

Mineral Geochemical Compositions of Tourmalines and Their Significance in the Gejiu Tin Polymetallic Deposits, Yunnan, China

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Abstract: The Gejiu tin polymetallic deposits are located in the southeastern part of Yunnan Province in China. A detailed electronic microprobe study has been carried out to document geochemical compositions of tourmalines from the deposits. The results indicate a systematic change of mineral geochemical compositions, which might be used as a mineral geochemical tracer for post-magmatic hydrothermal fluid, basin fluid and their mixture. The tourmalines from granite are schorl with Fe/(Fe+Mg) ratios of 0.912–1.00 and Na/(Na+Ca) ratios of 0.892–0.981. Tourmalines as an inclusion in quartz from the ore bodies are dravite with Fe/(Fe+Mg) ratios of 0.212–0.519 and Na/(Na+Ca) ratios of 0.786–0.997. Tourmalines from the country rocks are dravite with Fe/(Fe+Mg) ratios of 0.313–0.337 and Na/(Na+Ca) ratio of 0.599–0.723. Tourmalines from cassiterite-tourmaline veins that occur in crannies within the country rocks show distinct optical zoning with alternate occurrence of dravite and schorl, Fe/(Fe+Mg)=0.374–0.843, Na/(Na+Ca)=0.538–0.987. It suggests that schorl in granite and dravite in carbonatite are related to magmatic fluid and basin fluid respectively. When magmatic fluid rose up and entered into crannies of the country rocks, consisting mainly of carbonatite, basin fluid would be constantly added to the magmatic fluid. The two types of fluid were mixed in structural crannies of the sedimentary basin accompanied with periodic geochemical oscillations to form material records in chemical composition zonings of tourmalines.

Key words: tourmaline, mineral geochemical zoning, geochemical oscillation, tin polymetallic deposit, Gejiu

1 Introduction

Tourmaline is stable over a wide range of pressures and temperatures, and has variable compositions while it is able to exchange components and volatile species with coexisting minerals and fluids as external conditions change. Tourmalines of different geneses, therefore, can be used as a mineral geochemical indicator of the physical and chemical environment of metallogenic fluids (Henry and Guidotti, 1985; Xiao and Zhong, 1988; Mao et al., 1993; Slack et al., 1993; London and Manning, 1995; Rozendaal and Bruwer, 1995; Smith and Yardley, 1996; Deb et al., 1997; Pesquera and Velasco, 1997; Xue et al., 1997; Keller et al., 1999; Jiang et al., 1999, 2002; Anani, 1999; Trumbull and Chaussidon, 1999; Harraz and Sharkawy, 2001;

Deksissa and Koeberl, 2002; Kawakami and Ikeda, 2003; Michael, 2003; Yu and Jiang, 2003). The mineral model of the Gejiu tin polymetallic deposits is that all of the mineralizations occur around the roof pendant of Cretaceous granites (equigranular granite and porphyritic granite), i.e., greisen-type, skarn-type, Manto-type cassiterite sulfides, and vein-type quartz-tourmaline mineralization from the outside contact zone (Mao et al., 2008). Tourmalines are widespread in different types of ores and the above rocks. This paper, giving account of mineral geochemical research on tourmaline compositions in the Gejiu tin polymetallic deposits, is very useful for us to better understand changes of physical and chemical conditions in their metallogenic process accompanied with the influence of basin fluid.

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2 Geological Setting

The Gejiu tin polymetallic deposits are located in the southeastern part of Yunnan Province in China., comprising five orefields from north to south: the Malage, Songshujiao, Gaosong, Laochang and Kafang orefields as shown in Fig. 1. Sedimentary rocks widely occur, more than 80% of the whole surface area, in southeast Yunnan Province. Precambrian to Quaternary strata except for Cretaceous strata exposed in the region. The pre-Triassic and Early Triassic strata are characterized by marine sediments, whereas the post-Triassic and Early Triassic strata are dominated by terrestrial sediments. The crust-scale faults include the N-S-trending Xiaojiang fault, N-S-trending Honghe, Ailaoshan and Shiping faults, N-S-trending Shizong-Mile and Nanpanjiang faults. Intrusive and volcanic rocks, distributed in the Ailaoshan, Shiping, Jiashui, Wenshan and Maguan areas, are mainly attached to acid-basic volcanic eruptive rocks and acid intrusive rocks (about 10% of the whole surface area). The magmatic activities are characterized by multiple periods and stages from the Proterozoic to the Cenozoic, which took place during main tectonic movements. Especially, the marine basic volcanic eruptions in Hercynian orogeny, basic to acid magmatic intrusion in Indochina-Yanshanian orogeny probable were the strongest magmatic activities in the region (Zhuang et al., 1996; Fang et al., 2002; Jia et al., 2004; Cheng et al., 2008a, 2008b; Mao et al., 2008).

3 Tourmaline Occurrences

Tourmalines in the Gejiu tin polymetallic deposits can be grouped into three categories according to the spatial relations between the granite and ore bodies. In order to study systematic geochemical compositional variations of tourmalines in different occurrences, we mainly chose representative fresh rocks or ore samples, which contain tourmalines from skarn-type deposit in Tangziwa and vein-type deposit in Dadoushan of the Laochang orefield. All of the tourmalines display distinct pleochroism with different colors on thin sections.

3.1 Tourmalines within granite

Granites related to mineralization are mainly equigranular and porphyritic ones, which generally change to leucogranite nearby orebodies due to post-magmatic hydrothermal alteration (Zhuang et al., 1996; Jia et al.,

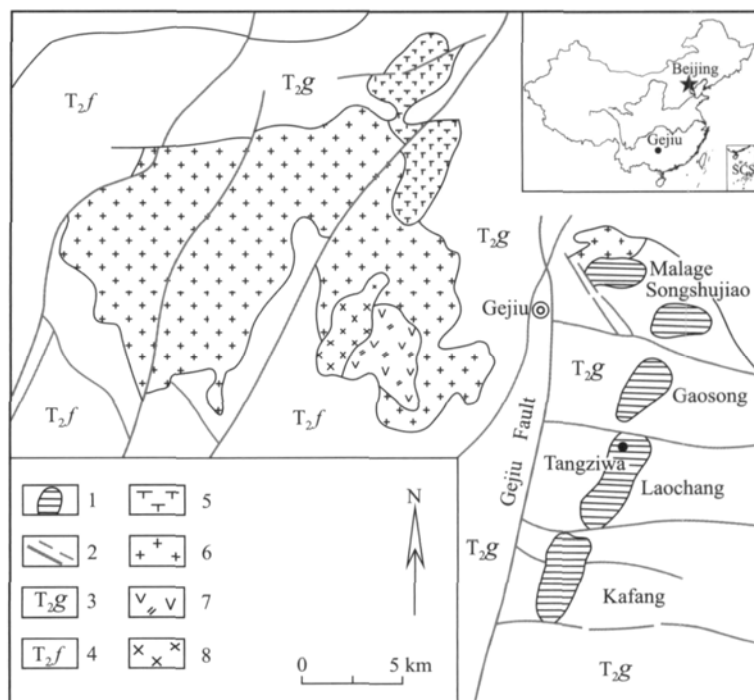


Fig. 1. A sketch showing distribution of the main tin polymetallic orefields in the Gejiu area (modified after Zhuang et al., 1996).

1. Main tin polymetallic orefields; 2. main fault; 3. Middle Triassic carbonate rock of the Gejiu Formation; 4. Middle Triassic sandstone, shale of the Falang Formation; 5. the late Yanshanian alkali rock; 6. the late Yanshanian granitoid; 7. monzonite; 8. gabbro.

2007). The tourmalines within granites sampled at the elevation of 1750 m in the Tangziwa tin polymetallic deposit in the Laochang orefield can be further classified into two sub-types according to their occurrences.

