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The distribution of lithium in some Cornish minerals: ion microprobe measurements

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ABSTRACT. Ion microprobe analyses of Li are presented for minerals of the Variscan granites and related rocks of west Cornwall. Together with electron microprobe data these provide insight into the behaviour of Li during the protracted late- and post-magmatic history of the granites. The role of the Mg-Fe tourmaline series is emphasized in this exploratory study.

Cornish granites and lithium geochemistry

The high-level, late Variscan granites of SW England are derived from highly differentiated melts rich in alkalis, volatiles, metalloids, and heavy metals (Floyd, 1972; Hawkes and Dangerfield, 1978). Pervasive alteration is indicative of late- and post-magmatic hydrothermal activity, involving substantial water-rock interaction with ample opportunity for mineralization (Plant *et al.*, 1980). The granites themselves may be broadly divided into biotite and Li-mica granites. This distinction need not be primary, as biotite may be converted to Li-mica by ion exchange of (MgFe) for (LiAl). The (MgFe) component may be fixed by boron to form tourmaline. The pelitic and basaltic country rock underwent low-grade regional metamorphism some 80 Ma before granite intrusion and the accompanying local metasomatism.

Li has a mean upper crustal concentration of 20 ppm (Norton, 1973), and Turekian and Wedepohl (1961) quote values of 40 and 24 ppm for high-Ca and low-Ca granites respectively. The small ionic radius (0.78 Å) of lithium aids substitution of Li^+ and Al^{3+} for Fe^{2+} and Mg^{2+}. The richest primary sources of Li on a world scale are pegmatites associated with granitic intrusions. Stewart (1978) points out that Li-rich pegmatites typically occur in granites which contain < 100 ppm Li, and that to form a typical (7100 ppm) Li pegmatite by extreme fractionation is a strained hypothesis. He advocates anatectic origins by partial melting of Li-rich metasediments. Meldon, the only Cornubian locality with a range of typical Li-rich phases, has a relatively high Li(pegmatite): Li(granite) ratio—a unique occurrence in a region where Li-mica is commonly the only Li-rich phase. In this context, the Li phosphate amblygonite has been noted as a significant phase in part of the Tregonning-Godolphin mass (Stone and George, 1978).

Data on Li occurrence and abundance are widely scattered in the literature. Some mineral data for comparison with the Cornish results are given in Table I. Much higher values can be found in some Li-mineralized provinces (e.g. Vlasov, 1964). Beer *et al.* (1978) have published a résumé of Li analyses available for British rocks and minerals.

Excluding varieties rich in Li-mica, the mean Li concentration in the Cornish granites is roughly 300 ppm (Dangerfield *et al.*, 1980). Within-grain analyses of Li provide fresh information on the geochemistry of an element for which published analyses on mineral separates are still relatively sparse.

Analytical methods

The samples were prepared as 30 μm sections mounted on 25 × 30 mm glass slides. Major elements were determined by electron microprobe analysis (EPM) using an Li-Si energy-dispersive detector.

TABLE I. *Some values for Li in minerals, taken from the literature*

Minerals		Li ppm	Ref.
Feldspars		Usually ≲ 5	1
Mica	muscovite	mean 1200	2
	biotite	mean 3300	2
	lepidolite	mean 23 000	2
Quartz	smoky	mean 22	3
	colourless	mean 45	3
	vein	mean 73	4
Tourmaline (Mg; Fe, Cornish)		78-1640	5

1. Heier and Billings, 1973.
2. Stevens and Schaller, 1942.
3. Frondel, 1962.
4. Konno, 1969.
5. Power, 1968.

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The concentrations of Li in bulk samples were determined by atomic absorption spectrophotometry (AAS). 100 mg aliquots of crushed and finely ground whole-rock samples were decomposed by NH_4F fusion followed by acid dissolution of the residue at atmospheric pressure. This proved adequate even for tourmaline-rich samples. Dilute solutions were analysed on a Pye Unicam SP1900 instrument, using an air-acetylene flame and tuning on the doublet at 6708 Å. All solutions contained a KCl ionization buffer. A standard addition procedure confirmed that matrix effects were not significant at the dilutions used (final volume 50–1250 cm^3). A bracketing method with alternating standards and unknowns was used to compensate for possible instrumental drift. Replicate analyses on synthetic glass standards gave a repeatability of better than $\pm 2\%(2\sigma)$.

