Chemical variation in tourmalines from south-west England

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It has long been recognised that tourmaline from south-west England shows complex compositional variation on all scales. Individual crystals often show spectacular colour zoning which is related to compositional changes, and compositions vary for samples taken from different geological environments. In this study, tourmaline has been sampled from magmatic, pegmatitic, contact metamorphic and hydrothermal environments throughout the province, and has been subjected to electron microprobe analysis. Essentially three suites of samples can be distinguished. First, tourmaline from granitic rocks and pegmatites (khaki green-brown in thin section) shows limited chemical variation about a schorl-dravite composition which is alkali or proton deficient; these are regarded as magmatic compositions. Hydrothermal tourmaline (typically blue needles) associated with granitic rocks is similar, but forms a trend which extends from magmatic tourmaline towards stoichiometric schorl. Finally tourmaline from the breccia pipes and from within contact metamorphic aureoles (very deep blue, strongly zoned grains) continues the hydrothermal trend away from magmatic compositions beyond schorl towards a Ca-rich end member, uvite, and contains high inferred Fe" contents. This variation reflects the increasing degree to which the magmatic-hydrothermal system becomes open to the influence of comparatively oxidising fluids derived from or hosted by the granite's country rock, emphasising both the potential value of tourmaline as a petrogenetic indicator and the need for caution in its use.

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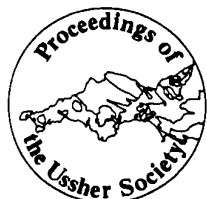
Introduction

The Hercynian granite province of south-west England is famous for its long history of mineral extraction and for the range and intensity of hydrothermal phenonema associated with the mineral deposits (for recent reviews see Willis-Richards and Jackson 1989; Jackson *et al.* 1989). Of particular interest is the association between hydrothermal tourmalinisation and the occurrence of economic deposits of tin, which has led to postulated genetic models which involve the transport of tin in fluids responsible for tourmalinisation. The five major granite outcrops all show the presence of tourmaline, but the mineral is particularly common in the St Austell granite and in its satellite minor stocks (Manning 1985). The modes of occurrence of tourmaline are as widespread as those of quartz - it may be magmatic or hydrothermal, and it contributes to secondary sedimentary placer deposits. Numerous studies have already identified tourmaline as apotential petrogenetic indicator (eg. Henry and Guidotti 1985), and have addressed the occurrence of the mineral in south-west England (Power 1968; Lister 1979). The purpose of this paper is to report the preliminary results of an investigation of the chemical variability of tourmaline and to assess its potential as a petrogenetic indicator in south-west England, using electron microprobe data for samples from throughout the peninsula.

The crystal chemistry of tourmaline

Tourmaline is a chemically complex borosilicate mineral, with the following simplified formula:

$$R^+R^{2+}_3R^{3+}_6(BO_3)_3Si_6O_{18}(OH)_4$$
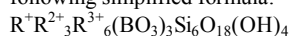
where:

$R^+ = Na, \frac{1}{2} Ca$ in the X site,

$R^{2+} = Fe^{2+}, Mg, Mn$ in the Y site,

$R^{3+} = Al, Fe^{3+}, \frac{4}{3} Ti$ in the Z site.

This gives the common end-members:

schorl	$NaFe_3Al_6(BO_3) Si_6O_{18}(OH)_4$
dravite	$NaMg_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$

the less common:

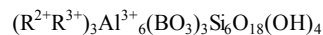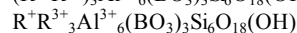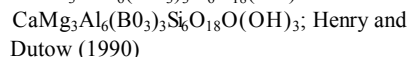|	
uvite	$CaMg_3MgAl_5(BO_3)_3Si_6O_{18}(OH)_4$
feruvite	$CaFe_3MgAl_5(BO_3)_3Si_6O_{18}(OH)_4$
ferridravite	$NaMg_3Fe^{3+}_6(BO_3)_3Si_6O_{18}(OH)_4$
elbaite	$Na(Li,Al)_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$
liddicoatite	$Ca(Li,Al)_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$

and the hypothetical:

alkali-free	$(R^{2+}R^{3+})_3Al^{3+}_6(BO_3)_3Si_6O_{18}(OH)_4$
proton deficient	$R^+R^{3+}_3Al^{3+}_6(BO_3)_3Si_6O_{18}(OH)$
unnamed	$CaMg_3Al_6(B0_3)_3Si_6O_{18}O(OH)_3$; Henry and Dutow (1990)

These substitutions appear to be complex, but can be simplified on the assumption that substitution predominantly only takes place in the X, Y and Z sites. They are described in detail by Foit and Rosenberg (1977), Rosenberg and Foit (1979), Grice and Robinson (1989) and Henry and Guidotti (1985). There are no commonly known substitutions for B or Si. The extent of chemical variation within tourmaline can be determined only partially by electron microprobe, because H, Li and B cannot be detected. However, this analytical technique is essential in view of the complex zoning that is characteristic of tourmaline. The interpretation of electron microprobe data for tourmaline can therefore only be carried out according to the rules of substitution within the X, Y and Z sites, and may involve indirect evidence for the presence of Li or site vacancies.