(1) Grain-shaped tourmalines: tourmalines disseminated in leucogranite (sample TZ-1) are euhedral and shown as acicular or elongated grains displaying blue-green color (Ne) to colorless (No) on thin sections, with their grain size varying from 0.2 to 0.8 mm.

(2) Vein-shaped tourmalines: tourmalines in tourmaline-quartz veins within leucogranite (sample TZ-2) are mainly associated with quartz, with the width of the tourmaline-quartz veins varying from 2 to 5 mm. Single tourmaline in the veins is generally exposed as acicular grain or elongated grain with their grain size varying from 0.02 to 0.3 mm. Fine-grained tourmalines displays light blue-green color (Ne) to colorless (No) and coarse-grained tourmalines exhibits blue-green color (Ne) to colorless (No) on thin sections.

3.2 Tourmalines within skarn orebodies

The skarn orebodies between leucogranite and carbonate rock in the Gejiu tin polymetallic deposits mainly consist of pyrite, pyrrhotite, chalcopyrite, sphalerite, cassiterite, quartz, tremolite and minor other skarn minerals. Tourmalines are very abundant and generally exists as

euhedral inclusions in euhedral quartz (sample TZ-5), displaying light olivine (Ne) to colorless (No) on thin sections, with the grain size varying from 0.01 to 0.15 mm (Jia et al., 2007).

3.3 Tourmalines in country rocks

Tin polymetallic vein-type orebodies from the outside contact zone in the Gejiu district are generally located at the top of skarn orebodies nearby granite (Xiao and Zhong, 1988; Zhuang et al., 1996; Mao et al., 2008). There are large amounts of tourmaline veins developed in the cranny of carbonate rock in the Dadoushan deposit of the Laochang orefield. The tourmaline veins can be further classified into two sub-types according to their widths and mineral assemblages.

(1) Tourmaline veins (sample GR-57, sample GR-59): The width of tourmaline veins in carbonate rock generally vary from 10 to 70 cm with a few of them more than 1 m. Statistics show that there are about five tourmaline veins observed in 1 m-width carbonate rock, the tourmaline veins are composed mainly of blue tourmaline (70%–80%), quartz, cassiterite, calcite, titanite and minor other minerals. Blue tourmalines from tourmaline veins are generally exposed as elongated grains or radiated aggregates displaying light purple (Ne) to blue (No) on thin sections, with the grain size generally varying from 0.4 to 6 mm or more than 10 mm. Three to five optical and chemical zones, showing alternate light blue and bright white colors from core to rim, can be observed in transverse sections of blue tourmalines, which are mainly shown as triangles and a few as anomalous polygons.

(2) Tourmaline veinlets (sample GR-55): The width of tourmaline veinlets in carbonate rock is no more than 10 cm, generally varying from 0.2 cm to 0.5 cm. Statistics show that there are about 38 tourmaline veinlets observed within 1 m-width carbonate rock, the tourmaline veinlets consist mainly of iron-manganese oxide, calcite, lesser amounts of tourmaline, and minor fluorite. Tourmalines generally associated with limonites from these veinlets have subeuhedral to irregular forms with grain sizes varying from 0.1 to 0.8 mm and colors of blue-green to colorless on thin sections.

4 Analytic Method and Results

Tourmalines were analyzed by the wavelength-dispersive electronic microprobe method (Yu and Jiang, 2003; Wang et al., 2008). The analyses were carried out at the Chinese Academy of Geological Sciences using a JXA-8800 superprobe after choosing the analytic spots by the scanning electron microscope, determining minerals by X-ray photoelectronic energy spectra and taking pictures of

back-scattered electron images for tourmaline on thin sections, operated at a beam current of 2×10^{-8} A, accelerating voltage of 20 kV, beam spot size of 2 μ m and counting time of 20 s for major elements (Na, K, Mn, Mg, Ca, Fe, Al, Ti, Cr, Si) and 50 s for trace elements (F, Cl, Sn, V, Ni). The standards used are natural minerals and synthetic compounds, including K-feldspar (K, Al, Si), albite (Na), wollastonite (Ca), olivine (Mg), apatite (F), salt (Cl), FeO (Fe), MnO₂ (Mn), TiO₂ (Ti), Cr₂O₃ (Cr), SnO₂ (Sn), V₂O₃ (V), and NiO (Ni).

Representative results of electron microprobe analyses for different types of tourmaline and their corresponding chemical zoning from the Gejiu district are given in Tables 1 and 2. Back-scattered electron images of tourmalines and their corresponding chemical zoning are seen in Figs. 2 and 4, respectively.

5 Mineral Geochemistry of Tourmaline

The general formula for tourmaline group minerals is $XY_3Z_6(BO_3)_3Si_6O_{18}(OH, F)_4$ or $(R1)(R2)_3(R3)_6(BO_3)_3Si_6O_{18}(OH, F)_4$, where the common site occupancies include X (R1)=Na, Ca, K, or vacancy; Y(R2) = Fe²⁺, Mg, Mn²⁺, Fe³⁺, Al, Li (when coupled with Al); Z(R3) = Al, Fe³⁺, Mg (when coupled with Ca in X), or 1.33Ti⁴⁺ (London and Manning, 1995). Tourmalines can be further classified as schorl, dravite and elbaite by the Y(R2)-site mainly occupied by Fe²⁺, Mg or Al³⁺ and Li⁺ respectively. In nature, tourmalines are generally attributed to the dravite-schorl and schorl-elbaite series, but the elbaite-dravite series and elbaite-uvite series of tourmalines are very few.

Based on 31 anions (Jiang et al., 2002) and assumed that B=3, HO+F+Cl=4.00 apfu, Li=3– Σ Y (the total cation amount on Y-site) in the unit structural formula of tourmaline, we can calculate the compositional data of B₂O₃, H₂O and Li₂O in tourmaline, which cannot be detected by the electron microprobe.

5.1 Geochemistry of tourmalines from different occurrences

Overall, tourmalines from the Gejiu tin polymetallic deposits belong to the dravite-schorl series. On the ternary, in the Al-Fe-Mg diagram (Fig. 3) of Henry and Guidotti (1985), tourmalines are plotted in three areas, indicating their different formation environments. The tourmalines within leucogranite fall in fields 2 and 1 in the plot, which suggests that they were formed from magmatic fluids derived from granitoid bodies that occur in the mine area. The tourmalines as euhedral inclusions in euhedral quartz and the tourmalines from tourmaline veinlets in carbonate rock are plotted in fields 4, 5 and 6, which implies that these tourmalines might be formed from fluids generated by

Table 1 Representative electron microprobe analyses of tourmaline from the Gejiu tin deposit (wt%)