The mineral analyses were carried out using an extensively modified AEI IM20 ion microprobe. Borosilicate glass standards (containing $\sim$ 2000 ppm Li, determined by AAS) were used to normalize the Li count rates from the samples, the absolute values of which are influenced by instrumental parameters. The ion probe has several advantages over EPM for trace-element analysis, including a low background and the potential for examining all elements from H to U. A high secondary-ion yield and the absence of serious molecular interference peaks at mass 7 makes the technique especially sensitive for Li. Matrix effects constitute a major problem in quantitative ion probe analysis, the bulk composition of a sample affecting the sensitivity for a given element by a factor of up to $\sim$ 2–3 within silicates. The use of standards of composition appropriate to all samples to be analysed is not generally practicable for such complex materials as tourmalines and micas. The correction procedure used here involved determination of Li introduced to minerals and standards by ion implantation. 'Matrix factors' were derived to quantify the variation in sensitivity of the ion probe for Li in different matrices. The methodology is described by Wilson and Long (1982) and Wilson (1982).

Polished glass standards were mounted in the centre of each thin section, the polished surfaces of section and standard being held coplanar. All specimens were sputter-coated with $\sim$ 50 Å of Au. The primary beam was 3–12 nA $^{16}O^-$, mass-filtered and focused to a diameter of about 15 μm at the sample surface. Sample chamber pressure was $\sim 10^{-6}$ torr, and a liquid nitrogen cold trap was used to minimise contamination. The specific count rate for ^{7}Li, obtained with a primary beam current of 10 nA on the glass standard, was $\sim$ 50 counts per second per ppm(wt) Li. The background count rate was negligible at $\sim$ 10 counts hr^{-1}. All measurements were made at a mass resolution, M/ΔM, of $\sim$ 450.

Measurements of the ^{6}Li count rate on the standard were alternated with counts on sets of four points on the adjacent section. The lithium concentration at each point is then given by

$$C_{SPEC} = C_{STD} \times (N_{SPEC}/N_{STD}) \times 1/F$$

where F is the matrix factor appropriate to the specimen composition determined by electron probe analysis. Some 6–8 Li analyses can be made per hour.

Uncertainties in the method are partly due to problems of matrix factor determination and partly to instrumental instability. Comparison with published data on similar samples suggests an accuracy of the order of $\pm 20\%$ for tourmaline containing $\gtrsim$ 100 ppm Li (data are quoted here in element ppm [or oxide %, for major elements] by weight). Thus Power (1968) quotes Li analyses averaging 462 ppm for twenty-one tourmalines. The twenty-six values listed here (see Table III) average 523 ppm. Quartz data are subject to greater overall error, as the mineral generally contains less Li, has a lower matrix factor than tourmaline (i.e. the ion yield is less) and contains a variable density of μm-scale inclusions, some of which will inevitably be sampled by the beam in particular grains. Matrix factors are quoted relative to the standard glass, of approximate composition (wt %) FeO 10.4, MgO 8.7, SiO_2 5.8, Na_2O 22.9, B_2O_3 51.4 and LiF 0.8. For quartz the mean matrix factor was found to be $0.5 \pm 0.2(2\sigma)$. The factor for tourmaline, also determined by ion implantation, varied with $Mg/(Mg+Fe)_{ionic}$ from 0.9 ± 0.3 at $Mg/(Mg+Fe) = 0$ to a maximum of 1.8 ± 0.3 at $Mg/(Mg+Fe) = 0.59$, falling again to 1.0 ± 0.3 at $Mg/(Mg+Fe) = \infty$. Matrix factors for other minerals have not yet been determined and data for mica and feldspars are quoted with a nominal factor of 1.00.

Results

Some 500 ion probe analyses of Li are presented in histogram form in figs. 1–5, corresponding to the five broad petrological divisions discussed below. Selected EPM analyses (EPM1-8) are given in Table II, and a summary of sample localities and of Li concentrations in tourmaline and quartz is given in Table III. Mineral colours quoted in the following refer to thin sections viewed in plane polarized light. The relative enrichment of Li in the Cornish granites is indicated by ion probe results for a quartz-tourmaline rock associated with the Caledonian Ross of Mull granite in West Scotland. Pale yellow tourmaline (EPM1) and clear quartz are the essential phases, with accessory feldspar and rutile. The average Li concentrations in the tourmaline and quartz are 15 and 4 ppm respectively, at least an order of magnitude below typical Cornish values.

