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Chemistry of tourmaline from the emerald-hosting rocks in Swat, NW Pakistan

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ABSTRACT: *The ophiolitic emerald-hosting carbonated ultramafic rocks (magnesite + talc and/ or quartz ± chrome spinel) in the Swat valley contain disseminated grains, clusters and veins of tourmaline and/ or fuchsite. These late-stage hydrothermal minerals are especially abundant where the host rocks are traversed by ubiquitous veins and stockworks of quartz. Crystals of emerald, tourmaline and fuchsite also occur in the quartz veins. Besides, the metasedimentary rocks that are spatially associated with the emerald's host rocks also contain tourmaline. In contrast to that in the metasediments, tourmaline in the emerald-hosting altered ultramafic rocks and the invading quartz veins contain variable but distinctly high amounts of* Cr_2O_3, MgO *and* NiO, *and relatively low concentration of* TiO_2. *These chemical features, mode of occurrence and nature of associated phases suggest that the tourmaline may have been deposited from Si-rich, Al-, Be-, B- and K-bearing hydrothermal fluids which passed through and extracted Mg, Cr and Ni contents from the host carbonated ultramafic rocks.*

INTRODUCTION

The magnesite-rich assemblages containing variable amounts of talc and/or quartz, with or without accessory amounts of chrome spinel, ferritchromite and/ or Cr-magnetite, occur at a number of places in the Swat valley (Fig. 1). These rocks are of great economic significance for hosting deposits which have been producing one of the world's finest gemstone quality emeralds for the last several decades. Grains of emerald are locally associated with those of tourmaline in the host rocks as well as in the quartz veins that traverse them. In addition, tourmaline occurs in the metasedimentary rocks which are spatially associated with the emerald's host rocks. A detailed petrgogarphic and chemical investigation of the tourmaline from these different parageneses - subject of the present study - would not only help in understanding the processes involved in its formation but is also likely to throw light on the genesis of emerald in the region.

GENERAL GEOLOGY

The westward extension of the Indus-Tsangbo Suture Zone, known as the Main Mantle Thrust (MMT), marks the boundary between the Indo-Pakistan plate and the Kohistan arc sequence in northern Pakistan (Treloar et al., 1989). The MMT assumes a wedge-shaped zone in the Swat valley and contains an assortment of rock assemblages that are bounded by faults (Fig. 1). These rocks, collectively known as the MMT Melange Group (MMTMG) (Arif & Moon, 1996), are grouped into three principal types of melanges: the Shangla blueschist melange, the Charbagh greenschist melange, and the Mingora ophiolitic melange (cf. fig. 2, Kazmi et al., 1984).

