Alkali-deficient tourmaline from the Sullivan Pb-Zn-Ag deposit, British Columbia

SHAO-YONG JIANG[1,2], MARTIN R. PALMER[1] AND JOHN F. SLACK[3]

[1] Department of Geology, University of Bristol, Bristol, BS8 1RJ, UK
[2] Max-Planck-Institut für Chemie, Abt. Geochemie, Postfach 3060, 55020 Mainz, Germany
[3] U.S. Geological Survey, National Center, MS 954, Reston, VA 20192, USA

Abstract

Alkali-deficient tourmalines are found in albitized rocks from the hanging-wall of the Sullivan Pb-Zn-Ag deposit (British Columbia, Canada). They approximate the Mg-equivalent of foitite with an idealized formula $\square(Mg_2Al)Al_6Si_6O_{18}(BO_3)_3(OH)_4$. Major chemical substitutions in the tourmalines are the alkali-defect type $[Na^*_{(X)} + Mg^*_{(Y)} = \square_{(X)} + Al_{(Y)}]$ and the uvite type $[Na^*_{(X)} + Al_{(Y)} = Ca_{(X)} + Mg^*_{(Y)}]$, where $Na^* = Na + K$, $Mg^* = Mg + Fe + Mn$. The occurrence of these alkali-deficient tourmalines reflects a unique geochemical environment that is either alkali-depleted overall or one in which the alkalis preferentially partitioned into coexisting minerals (e.g. albite).

Some of the alkali-deficient tourmalines have unusually high Mn contents (up to 1.5 wt.% MnO) compared to other Sullivan tourmalines. Manganese has a strong preference for incorporation into coexisting garnet and carbonate at Sullivan, thus many tourmalines in Mn-rich rocks are poor in Mn (<0.2 wt.% MnO). It appears that the dominant controls over the occurrence of Mn-rich tourmalines at Sullivan are the local availability of Mn and the lack of other coexisting minerals that may preferentially incorporate Mn into their structures.

KEYWORDS: alkali-deficient tourmaline, Mn enrichment, hydrothermal alteration, Sullivan mine, Pb-Zn-Ag deposit, British Columbia.

Introduction

TOURMALINE is a structurally and chemically complex borosilicate mineral with the general formula $XY_3Z_6Si_6O_{18}(BO_3)_3W_4$, where $X = Na^+$, Ca^{2+}, K^+, vacancy $(\square)$; $Y = Mg^{2+}$, Fe^{2+}, Mn^{2+}, Al^{3+}, Fe^{3+}, Mn^{3+}, Cr^{3+}, Li^+; $Z = Al^{3+}$, Mg^{2+}, Fe^{3+}, Cr^{3+}, V^{3+}, and $W = O^{2-}$, OH^-, F^-, Cl^-. The main compositional varieties in nature are Na- and Mg-rich dravite, Na- and Fe-rich schorl, Ca- and Mg-rich uvite, and Na- and Li-rich elbaite (e.g. Deer et al., 1962; Dietrich, 1985). Alkali-deficient tourmaline in which a vacancy is dominant in the X-site (i.e. $0 \leqslant X_{total} < 0.5$) has been synthesized in the laboratory (Rosenberg and Foit, 1979; Werding and Schreyer, 1984). However, highly alkali-deficient tourmalines in nature are relatively uncommon and only a limited number of occurrences have been reported (El-Hinnawi and Hofmann, 1966; Byerly et al., 1986; Bandyopadhyay et al., 1993; MacDonald et al., 1993; Fuchs and Maury, 1995; Selway et al., 1995), although tourmaline with substantial X-site vacancies (i.e. $0.5 < X_{total} < 1$) are found in many rock types (e.g. Werding and Schreyer, 1984; Byerly et al., 1986; Henry and Dutrow, 1990). In this paper, we report an occurrence of alkali-deficient tourmaline from the Sullivan Pb-Zn-Ag deposit, British Columbia, and emphasize its compositional variations, chemical substitutions, and significance in constraining its formational environment.