Granites and pegmatites. Ample petrographic evidence supports the observations of Stone (1979) on the paragenesis of local megacrystic granites. Xenocrystic resistate phases are overgrown by magmatic feldspars and quartz, with late development of K feldspar megacrysts and of secondary tourmaline, muscovite, and quartz. Primary tourmaline also occurs (in accessory amounts) in many granites. Interrupted megacryst growth is sometimes suggested by concentric zones of fine-grained inclusions (commonly biotite), as at Lamorna and Tregarden. Tourmaline is an almost ubiquitous accessory phase in rocks associated with the granites, and locally assumes rock-forming proportions. In particular, veins, stocklike

TABLE II. *Electron microprobe analyses; oxide and cation contents and MF* $[Mg/(Mg+Fe)_{ionic}]$ *ratios. Analysis EPM3 is of biotite, the rest are of tourmaline*

Analysis Sample number	EPM1 —	EPM2 S2	EPM3 S2	EPM4 S6	EPM5 S11	EPM6 S15	EPM7 S15	EPM8 S15
SiO_2	37.20	35.14	37.07	34.42	35.83	34.01	37.19	33.53
TiO_2	0.61	0.45	2.05	0.41	0.17	0.44	0.17	—
(B_2O_3)	(10.92)	(10.46)	—	(10.82)	(10.10)	(10.33)	(10.56)	(10.89)
Al_2O_3	32.46	35.02	22.00	29.42	29.58	35.88	37.94	26.06
$FeO+Fe_2O_3$	3.76	11.47	20.54	10.86	11.22	12.34	0.22	18.03
MnO	—	—	0.35	—	—	—	—	—
MgO	8.38	1.72	3.56	6.19	5.89	1.29	8.27	4.49
CaO	0.21	0.18	—	2.21	1.41	0.13	—	1.03
Na_2O	2.14	1.44	—	1.50	1.90	1.58	1.59	1.77
K_2O	—	0.08	9.46	—	—	—	—	—
(H_2O)	(4.21)	(4.03)	(3.55)	(4.17)	(3.90)	(3.99)	(4.07)	(4.20)
Partial total	84.76	85.51	95.03	85.01	86.00	85.68	85.37	84.91
Si	5.97	6.13	5.57	5.75	6.01	5.67	5.87	5.78
(B)	(3.03)	(3.15)	—	(3.12)	(2.92)	(2.97)	(2.87)	(3.24)
Al	6.13	7.20	3.90	5.79	5.85	7.04	7.05	5.29
Mg	2.01	0.45	0.80	1.54	1.47	0.32	1.94	1.15
Ti	0.07	0.06	0.23	0.05	0.02	0.06	0.02	—
Total Fe	0.50	1.67	2.58	1.52	1.57	1.72	0.03	2.60
Mn	—	—	0.04	—	—	—	—	—
Na	0.67	0.48	—	0.49	0.62	0.51	0.49	0.59
Ca	0.04	0.03	—	0.40	0.25	0.02	—	0.19
K	—	0.02	1.81	—	—	—	—	—
(OH,F)	(4.51)	(4.69)	(3.56)	(4.65)	(4.35)	(4.43)	(4.25)	(4.83)
Total	22.94	23.88	19.35†	23.31	23.06	22.74	22.52	23.67
MF	79.9	21.1	23.6	50.4	48.3	15.7	98.5	30.8

Taken from Wilson (1980), analyses 57,26,25,42,54,58,59,60. EPM6-8; brown core, wide pale outer zone and narrow green rim of a large tourmaline grain. Cation totals for tourmaline and biotite are respectively based on 31 and 24 (O,OH,F).

Estimated values of (H_2O,F,B_2O_3) are given in parentheses. †EPM3 includes an estimated (see Fig. 1) 0.86 Li ≡ 1.42 wt. % Li_2O. The estimated maximum Li_2O in the tourmalines is ~ 0.06 wt. % (see Table).

TABLE III. *List of Cornish samples, indicating rock type, locality (place name, O.S. grid reference and associated granite mass), and mean values (ppm) for Li in tourmaline and quartz*

				Tourmaline 'generations'		Quartz
				First	Subsequent	
S1 Granite	Longdowns Quarry	SW741338	Carnmenellis	260	—	160
S2 Granite	Imperial Pit, Goonbarrow	SX009583	St. Austell	140	—	100
S3 Luxullianite	Conce Moor	SX040617	St. Austell	220	1300	30
S4 Pegmatite	Priests Cove	SW352323	Land's End	220	—	100
S5 Schist	Cligga Head	SW739537	Cligga Head	150	—	50
S6 Metabasalt	Crowns, Botallack	SW362335	Land's End	150	—	—
S7 Greisen	Cligga Head	SW735536	Cligga Head	470	—	80
S8 Greisened elvan	Main Pit, Goonbarrow	SX007583	St. Austell	170	—	90
S9 'Topaz rock'	St. Mewan Beacon	SW986535	St. Austell	450	—	26
S10 Quartz-tourmaline rock	Roche Rock	SW992596	St. Austell	340	—	210
S11 Tourmaline rock	Grylls Bunny, Botallack	SW364334	Land's End	180	—	120
S12 Quartz-tourmaline rock	Levant Mine area	SW366343	Land's End	270	350	29
S13 Quartz-tourmaline rock	Imperial Pit, Goonbarrow	SX013578	St. Austell	740	500	100
S14 Quartz-tourmaline rock	Rosewall Hill	SW496393	Land's End	410	120	120
S15 Quartz-tourmaline rock	Providence Mines area	SW522386	Land's End	300	270/140	50
S16 Hydrothermal breccia	Trelavour Downs	SW962572	St. Austell	320	1600	60
S17 Hydrothermal breccia	Wheal Remfry	SW924573	St. Austell	230	1400/2900	50

