Coupled substitutions in schorl–dravite tourmaline: new evidence from SE Ireland

V. GALLAGHER*

Geology Department, University College, Dublin, Ireland

Abstract

Analyses of tourmaline and coexisting muscovite in tourmaline-bearing rocks from SE Ireland indicate that the content of Si in tourmaline is not fixed but is dependent on bulk chemistry, varying inversely with Al. Zoning patterns within tourmaline reflect this and, despite theoretical objections, substitution of Si by Al in the tetrahedral site must occur in nature. Ti may also substitute for Si. Ca and Ti are generally involved in a coupled substitution. Estimates of the degree of alkali-defect and proton-loss substitution in SE Ireland tourmalines indicate that the former process is at least as important as the latter and that bulk chemistry is important in determining which substitution occurs. The general importance of alkali-defect substitution and $Al \rightleftharpoons Si$ suggests that the most useful way to treat microprobe data for schorl–dravite tourmalines is to assume the presence of 3B and 4(OH) and calculate on the basis of 24.5 oxygen atoms.

KEYWORDS: coupled substitutions, schorl–dravite, tourmaline, Ireland.

Introduction

RECENT studies of the chemistry of tourmaline from a variety of settings have established its value as a petrogenetic indicator (e.g. Shearer *et al.*, 1984; Henry and Guidotti, 1985; Jolliff *et al.*, 1986) while others have helped refine our knowledge of its crystallochemistry (Foit and Rosenberg, 1977; Fortier and Donnay, 1975; Nuber and Schmetzer, 1979). It is clear that the chemistry of tourmaline reflects the bulk chemistry of the system in which it forms (*cf.* Ayuso and Brown, 1984; Ethier and Campbell, 1977; Peltola *et al.*, 1968) but few studies of tourmaline, apart from those of pegmatitic tourmaline, have considered variations in the crystallochemistry of tourmaline in the light of changes in bulk chemistry of its host.

In this paper, analyses of tourmaline and associated muscovite from a variety of environments in SE Ireland are used to place further constraints on substitutions and substitutional mechanisms in tourmaline. The results have implications for the treatment of tourmaline microprobe data.

Crystallochemistry of tourmaline

The general formula of tourmaline is $XY_3Z_6Si_6B_3O_{27}(OH,O,F)_4$, where the polyhedral X site is generally regarded as being occupied by alkalis (Na, Ca, K) and the octahedral Y and Z sites by divalent and trivalent cations such as Fe^{2+}, Mg^{2+}, Fe^{3+} and Al^{3+}. Si is in fourfold co-ordination with oxygen, boron threefold. Tourmaline's chemical variability results from the ability of its structure to withstand extensive substitution, particularly in the Y and Z sites. Mutual substitution in the Y site of Fe and Mg gives rise to the schorl–dravite series with end members

$$NaFe_3^{2+}Al_6Si_6B_3O_{27}(OH,F)_4 \text{ (schorl)}$$

and

$$NaMg_3Al_6Si_6B_3O_{27}(OH,F)_4 \text{ (dravite)}.$$

Other end members include

elbaite, $Na(Li,Al)_3Al_6Si_6B_3O_{27}(OH,F)_4$,

liddicoatite, $Ca\,(Li_2,Al)\,Al_6Si_6B_3O_{27}(OH,F)_4$,

uvite, $CaMg_3MgAl_5Si_6B_3O_{27}(OH,F)_4$,

ferridravite, $NaMg_3Fe_6^{3+}Si_6B_3O_{27}(OH,F)_4$

and

buergerite, $NaFe_3^{3+}Al_6Si_6B_3O_{30}(OH,F)$.

None of the pure end members are known in nature and they may be less stable configurations than their solid solutions (Foit and Rosenberg, 1977). Substitution of a cation by one of higher

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* Present address: Department of Geology, University College, Cork, Ireland.

charge (e.g. $Al^{3+} \rightleftharpoons (Fe^{2+}, Mg^{2+})$) requires charge balancing. This may occur by a compensating cation exchange but also by loss of a proton from the $(OH)^-$ anion (proton-loss substitution) or creation of a vacancy in the *X* site (alkali-defect substitution); where a cation is substituted by one of lower charge, the reverse applies. Alkali-defect substitution and proton-loss substitution are prevalent in natural tourmalines of the schorl–dravite series and previous studies (Foit and Rosenberg, 1977) have suggested that proton loss is more common than alkali deficiency. Buergerite, which may be regarded as a schorl–dravite tourmaline in which the loss of three protons balances the substitution of divalent cations by Fe^{3+}, is an extreme example of proton-loss substitution.

Because of its small size B is unlikely to be substituted by other cations to any significant degree although some chemical analyses reveal deficiencies in the calculated contents of B (e.g. Deer *et al.*, 1962). Whether these reflect defects in the trigonal site, substitution by other cations (including unanalysed elements such as Be; *cf.* Harder, 1959), or analytical error, is unclear. Loewenstein (1956) has suggested that B may substitute for Si in the tetrahedral site and noted that it shared a bridging oxygen with Si in any case. Because of the shared bridging oxygen a potential -Al-O-Si bond would be very weak and thus Al could not substitute for Si (Loewenstein, 1956). However, many analyses of tourmaline indicate a deficiency of Si and an excess of Al with respect to ideal cation contents and these are usually interpreted as indicating $Al \rightleftharpoons Si$ (Foit and Rosenberg, 1977; Henry and Guidotti, 1985). Substitution of tetrahedral Si by Al occurs in pyroxenes and in ring silicates such as cordierite (see analyses in Deer *et al.*, 1978 and 1986). Nevertheless, Jolliff *et al.* (1986) have argued for full occupation of the tetrahedral site in tourmaline by Si and suggested that microprobe analyses be normalized to 6Si. The issue is of importance for the treatment of microprobe data and new evidence is presented below for substitutions involving the tetrahedral site in tourmaline. A summary of tourmaline substitutions is given in Table 1.

TABLE 1.

TOURMALINE SUBSTITUTIONS

1. $Mg_Y \rightleftarrows Fe^{2+}_Y$ (schorl-dravite series)
2. $Li^{+}_Y + Al^{3+}_Y \rightleftarrows 2Fe^{2+}_Y$ (elbaite-schorl)
3. $2Na_x + Al^{3+}_Y \rightleftarrows 2Ca^{2+}_x + Li^{+}_Y$ (elbaite-liddicoatite)
4. $Ca_x + Mg_z \rightleftarrows Na_x + Al_z$ (uvite-dravite)
5. $Fe^{2+}_Y + (OH)^- \rightleftarrows Fe^{3+}_Y + O^{2-}$ (schorl-buergerite)
6. $Mg_Y + Al^{3+}_z \rightleftarrows Mg_Y + Fe^{3+}_z$ (dravite-ferridravite)
7. $R^{+}_x + R^{2+}_Y \rightleftarrows R^{3+}_Y + \square_x$ (alkali-defect)
8. $R^{2+}_Y + (OH)^- \rightleftarrows R^{3+}_Y + O^{2-}$ (proton-loss)
9. $(R^{2+}, R^{3+})_{Y,z} \rightleftarrows (Ti^{4+}, Cr^{3+}, V^{3+}, M^{2+}, Mn^{3+})_{Y,z}$
10. $Na^{+}_x + 2Mg_Y \rightleftarrows 2Al^{3+}_Y + Mg_x$
11. $R^{2+}_Y + Si_T \rightleftarrows Al_Y + Al_T$ (?)
12. $B_T \rightleftarrows Si_T$ (?)