Tourmalines from south-west England

There are many descriptions of tourmaline from south-west England, but in view of its abundance there are very few chemical data to illustrate the extent of compositional variation, and those which are available concentrate on granite-associated tourmalinisation (eg. Power 1968; Lister 1979; Charoy 1979). In addition, most attention has been oriented towards the major components, schorl and dravite, and the possible role played by minor components, such as Ti, in influencing the colour of the mineral.

In this study, a suite of samples has been collected from localities representative of main stage and minor, late-stage granitic rocks, pegmatites, quartz-tourmaline rocks, greisens, hydrothermal breccias and contact metamorphic rocks throughout the peninsula. The locations used in this study are summarised in Table 1.

The petrographic characteristics of tourmaline from these samples vary considerably. Compositional variation within grains is best shown using back-scattered electron images obtained using a scanning electron microscope (Jeol JSM-35), in which the grey level relates to the mean atomic number of the material at the
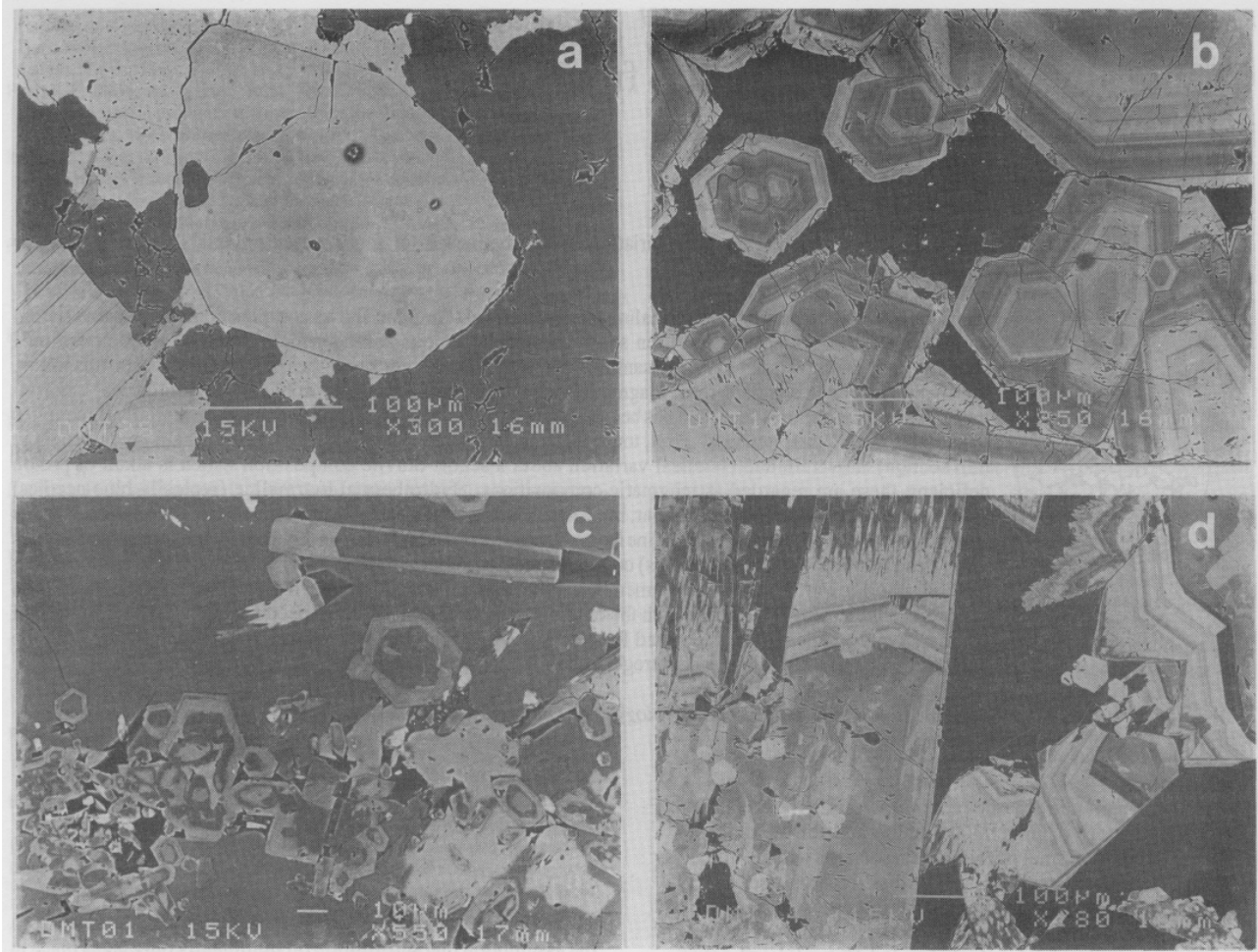
Figure 1. Back-scattered electron micrographs of tourmaline from selected geological environments in south-west England. (a) Weakly zoned magmatic tourmaline, aplite, De Lank quarries, Bodmin Moor; (b) strongly zoned hydrothermal vein tourmaline, Old Beam mine, Goonbarrow china clay pit; (c) Mg-rich cores with Fe-rich rims, set in quartz, Wheal Remfry tourmaline breccia (note that the BSE intensities of quartz and Mg-rich tourmaline are very similar); (d) contact aureole tourmaline, Grylls Bunny; Fe-rich rims and overgrowths on Ca-Mg - rich cores.