and pipelike masses, and certain tourmalinized granites and country rocks are essentially composed of quartz and tourmaline. Cornish tourmaline has been divided into 'magmatic' and 'hydrothermal' (blue, Mg-rich) affinites, a useful concept but misleadingly simple. In fifty or so rocks studied by EPM all tourmalines can be approximated chemically to the schorl–dravite series; a continuous variation between Fe and Mg endmembers has been noted. In the granites the 'MF' ratio, $Mg/(Mg+Fe)_{ionic}$, is more or less constant between coexisting primary tourmaline and biotite (e.g. EPM2-3). In terms of whole-rock Li we may note values of 107 ppm (fine-grained biotite granite, Hingston Down, east Cornwall), 1160 ppm (fine-grained granite with tourmaline and topaz, Castle-an-Dinas, north of the St. Austell mass), and 1710 ppm (Li-mica granite from Rinsey Cove, in the Tregonning–Godolphin outcrop). Microprobe results from four samples are described below, and illustrated in fig. 1.

Sample S1 is a Carnmenellis granite specimen divisible into two components; one fine-grained, porphyritic and biotite-rich, the other coarser and tourmaline-bearing. Textural relations suggest the partial tourmalinization of feldspar, and the development of tourmaline, muscovite, and fine-grained quartz after the primary biotite–quartz–feldspar sequence. The boundary of the two components is marked by a darkening of the feldspar in the coarser rock, due at least in part to the development of minute grains of iron oxide, perhaps representing an initial stage in tourmalinization (Lister, 1978). The two lithologies may differ only in the extent to which they were penetrated by a late B-rich fluid, the whole developing in one protracted episode of (re)crystallization and cooling. The Li data can be compared (fig. 1) with that for sample S2 (Goonbarrow Pit, St. Austell), a medium-grained feldsparphyric granite containing small amounts of muscovite and anhedral brown tourmaline. No distinction can be made in either S1 or S2 between Li concentrations in early- and late-crystallized portions of any one mineral, although the distribution between the species appears to be

$$\text{feldspar} < \text{quartz} < \text{tourmaline} < \text{muscovite} < \text{biotite}$$

with the bulk of Li concentrated into the volumetrically minor micas. Kaolinization does not appear to affect Li count rates in feldspars, whereas sericitization produces a sevenfold increase, indicative of Li concentration in the micaceous alteration product.

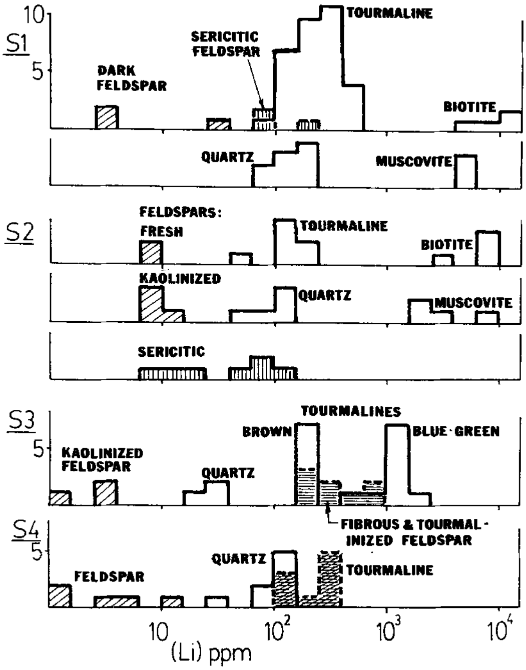

FIG. 1. Logarithmic–linear histograms of 141 ion microprobe Li analyses of minerals in Cornish granitic rocks. In figs. 1-5 only quartz and tourmaline analyses are corrected for matrix effects. Overlapping distributions are represented by dashed lines and shading.