Subscripts: T = tetrahedral site
Z = Z site, octahedral
Y = Y site, octahedral
X = X site, octahedral

(Modified after Henry & Guidotti (1985)).

Analytical methods and data treatment

Tourmaline and associated muscovite from pegmatitic, metasomatic and submarine-exhalative tourmaline-bearing rocks in SE Ireland (Fig. 1) were analysed using a Cambridge Instruments Geoscan at the Geology Department, Manchester University, and a laboratory-constructed probe at the Department of Mineralogy and Petrology, Cambridge University. The Manchester instrument employed a take-off angle of 75° and accelerating voltage of 15 kV, that at Cambridge a take-off angle of 40° and voltage of 20 kV. Replicate analyses indicate reasonable agreement with the levels of precision and accuracy found for these instruments by Sweatman and Long (1969) and by Dunham and Wilkinson (1978). No evidence of beam damage (Reed, 1975; Ethier and Campbell, 1977) was observed during analyses.

Cation contents have been calculated on the basis of 31 oxygen atoms with 3B and 4(OH) assumed so that the actual factor used is 24.5 oxygen atoms. The model of site filling follows others (e.g. Foit and Rosenberg, 1977; Shearer *et al.*, 1984; Henry and Guidotti, 1985): B is assumed to fill the 3-fold site, 6Al are placed in the *Z* site, Si is in the tetrahedral site. If calculated Si is less than 6, as is true of most schorl–dravite analyses, excess Al over 6 is used to top up the tetrahedral site ($Si \rightleftharpoons Al$ is assumed). Any remaining Al not assigned is placed in the *Y* site. Fe, Mg and other non-alkali cations are placed in the *Y* site and alkalis in the *X* site. It should be noted that distinctions between the two octahedral sites are a matter of convenience—in reality cations are to some degree randomly distributed between them (e.g. *cf.* Fortier and Donnay, 1975; Nuber and Schmetzer, 1979).

Frequently, calculated cation contents leave a deficiency in the octahedral sites. Foit and Rosenberg (1977) suggest that such defects would lead to instability and probably reflect proton-loss substitution ($R^{2+} + (\mathrm{OH})^{-} \rightleftharpoons \mathrm{Al}^{3+} + \mathrm{O}^{2-}$) and consequent underestimation of non-hydroxyl oxygen in the formula unit—the 24.5 factor would thus be too low. Henry and Guidotti (1985) estimated the extent of proton deficiency by normalizing octahedral and tetrahedral site contents to 15 (i.e. full occupancy). The upper limit on this should be Si = 6 (although some analyses suggest Si > 6, these are uncommon and for most purposes a maximum of 6Si is reasonable). Consideration of published analyses indicates that normalization to 6Si (as advocated by Jolliff *et al.*, 1986) does not, however, remove the apparent octahedral site deficiency in all cases and in some gives rise to an excess of cations in octahedral sites. Foit and Rosenberg (1977) would place such excess cations in the *X* site. In some microprobe analyses, apparent defects in the octahedral sites could reflect a significant aggregate content of unanalysed elements (either below the detection limit and/or of atomic number < 11), genuine vacancy or analytical error. Evidence that proton-loss substitution is far more important than alkali-defect substitution (Foit and Rosenberg, 1977) provides some justification for normalizing octahedral site cation contents to full occupancy since the presence of proton-loss substitution leads to an underestimation of all cation contents.

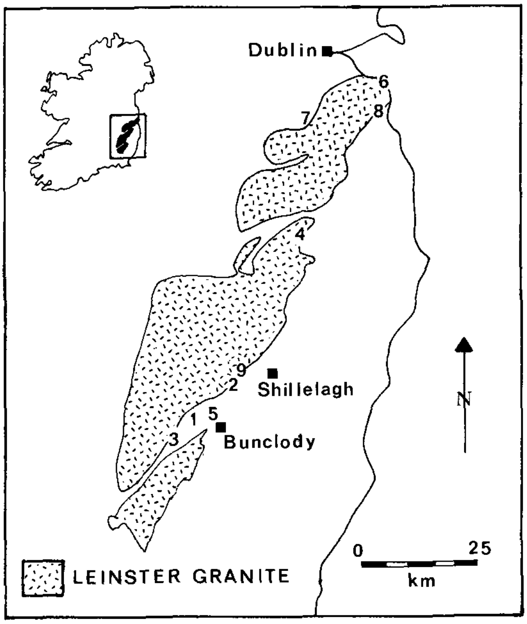

FIG. 1. Localities of samples from SE Ireland mentioned in the text and in figures: 1, Aclare, Co. Carlow; 2, Aghowle, Co. Wicklow; 3, Coolasnaghta, Co. Carlow; 4, Glendasan, Co. Wicklow; 5, Kilcarry Bridge, Co. Carlow; 6, Killiney, Co. Dublin; 7, Rathmichael, Co. Dublin; 8, Piperstown Hill, Co. Dublin; 9, Stranakelly, Co. Wicklow.

Regional setting

The geology of SE Ireland is dominated by the Leinster Granite batholith (Fig. 1) which is flanked by Lower Palaeozoic sediments (Brindley, 1973; Brück *et al.*, 1979). Tourmaline is a distinctive mineral of the granite margin, occurring both in pegmatite, aplite and quartz bodies and in their surrounding sediments (Brindley, 1957; McArdle, 1984). Where associated with pegmatites, aplites or quartz rocks, tourmaline in sediments is generally a metasomatic product of pegmatite–wallrock interaction (Brindley, 1957; Gallagher, 1987; Gallagher and Kennan, in prep.). Recently, tourmaline has been recognized as a constituent of stratiform, apparently pre-D1 quartz–tourmaline rocks ('tourmalinites' of Slack *et al.*, 1984) in SE Ireland (Kennan, 1983).

The tourmalines analysed for this study (Fig. 1) include samples from Li-rich pegmatites and their wallrocks (at Coolasnaghta, Aclare, Aghowle and Stranakelly), hydrothermal/metasomatic tourmaline from the margin of the Leinster Granite where it is related to small aplite and quartz bodies (Glendasan, Killiney and Rathmichael) and stratiform 'tourmalinites' (Kilcarry Bridge and Piperstown Hill). The Li pegmatites are part of the Li pegmatite province defined by Steiger and von Knorring (1974). Tourmaline occurs in coarse-grained quartz–tourmaline rocks and in flanking schists where it replaces biotite. It has also been found in granite which hosts pegmatite. Although clearly of pegmatitic origin the tourmalines are not rich in Li. Li cannot be measured by microprobe but an increasing elbaite component implies increasing Al content (Table 1) and when plotted on the Al–Fe–Mg discrimination diagram of Henry and Guidotti (1985), the tourmalines generally fall into the Li-poor granitoid field, away from the elbaite zone. Analyses by McArdle (1984) of some whole-rock, tourmaline-rich (50%+) samples from the pegmatites reveal Li contents of less than 250 ppm. These samples included muscovite-rich schist and hence muscovite associated with pegmatitic tourmaline is also Li-poor. All tourmalines analysed are members of the

TABLE 2. Representative analyses of tourmaline and muscovite.