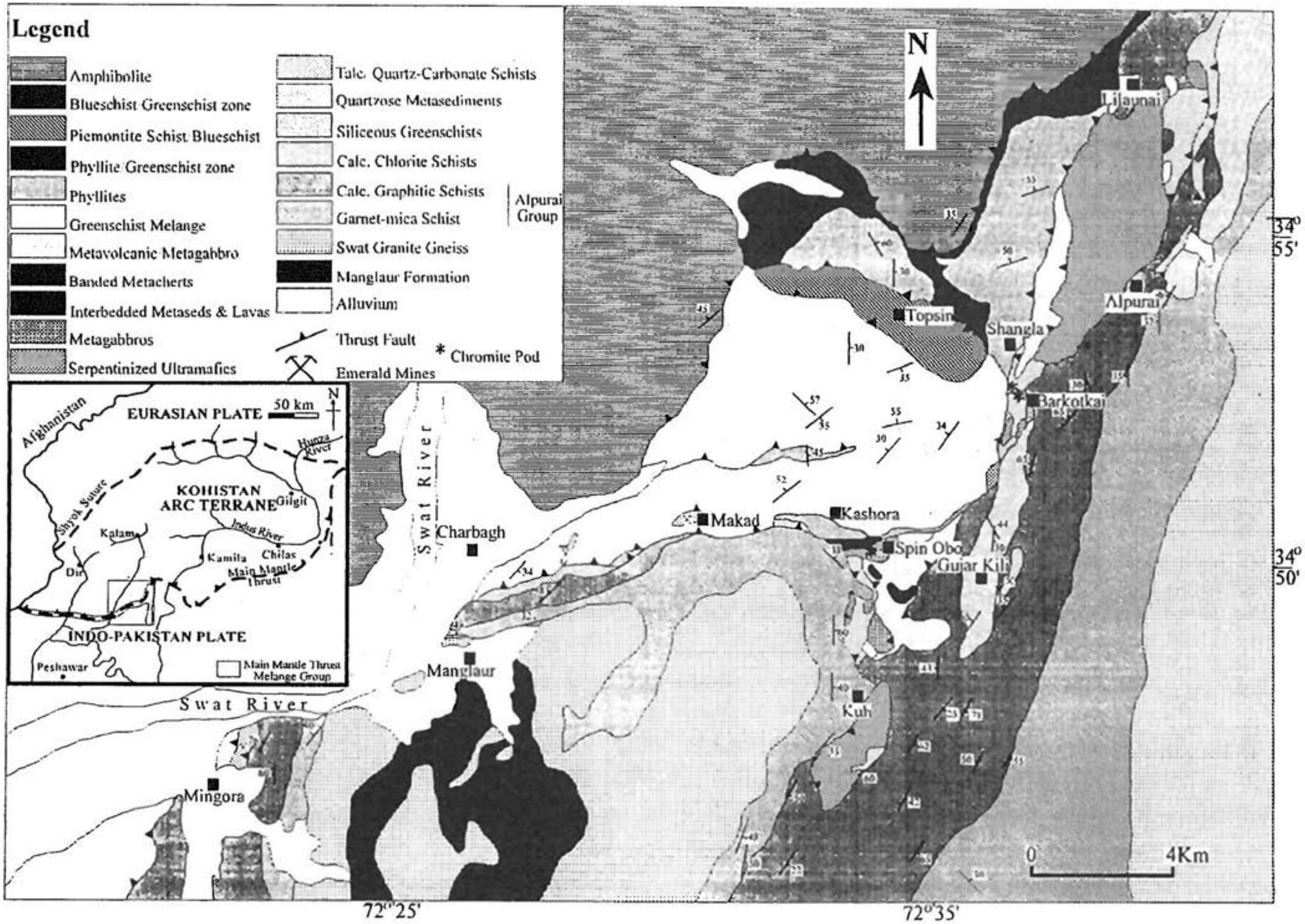

Fig. 1. Geological map of the Lilaunai-Mingora area, Swat, northwestern Pakistan (modified after Kazmi et al., 1984). The inset map shows general location of the study area.

The magnesite-rich lithologies, locally hosting emerald deposits, belong to the ophiolitic member of the MMTMG. These rocks mostly occur as lenses along the contact of the serpentinized ultramafic rocks with the metasediments of the Indo-Pakistan plate. At places, small patches and thin veins of these assemblages also occur within the serpentinized ultramafic rocks. Conversely, megnesite-rich lensoidal bodies containing relict patches of serpentinites occur at differently localities (e.g. Mingora emerald mines area). This characteristic mode of occurrence strongly suggests that these assemblages might have formed by carbonation of the previously serpentinized ultramafic rocks (Arif et al., 1996).

SAMPLES AND METHODS

Samples of carbonated ultramafic rocks and metasediments were collected from the two emerald mine areas in the Swat valley (Fig. 1). Besides, tourmaline-bearing quartz veins cutting the emerald-hosting rocks elsewhere in the region (e.g. Spin Obo-Kuh area) were also sampled. After detailed petrographic examinations, polished thin sections of representative samples were made for the purpose of SEM studies and analyses with electron microprobe.