Geology

The Sullivan Pb-Zn-Ag deposit is a giant, stratiform, sediment-hosted exhalative (sedex-type) sulphide orebody, hosted within clastic metasedimentary rocks of the Middle Proterozoic Aldridge Formation (Hamilton et al., 1982; Höy, 1993). Tourmaline is abundant at Sullivan, particularly in the footwall, where a large funnel-shaped tourmalinite pipe extends to a depth of at least 550 m below the massive sulphide orebody (Shaw et al., 1993a). In the upper portion of the tourmalinite pipe is a discordant fragmental body of breccias (tourmalinite, sedimen-

tary rocks, and sulphide ores) and an extensive network of irregular sulphide-quartz-carbonate veinlets (<50 m from the base of the orebody). Chlorite-pyrrhotite alteration is present in the upper portion of the tourmalinite pipe, and usually is in contact with or cuts the tourmalinite.

Tourmaline occurs in the hanging-wall of the deposit in lesser amounts as relict facies of tourmalinite that have been overprinted by albite-chlorite-pyrite alteration, or as disseminated grains in albite-chlorite-pyrite altered rocks and in sulphide ores. The albite-chlorite-pyrite alteration forms an irregular zone 900 m in diameter and up to 150 m thick (Shaw *et al.*, 1993*b*). This zone comprises a basal layer of intensely altered chlorite-pyrite rocks, an overlying zone of massive, bedded, or brecciated albite-rich rocks, and a peripheral zone of slightly to intensely altered rocks rich in albite, chlorite, and pyrite that surrounds and overlies the albite rocks (Hamilton *et al.*, 1982; Shaw *et al.*, 1993*b*). The absence of base metals in this assemblage suggests that this alteration was not directly related to ore formation, but was associated with intrusion of a postore gabbro sill (Hamilton *et al.*, 1982; Turner and Leitch, 1992).

Sampling and analytical methods

Alkali-deficient tourmaline has mainly been found in two samples (JS-93-22D and SY-5864-2) from the hanging-wall of the deposit. JS-93-22D is a tourmaline-rich albitized rock, and SY-5864-2 is a tourmaline-bearing albitite breccia, both collected from the heart of the hanging-wall albite-chlorite-pyrite alteration zone ~15 m stratigraphically above the massive sulphide orebody. Analyses of these two samples come from a large electron microprobe database acquired on ~40 samples from Sullivan, including > 1000 analyses of tourmaline (Jiang, 1995).

Microprobe analyses were obtained by wavelength dispersive spectrometry method (WDS) at the University of Bristol, using a JEOL JXA-8600 Superprobe equipped with a Link AN 10/85s analyzer and LEMAS automation, operated at 15 kV accelerating voltage, a beam current of 15 nA, a beam diameter of 1−2 μm, and a ZAF correction scheme. Standards used were natural minerals and synthetic compounds, including; SiO_2 (Si), $MgAl_2O_4$ (Al), $SrTiO_3$ (Ti), Fe_2O_3 (Fe), olivine (Mg), MnO (Mn), $CaSiO_3$ (Ca), albite (Na), adularia (K), MgF_2 (F), and a pantellerite glass (Cl).

Petrography

Sample JS-93-22D has a simple mineral assemblage consisting mainly of albite (An_0), quartz, and tourmaline. Sulphides (pyrrhotite and pyrite) locally are enriched in the sample as irregular patches or layers. The sample shows a typical annealed texture between albite and tourmaline. Tourmaline comprises ~20% by volume of the sample, forming euhedral to subhedral crystals with a yellowish colour. A slight optical zonation can be seen in the tourmaline, with a pale core and dark rim. The size of the tourmaline grains is generally 15−35 μm in the cross-sectional dimension, which is slightly coarser than the majority of the fine-grained tourmalines (<10 μm) at Sullivan (Jiang, 1995).

