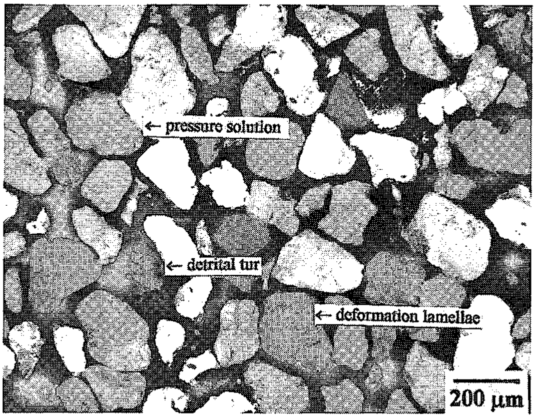

FIG. 1. Red-bed sandstone with a framework of detrital quartz and tourmaline (tur) and containing a cement of berthierine, hematite and epigenetic quartz. Note the development of pressure solution between some adjacent detrital grains of quartz and the occurrence of deformation lamellae within individual grains of detrital quartz. Transmitted-light photomicrograph, with partially crossed polars.

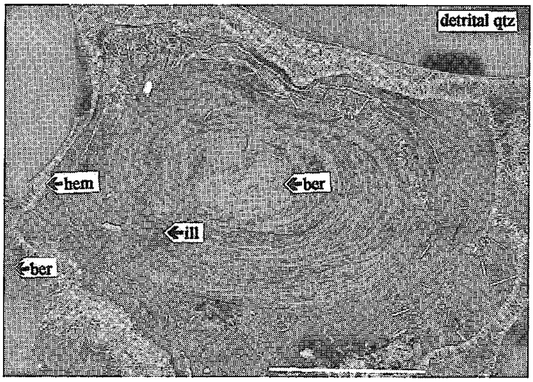

FIG. 2. Spheroidal ooid with mixtures of berthierine (ber) and illite (ill). Note the multiple generations of berthierine and hematite (hem) in the matrix between the detrital quartz (qtz) and ooid. Back-scattered electron image; scale bar 100 µm.

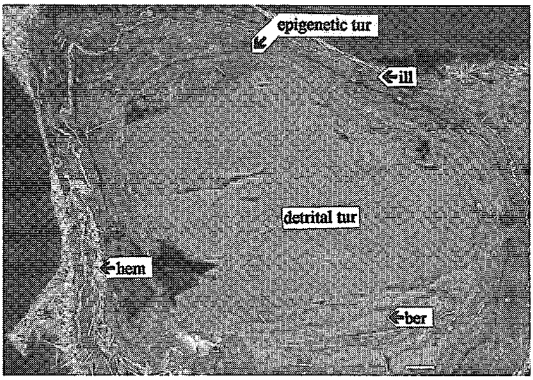

FIG. 3. Detrital tourmaline with epigenetic overgrowths of blue acicular tourmaline in a berthierine–illite ooid. Back-scattered electron image; scale bar 10 μm.

attributed to dislocation flow, such as undulatory extinction and deformation lamellae (*cf.* Onasch & Dunne 1993). Detrital grains of quartz contain rare tourmaline, ilmenite, pyrrhotite, and chalcopyrite inclusions. There are minor amounts of elongate subrounded detrital chert fragments. The balance of the framework grains is made up of small amounts of clay mineral ooids (Fig. 2), as well as trace amounts of rounded to subangular detrital grains of tourmaline and berthierine pseudomorphs after angular, detrital Fe–Mg silicate minerals. Some oolitic spheres are cored by detrital tourmaline (Fig. 3). The ooids are primarily composed of concentrically oriented fine plates of berthierine that apparently replace mixtures of illite and chlorite. Small amounts of hematite are found in the ooids (Fig. 2), but there is no evidence for massive alteration of the ooids to hematite (*cf.* Cotter 1992). Detrital framework grains are cemented (Fig. 4) by undeformed, randomly oriented laths of berthierine (20–40 μm), blades of hematite (5–10 μm), and euhedral epigenetic quartz (20–70 μm). The berthierine is pleochroic from pale brown to brown, with first-order green or red interference colors. Matrix minerals crystallized after the pressure solution; the most intense deformation is exhibited in the framework grains of quartz. Deformation is lacking in the berthierine and hematite, and only minor undulatory extinction and kinking are noted in the epigenetic quartz (Figs. 1, 2, 4). Multiple generations of hematite and berthierine are developed in the cement, and epigenetic quartz postdates hematite formation (Fig. 2). X-ray diffractometry of the <2 μm clay fraction confirms that the dominant layer silicate is berthierine, but the presence of a very small 14 Å peak relative to the 7 Å peak suggests the occurrence of minor amounts of admixed chlorite. A comparison of X-ray diffractograms of air-dried and ethylene-glycol-treated samples indicates that the minor amounts of illite are relatively pure, without a significant interlayered smectite-group mineral.