Sample type	Tourmaline within granite					Tourmaline within skarn orebody					Tourmaline in country rock				
	Tourmaline grain			Tourmaline vein		Tourmaline as inclusion in quartz					Vein	Veinlet			
Sample No.	TZ-1			TZ-2		TZ-5					GR-59	GR-55			
Detecting spot	1	2	3	1	2	1	2	3	4	5	1	1	2	3	4
SiO ₂	34.28	36.07	36.08	36.32	35.94	37.15	36.98	37.68	37.35	36.28	35.45	35.78	36.46	36.15	36.37
Al ₂ O ₃	34.34	36.08	32.67	33.63	34.39	30.77	29.45	28.34	30.19	28.88	31.19	30.99	29.66	28.92	28.48
Cr ₂ O ₃	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.02	0.01	0.09	0.02	0.00	0.02	0.00	0.00
TiO ₂	0.09	0.01	0.15	0.00	0.00	0.07	0.70	1.21	0.21	0.63	0.01	0.07	0.10	0.13	0.13
SnO ₂	0.01	0.01	0.04	0.01	0.04	0.02	0.05	0.01	0.02	0.13	0.04	0.02	0.03	0.05	0.02
FeO	12.95	11.66	14.04	14.57	12.35	8.52	5.75	7.02	9.94	4.48	8.42	6.41	7.05	7.22	7.07
MgO	0.04	0.00	0.76	0.21	0.21	6.02	8.46	8.47	5.16	9.35	5.10	7.06	7.91	8.27	8.69
MnO	0.01	0.05	0.07	0.01	0.01	0.00	0.02	0.02	0.01	0.05	0.08	0.08	0.10	0.09	0.12
CaO	0.33	0.14	0.18	0.04	0.14	0.01	0.45	0.81	0.07	0.89	1.05	1.44	1.78	2.00	1.93
Na ₂ O	1.53	0.73	1.44	1.21	1.35	2.26	2.54	2.38	2.27	1.80	1.58	2.08	1.86	1.65	1.65
K ₂ O	0.03	0.02	0.09	0.03	0.04	0.01	0.03	0.03	0.01	0.03	0.05	0.04	0.03	0.03	0.04
F	0.32	0.08	0.13	0.29	0.33	0.19	0.62	1.16	0.16	0.68	0.25	0.55	0.64	0.78	0.83
Cl	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
B ₂ O ₃ (calc.)	11.74	10.38	10.86	10.77	10.98	10.27	10.44	10.22	10.29	11.30	11.41	10.89	10.65	11.16	11.15
Li ₂ O (calc.)	1.09	0.43	0.63	0.48	0.74	0.41	0.34	0.31	0.57	0.43	0.79	0.45	0.31	0.35	0.36
H ₂ O (calc.)	3.45	3.56	3.54	3.47	3.44	3.51	3.31	3.05	3.53	3.28	3.49	3.34	3.30	3.23	3.21
O-F	0.27	0.07	0.06	0.24	0.28	0.16	0.52	0.98	0.13	0.29	0.21	0.46	0.54	0.66	0.69
O-Cl	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	99.94	99.17	100.62	100.80	99.70	99.06	98.60	99.74	99.65	97.99	98.72	98.74	99.36	99.38	99.34
Cations calculated on the basis of 31 anions															
Al (tol.)	6.74	7.08	6.41	6.60	6.75	6.04	5.78	5.56	5.92	5.66	6.12	6.08	5.82	5.67	5.59
Fe (tol.)	1.80	1.62	1.95	2.03	1.72	1.19	0.80	0.98	1.38	0.62	1.17	0.89	0.98	1.00	0.98
T-site															
Si	5.71	6.0	6.00	6.05	5.98	6.18	6.15	6.27	6.22	6.04	5.90	5.95	6.07	6.02	6.05
Al	0.29	0	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.10	0.05	0.00	0.00	0.00
Z-site															
Al	6.00	6.00	6.00	6.00	6.00	6.00	5.78	5.56	5.92	5.66	5.92	6.00	5.82	5.67	5.59
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Fe	0.00	0.00	0.00	0.00	0.00	0.00	0.22	0.44	0.08	0.32	0.08	0.00	0.18	0.33	0.41
Y-site															
Al	0.44	1.08	0.41	0.60	0.73	0.04	0.00	0.00	0.00	0.00	0.10	0.03	0.00	0.00	0.00
Ti	0.01	0	0.02	0.00	0.00	0.01	0.09	0.15	0.03	0.08	0.00	0.01	0.01	0.02	0.02
Sn	0.00	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Fe	1.80	1.62	1.95	2.03	1.72	1.19	0.58	0.54	1.31	0.30	1.10	0.89	0.80	0.68	0.57
Mg	0.01	0	0.19	0.05	0.05	1.49	2.10	2.10	1.28	2.32	1.27	1.75	1.96	2.05	2.16
Mn	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.02
Σ	2.27	2.71	2.58	2.68	2.50	2.73	2.77	2.79	2.62	2.71	2.47	2.70	2.79	2.76	2.76
Li	0.73	0.29	0.42	0.32	0.50	0.27	0.23	0.21	0.38	0.29	0.53	0.30	0.21	0.24	0.24
Fe/(Fe+Mg)	0.99	1.00	0.91	0.98	0.97	0.44	0.28	0.32	0.52	0.21	0.48	0.34	0.33	0.33	0.31
X-site															
Ca	0.06	0.02	0.03	0.01	0.02	0.00	0.08	0.14	0.01	0.16	0.19	0.26	0.32	0.36	0.34
Na	0.49	0.24	0.46	0.39	0.43	0.73	0.82	0.77	0.73	0.58	0.51	0.67	0.60	0.53	0.53
K	0.01	0.00	0.02	0.01	0.01	0.00	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01
Vacancy	0.44	0.74	0.48	0.60	0.53	0.27	0.10	0.08	0.25	0.26	0.29	0.06	0.08	0.10	0.12
Na/(Na+Ca)	0.89	0.90	0.93	0.98	0.95	1.00	0.91	0.84	0.98	0.79	0.73	0.72	0.65	0.60	0.61
W-site															
OH	3.83	3.96	0.00	3.85	3.82	3.90	3.68	3.39	3.92	0.00	3.87	3.71	3.66	3.59	3.57
F	0.17	0.04	3.93	0.15	0.17	0.10	0.32	0.61	0.08	3.64	0.13	0.29	0.34	0.41	0.43
Cl	0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.36	0.00	0.00	0.00	0.00	0.00
Σ	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00

dehydration of the country rocks during regional and/or contact metamorphism (Jiang et al., 2002). The tourmalines with optical and geochemical zoning from tourmaline-cassiterite veins in carbonate rock display compositions between granitoids and country rocks, and the data are plotted in fields 2, 4 and 5.

The projection of the Gejiu tourmalines plotted in the Ca-Fe-Mg ternary diagram (Fig. 3) is similar to that in the Al-Fe-Mg ternary diagram. Tourmaline within leucogranite mainly falls in field 2 near the end-member of schorl; in contrast, tourmaline as euhedral inclusions in euhedral quartz and tourmaline from tourmaline veinlets in

carbonate rock are plotted in field 9 of dravite. The tourmalines with optical and chemical zoning from tourmaline-cassiterite veins in carbonate rock are plotted in the middle region of fields 2 and 9 between schorl and dravite.

The distribution of Gejiu tourmalines plotted in the above two ternary diagrams shows that the compositions of tourmalines within leucogranite are mainly related to the magmatic hydrothermal system, the compositions of tourmalines in skarn ore and tourmalines from tourmaline veinlets in carbonate rock were derived from country rocks, and the tourmalines from tourmaline-cassiterite veins in