	1.	2.	3.	4.	5.	6.
SiO_2	37.14	36.69	38.08	35.59	36.31	38.10
TiO_2	0.81	1.48	0.48	1.16	0.66	0.95
Al_2O_3	34.44	34.04	33.72	32.59	35.23	35.50
FeO_{tot}	7.67	14.32	9.35	9.17	6.40	9.65
MgO	5.37	1.81	4.36	4.66	5.71	4.32
CaO	0.71	0.67	0.41	1.13	0.42	0.37
Na_2O	1.85	1.86	1.84	1.56	1.64	1.92
K_2O	n.d.	0.15	n.d.	n.d.	n.d.	n.d.
TOTAL	87.99	91.02	88.24	85.86	86.37	90.81
Cations per 24.5 oxygen atoms						
Si_T	5.933	5.872	6.000	5.892	5.859	5.940
Al_T	0.067	0.128	-	0.108	0.141	0.060
Al_Z	6.000	6.000	6.000	6.000	6.000	6.000
Al_Y	0.417	0.294	0.363	0.262	0.562	0.464
Fe	1.024	1.918	1.251	1.274	0.864	1.258
Mg	1.280	0.432	1.040	1.152	1.374	1.004
Ti	0.097	0.179	0.058	0.147	0.080	0.111
Si_Y	-	-	0.097	-	-	-
Na	0.573	0.577	0.570	0.196	0.073	0.062
Ca	0.122	0.114	0.070	0.502	0.515	0.580
K	-	0.030	-	-	-	-
TOTAL	15.513	15.544	15.449	15.533	15.468	15.479

	7.	8.	9.	10.	11.
SiO_2	47.78	47.49	45.63	45.76	47.51
TiO_2	0.51	0.31	0.81	0.52	0.67
Al_2O_3	35.12	34.98	29.78	35.30	34.71
FeO_{tot}	1.78	1.20	4.10	1.05	2.60
MgO	0.44	0.54	2.27	0.72	0.87
CaO	n.d.	n.d.	n.d.	n.d.	n.d.
Na_2O	0.85	0.90	n.d.	0.59	0.26
K_2O	10.25	9.46	10.27	9.18	11.20
TOTAL	96.73	94.88	92.86	93.12	97.82
Cations per 22 oxygen atoms					
Si	6.260	6.294	6.334	6.173	6.212
Ti	0.050	0.031	0.085	0.053	0.066
Al	5.423	5.464	4.873	5.613	5.349
Fe	0.195	0.133	0.475	0.118	0.284
Mg	0.087	0.106	0.469	0.146	0.169
Ca	-	-	-	-	-
Na	0.215	0.231	-	0.154	0.066
K	1.713	1.599	1.818	1.580	1.869
TOTAL	13.943	13.858	14.053	13.837	14.015

MnO less than detection limit in all cases. n.d. = not detected

1. Pegmatitic tourmaline, quartz-tourmaline rock, Coolasnaghta; core zone.
2. As no. 1; outer zone.
3. Metasomatic schist-hosted tourmaline, muscovite-tourmaline schist, Coolnasnaghta.
4. Tourmaline in altered granite hosting Aclare Li-pegmatite.
5. Schist-hosted, metasomatic tourmaline, Aclare Li-pegmatite complex.
6. Schist-hosted, metasomatic tourmaline, Rathmichael.
7. Muscovite in pegmatitic quartz-tourmaline rock, Coolasnaghta.
8. Muscovite in muscovite-tourmaline schist, Coolasnaghta.
9. Muscovite in altered, tourmaline-bearing granite, Aclare.
10. Muscovite in muscovite-tourmaline schist, Aclare
11. Muscovite in altered aplite, Strandkelly Li-pegmatite complex.

schorl-dravite series with Fe/(Fe + Mg) ranging between 0.3 and 0.9. Representative analyses are given in Table 2. A more detailed description of the geology and chemistry of tourmaline in SE Ireland is given by Gallagher (1987), Gallagher and Kennan (in prep.), and McArdle (1984).

Tetrahedral site occupancy

Muscovite analysed from tourmaline-bearing rocks in SE Ireland has, in most cases, grown with the tourmaline. These rocks include tourmaline-rich schists which, besides muscovite, also contain biotite, chlorite and quartz, and quartz-tourmaline rocks of pegmatitic origin in which muscovite and garnet are relatively minor constituents.

In most instances, tourmaline chemistry reflects that of the host rock. Muscovite compositions show parallel trends with high values of sensitive minor elements such as Ti correlating with elevated values of these elements in tourmaline. In Fig. 2, Al/Si of coexisting tourmaline and muscovite are positively correlated. Al/Si ratios are used because uncertainties in normalization factors for both minerals make direct comparison of calculated Al or Si contents meaningless where the normalization is not accurate. Ratios of cations are fixed and do not depend on normalization factors chosen. The chemistry of muscovite in the samples analysed does not vary consistently with respect to proximity to tourmaline and hence the average of all muscovite analyses were used together with the average of tourmaline analyses in the same thin section where petrographic examination indicated equilibrium between the two phases. The average values should approach those of the bulk mineral chemical compositions where analyses were detailed enough to account for chemical variations within and between grains. The treatment is necessarily imprecise but other ratios, such as Al/Fe and Si/Fe, do not show a similar correlation so it can be concluded tentatively from Fig. 2 that the Si and Al contents of tourmaline vary with the bulk chemistry of the system and that Si and Al are related by a coupled substitution. If the Si content of tourmaline is thus variable, then the apparent deficiency in calculated Si contents of tourmalines cannot simply be regarded as due to proton-loss