surface of a polished section. Thus the problem commonly encountered in optical petrographic studies of interference between overlapping acicular grains or zones within a thin section is avoided. In BSE images bright areas are richer in higher atomic number elements than dull areas, so that, for example Fe-rich areas (Fe = 26) appear brighter than Mg-rich areas (Mg = 12).

Within the granitic rocks and pegmatites, primary tourmaline is predominantly present as pleochroic khaki green-brown euhedral-subhedral grains, varying in size from 0.1mm upwards. Secondary tourmaline occurs as overgrowths and acicular fracture fills (with quartz), and shows blue-colourless pleochroism. Opaque inclusions within primary tourmaline are often surrounded by a halo of radiation damage, giving a blue colour. Both optical and BSE petrography show that primary tourmaline from these samples is relatively weakly and subtly zoned, with minor variation in the shade of khaki (plane-polarised light) or grey level (BSE image; Fig. 1a).

The quartz tourmaline rocks again contain a coarse generation of tourmaline, > 0.1mm. The mineral also shows a khaki coloration, but pleochroism often involves shades of blue. The degree of zoning is variable, often showing patchy cores with strong zoning predominantly developed in overgrowths on these. Acicular tourmaline is characteristic of fracture fill and overgrowths, and BSE images confirm the overall simplicity of the zonation, which resembles that shown in Fig. 1a.

Greisen-associated tourmalines occur in two forms. First, both within the greisen selvages of hydrothermal quartz-tourmaline veins and within pervasive greisens, relics of pre-existing granitic tourmaline occur which are petrographically similar to tourmaline from ungreisened parts of the same granite. Secondly, within the vein, tourmaline is characteristically strongly zoned with bluecolourless pleochroism, as coarse and fine acicular needles. This hydrothermal tourmaline also occurs within the greisened vein border, and illustrates complex zoning both optically and with BSE imaging (Fig. 1b).

The hydrothermal breccias are characterised by a matrix of fine-grained tourmaline and quartz, which cements fragments of granite and country rock, including isolated grains of individual minerals from such rocks. Tourmaline in the cement is typically fine-grained and acicular (needles of the order of a few tens of microns in length). Within vugs it becomes an order of magnitude coarser, and it is characteristically blue-colourless although the grain size is so small that individual needles are often superimposed in thin section obscuring colour variation. BSE imaging shows the presence of considerable compositional variation (Fig. 1c).

Tourmaline from the contact metamorphic samples forms essentially two parageneses. In the metamorphosed killas slates, tourmaline-rich "beds" alternate with quartz-rich units on a scale measured in millimetres, giving rise to characteristically zebra-

Table 1. Locations of samples used in this study.

1) Granitic rocks
Porphyritic biotite granite, Tregarden quarry, Luxulyan SX 053 590
Tourmaline aplite, De Lank quarry, Bodmin Moor SX 105 750
Tourmaline granite, Hensbarrow, St Austell SX 000 565
Topaz granite, Hensbarrow, St Austell SX 005 565
Topaz granite, Nanpean, St Austell SW 942 553
Elvan, West Tremore, Bodmin SX 010 649

2) Pegmatites
Goonbarrow, St Austell SX 008 583
Megiliggar Rocks, Porthleven SW 611 266

3) Quartz-tourmaline rocks
Porthledden Beach, Lands End SW 354 320
Roche Rock SW 991 597
St Mewan Beacon SW 985 535

4) Greisens
Old Beam Mine, Goonbarrow, St Austell SX 008 585
Great Wheal Prosper Pit, Roche SX 000 586

5) Hydrothermal breccias
Wheal Remfry, St Austell SW 924 576
Gaverigan, St Austell SW 935 587
Leigh Tor, Dartmoor SX 712 715