A Jeol Superprobe model JXA-8600 and equiped with an on-line computer for ZAF corrections was used for carrying out analyses. Quantitative analyses were conducted using wavelength dispersive system and natural and synthetic standards under the following operating conditions: 15 Kv accelerating voltage; 30×10^{-9} Amp. probe current; 20 (2 x 10) seconds peak, 10 (2 x 5) seconds negative background and 10 (2 x 5) seconds positive background counting times. The accuracy of the ZAF correction is generally better than 2%.

PETROGRAPHY

Besides abundant magnesite, the emerald's host rocks contain variable amounts of talc and/ or quartz, dolomite, and accessory to trace amounts of spinel (mostly Cr-magnetite-ferritchromite and, in some cases, Cr-rich chromite). The rocks are traversed by abundant quartz veins locally producing stockworks. The quartz veins contain tourmaline, fuchsite and emerald.

The tourmaline possesses a black to greenish black colour in hand specimen and a brownish to light green colour in thin section and occurs as veins which traverse the magnesite-rich matrix of some of the emerald-hosting rocks. Some of the tourmaline veins also contain flakes of a bright green fuchsite (cf. fig 6.2, Hammarstrom, 1989). In some cases, tourmaline and fuchsite coexist as clusters. These two minerals also occur as fine-grained disseminations in the host magnesite-rich rocks and in the quartz veins that are injected into them. It is worth mentioning that markedly high concentrations of tourmaline and fuchsite occur in the zones of the carbonated ultramafic rocks which are invaded by abundant quartz veins or stockworks.

Small prismatic crystals of tourmaline also occur in the metasediments (calcite-bearing quartz-mica schists) that are spatially associated with the emerald-hosting rocks from the study area. Tourmaline in the metasediments is brown to colourless in thin section and occurs both as disseminated grains as well as thin veins that are dominantly composed of quartz.

ANALYTICAL RESULTS

Spot compositions of tourmaline were determined in eight samples including two metasediments (one each from the Mingora and the Gujar Kili mines), five carbonated ultramafic rocks (four from the Mingora emerald mines area and one from the Gujar Kili mine) and a quartz-tourmaline vein that cuts across the magnesite-rich rocks in the Spin Obo-Kuh area (Fig. 1). This is important to note that the chemistry of tourmaline from the last mentioned paragenesis is similar (except for being slightly richer in FeO) to that from within the magnesite-rich rocks. On the other hand, the composition of tourmaline occurring in the metasedimentary rocks is markedly different from that in magnesite-rich rocks. The most notable differences are (also see Table 1):

a. Tourmaline in the metasediments is virtually free of Cr_2O_3 (<0.04-0.18 wt.%) whereas that in the carbonated ultramafic rocks contains variable, but mostly high Cr_2O_3 (3.88-12.58 wt.%).
b. The FeO content of tourmaline in the carbonated ultramafic rocks is distinctly lower (0.71-2.62 wt. %) than that in the metasediments (3.54-9.65 wt.%).
c. Tourmaline in the metasediments contains more TiO_2 (0.3-1.12 wt.%) than that in the carbonated ultramafic rocks (<0.04-0.25 wt.%).
d. NiO is mostly higher in tourmaline from the carbonated ultramafic rocks (0.05-0.80 wt.%) than that from the metasediments (<0.05-0.08 wt.%).
e. Tourmaline grains in the metasedimentary rocks (such as sample G13) exhibit optical and chemical zoning: the margins are greenish and relatively enriched in CaO, Cr_2O_3 and have distinctly higher FeO/ (FeO + MgO) ratios than the colourless cores (Table 1).