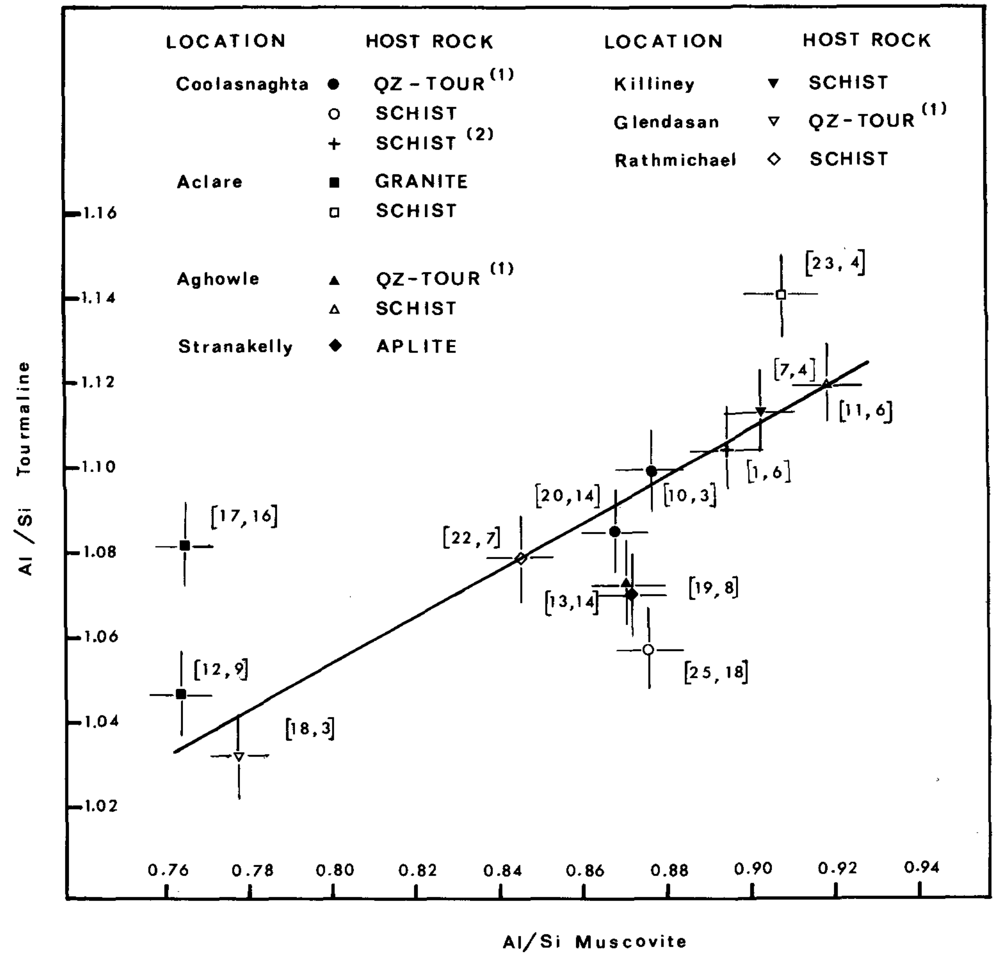

FIG. 2. Al/Si in tourmaline *vs.* Al/Si in muscovite for several localities in SE Ireland. Points represent the average Al/Si for all tourmaline and muscovite analyses in a given sample. See text. Figures in brackets are the number of points analysed in tourmaline and muscovite, respectively. Vertical and horizontal bars represent the precision (σ) for Al/Si. (1) Quartz-tourmaline rock (tourmaline > 40% by volume). (2) Tourmaline as accessory phase only—in other schist samples tourmaline is a major phase.

substitution affecting the calculations. Normalization of cation contents of tourmaline to 6Si is thus as likely to obscure the true composition as reveal it.

Most tourmaline grains were analysed at several points from core to rim. The resulting zoning patterns are further evidence for tetrahedral site occupancy (Fig. 3). Al apportioned to the Y site (Al_Y) after satisfying Z site requirements (Al_Z) and after topping up the tetrahedral site due to calculated Si deficiencies (Al_T) frequently shows a very good correlation with (Fe+Mg). It would be expected that Al should show some correlation with (Fe+Mg) since in most schorl-dravite tourmalines there is some substitution of divalent cations by Al. However, the size of the Al_Y term is controlled by the amount of the calculated Si content (or calculated Si deficiency) and is not immediately related to the total Al content. The good correlation with (Fe+Mg) indicates that Al_Y is a real term and not just a product of an arbitrary normalization scheme. Consequently, the Si deficiency which gives rise to the Al_Y term is also real and not just due to a failure to account for proton-loss substitution.

Two independent lines of evidence thus point to a deficiency of Si in tourmaline compared to the ideal 6Si and indicate that Si is substituted

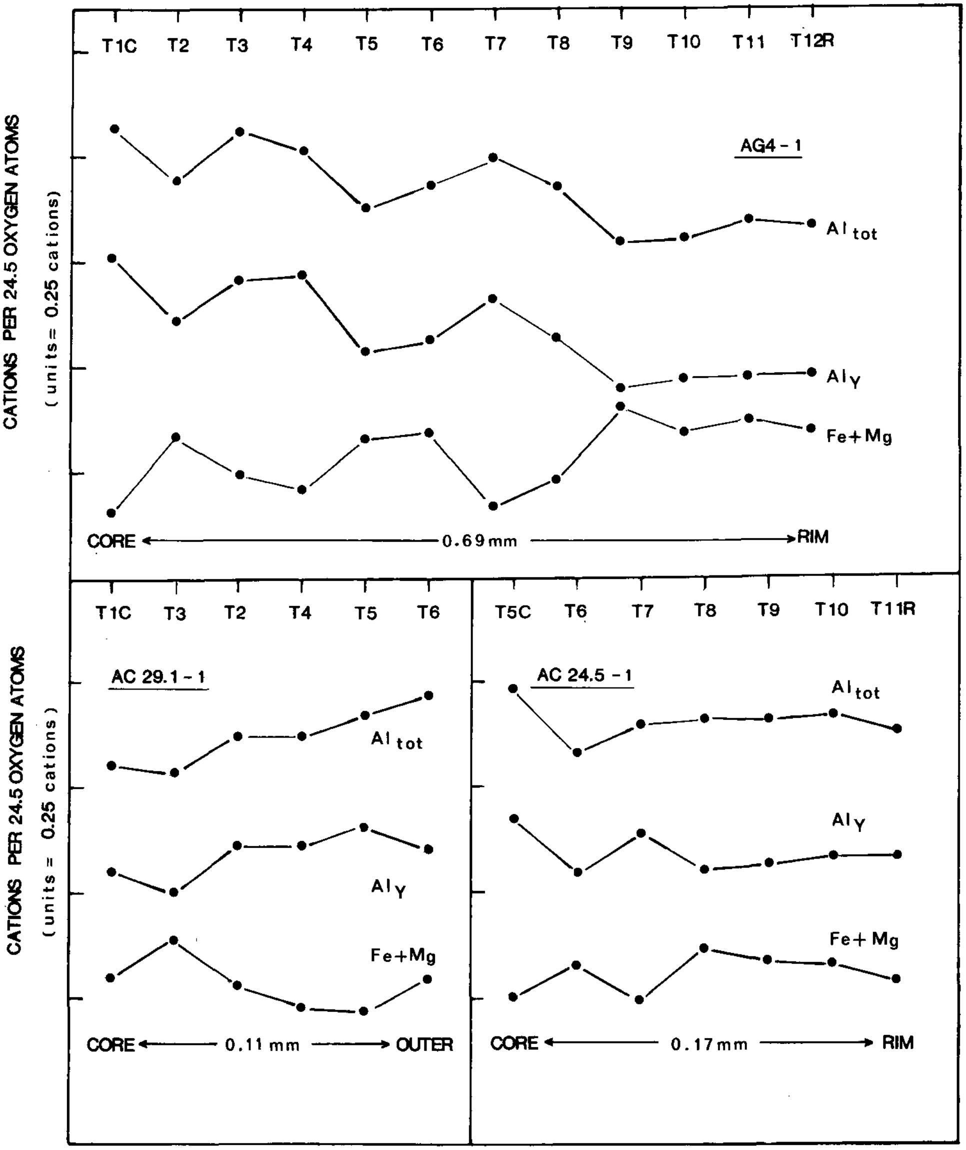

FIG. 3. Chemical zoning in tourmaline from quartz–tourmaline rock at Aghowle (AG4) and from altered granite and tourmaline-rich schist at Aclare (Ac 29.1 and Ac 25.4, respectively).

by Al. Other zoning patterns for SE Ireland tourmalines suggest that Ti may also replace Si. Assessing the relative importance of Al $\rightleftharpoons$ Si and proton-loss substitution for a given microprobe analysis with a calculated Si content below six is difficult but it is clear, as suggested by Weisbrod (1987), that overestimation of the degree of proton-loss substitution will occur if the possibility of Al $\rightleftharpoons$ Si is not acknowledged.