Tourmaline is present in the red-bed unit as detrital grains and very small overgrowths that nucleate on the detrital grains. Subrounded to subangular detrital grains of tourmaline are strongly pleochroic from light brown to very dark brown. Similar types of tourmaline are also found as euhedral inclusions in grains of detrital quartz. In contrast, the epigenetic tourmaline consists of fine, acicular light blue crystals (5–15 μm) that hemimorphically nucleated at the antilogous pole of the detrital grains and interfinger into the spheroidal texture in the berthierine–illite ooids (Fig. 3). There is a sharp textural and optical break at the interface of these two domains. Texturally, only a single stage of overgrowth development can be discerned.

MINERAL CHEMISTRY

Compositions of minerals associated with the tourmaline overgrowths reflect the Fe- and Al-rich nature of the diagenetic and epigenetic environments in the sandstone (Table 1). Analytical techniques and assumptions for calculation of Fe^{3+} in tourmaline are presented in the Appendix. The berthierine is Fe-rich, with $0.84 < Fe/(Fe+Mg) < 0.88$. The proportion of ^{VI}Al exceeds ^{IV}Al in the berthierine and is offset by a significant proportion of vacancies in the octahedrally coordinated sites, in accordance with the suggestion of Brindley (1982). Minor variations in chemistry exist, depending on where the berthierine nucleated (Table 1). However, the consistency of berthierine compositions in different modes of occurrence suggests that chemical equilibrium was approached locally during the last stages of epigenesis. The finer-grained berthierine in the ooids is poorer in Si and

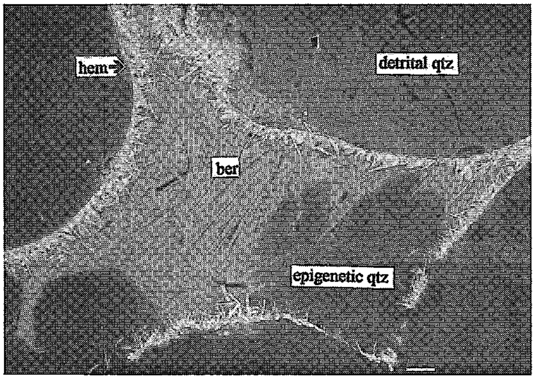

FIG. 4. Epigenetic berthierine, hematite, and quartz in the matrix of detrital quartz. Back-scattered electron image; scale bar 10 μm.