Sample SY-5864-2 is from an albitite breccia with minor tourmaline (~10% by volume). The tourmaline is very fine-grained (6−15 μm in length), subhedral to anhedral, and amber in colour. No optical zoning has been observed in the sample.

Chemical compositions

Representative microprobe data for alkali-deficient tourmaline from Sullivan are listed in Table 1, with calculations of unit formulae based on 24.5 oxygens. Large compositional variations occur for FeO (4.14−8.00 wt.%), MgO (4.08−6.88 wt.%), CaO (0.96−2.12 wt.%), and Na_2O (0.16−1.03 wt.%). TiO_2 contents are generally low (0.09−0.78 wt.%). Concentrations of F and Cl are negligible. The MnO contents of the tourmaline in sample SY-5864-2 are very low, but are unusually high in sample JS-93-22D (0.21−1.48 wt.%) compared to the generally low-Mn nature of the other Sullivan tourmalines (typically <0.2 wt.% MnO) (Jiang, 1995). In sample JS-93-22D, tourmalines associated with or included in sulphides have lower MnO (0.21−0.37 wt.%) than those without associated sulphides (0.94−1.48 wt.%) (Table 1).

Tourmaline compositions at Sullivan belong largely to two common solid-solution series: (Na−Fe) schorl–(Na−Mg) dravite and (Na−Mg) dravite–(Ca−Mg) uvite (Ethier and Campbell, 1977; Leitch, 1992; Jiang, 1995). Most of the tourmalines from the hanging-wall belong to the dravite–uvite solid solution series (Jiang, 1995). Tourmalines in samples JS-93-22D and SY-5864-2 have unusually low X-site totals (mostly <0.5 apfu), indicating a dominant vacancy (□) has replaced Na or Ca (Table 1, Fig. 1). This suggests that tourmaline in the samples is not part of the dravite-uvite solid-solution, but rather belongs to the alkali-deficient tourmaline series.

Chemical substitutions

Chemical substitutions in tourmaline occur predominantly in the X, Y, and Z sites. They take place as homovalent cation exchanges at a single site, such as

TABLE 1. Representative electron-microprobe analyses of the alkali-deficient tourmalines at Sullivan

	JS-93-22D 2a core	JS-93-22D 2b rim	JS-93-22D 7a core	JS-93-22D 7b rim	JS-93-22D 9a core	JS-93-22D 9b rim	SY-5864-2 1	SY-5864-2 4
SiO_2	35.96	35.92	36.87	35.25	36.28	36.31	36.37	36.81
TiO_2	0.09	0.37	0.22	0.62	0.24	0.78	0.22	0.35
Al_2O_3	35.60	34.30	34.77	34.50	35.71	34.21	35.28	33.90
FeO*	4.77	5.63	5.14	6.89	6.74	7.58	8.00	4.14
MgO	5.27	5.67	5.34	4.93	4.77	5.59	4.08	6.88
MnO	1.48	1.25	0.94	1.10	0.37	0.21	–	0.05
CaO	1.18	1.36	1.16	2.12	1.44	1.73	0.96	1.44
Na_2O	0.82	1.03	0.78	0.16	0.40	0.40	0.88	0.68
K_2O	0.05	0.06	0.06	0.06	0.09	0.09	0.08	0.04
F	0.09	–	–	–	–	–	–	0.34
Cl	–	0.01	0.01	0.02	–	0.02	0.03	–
Total	85.31	85.60	85.28	85.65	86.03	86.91	85.90	84.64

