

Tin partition behavior and implications for the Furong tin ore formation associated with peralkaline intrusive granite in Hunan Province, China

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Abstract Tin deposits are often closely associated with granitic intrusions. In this study, we analyzed tin partition coefficients between different fluids and melts ($D_{Sn}^{aq.fl./melt}$) as well as various crystals and melts ($D_{Sn}^{aq.fl./melt}$ ($D_{Sn}^{crystal/melt}$)) from the Furong tin deposit associated with the Qitianling A-type granite. Our experimental results indicate that tin partition behavior is affected by the chemical compositions of fluids, melts, and minerals. Tin is prone to partitioning into the residual magma in fractional crystallization or other differential magmatic processes if the magma originated from crustal sources with high alkali content, high volatile content, and low oxygen fugacity. Highly evolved residual peralkaline granitic magma enriched in tin can lead to tin mineralization in a later stage. Furthermore, the volatiles F and Cl in the magma play important roles in tin partitioning behavior. Low F contents in the melt phase and high Cl content in the aqueous fluid phase are favorable factors for tin partitioning in the aqueous fluid phase. High Cl content in the aqueous fluid catalyzes water–rock interaction and leads to the extraction of tin from tin-bearing minerals. All these findings support a hydrothermal origin for the tin deposits. In light of the geotectonic setting, petrochemical characteristics, and mineralizing physicochemical conditions of the Furong tin deposit, it is inferred that the ore-forming fluid of the Furong tin ore

deposit could have derived from the Qitianling peralkaline intrusion.

Keywords Tin · Partition · Peralkaline granite · Hunan Province

1 Introduction

Tin deposits are typically closely related to granite spatially, temporally, and metallogenically (Lehmann 1990; Xia and Liang 1991). Most granites associated with tin deposits display an extreme degree of differentiation and generally share the petrochemical characteristics of being peraluminous, enriched in K (relative to Na), and high in Si content, but lower in Ca, Fe, Mg, and Ti content (Lehmann 1990; Xia and Liang 1991; Chesley et al. 1993; Yeap 1993; Sun and Higgins 1996; Botelho and Moura 1998; Bettencourt et al. 2005). Historically, tin mineralization has been thought to be tied to peraluminous, K-rich, orogenic S-type granites. However, in recent decades, important economic tin deposits associated closely with A-type granites have been found (Taylor 1979; Mitchell and Carson 1981; Sawkins 1990; Bi et al. 1993; Botelho and Moura 1998; Liverton and Botelho 2001; Haapala and Lukkari 2005). For example, the Furong superlarge tin deposit in Hunan Province, southeast China is closely associated with the Qitianling peralkaline A-type granite intrusion (Zhao et al. 1998, 2000; Zheng and Jia 2001; Wang et al. 2003a, b; Li 2006; Shuang et al. 2006). A-type granite is generally characterized as peralkaline and anorogenic. Nearly all peralkaline intrusive granites contain alkalis more than 8 wt% more than those in calc-alkali anorogenic granites (Tu 1989). It is important to research the metallogeny of this new type of tin deposit. While there has been some

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research on the new type of tin deposit associated with A-type granite, the question of whether tin-rich aqueous fluid could be derived through peralkaline intrusion remains unsettled. One point of view is that the mineralized fluids of the Furong tin deposit were derived directly from later highly evolved magma (Wang et al. 2004; Li and Liu 2005; Shuang et al. 2006; Li et al. 2007a, b), but another is that the tin-bearing fluids were provided by post-magmatic hydrothermal alteration of the Qitianling granite (Zhao et al. 2005; Jiang et al. 2006).

Metal mineralization associated with intrusions depends to a great extent on fractional crystallization of the magma and partitioning of metallic elements between the melt and aqueous fluid phases in the evolution of the magma. The fractional crystallization of magma and the partition behavior of its metallic elements depend on the composition of the melt, the composition of fluid derived from the melt, and the physicochemical conditions under which the partitioning occurs (Holland 1972; Feiss 1978; Candela and Holland 1984; Urabe 1985; Candela 1989; Keppler and Wyllie 1991; Lowenstern et al. 1991; Peiffert et al. 1994; Candela and Piccoli 1995; Chantal et al. 1996; Webster 1997; Bai et al. 1998; Halter et al. 2002). Existing experimental data of tin partitioning behavior have been collected for this paper. These data include the tin partition coefficients between the crystals and liquids between different granitic melts and aqueous fluid phases in known experimental physicochemical conditions. Based on the existing data, geochemical behavior of tin throughout magma evolution and the factors leading to the tin-bearing granite's petrochemical characteristics are discussed. Furthermore, whether the mineralized aqueous fluids of the Furong tin deposit were derived from the Qitianling peralkaline intrusion is discussed in the context of the petrochemical characteristics of the Qitianling A-type granite, the mineralizing physicochemical conditions, and the geotectonic setting. Finally, the favorable factors of tin mineralization associated with the peralkaline granites are summarized, a significant step in understanding the mechanism of tin ore-forming processes related to peralkaline intrusive granite.