TABLE 1. REPRESENTATIVE COMPOSITIONS OF BERTHIERINE AND ILLITE

	Berthierine			Illite
Analysis no.	Ber-1	Ber-2	Ber-3	Ill-1
SiO_2 (wt%)	24.22	24.75	26.73	43.42
Al_2O_3	23.28	23.29	23.30	29.49
TiO_2	0.02	0.02	0.02	0.05
Cr_2O_3	0.01	0.01	0.01	0.01
*FeO	35.61	37.76	35.92	8.90
MnO	0.04	0.08	0.05	0.01
MgO	3.68	3.39	2.82	1.04
CaO	0.15	0.06	0.15	0.25
Na_2O	0.05	0.09	0.23	0.15
K_2O	0.25	0.38	0.18	7.96
TOTAL	87.31	89.83	89.41	91.28
Si	2.706	2.711	2.890	6.221
^{IV}Al	1.294	1.289	1.110	1.779
^{VI}Al	1.771	1.718	1.859	3.200
Ti	0.002	0.002	0.002	0.005
Cr	0.001	0.001	0.001	0.001
Fe^{2+}	3.327	3.459	3.248	1.066
Mn	0.004	0.007	0.005	0.001
Mg	0.613	0.554	0.455	0.222
^{VI}Total	5.718	5.740	5.569	4.497
Ca	0.018	0.007	0.017	0.038
Na	0.011	0.019	0.048	0.042
K	0.036	0.053	0.025	1.455
^{XII} Total				1.535
Oxygens	14	14	14	22
Fe/(Fe+Mg)	0.844	0.862	0.877	0.828
Mg/Fe	0.184	0.160	0.140	0.208

*All Fe is calculated as FeO. Ber-1: Berthierine in ooid proximal to detrital tourmaline; Ber-2: berthierine in core of an ooid; Ber-3: late-stage berthierine in matrix; Ill-1: illite in ooid.

richer in Mg relative to the coarser-grained berthierine in the matrix. The small amounts of Ca, Na, and K are interpreted as being due to a finely interlayered smectite-group phase or a mica (*cf.* Slack *et al.* 1992). A minor amount of illite is interlayered with berthierine in the ooids. On the basis of locations established by back-scattered electron imagery, an electron-microprobe analysis of the most homogeneous material indicates that it generally is an Fe-rich illite, probably mixed with minor amounts of other layer silicates on a very fine scale.

The dark brown grains of detrital tourmaline are very rich in Fe^{2+}, Fe^{3+} (inferred) and Ti, but poor in Al, Ca and $^{X}\square$ (Tur 1 and 2 in Table 2). Individual detrital grains exhibit considerable compositional heterogeneity. These unusual compositions, with elevated levels of Fe^{3+} and some of the lowest levels of Al recorded (Al = 3.71 atoms per formula unit, apfu), imply that the tourmaline has a substantial povondraite component $[NaFe^{3+}_3Fe^{3+}_6(BO_3)_3(Si_6O_{18})(O_3OH)]$. The significant amount of K in this tourmaline (>0.16 wt% K_2O) is consistent with this interpretation (see Grice *et al.* 1993). In accordance with the preferred site assignments in Fe-rich tourmalines (Grice *et al.* 1993), a large proportion of the Mg should be assigned to the distorted octahedrally coordinated *Z* site, such that some of the apparent deficit in the *Z* site is probably due to occupancy by Mg. However, the *Z* site may also contain an appreciable amount of Fe^{2+} (Foit *et al.* 1989). The unusual chemistry of the detrital grains is consistent with derivation of the tourmaline from highly oxidized, Al-poor environments such as hydrothermally altered granitic rocks or quartz–tourmaline veins (Henry & Guidotti 1985, Henry & Dutrow 1992, Grice *et al.* 1993).

TABLE 2. REPRESENTATIVE COMPOSITIONS OF DETRITAL CORE AND EPIGENETIC OVERGROWTH IN TOURMALINE

	Detrital core		Epigenetic overgrowth
Analysis no.	Tur-1[a]	Tur-2	Tur-3
B_2O_3[b] (wt%)	9.70	9.56	10.35
SiO_2	33.33	32.99	35.56
Al_2O_3	20.20	17.34	31.88
TiO_2	1.54	2.44	0.10
Cr_2O_3	0.03	0.01	0.01
Fe_2O_3 (min)[c]	10.26	11.72	1.27
FeO	16.50	17.88	11.59
MnO	0.08	0.08	0.00
MgO	2.56	2.27	3.65
CaO	0.02	0.01	0.01
Na_2O	2.72	2.73	1.67
K_2O	0.16	0.21	0.04
F	0.19	0.21	0.02
Cl	0.01	0.15	0.02
TOTAL	97.22	97.33	96.15
Atomic proportions on the basis of 15 cations (except Na+Ca+K)			
B	3.000	3.000	3.000
Si	5.972	5.998	5.973
^{IV}Al	0.028	0.002	0.027
^{Z}Al	4.237	3.714	6.000
$^{Z}Fe^{3+}$	1.383	1.604	
^{Y}Al	0.000	0.000	0.284
Ti	0.207	0.334	0.013
Cr	0.004	0.001	0.001
Fe^{3+}	0.000	0.000	0.161
Fe^{2+}	2.472	2.719	1.628
Mn	0.012	0.012	0.000
Mg	0.684	0.616	0.914
^{Y}Total	3.379	3.682	3.000
Ca	0.004	0.002	0.002
Na	0.945	0.962	0.544
K	0.037	0.049	0.009
$^{X}\square$	0.015	0.000	0.446
F	0.108	0.086	0.011
Cl	0.003	0.000	0.006
$Fe_T/(Fe_T + Mg)$	0.849	0.875	0.662
Mg/Fe_T	0.177	0.142	0.511