Alkali-defect *vs.* proton-loss substitution

Al generally substitutes for Fe and Mg in schorl–dravite tourmalines and the resulting positive charge imbalance must be compensated for. Foit and Rosenberg (1977) concluded that two coupled substitutions, alkali-defect and proton-loss substitution, are involved. They concluded, on the basis of a survey of published analyses, that proton loss

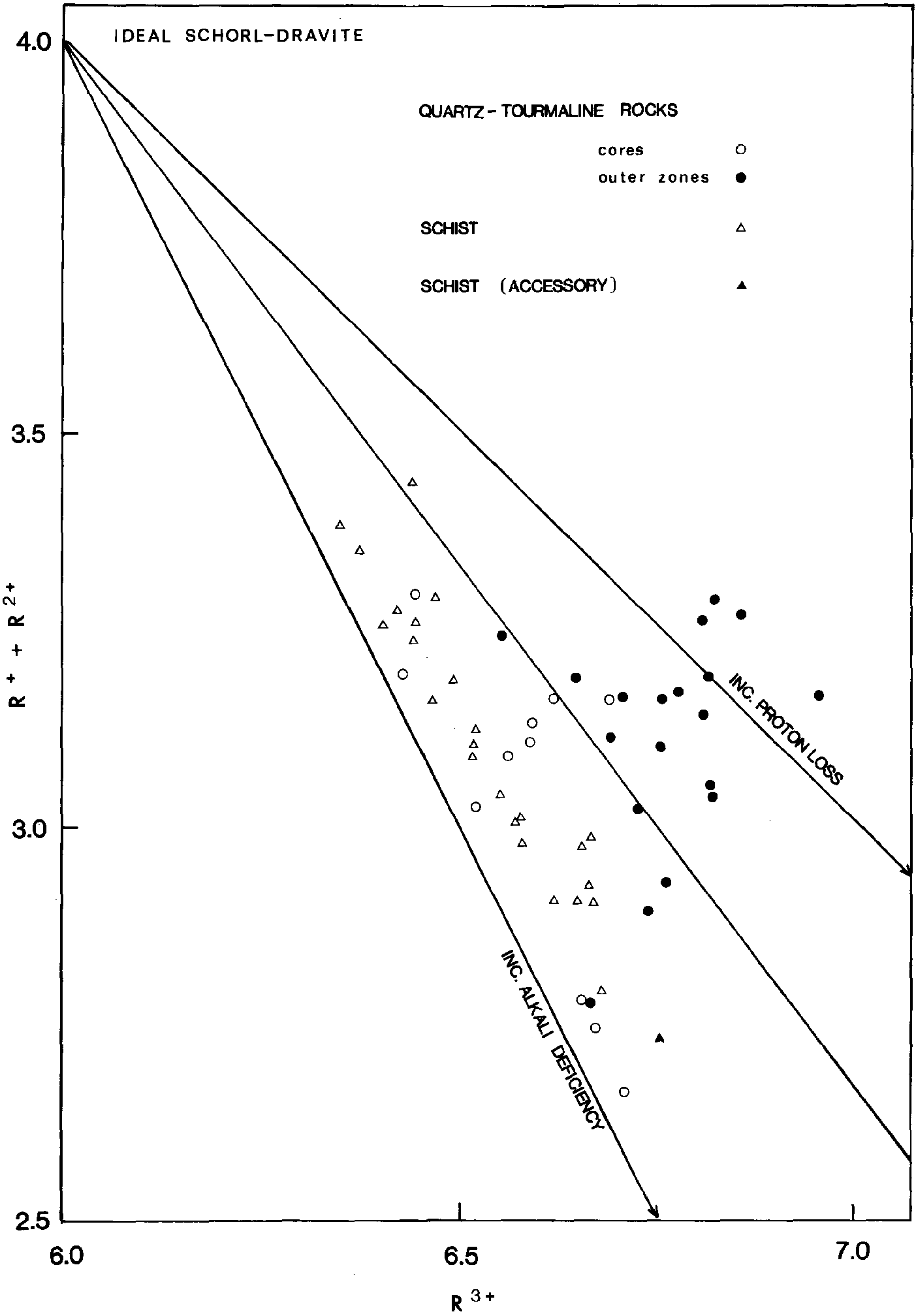

FIG. 4. Proton-loss substitution *vs.* alkali-defect substitution in tourmalines from Coolasnaghta showing dominance of alkali-defect substitution in tourmaline which grew in H_2O-rich schist or in equilibrium with it.

is much more significant than vacancies in the alkali site. Both substitutions improve local charge balance but proton loss does so more effectively and alkali-defect tourmalines are inherently unstable (Foit and Rosenberg, 1977). The degree of replacement of divalent cations by Al^{3+} was found to increase with decreasing temperature (Rosenberg and Foit, 1979; Manning, 1982).

Alkali-defect and proton-loss substitution in SE Ireland tourmalines are illustrated in Figs. 4 and 5. In these diagrams trivalent cation contents are plotted against univalent and divalent cation contents. Substitution involves charge balancing between sites, so charge occupancy rather than simple cation contents are used (Foit and Rosenberg, 1977):

$$(R^{+} + R^{2+}) = (Na^{+} + 2Ca^{2+} + K^{+} + Fe^{2+} + Mg^{2+} + Mn^{2+} + \ldots)$$

$$R^{3+} = (Al^{3+} + Cr^{3+} + V^{3+} + 4/3Ti^{4+} + \ldots)$$

The theoretical end members are

$$R^{+}R_{3}^{3+}R_{6}^{3+}Si_{6}B_{3}O_{30}(OH) \text{ (proton loss)}$$

and

$$\square(R_{2}^{2+}R^{3+})R_{6}^{3+}Si_{6}B_{3}O_{27}(OH)_{4} \text{ (alkali defect);}$$

$\square$ = vacancy). Because $Al \rightleftharpoons Si$ substitution and proton loss can occur together and have opposite effects on the calculated cation contents and because it is not possible to estimate the precise amount of either from microprobe data, it is necessary to refine further the $(R^{+} + R^{2+})$ *vs.* R^{3+} diagram if it is to be useful for most analyses. After calculating cation contents on the basis of 24.5 oxygen atoms the $(R^{+} + R^{2+})$ *vs.* R^{3+} plots would be too near the alkali-defect side of Figs. 4 and 5 if proton-loss had occurred. This is because calculating on the basis of 24.5 oxygen atoms is to assume that no proton loss has occurred, thus exaggerating the relative importance of alkali-defect substitution. One way to allow for proton-loss substitution is to assume that any calculated Si deficiency is due solely to proton-loss and then normalize cation contents to 6Si (6Si being taken as the maximum number of Si possible). However, if $Al \rightleftharpoons Si$ has taken place the resulting plots would, after normalization to 6Si, be too near the proton-loss side of the diagram since normalization to 6Si does not allow for $Al \rightleftharpoons Si$ substitution. Normalization to 24.5 oxygens and normalization to 6Si represent extreme positions not attained in natural tourmalines which have undergone a degree of both alkali-defect and proton-loss substitution. The true position of tourmaline points on the $(R^{+} + R^{2+})$ *vs.* R^{3+} diagram are likely to lie between the points fixed by normalization to 24.5 oxygens and normalization to 6Si. Using the latter, the resulting diagram can be used to show the maximum degree of proton-loss substitution in a given tourmaline and the minimum degree of alkali-defect substitution. The diagrams used in this paper (Figs. 4–7) thus involve normalization to 6Si.