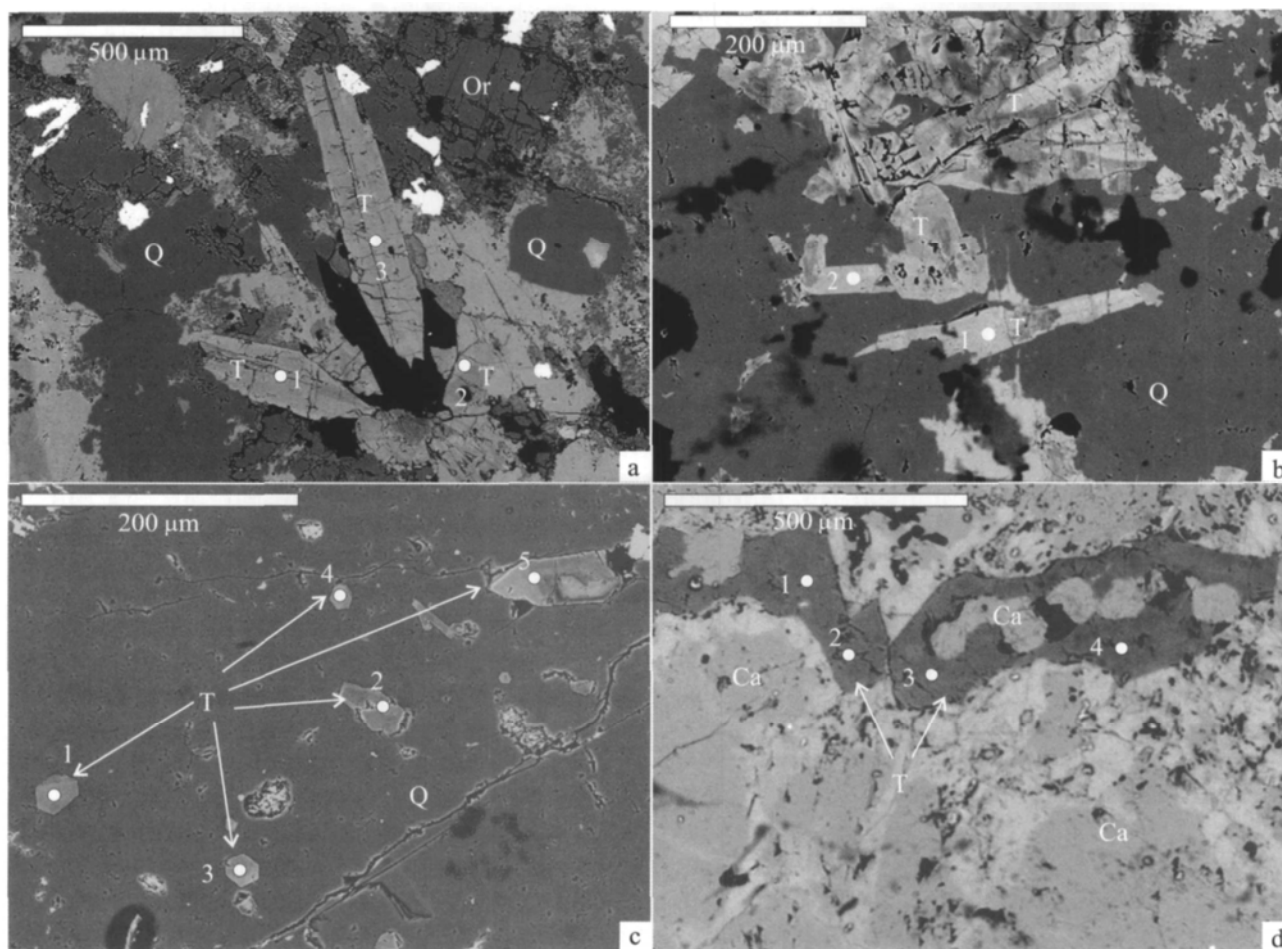


Fig. 2. Back-scattered electron images of different occurrences of tourmaline from the Gejiu tin deposits.

(a) Tourmaline within leucogranite from sample TZ-1; (b) tourmaline in tourmaline-quartz vein within leucogranite from sample TZ-2; (c) tourmaline as euhedral inclusion in euhedral quartz of skarn ore from sample TZ-5; (d) tourmaline of tourmaline veinlet in carbonate rock from sample GR-55; T – tourmaline; Q – quartz; r – Orthoclase; Ca – Calcite; 1, 2, 3, 4 and 5 represent detecting spots by electron microprobe from different tourmaline samples.

carbonate rock are composed of mixed materials derived from the magmatic hydrothermal system and the country rocks.

The characteristic ratios of $Fe/(Fe+Mg)$ and $Na/(Na+Ca)$ and Al cations in R_2 -site for the Gejiu tourmalines in different occurrences are also different. (1) the average ratios of $Fe/(Fe+Mg)$ for tourmaline grains and tourmaline veinlets within leucogranite are 0.967 (0.912–1) and 0.973 (0.970–0.975) respectively, the average ratios of $Na/(Na+Ca)$ for them are 0.910 (0.892–0.934) and 0.963 (0.946–0.981) respectively, and Al cations in R_2 -site are 0.642 (0.409–1.08) apfu and 0.663 (0.598–0.727) apfu respectively, which suggest their distinct magmatic genesis. (2) Tourmalines as inclusions in quartz from skarn sulfide ores are mainly dravite with the $Fe/(Fe+Mg)$ ratio varying from 0.212 to 0.519 (averaging 0.353), $Na/(Na+Ca)$ ratio from 0.786–0.997 (averaging 0.904) and Al cations in R_2 -site varying from 0 to 0.036 (averaging 0.007) apfu. The composition of Mg-rich tourmalines in sulfide ores of the Gejiu tin deposits is similar to that observed in

massive sulfide ore deposits worldwide (Jiang et al., 1999; Jiang et al., 2002; Yu and Jiang, 2003). The enrichment of Mg of tourmalines associated with sulfides may be due to metasomatism or metamorphism, during which element Fe was incorporated into sulfides such as pyrite and pyrrhotite, leaving coexisting silicates such as dravite more Mg-rich. (3) Tourmalines from tourmaline veinlets in the country rocks is mainly dravite with the $Fe/(Fe+Mg)$ ratio varying from 0.313 to 0.337 (averaging 0.328), $Na/(Na+Ca)$ ratio from 0.599 to 0.723 (averaging 0.646) and Al cations in R_2 -site varying from 0 to 0.032 (averaging 0.009) apfu. Previous studies (Slack et al., 1993; Tiwary and Palmer, 1997; Jiang et al., 1999) argued that the compositions of tourmalines developed in the country rocks are mainly related to basin fluid (Gu et al., 2007). (4) The compositions of tourmalines with different optical zonings from cassiterite-tourmaline veins in the country rocks are very different from core to rim on thin sections, with the $Fe/(Fe+Mg)$ ratio varying from 0.374 to 0.843 (averaging 0.561), $Na/(Na+Ca)$ ratio from 0.538 to 0.987 (averaging

Table 2 Representative electron microprobe analyses of tourmaline zoning from the Gejiu tin deposit (wt%)