Structural formulae on the basis of 24.5 Oxygens

Si	5.866	5.877	5.997	5.800	5.883	5.875	5.934	6.009
Al	6.845	6.614	6.666	6.688	6.824	6.524	6.784	6.523
$Al_{(T)}$	0.134	0.123	0.003	0.200	0.117	0.125	0.066	0.000
$Al_{(Z)}$	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000
$Al_{(Y)}$	0.711	0.491	0.663	0.488	0.708	0.399	0.719	0.523
Ti	0.011	0.046	0.027	0.077	0.029	0.095	0.027	0.043
Fe	0.650	0.770	0.699	0.948	0.914	1.025	1.091	0.565
Mg	1.283	1.383	1.295	1.208	1.153	1.348	0.993	1.674
Mn	0.204	0.173	0.129	0.153	0.050	0.029	0.000	0.007
$Y_{(Total)}$	2.859	2.862	2.813	2.873	2.854	2.897	2.830	2.812
Fe/(Fe+Mg)	0.336	0.358	0.350	0.440	0.442	0.432	0.524	0.252
Ca	0.207	0.239	0.202	0.373	0.250	0.299	0.168	0.252
Na	0.260	0.326	0.245	0.052	0.125	0.124	0.279	0.215
K	0.010	0.013	0.012	0.014	0.019	0.018	0.017	0.009
$X_{(Total)}$	0.477	0.579	0.458	0.439	0.393	0.442	0.464	0.476
Na/(Na+Ca)	0.557	0.577	0.548	0.121	0.333	0.293	0.624	0.460

* Total iron as FeO
– Below detectable limit

substitution of Mg^{2+} for Fe^{2+} in the Y site, or as heterovalent coupled substitutions among several sites, such as the alkali-defect type of substitution: $R^+_{(X)} + R^{2+}_{(Y)} = \square_{(X)} + R^{3+}_{(Y)}$, where $R^+ = Na$, $R^{2+} = Fe$ or Mg, $R^{3+} = Al$, and $\square$ = vacancy (Foit and Rosenberg, 1977; Henry and Guidotti, 1985).

Alkali-deficient tourmaline (foitite) has been reported by Foit et al. (1989) and MacDonald et al. (1993) with the ideal formula $\square[Fe^{2+}_2(Al,Fe^{3+})]Al_6Si_6O_{18}(BO_3)_3(OH)_4$. Foitite can be derived from schorl [$NaFe^{2+}_3Al_6Si_6O_{18}(BO_3)_3(OH)_4$] by the substitution $\square_{(X)} + Al_{(Y)} = Na_{(X)} + Fe^{2+}_{(Y)}$ (MacDonald et al., 1993). Selway et al. (1995) reported another alkali-deficient tourmaline with the ideal formula $\square(Al_2Li)Al_6Si_6O_{18}(BO_3)_3(OH)_4$. This alkali-deficient Li-tourmaline can be derived either from the

foitite formula by the substitution $2Fe^{2+} = Li + Al$ or from the elbaite formula $Na(Al_2Li)Al_6Si_6O_{18}$ $(BO_3)_3(OH)_4$ by $Na = \square$. Hence, the only unreported alkali-deficient tourmaline in nature is the Mg-equivalent of foitite with $Y = Mg_2Al$ (cf. MacDonald et al., 1993), although this composition has been synthesized in the laboratory (Rosenberg and Foit, 1979; Werding and Schreyer, 1984) and its relationship to general tourmaline stoichiometry has been discussed (Burt, 1989; Foit et al. 1989). In the alkali-deficient tourmaline from Sullivan, Mg is predominant (i.e. Mg > Fe) in the Y site (Table 1), indicating that this tourmaline belongs to the Mg equivalent of foitite with an idealized formula $\square(Mg_2Al)Al_6Si_6O_{18}(BO_3)_3(OH)_4$ (cf. MacDonald et al., 1993).