Analyses of tourmalines from Coolasnaghta (Fig. 1) (see Gallagher, 1987; Gallagher and Kennan, in prep.) illustrate the main results for SE Ireland (Fig. 4). Three tourmaline types are present, a zoned tourmaline from pegmatitic quartz–tourmaline bodies, a metasomatic tourmaline from wallrock schist and accessory tourmaline from country-rock schist. The cores of quartz-hosted tourmalines have a similar chemistry to schist-hosted tourmalines and both grew in equilibrium, their chemistry reflecting that of the schist. Outer zones of quartz-hosted tourmalines reflect a more evolved, pegmatitic chemistry (Gallagher and Kennan, in prep.). The $(R^{+} + R^{2+})$ *vs.* R^{3+} diagram reveals sharp distinctions which parallel the chemical differences in these tourmalines (Fig. 4). Schist-hosted tourmalines and the chemically similar cores of quartz-hosted tourmalines are dominated by alkali-defect substitution. The outer zones of quartz-hosted tourmalines have a greater degree of proton-loss substitution. The differences have been interpreted (Gallagher, 1987; Gallagher and Kennan, in prep.) as reflecting growth of the schist-hosted tourmalines and the cores of quartz-hosted tourmalines in a water-rich environment during metasomatism of the wallrock schist so that alkali deficiency was dominant over proton loss. Later tourmaline which grew in equilibrium with the pegmatitic melt was buffered more readily with respect to alkalis than H_2O.

Four out of five tourmalines which grew in schist show a greater degree of alkali-defect substitution than proton-loss substitution (Fig. 5). For all analysed tourmalines from SE Ireland, alkali-defect substitution is at least as important as proton-loss substitution (Fig. 6) and when normalization to 6Si is allowed for, it seems likely that alkali-defect substitution may be the more important of the two.

The degree of trivalent-for-divalent substitution is at least partly dependent on bulk chemistry, with tourmalines which grew in an Al-rich environment having high Al contents. This is illustrated by Aclare tourmalines (Figs. 1 and 7), the material in relatively Al-rich schist (mean 22.4% Al_2O_3, $n = 32$) showing a high degree of substitution compared to tourmaline in granite which has a relatively low Al_2O_3 content (mean 16.5% Al_2O_3, $n = 20$) (see Scoon, 1978, for whole rock analyses). No evidence is available for the temperature of formation of these tourmalines and hence the

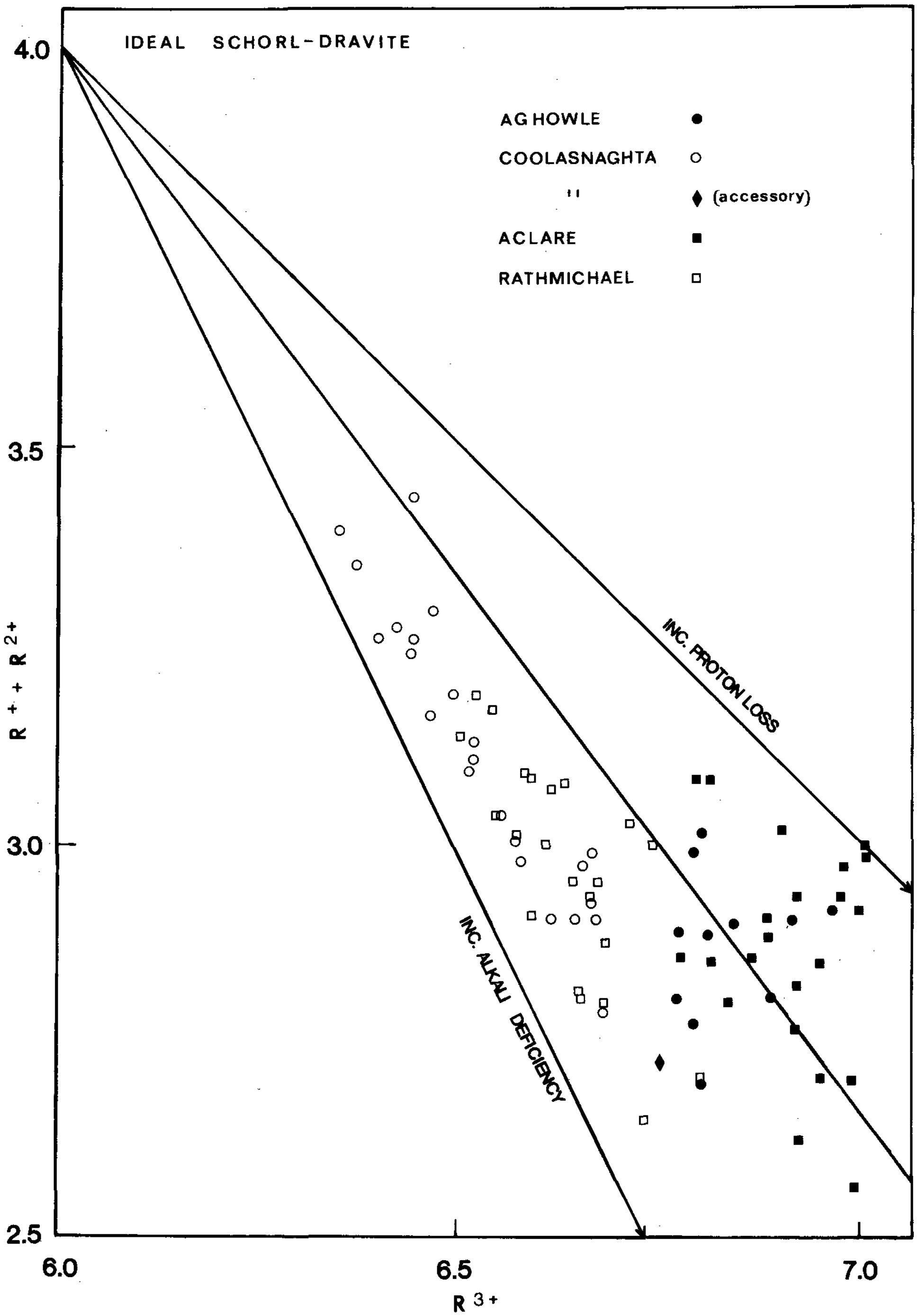

FIG. 5. Alkali-defect *vs.* proton-loss substitution in all schist-hosted tourmalines analysed from SE Ireland. Alkali-defect substitution is dominant, reflecting the availability of H_2O during growth of tourmaline.