6) Contact metamorphic
Grylls Bunny, Botallack SW 364 335
Mine dumps, Botallack SW 364 335

striped hand specimens. In thin section this material is extremely fine grained (<10μm), but occasional coarser patches show the development of a deep blue colour. Blocks of tourmalinised killas of this type are common components of the breccias described above, which occur widely within the aureole of the St Austell granite in particular (Manning 1985), and at Leigh Tor. The second paragenesis is represented by much coarser tourmaline such as that present within samples from Botallack. The material from Grylls Bunny (Jackson 1974) is coarsely granular (<5mm) and shows pleochroism between an intense blue and a khaki brown, with abundant zoning (Fig. 1d). The other sample from Botallack was collected from mine dumps and not seen in situ; it is remarkable in that it is composed of a small number of spheroids, each up to 100mm in diameter. Within this sample tourmaline shows petrographic characteristics similar to those of material from Grylls Bunny.

In general there is an increase in the extent of compositional zoning and the abundance of optically deep blue tourmaline as this suite of samples varies from non-hydrothermally altered granitic to greisened granites to tourmalinised non-granitic, or killas, members. Chemical variation associated with this variation has been determined by electron microprobe analysis, using a Cameca Camebax/Link Systems energy dispersive (ED)/wavelength dispersive (WD) system. Mn, Ca, K and F were determined by WD analysis, with detection limits of approximately 0.02% oxide for Mn, Ca and K and 0.1% for F; other elements were determined by ED analysis, with detection limits of approximately 0.2% oxide for Ti, Mg and Fe and 0.25% oxide for Na. Li, of course, cannot be detected. Weight data have been recalculated to atomic proportions assuming the presence of 24.5 oxygen atoms, and these rather than the raw weight data have been used for interpretative purposes.

Chemical variation - general observations
Representative analyses of tourmalines from the samples considered here are given in Table 2. There is considerable variation within individual samples, and this is best expressed graphically. It should however be noted that the granitic and greisen tourmalines

are generally poorer in Ca than those derived from country rocks, even as components of breccias. The substitution of Ca within granitic and greisen tourmalines can in general be regarded as negligible, but must be considered as significant for the country rock tourmalines.

The initial approach taken here is to use the plot of $R^+ + R^{2+}$ v. R^{3+} to compare the data for this suite of samples. This plot allows the samples to be compared according to major substitutions other than Fe-Mg (schorl-dravite), which has already been shown to occur (Power 1968; Lister 1975). It has also been used for other granitic tourmalines (Manning 1982; Gallagher 1988) and has considerable potential for the interpretation of tourmaline compositions. Ideal compositions and compositional vectors for dominant substitutional trends are shown in Fig. 2, which provides a reference point for comparison of subsequent analytical data:

a) The granite tourmalines plot as a tight cluster of points (Fig. 3a), but lie close to trends extending towards the hypothetical alkalifree and proton deficient end-members - they have excess Al, between 6.6 and 7.2 (Ti is negligible in comparison). Within this plot the topaz granites are more extreme than the biotite and tourmaline granites. On closer inspection of the data, the biotite granite and tourmaline granite tourmalines clearly show a deficiency in the X site, with <1 atom of Na, whilst the X site for the topaz granites is fully occupied. This means that the deficiency in $R^+ + R^{2+}$ for the topaz granite tourmalines represents a deficiency in R^{2+} alone, ie. a deficiency in Fe+Mg. Taken together with an excess in Al^{3+} of up to one atom, these observations provide indirect evidence that the topaz granite tourmalines are Li-rich and contain up to approximately 30% of the elbaite end-member. In terms of schorl-dravite substitution, the granitic tourmalines overall show a range from 70-95% schorl.

b) The pegmatitic tourmalines overlap with the granitic tourmalines (Fig. 3b), and have low alkali site occupancy - there is no evidence for Li enrichment from these analyses. In terms of schorl-dravite they are also similar to the granitic samples, but are more schorl rich (80-100% schorl).

c) The tourmalines from quartz tourmaline rocks again overlap with those from the granites (Fig. 3c), but begin to extend towards the schorl-dravite end member composition. Again, there is no evidence of Li enrichment for these samples, and in terms of schorl-dravite they are consistently schorl rich.

d) Greisen tourmalines, and those from associated hydrothermal veins, show considerable variation in the $R^+ + R^{2+}$ v. R^{3+} plot, extending from the field occupied by the granites towards
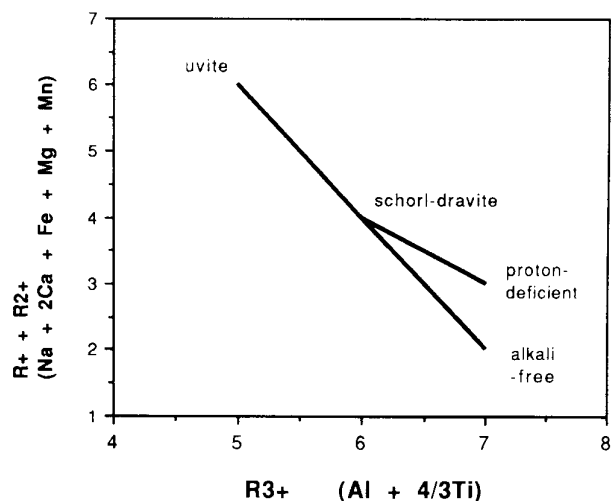