All the studied tourmalines are characterized by high, although variable, contents of MgO (i.e. all are more or less dravitic in composition). But as tourmalines from the metasedimentary rocks are rich in FeO, their Fe #s {=FeO/(FeO + MgO)} are consistently higher than that in the carbonated ultramafic rocks. However, the Fe #s of tourmaline grains in one of the latter rock type are variable and markedly high (although still distinctly lower than in the metasediments) relative to other samples of similar mineralogical composition. This difference in the composition of tourmaline between and within the two categories of rocks (metasediments and carbonated ultramafics) reflects differences in bulk composition (i.e. FeO/MgO ratios) among the rocks.

The compositional variation of the studied tourmalines is shown in Figs. 2 and 3. Although Cr most probably replaces Al in the tourmaline structure (Fig. 2a), it appears that the Cr for Al and Mg for Fe^{2+} substitutions are strongly inter-related. Such a conception is favoured by the reduced scatter in the data points and improved correlation coefficient when Al + Fe^{2+} and Cr + Mg pairs are plotted against each other (Fig. 2b). Tourmaline analyses from the two different parageneses noted in the present investigation plot in their respective compositional fields (Fig. 3a, b).

DISCUSSION AND CONCLUSIONS

The occurrence of tourmaline (± fuchsite) in veins which cut across the main matrix of the carbonated ultramafic rocks suggests that its formation probably took place after the main episode of talc-carbonate alteration. The distinctly high concentrations of Cr, Ni and Mg in the tourmaline occurring in the carbonated ultramafic rocks, relative to that in the metasediments, strongly demonstrate that these components were extracted by the tourmaline-forming hydrothermal solutions from the host ultramafic rocks. The greater within sample variability in the concentration of Cr in the tourmaline compositions is probably due to the extremely low mobility of this metal.

The coexistence of tourmaline and fuchsite within the rock matrix as well as along one and the same vein suggests that both of them formed as a result of one phase of hydrothermal activity.

TABLE 1. REPRESENTATIVE ANALYSES OF TOURMALINE