Alkali-deficient tourmaline
(X =□)

Dravite (or Schorl)   50   Uvite
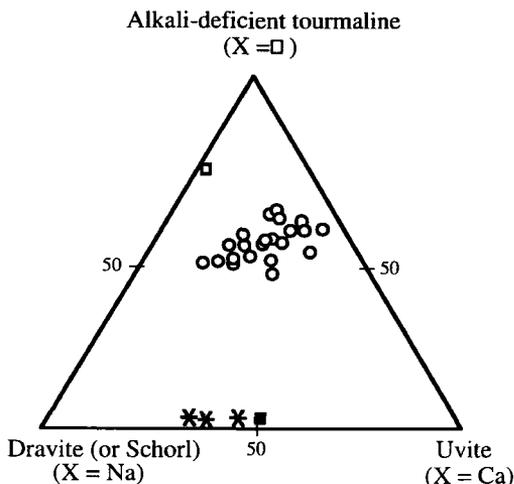(X = Na)   (X = Ca)

FIG. 1. Ternary plot of electron-microprobe data outlined by the end-members alkali-deficient tourmaline, dravite (or schorl), and uvite. Open circles represent alkali-deficient tourmaline from the Sullivan mine (this study); open square represents foitite from southern California (MacDonald et al., 1993); solid square represents Mn-rich uvite from the Arnold mine, New York (Ayuso and Brown, 1984); asterisks represent Mn-rich dravite–uvite from the Olary district, South Australia (J.F. Slack, unpub. data).

On plots of $Na^*_{(X)} + Mg^*_{(Y)}$ vs. $\square + Al_{(Y)}$ (Fig. 2) and $Ca_{(X)} + Mg^*_{(Y)}$ vs. $Na^*_{(X)} + Al_{(Y)}$ (Fig. 3) , where $Mg^* = Mg + Fe + Mn$, $Na^* = Na + K$, $\square = $ X-site vacancy, the Sullivan tourmaline data fall on approximately linear arrays, suggesting that the major chemical substitutions are the alkali-defect type ($\square AlNa^*_{-1}Mg^*_{-1}$) and the uvite type ($Na^*AlCa^*_{-1}Mg^*_{-1}$), although there maybe other substitutions that contribute to the antithetical relations (cf. Foit and Rosenberg, 1977; Henry and Guidotti, 1985). In addition, the slight dispersion of data involving the Mg* constituents in Figs 2 and 3 may partly be caused by unknown proportions of Fe^{3+} in the tourmalines. Where X-site vacancy develops via the substitution $\square AlNa^*_{-1}Mg^*_{-1}$, another important mechanism of Ca-incorporation in aluminous tourmaline is the substitution $CaMg^*_{-1}Al_{-1}(OH)_{-1}$ as suggested by Henry and Dutrow (1990). However, the poor correlation between Ca and X-site vacancy ($\square$) (Fig. 4b) suggests that this substitution is not important at Sullivan, whereas the inverse correlation between Ca and Na (Fig. 4a) indicates that the uvite type substitution is important.
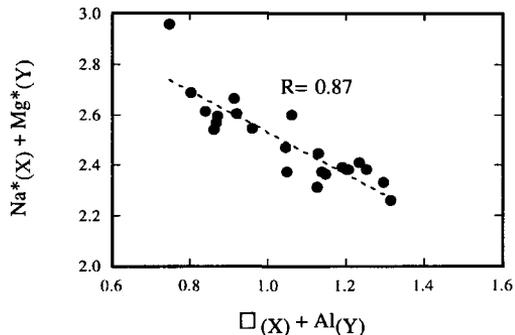

FIG. 2. Plot of $\square_{(X)} + Al_{(Y)}$ vs. $Na^*_{(X)} + Mg^*_{(Y)}$, showing alkali-defect substitution in tourmaline. The * denotes multicomponent compositions: $Na^* = Na + K$, $Mg^* = Mg + Fe + Mn$. Dashed line represents a linear least squares fit to the data.