Figure 2. Tourmaline compositional end-members and variation trends within the $R^+ + R^{2+}$ v. R^{3+} plot.
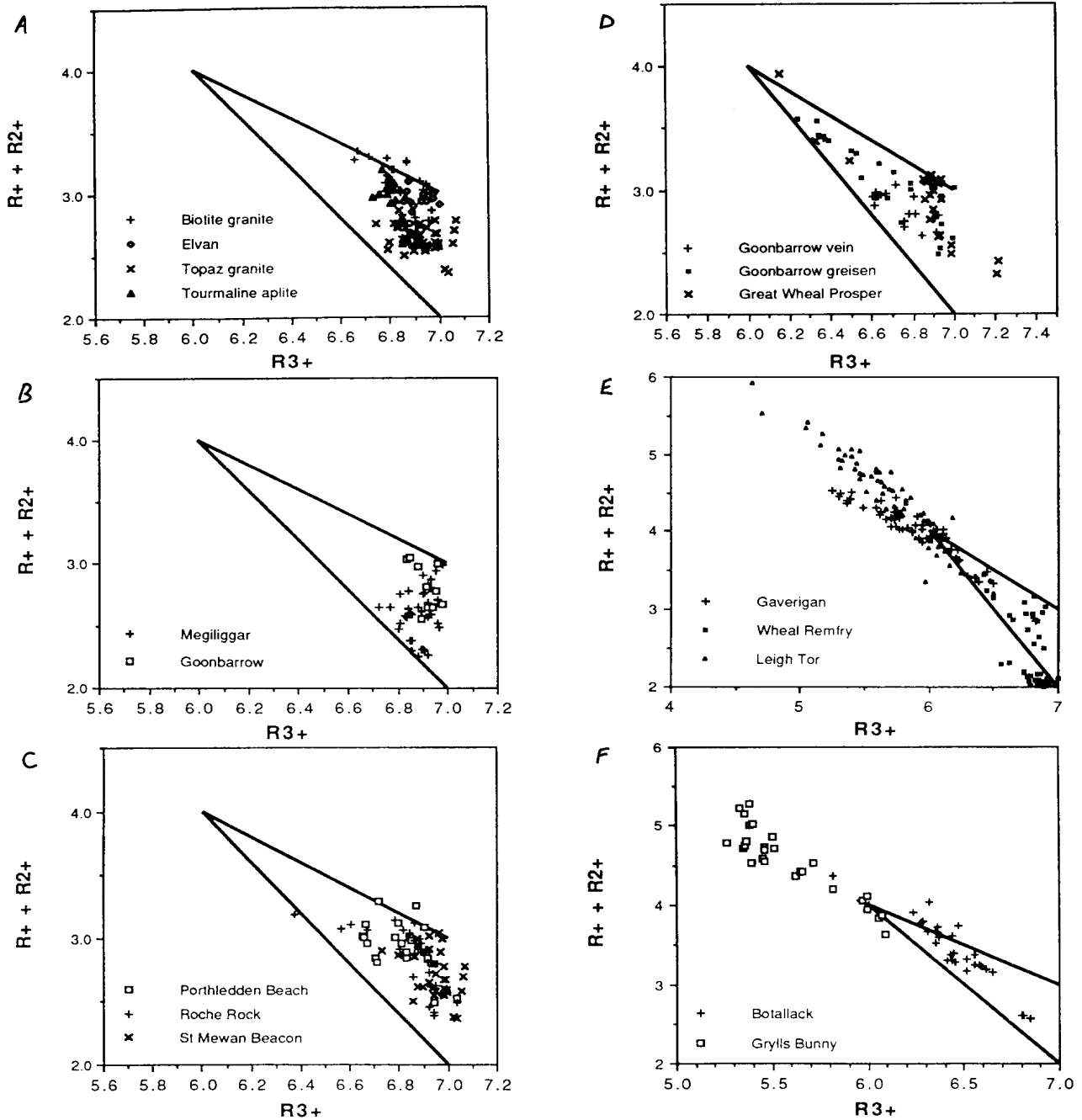
Figure 3. Compositional variation shown by tourmalines from contrasting geological environments in south-west England. (a) From granitic hosts, (b) from pegmatitic hosts, (c) from quartz-tourmaline rocks, (d) from greisens and quartz-tourmaline veins, (e) from hydrothermal breccias and (f) from metamorphic aureole rocks.