Sample No. Detecting spot	GR-57-A					GR-57-B					GR-57-C					GRJ-3				
	A1	A2	A3	A4	A5	B1	B2	B3	B4	B5	C1	C2	C3	C4	C5	D1	D2	D3	D4	D5
SiO ₂	35.73	35.03	34.07	36.05	35.95	36.23	35.48	35.23	35.80	35.18	34.73	34.99	34.02	35.25	34.66	36.58	34.73	35.33	35.14	35.74
Al ₂ O ₃	32.01	31.65	31.78	29.81	29.91	29.99	31.94	31.08	31.71	30.10	29.82	31.06	32.84	31.14	31.24	30.66	33.19	31.39	32.28	30.27
Cr ₂ O ₃	0.02	0.01	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.01	0.02	0.02	0.00	0.01	0.02	0.03	0.04	0.00
TiO ₂	0.03	0.01	0.03	0.03	0.01	0.03	0.00	0.01	0.01	0.01	0.03	0.01	0.01	0.00	0.01	0.04	0.03	0.03	0.03	0.01
SnO ₂	0.24	0.03	0.15	0.13	0.03	0.08	0.01	0.04	0.02	0.06	0.15	0.01	0.03	0.01	0.03	0.15	0.05	0.03	0.02	0.02
FeO	9.02	12.62	10.30	9.10	7.44	8.93	12.97	7.97	10.60	8.14	8.34	12.40	8.98	10.46	7.97	9.97	9.73	9.70	12.42	8.41
MgO	4.35	1.89	4.42	5.92	6.98	5.87	1.36	5.59	2.77	6.26	5.95	2.16	4.09	3.58	5.72	4.98	4.06	5.13	1.93	6.23
MnO	0.32	0.85	0.45	0.16	0.26	0.16	0.68	0.19	0.63	0.36	0.14	0.18	0.11	0.18	0.11	0.08	0.11	0.11	0.21	0.12
CaO	0.56	0.11	1.75	1.32	1.36	1.10	0.04	1.35	0.04	1.54	1.80	0.28	1.64	0.20	1.28	0.77	1.28	1.47	0.15	1.58
Na ₂ O	1.47	1.88	1.13	1.44	1.37	1.43	1.73	1.29	1.84	1.42	1.75	2.37	1.61	2.50	1.96	2.01	1.85	1.85	2.44	1.75
K ₂ O	0.04	0.06	0.05	0.04	0.04	0.04	0.03	0.03	0.05	0.06	0.04	0.05	0.07	0.07	0.06	0.04	0.03	0.02	0.05	0.04
F	0.00	0.61	0.49	0.45	0.43	0.15	0.67	0.37	0.47	0.50	0.57	0.75	0.27	0.60	0.53	0.16	0.46	0.46	0.58	0.35
Cl	0.02	0.03	0.00	0.02	0.02	0.02	0.00	0.01	0.02	0.01	0.02	0.01	0.02	0.01	0.01	0.00	0.00	0.00	0.00	0.00
B ₂ O ₃ (calc.)	11.00	12.07	11.77	11.37	11.37	11.12	11.94	11.57	11.67	11.74	12.01	12.27	11.44	11.87	11.68	10.56	10.93	11.02	11.59	11.12
Li ₂ O (calc.)	0.57	0.92	0.73	0.57	0.51	0.58	0.88	0.76	0.85	0.74	1.05	1.19	0.91	0.97	0.83	0.51	0.48	0.47	0.86	0.57
H ₂ O (calc.)	3.60	3.31	3.37	3.39	3.40	3.53	3.28	3.43	3.37	3.36	3.33	3.24	3.47	3.32	3.35	3.53	3.38	3.38	3.33	3.44
∑O=F	0.00	0.26	0.21	0.19	0.18	0.06	0.28	0.16	0.20	0.21	0.48	0.63	0.22	0.51	0.45	0.14	0.39	0.39	0.49	0.29
∑O=Cl	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	98.95	100.80	100.28	99.61	98.88	99.19	100.75	98.77	99.65	99.28	99.24	100.33	99.29	99.67	98.98	99.88	99.94	100.04	100.56	99.35
Cations calculated on the basis of 31 anions																				
Al (tol)	6.28	6.21	6.23	5.85	5.87	5.88	6.26	6.10	6.22	5.90	5.85	6.09	6.44	6.11	6.13	6.01	6.51	6.16	6.33	5.94
Fe (tol)	1.25	1.76	1.43	1.27	1.03	1.24	1.81	1.11	1.47	1.13	1.16	1.73	1.25	1.46	1.11	1.39	1.35	1.35	1.73	1.17
T-site																				
Si	5.95	5.83	5.67	6.00	5.98	6.03	5.90	5.86	5.96	5.85	5.78	5.82	5.66	5.87	5.77	6.09	5.78	5.88	5.85	5.95
Al	0.05	0.17	0.33	0.00	0.02	0.00	0.10	0.14	0.04	0.15	0.22	0.18	0.34	0.13	0.23	0.00	0.22	0.12	0.15	0.05
Z-site																				
Al	6.00	6.00	5.90	5.85	5.85	5.88	6.00	5.96	6.00	5.76	5.63	5.92	6.00	5.98	5.90	6.00	6.00	6.00	5.99	5.89
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Fe	0.00	0.00	0.10	0.15	0.15	0.12	0.00	0.04	0.00	0.24	0.37	0.08	0.00	0.02	0.10	0.00	0.00	0.00	0.00	0.11
Y-site																				
Al	0.23	0.04	0.00	0.00	0.00	0.00	0.17	0.00	0.18	0.00	0.00	0.00	0.11	0.00	0.00	0.01	0.29	0.04	0.18	0.00
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sn	0.02	0.00	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Fe	1.25	1.76	1.34	1.11	0.88	1.13	1.81	1.07	1.47	0.89	0.79	1.64	1.25	1.44	1.01	1.39	1.35	1.35	1.73	1.06
Mg	1.08	0.47	1.10	1.47	1.73	1.46	0.34	1.39	0.69	1.55	1.48	0.53	1.02	0.89	1.42	1.23	1.01	1.27	0.48	1.55
Mn	0.05	0.12	0.06	0.02	0.04	0.02	0.10	0.03	0.09	0.05	0.02	0.02	0.02	0.03	0.02	0.01	0.02	0.02	0.03	0.02
Σ	2.62	2.39	2.51	2.62	2.66	2.61	2.41	2.49	2.43	2.50	2.30	2.20	2.39	2.35	2.44	2.66	2.68	2.69	2.43	2.62
Li	0.38	0.61	0.49	0.38	0.34	0.39	0.59	0.51	0.57	0.50	0.70	0.80	0.61	0.65	0.56	0.34	0.32	0.31	0.57	0.38
Fe/(Fe+Mg)	0.54	0.79	0.57	0.46	0.37	0.46	0.84	0.44	0.68	0.42	0.44	0.76	0.55	0.62	0.44	0.53	0.57	0.51	0.78	0.43
X-site																				
Ca	0.10	0.02	0.31	0.24	0.24	0.20	0.01	0.24	0.01	0.27	0.32	0.05	0.29	0.04	0.23	0.14	0.23	0.26	0.03	0.28
Na	0.48	0.61	0.36	0.46	0.44	0.46	0.56	0.42	0.59	0.46	0.57	0.76	0.52	0.81	0.63	0.65	0.60	0.60	0.79	0.57
K	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Vacancy	0.42	0.36	0.31	0.29	0.31	0.33	0.43	0.34	0.39	0.26	0.10	0.17	0.18	0.15	0.13	0.21	0.17	0.13	0.18	0.14
Na/(Na+Ca)	0.83	0.97	0.54	0.66	0.65	0.70	0.99	0.63	0.99	0.63	0.64	0.94	0.64	0.96	0.74	0.82	0.72	0.69	0.97	0.67
W-site																				
OH	4.00	3.67	3.74	3.76	3.77	3.92	3.64	3.80	3.75	3.73	3.69	3.60	3.86	3.68	3.72	3.91	3.76	3.76	3.69	3.81
F	0.00	0.32	0.26	0.23	0.23	0.08	0.35	0.19	0.25	0.26	0.30	0.40	0.14	0.32	0.28	0.08	0.24	0.24	0.31	0.18
Cl	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Σ	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00

0.768) and Al cations in R₂-site varying from 0 to 0.293 (averaging 0.063) apfu, which shows that these compositions of tourmalines are related to two different metallogenic fluids (magmatic hydrothermal fluid and basin fluid) and their mixture in the tourmaline crystallization process.

Although the compositions of tourmalines in different occurrences are not consistent, all of them show a closely inherited relation with metallogenic fluid evolution. During the evolutionary process of metallogenic fluid near or within granite entering into the country rocks of carbonate, the Al and Fe contents in the metallogenic fluid tended to decrease, while the Ca and Mg contents would increase gradually, indicating that basin fluid might be constantly

added to and mixed with magmatic fluid as the magmatic fluid rose up and entered into cracks of carbonate rocks.

5.2 Optical and geochemical zonings in Tourmalines

Optical and geochemical zonings are well developed in tourmalines from cassiterite-tourmaline veins in the Gejiu tin deposits. Back-scattered electron images and detecting spots (white dots) for tourmalines with optical zoning in the Gejiu tin deposits are seen in Fig. 4. Compositions at different detecting spots from the core to the rim of the tourmalines are seen in Fig. 5, which display that all the tourmaline grains have similar variation trends, that is, almost no changes in K, Mn and Cl contents, relative minor changes in Al, Si, Na and Ca contents, normally Al>Si and