Sample S3 (Conce Moor, St. Austell) is a striking sample of 'luxullianite' affinity; microscopically it consists mainly of turbid feldspar, quartz, and tourmaline. The latter can be divided into large brown crystals (MF23) and thin borders, sheaves and individual small grains of variable (frequently blue) colouration, averaging MF27-30. Fracture planes cutting the brown tourmaline may be infilled with fibres of blue tourmaline oriented parallel to the *c*-axis of the pre-existing crystal. Aligned secondary fibrous tourmaline is quite common in the Cornish rocks. It grows from a bristly 'root zone' along (frequently straight) margins with the earlier material, sometimes forming rims up to 0.5 mm wide. There appears to have been overgrowth of irregular primary brown tourmaline by later fibrous material, with no evidence of concomitant corrosion (Lister, 1978). A magmatic assemblage subjected to a postmagmatic fluid rich in B and alkalis (Alderton, 1979; Lister, 1979) is indicated by the partial replacement of feldspar by tourmaline, and by the sixfold increase in Li content from the brown to the (later) blue-green tourmaline. (Table III).

Pegmatite rich in quartz and tourmaline was recovered from a small pod in granite at Priests Cove. The relative age of these pegmatites, whose

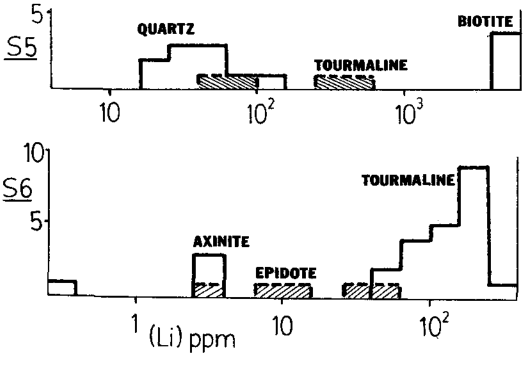

FIG. 2. Histograms of forty-eight Li analyses of minerals from rocks in the aureoles of two Cornish granites.

immediate surroundings are fine-grained albitized granite, is a matter for debate. By comparison with S1-3, the Li contents of S4 are consistent with a 'magmatic' origin.

Country rocks. Sample S5 is a tourmalinized biotite schist from the E contact of the Cligga Head granite stock. Analysis is hampered by the fine-grained nature of the rock, but the Li distribution between tourmaline and mica is clearly similar to that in the granites (fig. 2). Sample S6 is a metabasalt from the Crowns Rock, Botallack, in the aureole of the Land's End granite, substantially altered by CaFeB metasomatism. Large tourmaline grains, highly pleochroic in blues and browns, have grown in an epidote-rich matrix. Alderton and Jackson (1978) analysed seventeen local metabasalts by AAS, with Li from 15-241 ppm. An approximate mode for this rock and the apparent Li concentration (mostly found in tourmaline; 150 ppm) suggests a bulk composition for this sample of about 50 ppm.

Greisens and other F-rich rocks. Greisen S7 (Cligga Head) is a quartz-mica rock with minor tourmaline and accessory ores. The quartz occurs as small (0.1-0.2 mm) grains and as large (2-4 mm) hexagonal prisms containing elongate inclusions aligned about the *c*-axis. The mica is largely fine-grained muscovitic material, with a number of larger grains of protolithionite (substantially altered to muscovite). Both quartz fractions appear to contain the same amount of Li (80 ppm), and no Li zoning was detected in the large prisms, although both results may be limited by the poor analytical precision. Tourmaline and mica contain 470 and 4200 (apparent) ppm Li respectively, also undifferentiated by type. Sample S8 (Goonbarrow) is a tourmaline-bearing greisened elvan similar to an Li-rich specimen from the same china clay pit (two greisened elvans were each analysed twice by AAS, and found to have bulk Li contents of 43/45 and 4780/4800 ppm respectively; see discussion section). Similar partitioning between quartz, tourmaline and mica is indicated, with apparent concentrations of Li in discrete grains and fine-grained pseudomorphs of mica after feldspar of 3600 and 12 000 ppm respectively.

In the quartz-tourmaline-topaz rock from St. Mewan Beacon topaz and tourmaline have irregular mutual contacts, interpreted in terms of more or less simultaneous growth. Tourmaline in particular may display anhedral embayments in otherwise quite regular prism forms. The striking range in apparent Li concentrations (S9, fig. 3) seems to confirm that F is important in Li transport, and that F-rich materials may be either enriched or depleted in Li, depending on the affinity of Li for the crystallizing phases. F seems to associate with aluminosilicates at the melt stage (Manning, 1981). The apparent mean result of 0.4 ppm for topaz is consistent with Li preferentially substituting for (MgFe) wherever possible. It has been suggested that rock of this composition may have a magmatic origin at about 600 °C, a possibility attested by fluid inclusion work (Eadington and Nashar, 1978) and by some experimental studies (e.g. Manning, 1980).