Discussion

X-site vacancies are common in most natural tourmalines. However, tourmaline with more than 50% vacancy in the X site is relatively rare due to the unusual geochemical environment necessary for its formation, i.e. peraluminous and alkali deficient (Werding and Schreyer, 1984; Henry and Dutrow, 1990; MacDonald et al., 1993). Tourmalines within volcanic-hosted mineral deposits are particularly likely to show major alkali deficiencies (e.g. Foit et al., 1989; Slack and Coad, 1989; Barrett et al., 1993; Bandyopadhyay et al., 1993; Fuchs and Maury, 1995). These tourmaline compositions reflect hydrothermal leaching of Na, Ca, and generally K within the footwall rocks underlying the deposits, a process which may take place prior to and/or during tourmaline formation.
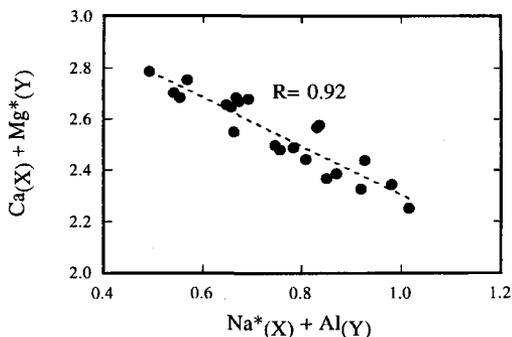

FIG. 3. Plot of $Na^* + Al_{(Y)}$ vs. $Ca_{(X)} + Mg^*_{(Y)}$, showing uvite substitution in tourmaline. Symbols as in Fig. 2.
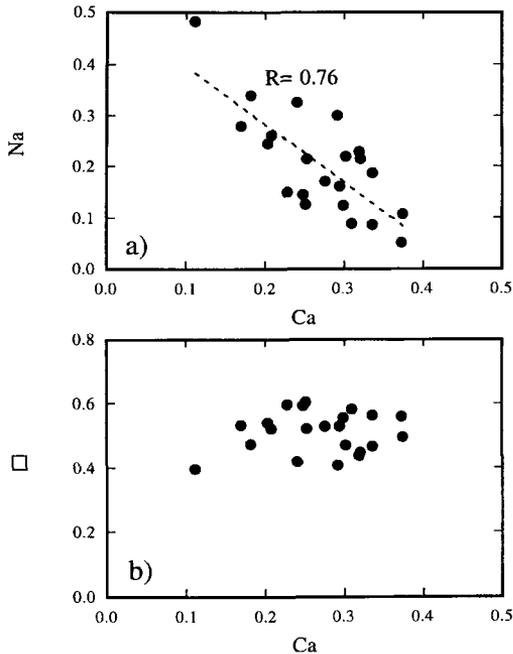
FIG. 4. (*a*) Correlation between Ca and Na in tourmaline; and (*b*) Correlation between Ca and □ in tourmaline. Symbols as in Fig. 2.

The majority of tourmalines from Sullivan have only limited X-site vacancies (i.e. X_{total} approaching unity) that records the Na- or Ca-enriched nature of the hydrothermal fluids responsible for their formation (see Ethier and Campbell, 1977; Jiang, 1995). A detailed microprobe study revealed that most of the tourmalines in the footwall of the Sullivan orebody belong to the dravite-schorl solid-solution series, while those from the hanging-wall mainly belong to the dravite-uvite series (Jiang, 1995). No significant X-site vacancy (i.e. $X_{total} < 0.5$) has been found in the footwall tourmalines, except for one feruvite sample that displays an X-site vacancy of 0.54 apfu (Jiang *et al.*, 1996*a*). In contrast, feruvite from the hanging-wall shows larger proportions of X-site vacancy and is more aluminous than that from the footwall. We suggest that this compositional difference reflects the nature of the evolved hydrothermal fluids responsible for the albitization. This is supported by the observation that the alkali-deficient feruvite (JS-93-10-5) is closely associated with albite (Jiang *et al.*, 1996*a*). The alkali-deficient tourmalines from the hanging-wall of the Sullivan orebody are from albitized rocks. Hence, these alkali-deficient tourmalines may have formed due to the partitioning of Na

into albite during albitization. However, this hypothesis needs to be tested further as there are many occurrences of Na-rich tourmaline coexisting with albitic plagioclase in metapelitic rocks (e.g. Henry and Guidotti, 1985). Alternatively, the alkali-deficient tourmalines at Sullivan may have crystallized from hydrothermal fluids that became depleted in alkalis as a result of forming albite.