stoichiometric schorl-dravite (Fig. 3d). In terms of schorl-dravite substitution they overlap with the granites (65-95% schorl), possible reflecting an inherited component, and again there is no evidence of Li enrichment.

e) Tourmalines from hydrothermal breccias extend the trend away from granitic compositions shown by the greisen tourmalines, but overshoot the schorl-dravite composition (Fig. 3e). In detail, their compositions reflect the nature of their host rock. Those from the granite-hosted Wheal Remfry breccia coincide with granitic tourmalines. Amongst this group are encountered for the first time Carich tourmalines, with Ca extending up to 0.55 atoms (Gaverigan) and 0.44 (Leigh Tor), both from country-rock hosted occurrences. In terms of schorl-dravite substitution these range from 10-100% schorl.

f) Contact metamorphic tourmalines are perhaps the most complex chemically, as they show very considerable variation involving substitutions other than those already considered (schorl-dravitealkali free-proton deficient). Samples taken from Grylls Bunny extend away from the schorl-dravite composition, and coincide with compositional field already shown by the Gaverigan and Leigh Tor breccias, which are hosted by contact metamorphic rocks (Fig. 3f). They are again Ca-rich, with up to 0.46 Ca atoms. In contrast, samples of an exceptionally coarse aggregate of tourmaline suns each 100mm in diameter taken from dumps at Botallack coincide with the field defined by the greisen tourmalines from granitic areas, and may be of analogous hydrothermal origin. In terms of schorl-dravite substitution the Botallack and Grylls Bunny samples vary from 20-90% schorl.

Table 2. Selected examples of electron microprobe analyses of tourmalines from south-west England.

sample	1	2	3	4	S	6	7	8	9	10	11	12
SiO_2	34.94	35.20	37.19	34.64	34.53	36.69	36.37	34.21	35.78	36.41	34.93	35.06
Al_2O_3	35.77	34.66	36.02	35.00	34.95	35.82	33.98	34.09	27.15	29.11	25.95	32.14
TiO_2	0.36	0.48	0.51	0.87	0.00	0.09	0.17	0.51	0.11	0.69	0.49	0.00
FeO	11.51	13.66	10.18	13.22	14.94	10.98	15.92	13.38	12.76	4.95	13.21	8.87
MgO	2.62	1.49	0.48	1.59	0.68	0.52	0.55	1.66	7.01	9.33	6.92	5.62
Mno	0.077	0.310	0.260	0.025	0.055	0.050	0.060	0.014	0.010	0.040	0.038	0.000
Na_2O	2.49	2.34	3.37	2.30	2.24	2.70	1.68	1.96	1.48	1.54	1.62	2.21
CaO	0.211	0.100	0.009	0.138	0.058	0.100	0.010	0.055	3.030	2.454	2.499	0.980
K_2O	0.037	0.050	0.034	0.032	0.032	0.040	0.030	0.027	0.030	0.019	0.025	0.029
F	0.52	1.2	2.02	0.58	0.57	1.14	0.19	1.10	0.88	0.56	0.97	0.35
Total	88.54	89.48	90.08	88.39	88.09	88.12	88.95	87.00	88.23	85.10	86.66	85.25
Si	5.710	5.799	6.011	5.722	5.766	6.009	5.984	5.776	6.023	6.046	6.021	5.885
Al	6.890	6.731	6.863	6.815	6.880	6.915	6.589	6.784	5.386	5.698	5.273	6.359
Ti	0.044	0.060	0.062	0.108	0.000	0.011	0.021	0.064	0.014	0.086	0.063	0.000
Fe	1.572	1.882	1.376	1.826	2.087	1.504	2.191	1.890	1.796	0.687	1.904	1.945
Mg	0.639	0.365	0.115	0.392	0.169	0.127	0.135	0.418	1.758	2.310	1.778	1.407
Mn	0.011	0.043	0.036	0.004	0.008	0.007	0.008	0.002	0.001	0.006	0.006	0.000
Na	0.790	0.747	1.056	0.737	0.725	0.857	0.536	0.640	0.481	0.496	0.543	0.719
Ca	0.037	0.018	0.002	0.024	0.010	0.017	0.002	0.010	0.547	0.437	0.462	0.176
K	0.008	0.010	0.007	0.007	0.007	0.008	0.007	0.006	0.006	0.004	0.006	0.006
F	0.266	0.627	1.033	0.304	0.302	0.589	0.097	0.585	0.468	0.295	0.531	0.185
R^+	0.864	0.783	1.06	0.785	0.745	0.891	0.540	0.660	1.575	1.370	1.467	1.071
R^{2+}	2.222	2.290	1.527	2.222	2.264	1.638	2.334	2.310	3.555	3.003	3.688	2.652
R^{3+}	6.949	6.811	6.946	6.959	6.880	6.930	6.617	6.869	5.405	5.813	5.357	6.359
$R^+ + R^{2+}$	3.086	3.073	2.587	3.007	3.009	2.529	2.874	2.970	5.130	4.373	5.155	3.723
F/F+M+M	0.707	0.822	0.901	0.822	0.922	0.918	0.939	0.818	0.505	0.229	0.516	0.469