Samp.	G13$_C$	G13$_M$	G13$_C$	G13$_M$	M12	M12	M12	M12	M12	M12	M12	M12	M12	Sp34	Sp34
SiO_2	36.42	36.25	36.04	36.42	37.03	37.09	37.01	36.94	36.97	36.65	36.51	36.54	36.56	36.34	36.67
TiO_2	0.83	0.78	1.12	0.85	0.54	0.57	0.61	0.64	0.60	0.52	0.60	0.37	0.62	0.06	0.25
Al_2O_3	31.22	31.03	31.52	31.11	29.86	29.95	30.18	29.55	29.32	28.97	29.45	29.20	28.63	26.54	27.69
Cr_2O_3	0.12	0.17	0.06	0.18	0.04	0.01	0.02	0.01	0.04	0.02	0.04	0.04	0.04	10.66	7.46
FeO*	8.58	7.01	9.19	6.89	5.93	6.37	6.35	6.97	7.45	7.85	8.16	9.01	9.58	0.78	1.04
MnO	0.01	0.04	0.03	0.01	0.02	0.01	0.02	0.00	0.02	0.02	0.00	0.00	0.01	0.02	0.04
MgO	5.8	7.26	5.09	7.14	8.63	8.52	7.99	8.06	8.07	7.84	7.56	7.09	7.08	8.14	8.82
CaO	0.04	0.47	0.01	0.5	0.31	0.34	0.32	0.30	0.17	0.17	0.16	0.06	0.07	0.06	0.06
Na_2O	2.57	2.48	2.44	2.44	2.66	2.66	2.56	2.76	2.82	2.82	2.87	2.99	2.93	2.63	2.72
K_2O	0.01	0.01	0.00	0.02	0.03	0.03	0.02	0.01	0.02	0.01	0.02	0.01	0.02	0.03	0.01
NiO	0.06	0.04	0.08	0.03	0.06	0.02	0.03	0.01	0.04	0.06	0.02	0.04	0.06	0.13	0.15
Total	85.66	85.54	85.58	85.59	85.11	85.57	85.11	85.25	85.52	84.93	85.39	85.35	85.60	85.39	84.91
Number of cations based on 24.5 oxygens															
Si	6.035	5.985	5.995	6.001	6.108	6.098	6.109	6.117	6.121	6.127	6.080	6.114	6.123	6.021	6.052
Ti	0.104	0.097	0.140	0.106	0.067	0.070	0.076	0.080	0.075	0.066	0.075	0.047	0.078	0.008	0.031
Al	6.098	6.038	6.180	6.043	5.806	5.804	5.872	5.768	5.722	5.708	5.781	5.759	5.652	5.182	5.390
Cr	0.016	0.022	0.008	0.023	0.006	0.002	0.002	0.002	0.006	0.002	0.006	0.006	0.006	1.397	0.974
Fe^{2+}	1.189	0.968	1.278	0.950	0.818	0.876	0.876	0.965	1.031	1.098	1.136	1.261	1.342	0.108	0.141
Mn	0.001	0.006	0.004	0.001	0.003	0.002	0.003	0.000	0.003	0.003	0.000	0.000	0.002	0.003	0.006
Mg	1.433	1.786	1.262	1.754	2.122	2.088	1.966	1.989	1.992	1.954	1.877	1.769	1.768	2.011	2.169
Ca	0.007	0.084	0.002	0.088	0.055	0.060	0.057	0.053	0.030	0.031	0.028	0.011	0.013	0.011	0.013
Na	0.826	0.794	0.787	0.780	0.850	0.848	0.820	0.886	0.906	0.914	0.927	0.971	0.952	0.846	0.870
K	0.002	0.002	0.000	0.004	0.006	0.006	0.004	0.002	0.004	0.002	0.004	0.002	0.004	0.006	0.000
Ni	0.008	0.006	0.011	0.004	0.008	0.002	0.004	0.002	0.006	0.008	0.002	0.006	0.008	0.017	0.018
Fe #	59.7	49.1	64.4	49.1	40.7	42.8	44.3	46.4	48.0	50.0	51.9	56.0	57.5	8.7	10.6