Quartz-tourmaline assemblages. The mode of a sample from the quartz-tourmaline mass of the Roche Rock (S10) is roughly 80% quartz (containing submicroscopic inclusions) and 20% pleochroic schorl (MFO-14). The average Li concentration was found to be 340 ppm (Power [1968]

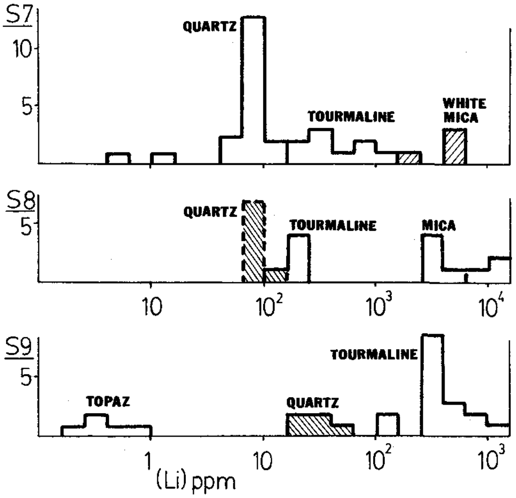

FIG. 3. Histograms of eighty Li analyses of minerals in Cornish F-rich rocks. The micas in S8 divide into two apparent groups; one with lower Li in lath-like discrete grains, and a second with higher Li in aggregates pseudomorphing feldspar phenocrysts.

quotes values of 294 and 319 ppm for Roche Rock tourmaline, determined by emission spectrography). Based on only four analyses, the mean quartz value of 220 ppm is the highest encountered in this study. Quartz data are discussed further later.

Sample S11 is notable for a 90% modal proportion of blue-brown pleochroic tourmaline. The tourmaline, which displays strong concentric zoning, forms an example of 'cockle' gangue overlying a 'carbonas', an irregular Sn-bearing ore body, near Botallack. Eight tourmaline analyses gave a mean Li concentration of 180 ppm, and four more, obtained by localized isotope dilution during the matrix factor determination, averaged 190 ppm. The nearby metasomatized metabasalt (S6) has tourmaline of similar appearance, Li (150 ppm) and major element composition (EPM4-5). This suggests that the two formed during the same metasomatic episode. These tourmaline-rich rocks are thought by Jackson (1974) to serve as a lithological control on later tin ore deposition.

In a coarse-grained quartz-schorl (MFO-16) rock from the Levant Mine area (S12), thin-zoned rims give a slightly higher Li value (350 as opposed to 270 ppm) than the central material in the tourmaline crystals. The quartz (which contains minor fibrous chalcedonic silica) has a mean Li concentration of 29 ppm. A sample (from the Wheal Edward Mine) of quartz-Fe oxide-chalcedony vein material gave a value of 47 ppm by isotope dilution. It is hard to judge from the few samples available whether or not low Li values correlate with the presence of chalcedonic silica in the veins.

The next three samples all display the phenomenon of multiple 'generations' of tourmaline seen in the luxullianite S3. S13 (Goonbarrow Pit) contains scattered yellow-brown schorl grains, a felted mass of fine-grained deep blue tourmaline, and acicular material in part aggregated into radial 'suns'. Unfortunately no analyses were obtained of the minor brown phase. The later forms are essentially pure schorl, an observation at variance with a straight correlation of magnesian compositions with 'hydrothermal' tourmaline. S14 (Rosewall Hill Mine, St. Ives) is somewhat similar, with large yellow grains, dark green to colourless granules and prisms, and pale needles in late quartz veinlets. Some of the large grains are fractured, and penetrated by the dark green material (containing disseminated minor cassiterite) which has a lower Li content.