[a] Each composition represents the average result of 3 analyses taken in close proximity.

[b] B_2O_3 calculated assuming 3 B atoms per formula unit.

[c] Minimum Fe_2O_3 calculated assuming no vacancies in the octahedrally coordinated site (cf. Hawthorne et al. 1993) and charge balance. Additional Fe_2O_3 is possible if Fe-oxidation involves H desorption.

The overgrowths of epigenetic tourmaline in one sample have a relatively uniform composition, strikingly different from the cores of Al-poor detrital tourmaline. The overgrowth is substantially richer in Al (Al = 6.31 apfu) and ${}^{X}\Box$ (45% alkali-deficient), but poorer in Ti (Tur 3 in Table 2). It is also relatively Fe-rich [$\mathrm{Fe_T/(Fe_T+Mg)} = 0.66$], with a minimum of 9% of the Fe as $\mathrm{Fe^{3+}}$, consistent with growth in a hematite-bearing assemblage. This epigenetic tourmaline composition is significantly richer in Fe than the epigenetic overgrowths reported by O'Connor (1990), owing to the Fe-rich bulk composition of the sample. However, both sets of data indicate that epigenetic tourmaline in each of the investigated sandstones is rich in Al and ${}^{X}\Box$, primarily reflecting the exchange vector: $\Box\mathrm{AlNa_{-1}Mg_{-1}}$. This exchange vector will be most strongly favored in those rocks that are both peraluminous and Na- and Ca-deficient, such as the aluminous berthierine-rich matrix of this red-bed sequence (*cf.* Werding & Schreyer 1984, Foit *et al.* 1989).

DISCUSSION AND CONCLUSIONS

Epigenetic tourmaline is responsive to reactions in the local chemical environments and can be an effective chemical monitor even at relatively low-temperature conditions. The composition of the epigenetic tourmaline in the Rose Hill Formation generally mirrors the Fe- and Al-rich, and Na- and Ca-poor nature of the red-bed matrix. Furthermore, Mg–Fe partitioning between tourmaline and associated proximal berthierine [$K_D^{\mathrm{Tur-Ber}} = \mathrm{(Mg/Fe)_{Tur}/(Mg/Fe)_{Ber}}$] is 2.77, which is similar to Mg–Fe partitioning between tourmaline and berthierine in hydrothermal massive sulfide deposits equilibrated at 350–400°C (Slack & Coad 1989, Slack *et al.* 1992). The compositions of layer silicates such as berthierine tend to adjust readily to the epigenetic conditions associated with tourmaline development (*cf.* Guidotti 1984). The systematic chemical characteristics suggest that chemical equilibrium was approached, at least locally, in the epigenetic setting of the Rose Hill Formation.

Monopolar growth of epigenetic tourmaline at the *c* pole proceeds with little or no chemical interaction with the substrate of detrital tourmaline. This hemimorphic growth contrasts with overgrowths that form under higher-temperature metamorphic conditions of the chlorite zone, in which tourmaline develops asymmetrically at both poles of a detrital grain of tourmaline, resulting in striking compositional differences between the poles (Henry & Dutrow 1992). With an increase in metamorphic grade, textural asymmetry and compositional polarity disappear roughly at staurolite-zone conditions (Henry 1992). The monopolar growth of tourmaline in the red-bed sample from the Rose Hill Formation reaffirms the low-temperature character of the reaction inferred for this sequence.