(Continued)

Samp.	Sp34	Sp34	G15	G15	G15	M9	M9	M9	M13	M13	M13	M19	M19	M19	M24
SiO_2	36.76	36.90	36.55	36.61	36.67	36.35	36.06	37.19	36.14	36.20	36.36	37.12	36.61	36.86	35.80
TiO_2	0.08	0.14	0.05	0.08	0.11	0.06	0.11	0.05	0.08	0.10	0.15	0.07	0.06	0.01	0.03
Al_2O_3	28.49	28.72	27.32	27.34	27.63	25.72	25.44	26.26	24.21	24.80	24.65	27.30	26.49	26.43	25.08
Cr_2O_3	6.97	5.81	9.68	7.97	7.22	9.84	9.01	7.89	10.98	10.61	9.11	7.93	9.53	8.92	9.61
FeO*	1.28	1.47	0.74	0.81	0.99	0.95	1.17	1.37	1.21	1.55	2.12	0.71	0.74	0.85	0.89
MnO	0.02	0.03	0.01	0.03	0.03	0.01	0.06	0.03	0.05	0.02	0.03	0.01	0.03	0.03	0.03
MgO	8.84	9.04	8.97	9.56	10.24	9.53	9.59	9.79	9.49	9.06	9.25	9.80	9.25	9.55	9.32
CaO	0.02	0.13	0.09	0.09	0.20	0.14	0.17	0.11	0.16	0.19	0.14	0.22	0.13	0.46	0.08
Na_2O	2.45	2.66	2.63	2.54	2.79	2.70	2.73	2.70	2.85	2.77	2.66	2.60	2.72	2.62	2.63
K_2O	0.03	0.02	0.02	0.00	0.02	0.04	0.02	0.02	0.03	0.02	0.02	0.03	0.02	0.03	0.03
NiO	0.31	0.28	0.05	0.06	0.10	0.07	0.09	0.10	0.15	0.15	0.22	0.10	0.15	0.18	0.13
Total	85.25	85.20	86.11	85.09	86.00	85.41	84.45	85.51	85.35	85.47	84.71	85.89	85.73	85.94	83.63
Number of cations based on 24.5 oxygens															
Si	6.036	6.052	5.984	6.033	5.988	6.026	6.044	6.122	6.044	6.040	6.108	6.059	6.029	6.052	6.057
Ti	0.010	0.017	0.007	0.012	0.014	0.008	0.013	0.006	0.010	0.013	0.019	0.009	0.007	0.002	0.004
Al	5.514	5.552	5.272	5.310	5.317	5.026	5.026	5.095	4.772	4.878	4.881	5.252	5.141	5.115	5.002
Cr	0.905	0.753	1.253	1.041	0.932	1.290	1.194	1.027	1.452	1.400	1.210	1.023	1.241	1.158	1.286
Fe^{2+}	0.176	0.202	0.101	0.110	0.136	0.131	0.164	0.188	0.169	0.217	0.298	0.097	0.102	0.117	0.126
Mn	0.003	0.004	0.002	0.006	0.004	0.001	0.009	0.005	0.007	0.003	0.004	0.002	0.004	0.004	0.004
Mg	2.164	2.211	2.189	2.346	2.492	2.355	2.395	2.402	2.365	2.254	2.316	2.384	2.271	2.338	2.350
Ca	0.004	0.023	0.016	0.018	0.035	0.025	0.030	0.019	0.028	0.034	0.025	0.039	0.023	0.081	0.014
Na	0.780	0.846	0.835	0.809	0.884	0.868	0.888	0.862	0.924	0.896	0.866	0.823	0.869	0.834	0.863
K	0.006	0.004	0.004	0.000	0.004	0.009	0.005	0.005	0.006	0.004	0.004	0.006	0.004	0.006	0.006
Ni	0.040	0.037	0.007	0.006	0.013	0.009	0.013	0.013	0.021	0.020	0.030	0.013	0.020	0.024	0.017
Fe #	12.7	14.0	7.6	7.8	8.8	9.1	10.9	12.3	11.3	14.6	18.7	6.8	7.4	8.2	8.7

Samples are designated after their localities: G= Gujar Kili mine area, M= Mingora emerald mines area and Sp= Spin Obo-Kuh area (Fig. 1). Samples G13 and M12 are metasedimentary rocks, Sp34 is a quartz vein traversing carbonated ultramafic rocks and the remaining are carbonated ultramafics themselves. The subscripts C and M with the analyses from sample G13 specify, respectively, the core and margin positions in the analysed grain; * Total iron as FeO; Fe# = 100 x FeO/ (FeO+MgO).