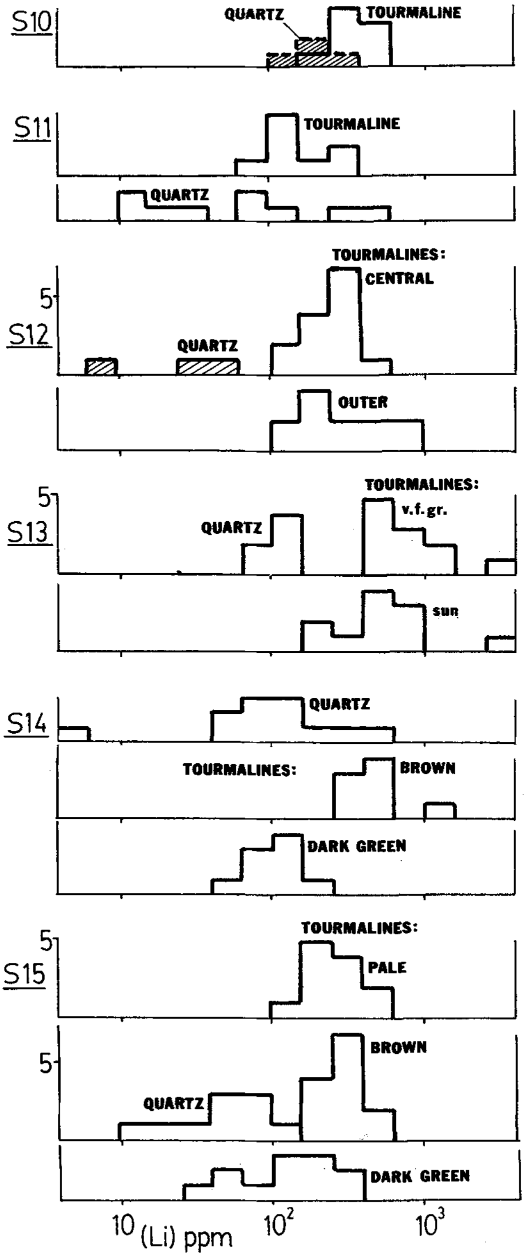

FIG. 4. Histograms of 167 Li analyses of minerals in Cornish quartz-tourmaline rocks. S11 data also include two quartz values in the 0.16–0.4 ppm range.

Sample S15 (Providence Mines area, St. Ives) shows clear evidence for multistage development of both quartz and tourmaline. Large euhedral crystals of clear quartz are surrounded by anhedral quartz granules and radial-fibrous growths of inclusion-filled chalcedonic silica. Mean Li concentration in the quartz is 50 ppm. Much of the tourmaline consists of composite grains with yellow cores surrounded by rims of colourless material, often with a break in optical continuity between the two. Dark green tourmaline, as thin outer rims and as small discrete prisms, constitutes a third 'generation'. Fibrous growths are seen along fractures, of the second form in the first, and of the third type in both of the earlier forms. The major element compositions (EPM6–8) vary widely, with mean MF values of 17, 96, and 37. Mean Li concentrations are 300, 270, and 140 ppm respectively (fig. 4).

Hydrothermal breccias. The previous examples have shown that point analyses of composite grains can reveal something of the evolution of vein fluids with time. Cornish hydrothermal breccias contain clasts of granite and country rock in quartz–tourmaline matrix material. The best-exposed example, that at Wheal Remfry on the west margin of the St. Austell granite, contains clasts of variable shape and size ranging from mm to tens of cm. The origin of such pipe-like bodies has commonly been ascribed to the upward-drilling action of a fluidized suspension of debris in a volatile-rich melt. Wolfe (1980) has proposed an alternative mechanism for the formation of near-surface breccia pipes of this sort by downward-propagating explosive fracturing initiated by magmatic superheating of meteoric waters. Jackson (1979) classified breccia pipes and CaFeB metasomatism (of the type mentioned for S6/11) in the earliest of four phases of mineralization associated with the granites.

Breccia S16 (Trelavour Downs) contains clasts of tourmalinized laminated schist and silicified granite and elvan-like material in a matrix of pale tourmaline and inclusion-filled quartz. The matrix tourmaline comprises scattered large brown crystals (MF18) in a seriate mixture of quartz and felted/acicular tourmaline (MF50). Oriented secondary blue fibres may develop on the large brown material. The fine-grained tourmaline displays a fivefold increase in Li relative to the earlier brown crystals (Table III). The fibrous material displays a similar enrichment and is probably contemporaneous; the greater scatter of results is probably due to the problems of marginal contamination inevitable with fine-grained material.

Breccia S17 is from Wheal Remfry, containing clasts of tourmalinized schist, kaolinized granite, and milky quartz. Topaz is an accessory in both matrix and granite clasts. Orthoclase and albite are turbid due to kaolinite and minor sericite, and EPM analyses reveal minor Fe. The tourmaline is pleochroic from a neutral or yellow shade to an intense inky blue, variably Fe-rich and often with incomplete deep blue margins. The largest tourmaline grains occur in the granite clasts; this material is the most irregular in form. Some fibrous blue tourmaline (M78) is present as the familiar overgrowths. There is a sixfold Li enrichment from the granite's coarse tourmaline to the fine-grained matrix material, and the average concentration in the fibrous material is twice that of the matrix, the overall sequence being 230–1400–2900 ppm (fig. 5). Low Li values for occasional large grains in the matrix support a xenocrystal origin. The mean value for the quartz is 50 ppm. Three isotope dilution results from quartz in a vein cutting the breccia gave a mean result of 64 ppm. This vein contains slivers of tourmalinized country rock; quartz (±tourmaline) veins were probably intruded in the area before, during and after the formation of the breccia body itself. The feldspars have an apparent Li content of 2 ppm, further evidence that Li is not significantly deposited during kaolinization.