The origin of the boron necessary to form the epigenetic tourmaline is uncertain; it could have been derived from four possible sources: (a) dissolution of detrital tourmaline, (b) dissolution of detrital K-feldspar with minor contents of B, (c) release of adsorbed boron from clay minerals undergoing the smectite-to-illite transformation or the $1M$ to $2M_1$ polytypic transition in illite (Reynolds 1965), or (d) introduction of boron from an external source, such as the probable late Paleozoic brines that affected these rocks (Hearn *et al.* 1987). Because of the refractory nature of tourmaline, the latter three possibilities are considered the most likely (*cf.* Henry & Dutrow 1992).

The source of the Fe and Al necessary for the formation of the diagenetic minerals is still enigmatic. The aluminum could have been derived locally through the breakdown of detrital K-feldspar or aluminous mafic silicates or from clays. However, Fe is more problematic in that the amount of Fe necessary to form the Fe-rich oxides and silicates of the matrix is greater than that which can be derived from local detrital grains and must have, in part, been derived externally (Lu 1994). The occurrence of berthierine as an apparently epigenetic mineral in the red-bed is relatively unusual in that berthierine commonly disappears during burial metamorphism at temperatures of <100°C (see discussions of Slack *et al.* 1992). However, berthierine has been identified as a stable phase in other, higher-temperature settings comparable to that of the red-bed (*e.g.*, Slack *et al.* 1992, Xu & Veblen 1993).

Epigenetic tourmaline is an ideal mineral to provide information on the diagenetic and very low grade metamorphic history of a sedimentary rock. Tourmaline has a wide range of possible chemical compositions that vary dramatically in response to local chemical reactions and, once formed, tends to retain that chemical imprint. However, there are few microanalytical data available on epigenetic tourmaline. Future studies of the diagenesis and epigenesis of sedimentary rocks should include systematic investigations of the compositions of any epigenetic tourmaline, as this mineral can aid in the evaluation of the geochemical evolution of the sedimentary rocks.

ACKNOWLEDGEMENTS

This work was supported by National Science Foundation Grants EAR 8805220 to Henry and Dutrow and EAR 900534 to McCabe. We thank Wanda LeBlanc for the X-ray-diffraction analysis. The manuscript benefitted greatly from insightful and rapid reviews by J.T. O'Connor, J.F. Slack and B.L. Dutrow. We are grateful to J.T. O'Connor for providing a preliminary version of his manuscript on epigenetic tourmaline.

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Received August 18, 1993, revised manuscript accepted November 17, 1993.

APPENDIX:
ELECTRON-MICROPROBE PROCEDURES

Minerals were quantitatively analyzed by wavelength-dispersion spectrometry (WDS) using the automated JEOL 733 electron microprobe at Louisiana State University. WDS analyses were done at an accelerating potential of 15 kV and a sample current of 10–15 nA. The electron beam was focused to a 1-μm spot for the microprobe traverse of the tourmaline, and was defocused to a 5-μm spot for the analyses of associated minerals. Well-characterized synthetic and natural silicates and oxides were used as standards, and the data were corrected on-line with the procedures of Bence & Albee (1968) and with the improved α-factors of Armstrong (1988). On the basis of replicate analyses of several secondary standards, analytical precision for selected oxides is estimated to be $\pm$ 0.17% SiO_2, $\pm$0.12% Al_2O_3, $\pm$0.04% FeO, $\pm$0.09% MgO, $\pm$0.02% CaO and $\pm$0.03% Na_2O. Tourmaline formulae were normalized on the basis of 15 cations excluding Na, Ca, and K, *i.e.*, assuming no vacancies in the tetrahedral or octahedral sites (*cf.* Hawthorne *et al.* 1993). A minimum value of Fe^{3+} was estimated assuming charge-balance constraints and maximal H in the OH site. Any dehydroxylation reactions involving Fe would produce additional Fe^{3+}. The amount of B_2O_3 necessary to produce three B cations in the structural formula was calculated from stoichiometric constraints.