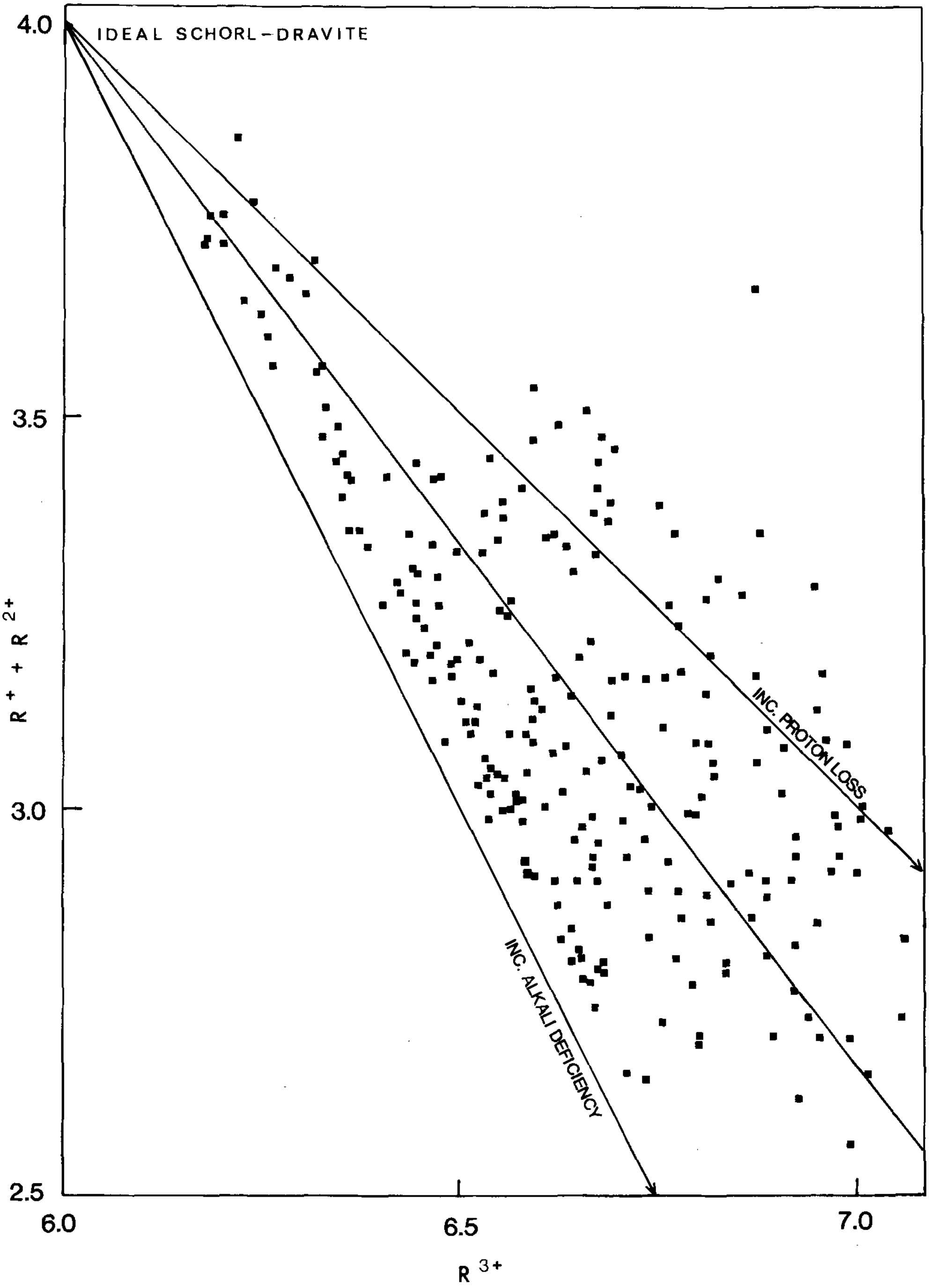

FIG. 6. Alkali-defect *vs.* proton-loss substitution for all tourmalines analysed from the localities in Fig. 1. Alkali-defect substitution is at least as important as proton-loss substitution, particularly when the normalization of cation contents to 6Si is taken into account.

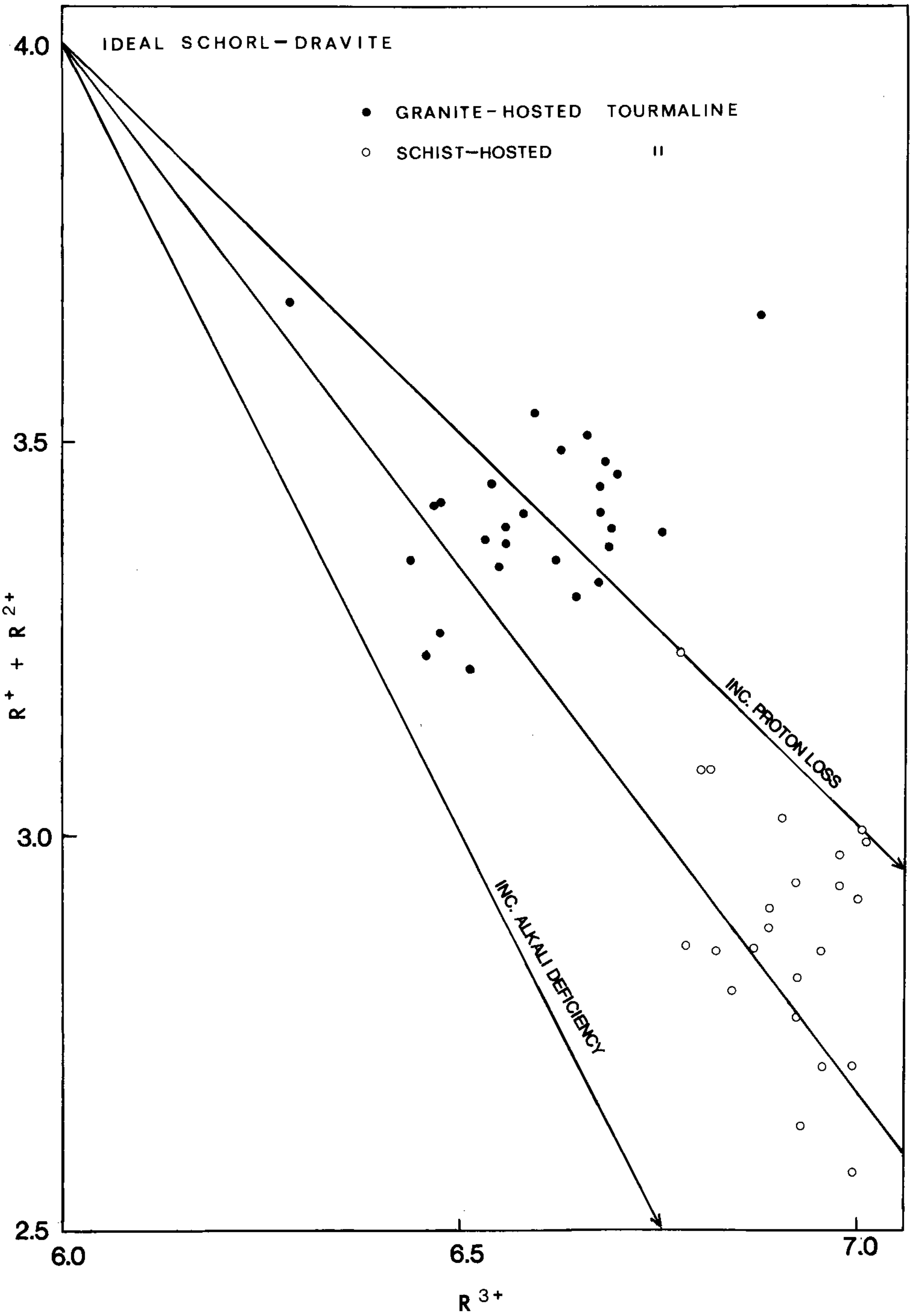

FIG. 7. Alkali-defect *vs.* proton-loss substitution in tourmaline in relatively Al_2O_3-rich schist and Al_2O_3-poor granite.