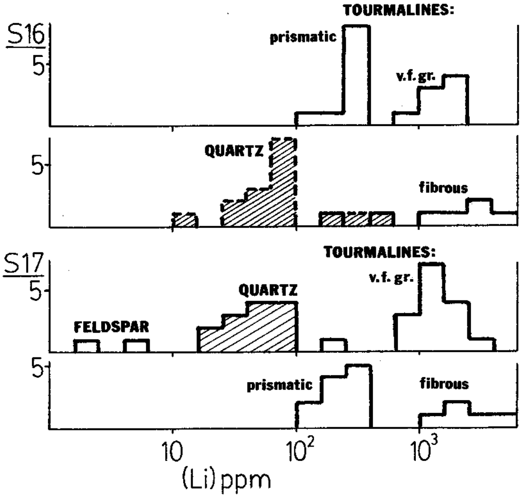

FIG. 5. Histograms of ninety Li analyses of minerals in Cornish hydrothermal breccias. S17 data also include two feldspar values in the 0.16–0.63 ppm range.

Discussion and conclusion

As stated earlier, analyses of quartz are likely to be somewhat less accurate than those of tourmaline. Most of the quartz results are in the 20–120 ppm range. The matrix factor for quartz is low (0.5 ± 0.2), but more important is the possible affect of Li-rich inclusions. On the basis of experience gained, it should be possible to define the matrix corrections more accurately in future.

Isotope dilution of schorl from a tourmaline granite at Porth Ledden near Cape Cornwall gave a Li result of 260 ppm. Suggestions have been made that this, the Priests Cove pegmatite and the Roche Rock outcrop are late magmatic products, due to processes of liquid immiscibility and/or solidus-lowering by volatiles in the granite system. In each case the Li concentration is consistent with these ideas; clearly it cannot prove the case either way. The same is true for the St. Mewan Beacon topaz rock, whose tourmaline gives higher and more scattered Li results.

Stable isotope work on O and H (Sheppard, 1977) indicates that much of the kaolinization may be of late, supergene origin. Charoy (1975) cited a case of a hydrothermal kaolin deposit in Brittany. Both possibilities must be considered for any particular example. Alderton *et al.* (1980) quote two Cornish examples in which Li content rises by factors of 1.87 and 7.38 in argillic and sericitic alteration respectively. Dangerfield *et al.* (1980) found that kaolinization had no systematic effect on whole-rock Li. Ion probe evidence reinforces the finding that whilst coarse-grained sericite is likely to be a hydrothermal development, there is no visible link between the kaolinization process and Li mobility.

Lowering of the granite solidus by H_2O, F, B, and Li may have retarded crystallization to some extent, allowing high-level emplacement with minimal contact metamorphism, as suggested for some Erzgebirge granites (Bankwitz, 1978). Greisens may be enriched or depleted in Li, as indicated by the data from Goonbarrow. The occurrence of such variation is probably indicative of discrete phases of greisen formation; the time scale is adequate, as some greisens clearly postdate the elvans, themselves intruded perhaps 20 Ma later than the granite (Hawkes and Dangerfield, 1978). It may also be noted that the general absence of Li minerals such as spodumene from Cornish rocks may be due to an overall activity for F much in excess of that of Li at the relevant time (cf. Palchen and Tischendorf, 1978).

The general association of Li with the volatiles B and F is no absolute guarantee of final distribution. Two factors must be considered; the preferred sites for Li in a given assemblage and the availability of Li. Axinite and tourmaline are both B cyclosilicates, yet in the Crowns metabasalt S6 most of the Li appears to reside in the latter. This may be evidence of genuine partitioning, or of an influx of Li-rich volatiles when the later tourmaline crystallized. The extra possibility of high mobility of Li in the presence of excess F may explain the very low topaz result, and certain low mica (greisen) data (cf. Dangerfield *et al.*, 1980 concerning 'gilbertite' mica).

In conclusion, this first application of the ion probe to trace element analysis in Cornish rocks demonstrates the value of the technique. An increasing Li content in the sequence

topaz < feldspar < quartz < tourmaline < mica

is convincingly displayed. It seems likely that Li concentrated in the residual fluids as the primary crystallization proceeded, and that the element was then distributed in receptive phases over a period of perhaps 30 Ma, with local concentration on a microscopic scale (e.g. high-Li fibrous tourmaline) and a whole-rock scale (e.g. greisens). It is probable that Li may be remobilized on occasion, as in the case of U released during tourmalinization of micaceous granites suggested by Simpson *et al.* (1979).

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