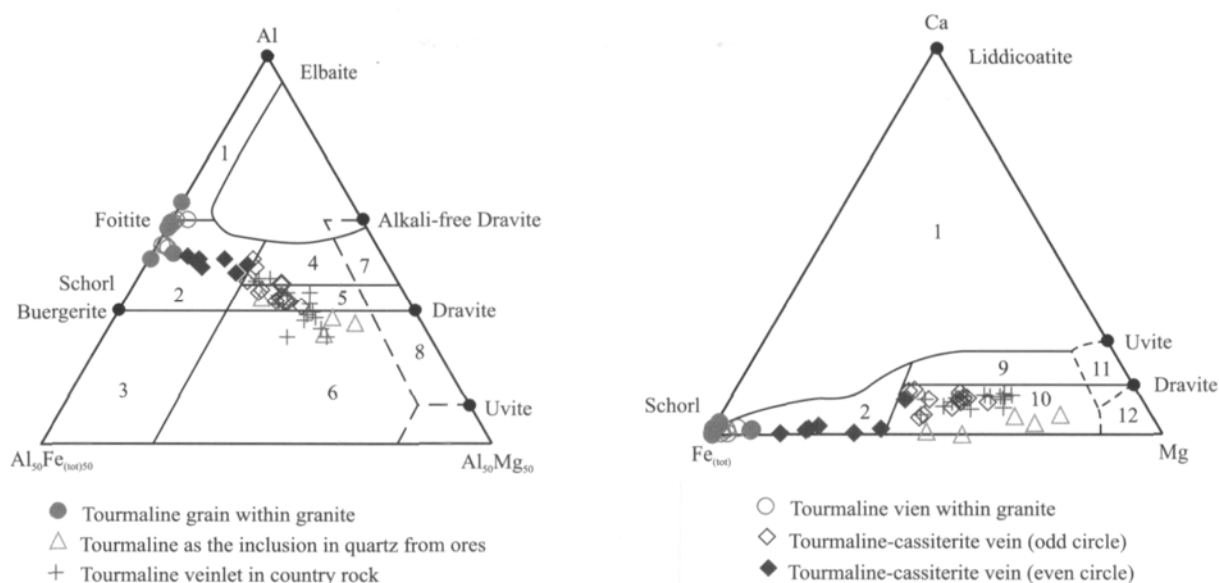


Fig. 3. Ternary Al-Fe-Mg and Ca-Fe-Mg plots of tourmaline compositions from the Gejiu tin deposits (the numbered fields are after Henry and Guidotti (1985)).

1. Li-rich granitoids and associated pegmatites and aplites; 2. Li-poor granitoids and associated pegmatites and aplites; 3. Fe^{3+} -rich quartz-tourmaline rocks; 4. metapelites and metapsammites coexisting with an Al-saturating phase; 5. metapelites and metapsammites not coexisting with an Al-saturating phase; 6. Fe^{3+} -rich quartz-tourmaline rocks, calcsilicate rocks, and metapelites; 7. low Ca metaultramafics and Cr, V-rich metasediments; 8. metacarbonates and metapyroxenites; 9. Ca-rich metapelites, metapsammites, and calc-silicate rocks; 10. Ca-poor metapelites, metapsammites, and quartz-tourmaline rocks; 11. metacarbonates; 12. metaultramafics.

$\text{Na} > \text{Ca}$, and large changes in Fe, Mg and F contents. The alternating changes of two types of optical zonings, light blue and bright white, in tourmalines are mainly due to their large variations of $\text{Fe}/(\text{Fe}+\text{Mg})$ ratios. Generally, the ratios of $\text{Fe}/(\text{Fe}+\text{Mg})$ and $\text{Na}/(\text{Na}+\text{Ca})$ for light blue zoning in tourmalines are smaller than those in bright white zoning, which may indicate that fluids responsible for tourmaline growth from tourmaline-cassiterite veins in the country rocks have periodic variations of $\text{Fe}/(\text{Fe}+\text{Mg})$ and $\text{Na}/(\text{Na}+\text{Ca})$ ratios during the hydrothermal process.

5.3 Correlation of Sn and other elements in tourmalines

As shown in Table 2, Sn mainly has an isomorphous form in tourmalines with low content varying from 0.01–0.24 wt% (averaging 0.08 wt%). The variation of the Sn content in tourmalines is related to $\text{Fe}/(\text{Fe}+\text{Mg})$ and $\text{Na}/(\text{Na}+\text{Ca})$ as well as the F content in tourmalines. The light blue zoning has slightly higher SnO_2 content (0.02–0.24 wt%, averaging 0.09 wt%) with lower ratios of $\text{Fe}/(\text{Fe}+\text{Mg})$ and $\text{Na}/(\text{Na}+\text{Ca})$ as well as higher F content, whereas the bright white zoning has very low SnO_2 content (0.01–0.05 wt%, averaging 0.02 wt%) with corresponding high ratios of $\text{Fe}/(\text{Fe}+\text{Mg})$ and $\text{Na}/(\text{Na}+\text{Ca})$ as well as low F content.

We chose the mole numbers of Sn and other corresponding elements of Mg, Fe, F, Cl, Ca, Na in tourmalines from different occurrences to plot correlation diagrams (Figs. 6, 7, 8, 9, 10 and 11), which show that Sn has positive correlations with Mg, Cl and Ca with different correlation coefficients of 0.6121, 0.4972 and 0.5915

respectively. In contrast, Sn has negative correlations with Fe, F and Na with corresponding correlation coefficients of 0.5576, 0.4044 and 0.4833 respectively. Therefore, the Sn content in tourmalines is closely related to variations of the Mg, Fe, F, Cl, Ca and Na contents in metallogenic fluid. We can see that there are abundant cassiterites around tourmalines (Fig. 4) from vein-type orebodies in the Gejiu tin deposits. Some studies (Muller et al., 2001; Michael et al., 2003) thought that SnO_2 precipitation in vein-type deposits might be related mainly to the mixing of high saline magmatic fluid and low-salinity waters of meteoric origin. This mixing produced sharp decrease in temperature and a sharp increase in f_{O_2} , which would have caused or favored cassiterite precipitation.

6 Discussion and Conclusions

Mineral geochemical compositions of tourmalines from different occurrences in the Gejiu tin polymetallic deposits are very different, implying mixing of post-magmatic hydrothermal fluid and basin fluid. Firstly, tourmalines within granite is mainly schorl with high $\text{Fe}/(\text{Fe}+\text{Mg})$ ratios of 0.912–0.975 and $\text{Na}/(\text{Na}+\text{Ca})$ ratios of 0.892–0.981. Secondly, tourmalines from tourmaline veinlets in the country rocks is mainly dravite with the $\text{Fe}/(\text{Fe}+\text{Mg})$ ratios varying from 0.212 to 0.519, $\text{Na}/(\text{Na}+\text{Ca})$ ratios varying from 0.786–0.997. Thirdly, tourmalines with optical zoning from cassiterite-tourmaline veins have wide varying ranges of $\text{Fe}/(\text{Fe}+\text{Mg})$ ratios and $\text{Na}/(\text{Na}+\text{Ca})$ ratios,