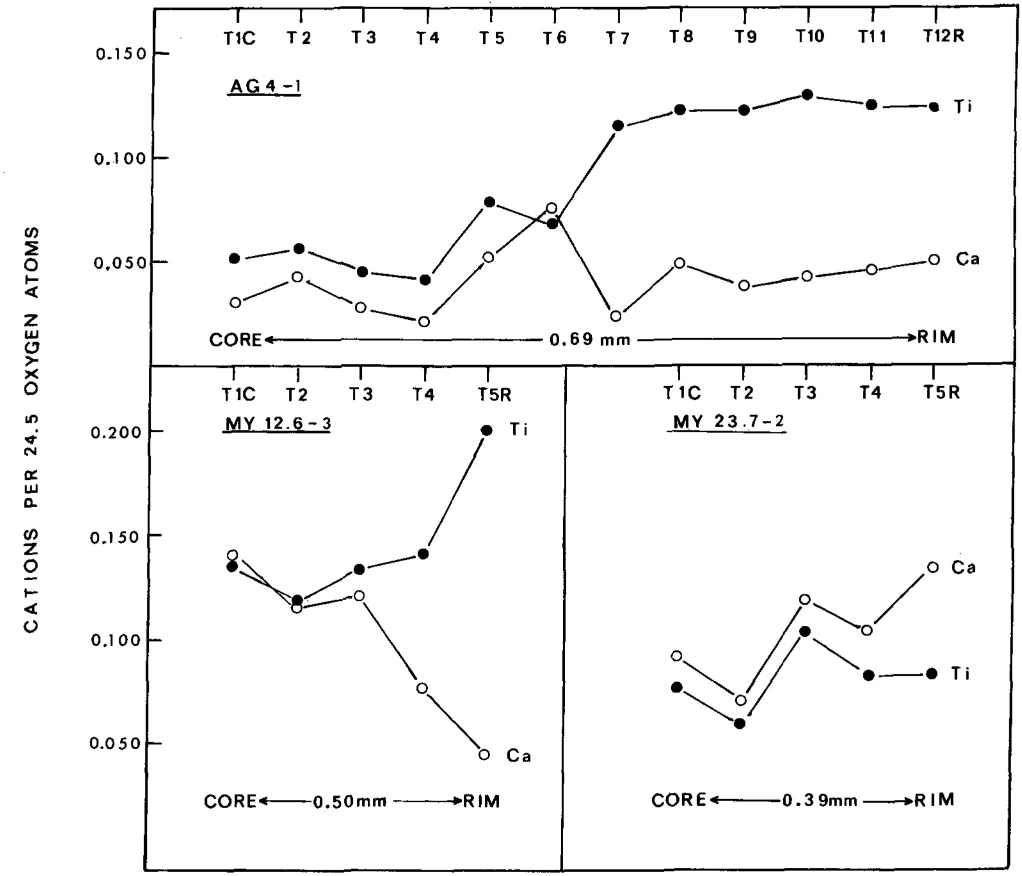

FIG. 8. Co-variation between Ca and Ti across some tourmaline grains from Aghowle (AG4) and Coolasnaghta (MY 12.6 and MY 23.7).

question of whether bulk chemistry or temperature (as suggested by Rosenberg and Foit, 1979, and by Manning, 1982) is more important in controlling the degree of trivalent-for-divalent substitution cannot be resolved for SE Ireland.

Other substitutions

Zoning diagrams were constructed for all tourmalines analysed at several points between core and rim (Gallagher, 1987) and several conclusions may be drawn. Ti and Ca show strong positive correlation in many tourmalines; in others they are negatively correlated (Fig. 8). Both trends imply a coupled substitution but the relatively low content of these elements does not allow the other cations involved to be identified.

Staatz *et al.* (1955) suggested that the Na content of tourmaline was governed not by bulk chemical control (or fractionation) but by charge-balance considerations. They found no relationship between the Na content of tourmaline and the degree of fractionation of the Brown Derby pegmatite, Colorado, in contrast to other elements such as Fe, Mg, etc., which showed strong correlation with fractionation. Similar observations hold for SE Ireland tourmalines—despite strong zoning patterns for some elements (especially Fe, Mg, Ca, Ti, Al), Na shows little consistent variation with respect to other elements within individual tourmalines or with respect to bulk chemistry (Gallagher, 1987).

Conclusions

The chemistry of tourmalines and coexisting muscovites in SE Ireland and chemical zoning patterns in tourmaline clearly demonstrate that the Si content of tourmaline is variable and Al substitutes for Si in tetrahedral sites despite objections based upon theoretical considerations. Limited zoning evidence also suggests replacement of Si by Ti. Covariation of Ca and Ti in most tourmalines is evidence for a coupled substitution involving these cations but any other cations involved are not known. The lack of a consistent zoning pattern for Na reinforces the view that Na contents are governed by charge-balance considerations rather than by bulk chemistry.

Without knowledge of the H_2O content of tourmaline it is not possible to assess accurately the true degree of proton-loss or alkali-defect substitution in schorl-dravite where they occur. Normalization of Foit and Rosenberg's (1977) diagram to 6Si indicates the maximum and minimum amount of proton-loss and alkali-defect substitution, respectively, and thus allows use of microprobe data for assessing these substitutions. On this basis, taking all tourmalines from SE Ireland together, alkali-defect substitution is as important as proton-loss substitution, in contrast to the conclusions of Foit and Rosenberg (1977). These substitutions are at least partly controlled by bulk chemistry, H_2O-rich environments favouring alkali-defect substitution. The degree of trivalent-for-divalent substitution present in tourmaline is also at least partly controlled by bulk chemistry.

Because of the complexity of competing substitutions and the presence of unanalysed components it is clear that no one normalization scheme can be satisfactory for all tourmalines analysed by microprobe. Normalization to 6Si may obscure significant tetrahedral site substitution and exaggerate the degree of proton-loss substitution in schorl-dravite tourmalines. Normalization to 24.5 oxygen atoms may do the reverse but when used in conjunction with the $(R^+ + R^{2+})$ *vs.* R^{3+} diagram (normalized to 6Si) provides a flexible scheme for treating tourmaline microprobe data. Further normalization (e.g. normalization of octahedral and tetrahedral contents to 15 cations) could be carried out after initial assessment of the degree of proton-loss substitution. Greater emphasis on defining chemical zoning within individual tourmalines may reveal trends which could be used to refine the microprobe data further.

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