Samples:
1. Megacrystic biotite granite, Luxulyan quarry, St. Austell pluton.
2. Tourmaline aplite, Hantergantick quarry, Bodmin Moor pluton.
3. Topaz granite, Kernick quarry, Nanpean stock, St. Austell pluton.
4. Pegmatite, Goonbarrow china clay pit, St. Austell pluton.
5. Quartz-tourmaline rock, Roche Rock, St. Austell aureole.
6. Greisen, Old Beam Mine, Goonbarrow china clay pit, St. Austell pluton.
7. Vein, Old Beam Mine, Goonbarrow china clay pit, St. Austell pluton.
8. Tourmaline breccia, Wheal Remfry, St. Austell pluton.
9. Tourmaline breccia, Gaverigan, St. Austell aureole.
10. Tourmaline breccia, Leigh Tor, Dartmoor aureole.
11. Tourmaline hornfels, Grylls Bunny, Lands End aureole.
12. Tourmaline sun, Botallack mine dumps.

ED determinations of major elements and WD determinations of F given to 2 decimal places, WD determinations of Ca, Mn and K given to 3 decimal places. Atomic proportions calculated to 24.5 oxygen atoms.

Chemical variation within tourmaline from country rock hosts

Quite clearly, substitution towards uvite is a potentially important component of the compositional trends observed for tourmalines derived from the country rock and breccias within the country rock. In the $R+ + R2+$ v. $R3+$ plot as constructed here, uvite lies at $R+ + R2+ = 6$ ($2Ca + 4Mg$) and $R3+ = 5$ (Al; Fig. 2). This construction artificially emphasises the substitution of Ca, as R^* is calculated as $Na + 2Ca$. It is not necessarily appropriate for high Ca tourmalines, because on closer inspection of the data the X site occupancy appears never to be significantly greater than one, with up to 0.5 Ca atoms. The excess positive charge involved in increasing Ca is balanced by a reduction in the Z site occupancy.

In the country rock tourmalines, there is clearly a loss of Al in comparison with the granitic tourmalines, as R'' decreases from 6 or more to as little as 4.64 (Leigh Tor). In compensation there is an increase in the calculated $R2+$ parameter, to values in excess of 3. This implies that significant quantities of Fe'' may be present in addition to Fe^{2+}, which cannot be distinguished on the basis of electron microprobe analysis and so is expressed as Fe' (low totals for the weight percent oxides also suggest that a significant proportion of Fe'' is present). This phenomenon is illustrated in Fig. 4 which shows the excess occupancy in the Y site for samples from Leigh Tor and Grylls Bunny. Substitution towards uvite can account for a proportion of the displacement away from schorldravite, but the Ca contents of the X sites are only sufficient to demonstrate substitution of up to 50% of the uvite component. However, substitution towards ferridravite extends the trend shown by the data towards a ferridravite end-member which would plot at $R3+ = 0$, $R2+ - 3 = 6$, with a slope of -1. Clearly this substitution could account for some of the observed compositional variation,

but the fact that the samples from Leigh Tor and Grylls Bunny lie on trends with slopes of -0.75 suggests that either additional unrecognised substitutions may also occur or that there may be a systematic artificial error in this method of interpretation.

Independent evidence for the presence of a significant proportion of Fe^{3+} is provided by Mössbauer spectroscopic studies of bulk samples, allowing comparison of a sample from Grylls Bunny with a sample form a granitic pegmatite from the St Austell topaz granite (Hensbarrow stock). Preliminary results in a continuing study suggest that the $Fe^{3+}/Fe2+ + Fe3+$ ratio for the pegmatite is no more than 10% whereas the value for the Grylls Bunny sample is around 50%.