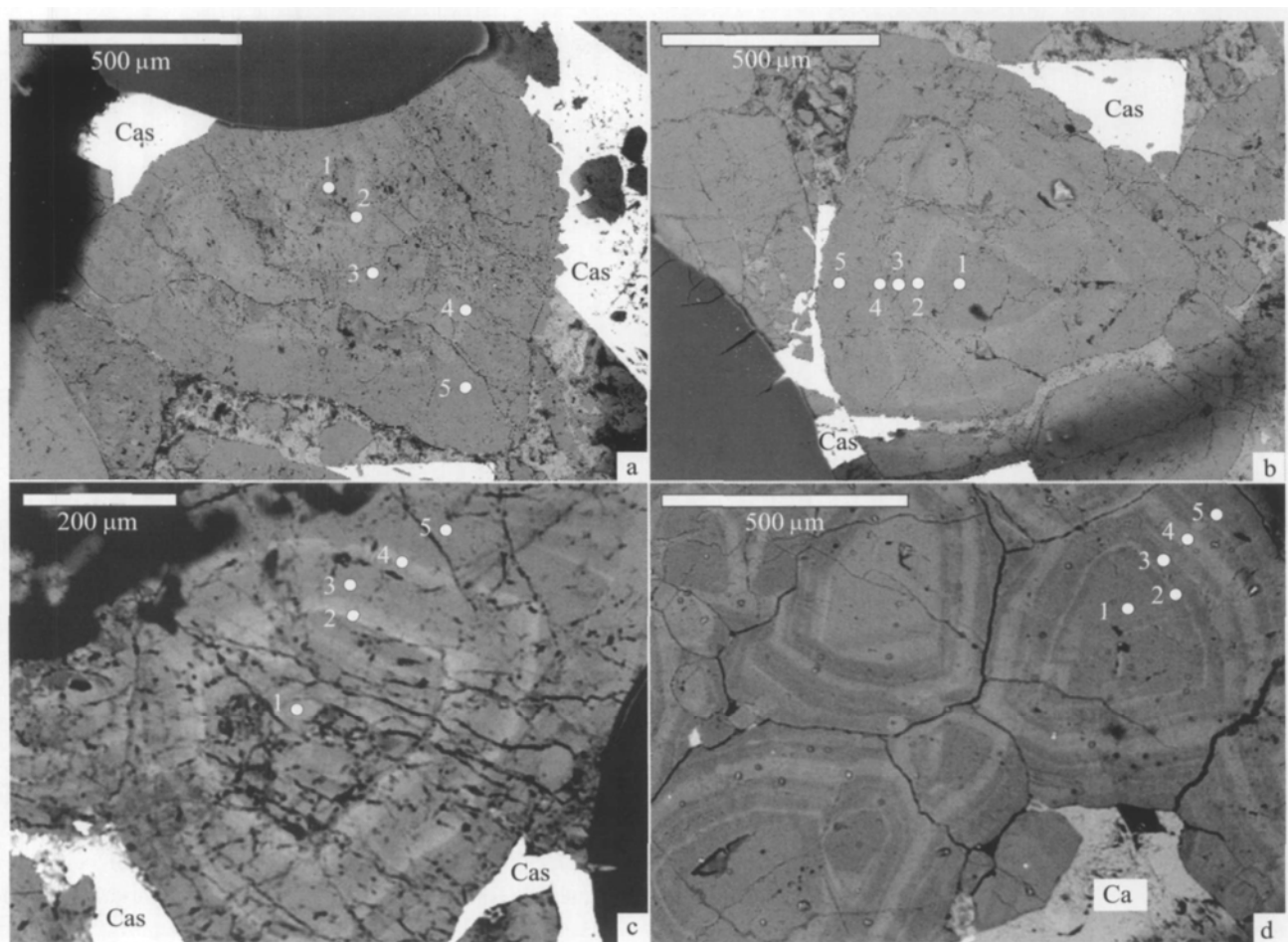


Fig. 4. Back-scattered electron images for tourmaline with optical zoning in the Gejiu tin deposits.

(a, b, c) from sample GR-57; (d) from sample GRJ-3; Cas – cassiterite; Ca – calcite, 1, 2, 3, 4 and 5 represent the detecting spots by electron microprobe from core to rim of tourmaline.

varying from 0.374 to 0.843, and from 0.786 to 0.997, respectively. Their compositions belong to the intermediate area between schorl and dravite with the corresponding high Fe/(Fe+Mg) ratio in bright white zone and low Fe/(Fe+Mg) ratio in light blue zone.

In many granite-related tin deposits, tourmaline compositions display systematic variation from Fe-rich schorl within or near granite bodies to Mg- and Ca-rich dravite-uvite away from granite and in the country sedimentary rocks (London and Manning, 1995; Trumbull and Chaussidon, 1999; Robert and Marc, 1999; Yu and Jiang, 2003). Tourmaline compositions in hydrothermal veins are strongly controlled by the host-rock type and fluid chemistry (Henry and Guidotti, 1985). Jiang (1999) suggested that tourmalines in stratiform host rocks were formed from deeply circulating submarine hydrothermal fluids, and that tourmalines from quartz-tourmaline veins in or near granite were formed from magmatic-hydrothermal fluids. The differences of chemical composition of tourmalines from granite and the country rocks of

carbonate in the Gejiu tin polymetallic deposits indicate that there are two different types of metallogenic fluids: one is post-magmatic hydrothermal fluid with relatively high temperature (represented by schorl), and the other is basin fluid of wall-rock-derived components with relatively low temperature (represented by dravite).

The formation of optical and mineral chemical zonings in tourmalines might be related mainly to the ratios of Fe/(Fe+Mg) (London and Manning, 1995; Deksissa and Koeberl, 2002; Torres-Ruiza et al., 2003; Yu and Jiang, 2003). Tourmalines with distinct optical and mineral chemical zonings can be widely developed in vein-type or bedded-type forms in different types of rock for different metallogenic geneses including magmatic hydrothermalism (London and Manning, 1995), submarine exhalative sedimentation (Xue et al., 1997) and regional metamorphism. Tourmalines in high-grade meta-sedimentary rocks have zonal structure of major element compositions with increasing ratios of Mg/(Mg+Fe) from the core to the outer rim (Pesquera and Velasco, 1997;

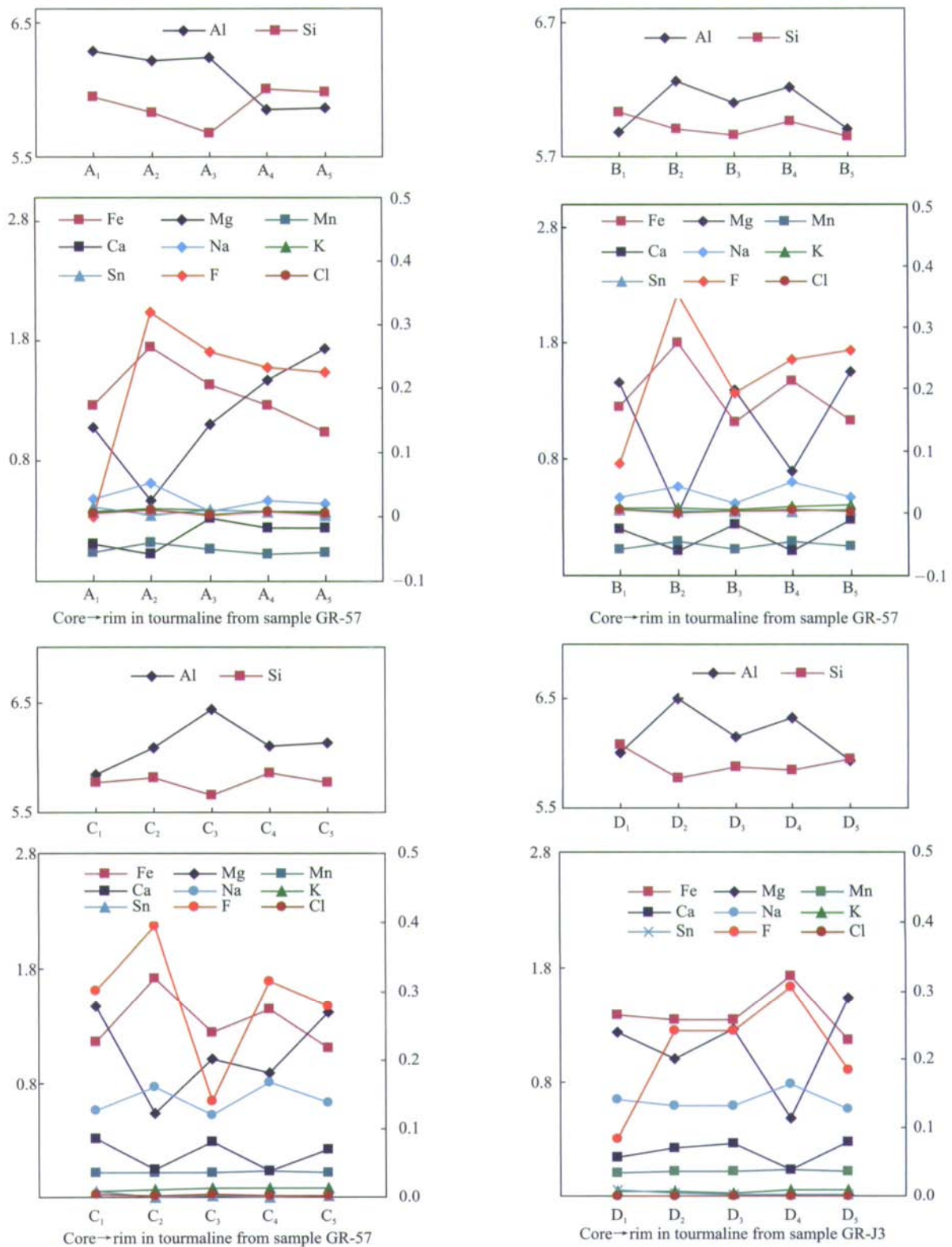


Fig. 5. Chemical composition variation for different optical zonings in tourmaline from the Gejiu tin deposits.