Some of the Sullivan alkali-deficient tourmalines (JS-93-22D) have unusually high Mn (up to 1.48 wt.% MnO) compared to other Sullivan tourmalines (typically <0.2 wt.% MnO) (Jiang, 1995). Tourmaline with a high Mn content is comparatively rare, and is generally associated with Na–Li pegmatites, where it occurs within the elbaite-schorl solid solution series (Slivko, 1961; Leckebusch, 1978; Sahama *et al.*, 1979). The highest Mn contents in this tourmaline variety are 8.21 wt.% MnO (Kunitz, 1929) and 8.86 wt.% MnO (Shigley *et al.*, 1986). Mn-rich tourmaline in the uvite–dravite solid-solution series was reported by Ayuso and Brown (1984) from the Arnold talc mine, New York, with up to 4.34 wt.% MnO. An Fe^{3+}-bearing dravite–uvite containing $1.1-1.6$ wt.% MnO has also been identified in piemontite-rich rocks of the Olary district, South Australia (cf. Ashley, 1984) by one of us (J.F. Slack, unpub. data, 1989). Both the Arnold mine and Olary district Mn-rich tourmalines lack X-site vacancies (Fig. 1). The only reported Mn-rich alkali-deficient tourmaline is foitite with 1.71 wt.% MnO described by MacDonald *et al.* (1993).

Compared to Mn-rich tourmalines elsewhere (Sahama *et al.*, 1979; Ayuso and Brown, 1984; Schmetzer and Bank, 1984; Shigley *et al.*, 1986; Burns *et al.*, 1994), the Mn content of the Sullivan alkali-deficient tourmalines (JS-93-22D) is not high. However, the presence of this relatively Mn-rich tourmaline, compared to the generally Mn-poor tourmaline at Sullivan, has important implications for its formational environments. The Mn-rich host rocks containing tourmaline are common in the immediate footwall at Sullivan, especially where Mn-garnet-bearing tourmalinite occurs locally (Slack, 1993; Slack *et al.*, 1995). Tourmaline is also locally associated with other Mn-rich minerals at Sullivan including chlorite, ilmenite, tremolite, and carbonate (Leitch, 1992; Jiang, 1995; Jiang *et al.*, 1996*b*). However, these tourmalines contain only minor Mn (<0.2 wt.% MnO), as Mn is preferentially incorporated into silicates, carbonates, oxides, and/or other coexisting phases (Jiang, 1995). The strong partitioning of Mn into coexisting silicates is supported by experimental synthesis work in the binary system tsilaisite–dravite (Haralampiev and Grover, 1993, 1994).

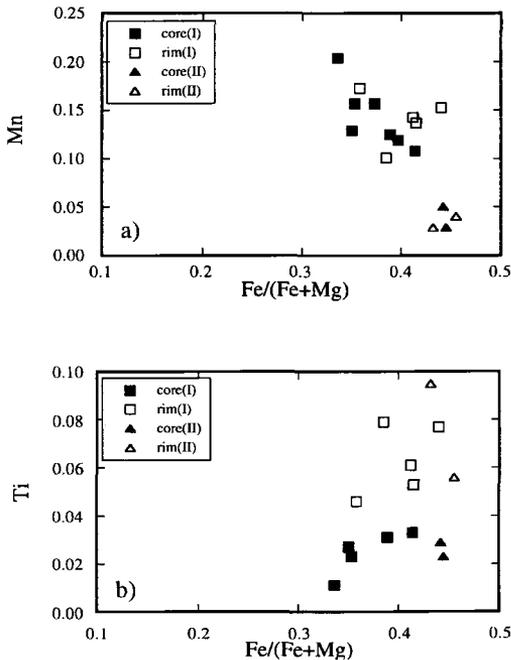The presence of Mn-rich alkali-deficient tourmaline at Sullivan appears to have been controlled by