Discussion and conclusions

This exploratory study has clearly demonstrated that tourmaline from different environments within the south-west England granite province shows considerable compositional variation which appears to be controlled by the nature of its host. Thus granitic tourmalines, from magmatic and pegmatitic rocks, are compositionally simple and show limited variation. These can be regarded as primary igneous tourmalines, and are essentially schorl-dravite solid solutions with a significant component of alkali-free or proton-deficient end-members; they predominantly show khaki brown-green colours in thin section. The tourmalines from greisens and granite-hosted breccias show increased zoning and more extensive variation extending away from the primary granitic compositions towards pure schorl-dravite. Tourmalines from country rocks and breccias within the country rocks clearly show additional substitution towards Ca-rich end-members, and contain a significant proportion of Fe'^*; they are commonly intensely zoned, with deep blue colours in thin section.
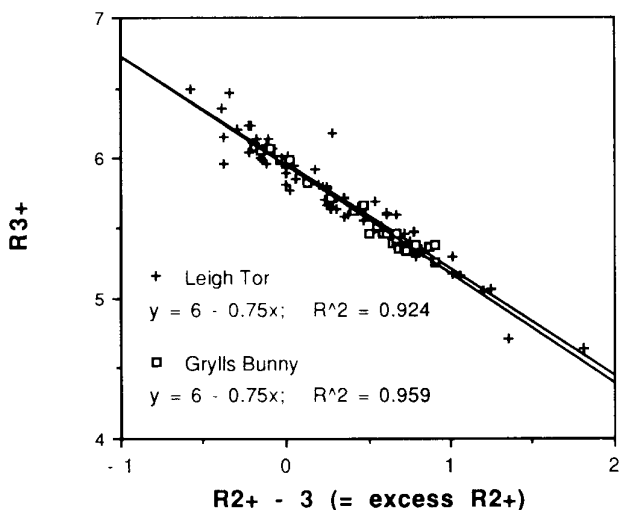
Figure 4. Excess R^{2+}, which indicates the presence of Fe^{3+}, within tourmaline from contact metamorphic hosts.

The conditions which dictate the stability and conditions of formation of the tourmaline group are not fully understood. It is known that tourmaline (schorl-dravite) can occur as liquidus phase within granitic systems (Benard *et al.* 1985) and it is reasonable to assume that magmatic tourmaline occurs within the granitic rocks. The composition of tourmaline crystallising from a magma is controlled by factors such as bulk composition as well as P and T; within a closed magmatic system these are relatively stable and result in simple compositional variation within the tourmaline. In contrast, conditions of tourmaline growth within hydrothermal systems are variable, involving fluctuations in fluid composition within dynamic systems of circulation, and relatively rapid growth can be invoked to account for the acicular nature of the grains. Hydrothermal systems derive components from a number of sources, and represent variable open systems allowing the growth of compositionally complex tourmaline.

Perhaps the most significant control of tourmaline composition overall is the bulk composition of the environment in which it grows. The granitic rocks of the south-west England peninsula are peraluminous, and this may account for the excess of Al within the tourmaline which is associated with the substitution towards alkali-free and proton-deficient end-members. Tourmaline from non-peraluminous granite provinces such as the Cheviot Hills (Northumberland) are less Al-rich than their equivalents from the south-west England granites, and share affinities with the southwest England Ca-rich tourmalines (Elyas 1988). The variable composition of tourmaline from the south-west England country rocks suggests that the growth of tourmaline involves relatively little transport of X, Y and Z site components (and Si) but is principally a consequence of the introduction of boron to an existing unstable mineral assemblage. If this is the case the observation that the country rock derived tourmalines are richer in FeII than those from granite-hosted greisens implies that they crystallised under relatively oxidising hydrothermal conditions. Thus within a static system the oxygen fugacity of a hydrothermal fluid within an aureole host may have exceeded that of a fluid within adjacent granite. In a dynamic system the oxygen fugacity of a fluid passing through a section from granite into country rock is controlled by the wallrock, and increases on entry into the country-rock hosted hydrodynamic system. This has implications for models for the transport and deposition of tin, which is believed to be transported in a reduced form as Sn^{2+} complexes, precipitating as cassiterite on oxidation (Wilson and Eugster 1990). It can be envisaged that the crystallisation of hydrothermal tourmaline within the south-west England granite

province provides a potential indicator of the oxidation state of potential ore forming fluids, although it remains to be calibrated. It is also apparent that the presence of Fe^{3+} - rich tourmaline within contact metamorphic rocks demonstrates their potential as an oxidising hydrothermal environment, which would favour the precipitation of cassiterite.

The use of tourmaline as an indicator of hydrothermal fluid (or to a lesser extent magmatic) oxygen fugacity depends on experimental calibration. The determination of the proportions of Fe^{2+} and Fe^{3+} within tourmaline can only be carried out using bulk methods at present, and this study has confirmed the long standing petrographic evidence that tourmaline shows considerable compositional variation within grains as well as between samples. Bulk analytical methods should only be undertaken with care. This applies equally to the use of bulk determinations of the isotopic composition of tourmaline, and variation in B, H and O isotopes should be expected to be as considerable as major element variation. Although this cautionary approach might restrict certain studies, it opens additional possibilities, perhaps extending the use of tourmaline in provenance studies within sedimentary rocks

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