Brocker and Franz, 2000; Nakano and Nakamura, 2001); on the contrary, a few tourmalines in relatively low-grade meta-sedimentary rocks such as blueschist facies show Fe-Ca enrichment and Mg depletion in the rim compared to the

core (Tiwary and Palmer, 1997; Brocker and Franz, 2000). This feature of tourmaline chemistry could be because part of the Fe from the core has diffused towards the rim during metamorphism, or because Fe has been incorporated in the

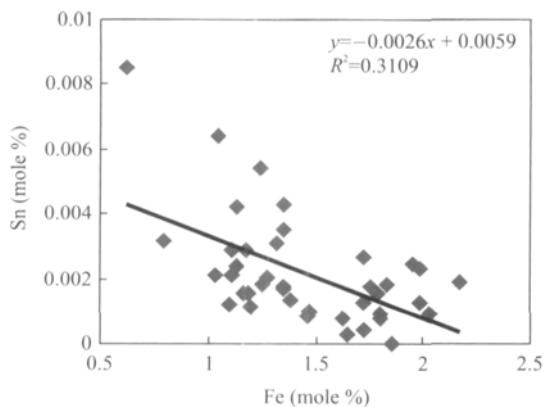


Fig. 6. Sn vs. Fe plot of tourmaline.

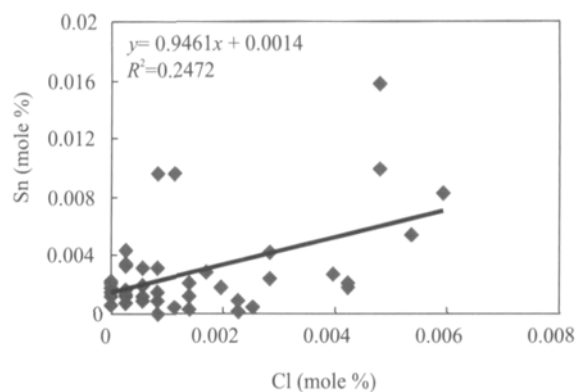


Fig. 9. Sn vs. Cl plot of tourmaline.

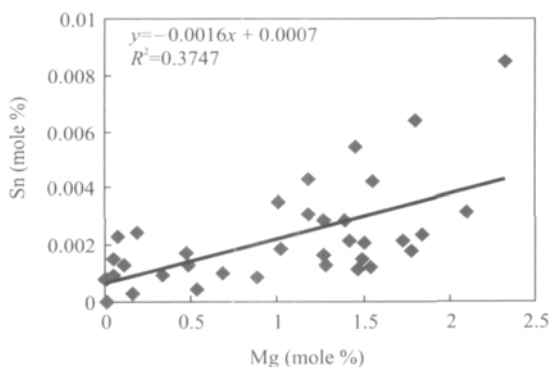


Fig. 7. Sn vs. Mg plot of tourmaline.

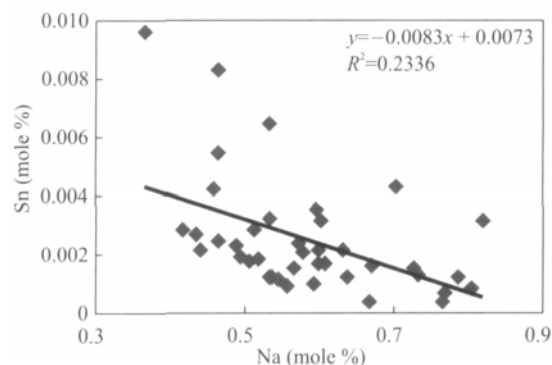


Fig. 10. Sn vs. Na plot of tourmaline.

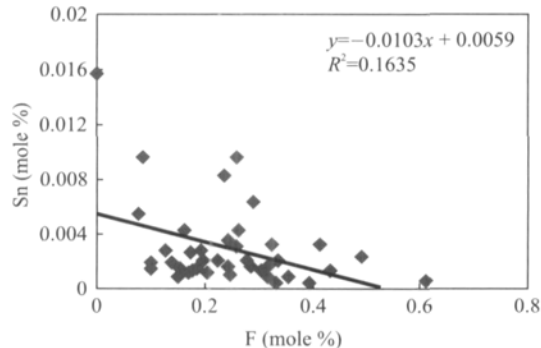


Fig. 8. Sn vs. F plot of tourmaline.

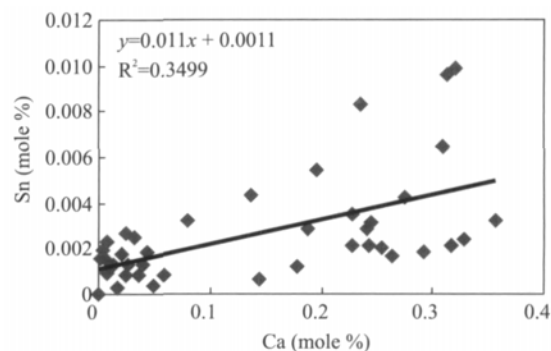


Fig. 11. Sn vs. Ca plot of tourmaline.

tourmaline rim from the surroundings during metamorphism (Tiwary and Palmer, 1997).

Structural characteristics of tourmalines with optical and chemical zoning are very useful for us to study the composition variation of metallogenic fluid during its evolution. Generally, oscillatory zonation in the tourmalines is most likely the result of changes in the P - T conditions of the fluid due to small-scale pressure variations caused by periods of dilation or by throttling of the fluid flow (Yardley et al., 1991). In addition, the oscillatory zonation can be further explained by repeated changes in crystal-fluid equilibrium due to sudden changes of temperature, pressure, H_2O saturation, and fluid composition, or on the basis of disequilibrium crystal

growth (Torres-Ruiza et al., 2003). London and Manning (1995) studied the Cornwall tin deposit and suggested that tourmalines in veins and breccias with chemical variation and fine-scale zoning are hydrothermal in origin formed from open systems by mixing of two fluids along fractures, one fluid derived from granite and the other derived from the host rocks. The occurrence of tourmalines from the Gejiu tin polymetallic deposits with optical and chemical zonings is very similar to that of tourmalines in the Cornwall tin deposit (London and Manning, 1995). Because of two differently derived fluids (magmatic fluid and basin fluid) and their mixing in tectonic crannies of carbonate rock, which lead to continuous change in pressure and temperature of metallogenic fluid, and

periodical oscillation of chemical compositions. Tourmalines with chemical zoning in the Gejiu tin polymetallic deposits may be the result of all changes of metallogenic fluid during its evolution process.

In summary, (1) in the process of sedimentary basin reconstructed by magmatic emplacement, post-magmatic hydrothermal fluid flowing into the sedimentary basin may be the origin of schorl within leucogranite; (2) there are abundant fluids filling in crannies of the sedimentary basin, which may be closely related to dravite developed in the country rock; (3) mixing of two different fluids, i.e. post-magmatic hydrothermal fluid and basin fluid, may result in periodic oscillations of chemical composition and a lot of cassiterites precipitation around tourmalines. All these changes were recorded by tourmalines with different chemical zonings in crannies of the country rock.

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