FIG. 5. (*a*) Plot of Fe/(Fe+Mg) *vs.* Mn; (*b*) Plot of Fe/(Fe+Mg) *vs.* Ti for the Mn-rich, alkali-deficient tourmaline at Sullivan (sample JS-93-22D). Squares represent tourmalines associated with silicates (I); triangles represent tourmalines associated with sulphides (II). Solid symbols represent tourmaline cores; open symbols represent tourmaline rims.

FIG. 6. (*a*) Plot of Fe/(Fe+Mg) *vs.* Na/(Na+Ca); (*b*) Plot of Fe/(Fe+Mg) *vs.* X-site vacancy (□) for the Mn-rich, alkali-deficient tourmaline at Sullivan (sample JS-93-22D). Symbols as in Fig. 5.

the local availability of Mn and the lack of other coexisting minerals that preferentially incorporated Mn into their structures. The scale of equilibration may be small as tourmalines immediately associated with, or included within, sulphides have lower Mn contents than those without associated sulphides in the same thin section (Table 1, Fig. 5*a*). The sulphide-related tourmalines are also characterized by higher Fe/(Fe+Mg) ratios. It is likely that this sulphide-related microenvironment has lower Mn but higher Fe than the silicate-related microenvironment. A slight chemical zoning also exists in the Mn-rich tourmalines as the cores have lower Ti contents, higher Na/(Na+Ca) ratios, and higher X-site vacancy (□) than the rims (Figs. 5*b*; 6*a,b*). This may indicate changing geochemical conditions during formation of the cores and rims.

Slivko (1961) suggested that the formation of Mn-rich tourmaline is largely restricted to pegmatites saturated in lithium and sodium, as shown by the common occurrence of Li−Mn elbaite in pegmatites
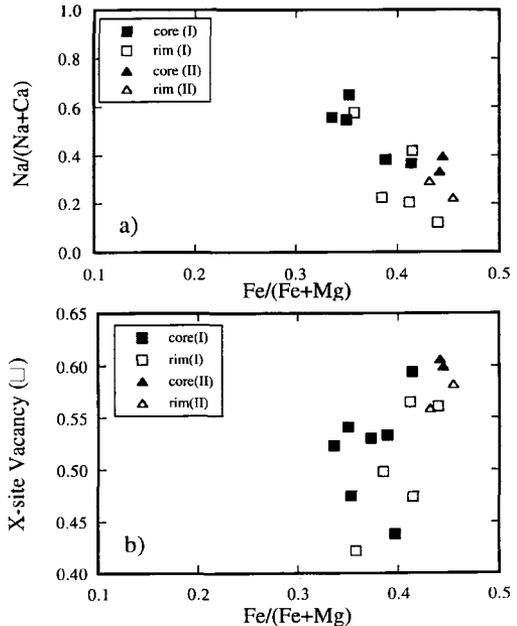
(Dietrich, 1985; Burns *et al.*, 1994). However, the presence of Mn-rich tourmaline in the hanging-wall of the Sullivan deposit suggests that this variety of tourmaline may also form from Li-poor hydrothermal fluids in sedex-type environments. Our study, and that of Ayuso and Brown (1984) of Mn-rich uvite from the Arnold talc mine (New York) indicate that substantial amounts of Mn may be accommodated in magnesian tourmaline, and that Mg and Mn do not necessarily behave antithetically, as suggested by Shimoda (1957) based on study of tourmalines from pegmatites.

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