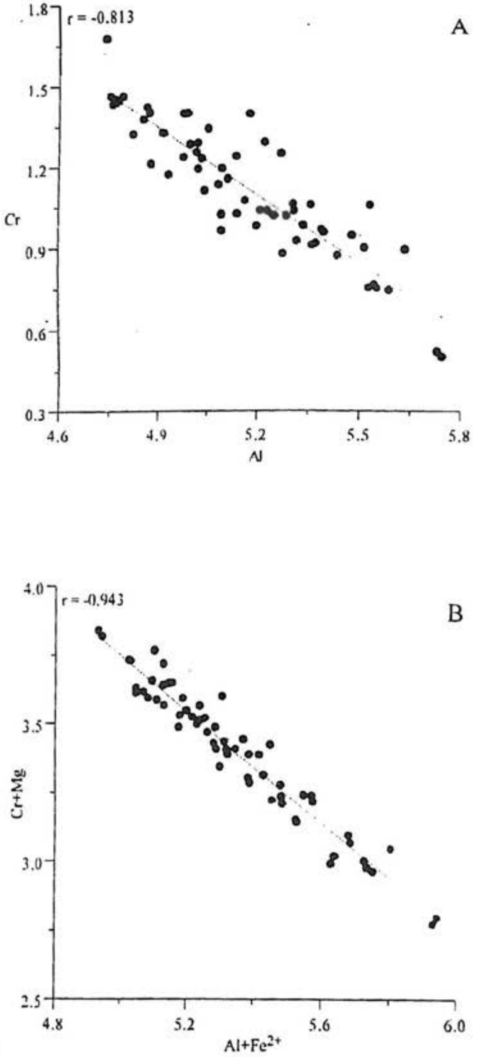

Fig. 2. Inter-element relationships in tourmalines from the studied ultramafic rocks and the invaded quartz vein.

As tourmaline of similar composition also occurs in quartz veins, the hydrothermal activity is probably related to the injection of the latter. The more frequent occurrence and increasing abundance of the tourmaline-fuchsite association in zones rich in quartz veins (i.e. stockworks) also indicate that the source of the hydrothermal solutions most probably lies in, or is at least related to, the quartz veins. It seems that tourmaline, fuchsite and emerald all are genetically related. One strong evidence in this regard is that emerald, like tourmaline, occurs in the same quartz veins and inclusions of fuchsite have been observed in emerald grains from the study area (see also Seal, 1989). Furthermore, a close chemical affinity, similar chemical characteristics and more or less identical geochemical behaviour of Be and B (as evident from the similar mode of occurrence and distribution of beryl and tourmaline, e.g. in late-stage magmatic products and pneumatolytic veins and pegmatites) during many geological processes support the hypothesis that emerald and tourmaline from the study area are genetically related. Emerald (or beryl) was not observed in any of the studied samples representing the metasedimentary rocks. However, based on the evidence from the chemistry of the associated and most probably genetically related tourmaline, it can be predicted that Cr for the emerald formation was also extracted from the host rock. In other words, the hydrothermal solutions were originally Cr-free and thus would have resulted in the formation of Cr-free tourmaline, muscovite and beryl rather than Cr-rich dravite, fuchsite and emerald, respectively, had they not encountered ultramafic rocks. Furthermore, the compositions of the resultant mineral phases (quartz, tourmaline, fuchsite and emerald) suggest that the hydrothermal fluids were Si-rich and they carried notable amounts of Al, Be, B and K.

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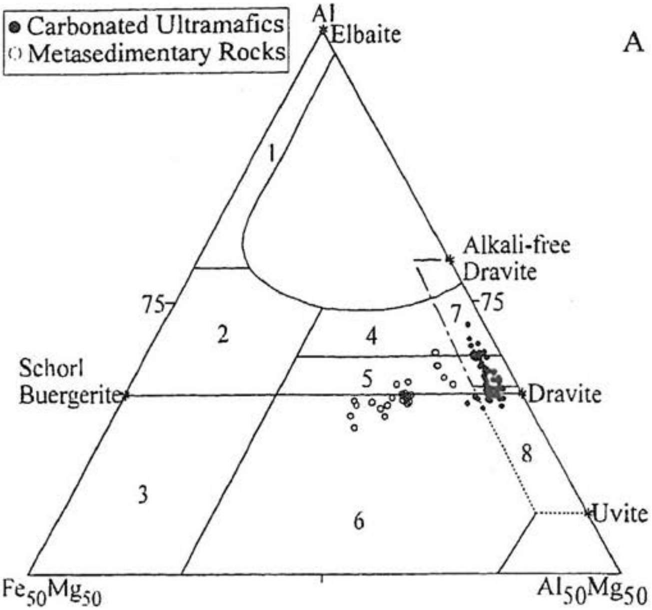
● Carbonated Ultramafics
○ Metasedimentary Rocks
A
Al
Elbaite
1
2
3
4
5
6
7
8
75
75
Alkali-free
Dravite
Schorl
Buergerite
Dravite
Uvite
Fe$_{50}$Mg$_{50}$
Al$_{50}$Mg$_{50}$

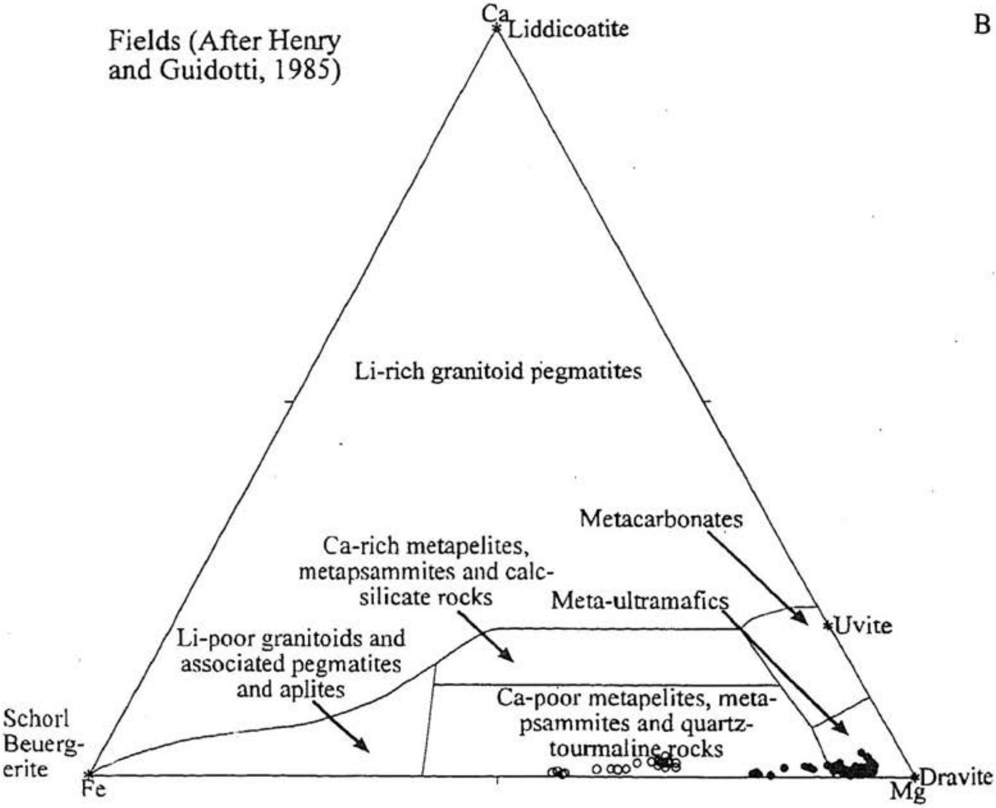
Fields (After Henry and Guidotti, 1985)
B
Ca
Liddicoatite
Li-rich granitoid pegmatites
Metacarbonates
Ca-rich metapelites, metapsammites and calc-silicate rocks
Meta-ultramafics
Li-poor granitoids and associated pegmatites and aplites
Uvite
Ca-poor metapelites, metapsammites and quartz-tourmaline rocks
Schorl
Beuergerite
Fe
Mg
Dravite

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Fig. 3. Compositional characteristics of the investigated tourmaline. The diagrams are based on cation proportions (after Henry & Guidotti, 1985) with symbols as indexed in (A). Fields in (A) are: (1) Li-rich granitoid pegmatites; (2) Li-poor granitoids and associated pegmatites and aplites; (3) Fe^{3+}-rich quartz-tourmaline rocks (hydrothermally altered granites); (4) metapelites and metapsammites associated with an Al-rich phase; (5) as (4) but not associated with an Al-saturating phase; (6) Fe^{3+}-rich quartz-tourmaline rocks, calc-silicate rocks and metapelites; (7) low-Ca meta-ultramafics and Cr-, V-rich metasediments; and (8) metacarbonates and metapyroxenites.