2 Tin partitioning behavior

2.1 Tin partition between minerals and melts

Fractional crystallization is the dominant petrogenetic process controlling magmatic evolution. The main tin carrier in tin deposits related to granitic rocks is cassiterite. Some accessory minerals such as biotite, hornblende, titanite, ilmenite, and magnetite are usually important hosts for tin in granitic rocks because of the preferential

substitution of major cations Ti^{4+} and Fe^{3+} in those crystals by Sn^{4+} (Barsukov 1957; Petrova and Legeydo 1965). These substitutions are possible because the coordination radii of Ti^{4+} , Fe^{3+} , and Sn^{4+} are similar (61, 65, and 69 pm, respectively) (Shannon 1976). In contrast, tin contents in feldspar and quartz are generally very low—much less than tin content in bulk granite rocks.

The compiled data of tin partition coefficients, $D_{Sn}^{crystal/melt}$, between different minerals and melts are shown in Table 1 (Gan 1993). Generally, tin tends to partition into biotite, magnetite, ilmenite, and amphibole rather than plagioclase, K-feldspar, and quartz. As the table shows, tin partition coefficients are affected by the melt composition. For example, the value 5.18 of $D_{Sn}^{crystal/melt}$ between amphibole and metaluminous andesitic melt is almost ten times that between amphibole and peralkaline rhyolitic melt (0.57). The bulk tin partition coefficients between the minerals and different melts are estimated roughly as the average of the coefficients of the individual minerals against the melts. The bulk tin partition coefficients between the minerals and peralkaline basaltic melt, metaluminous andesitic melt, peralkaline andesitic melt, metaluminous acidic melt, peralkaline rhyolitic melt, and peraluminous acidic melt are 0.92, 2.41, 1.04, 1.21, 0.50 and 1.03, respectively. The majority of the bulk tin partition coefficients between the minerals and the melts are near 1. The bulk tin partition coefficient between the minerals and the peralkaline rhyolitic melt is the lowest at 0.50. This implies that the residual magma is likely to be enriched in tin following fractional crystallization of peralkaline granitic magma. In contrast, when the magma is rich in Ti^{4+} , Fe^{3+} , Mg^{2+} , etc., the residual magma will be deficient in tin after abundant tin-

Table 1 Partition coefficients of tin between different minerals and melts

Melt:	I	II	III	IV	V	VI
Mineral						
Olivine	0.57		0.12			
Clinopyroxene	0.53	1.46	1.92	0.52	0.49	
Orthopyroxene		0.55				
Amphibole		5.18	4.29		0.57	
Biotite	2.24		2.59	3.19	2.81	9.90
Plagioclase	0.08	0.57	0.97	0.52	0.67	0.24
K-feldspar			0.37	0.24	0.21	0.10
Quartz		0.32		0.17	0.22	0.05
Magnetite	1.07	16.00	0.09	7.47		
Ilmenite	4.72					

I peralkaline basaltic melt, *II* metaluminous andesitic melt, *III* peralkaline andesitic melt, *IV* metaluminous acidic melt, *V* peralkaline rhyolitic melt, *VI* peraluminous acidic melt (Data collected by Gan 1993)

bearing minerals crystallize. For example, tin is depleted in melt from the mantle at 1000 °C for melts containing abundant olivine and pyroxene crystals, a result of a higher bulk tin partition coefficient (>1) (Lehmann (1990), and tin content in the melt generally is less than 1 $\mu\text{g/g}$ (Hamaguchi and Tin 1969). Tin enrichment in residual melt is almost impossible through andesitic magma evolution because of higher bulk tin partition coefficients between sphene/magnetite and andesitic melt (Petrova and Legeydo 1965; Gill 1978; Osborn 1979). However, peralkaline andesitic magma can differentiate tin-rich melt, as is the case in the Silsilah tin-bearing peralkaline granite in the northeast Arabia shield (Bray 1985), which implies that peralkaline melt is favorable for tin enrichment in the melt phase (Linnen et al. 1995, 1996). Furthermore, if a crustal source intrusion is initially rich in tin, the residual later stage magma will be more enriched in tin after highly evolving due to low initial Ti, Fe, and Mg contents in the intrusion. Therefore, tin transport and enrichment in residual magma should occur in peralkaline crustal source intrusions with a higher degree of fractionation.

High volatile content, particularly F and Cl, can increase tin solubility in the granite melt phase (Bhalla et al. 2005; Farges et al. 2006). F in melt can reduce the melt viscosity and liquidus and lower the crystallizing temperature (Baker and Vaillancourt 1995; Xiong et al. 1998). These factors decrease bulk $D_{\text{Sn}}^{\text{crystal/melt}}$ (with crystals including biotite, hornblende, titanite, ilmenite and magnetite, plagioclase, K-feldspar and quartz, etc.) because of the decreasing substitution by tin in the minerals for the higher crystal order under lower temperature conditions (Badejoko 1984; Xu et al. 1995). As a result, tin contents in the minerals are lower and tin becomes enriched in the melt phase when granitic magma contains more volatiles.

Magmatic oxygen fugacity is another very important factor influencing tin partitioning behavior between minerals and melts. The ionic radius of Sn^{2+} is 93 pm and is larger than that of Sn^{4+} (Huheey et al. 1993). Existing data show that $D_{\text{Sn}^{2+}}^{\text{crystal/melt}}$ is generally less than 1 and $D_{\text{Sn}^{2+}}^{\text{crystal/melt}} < D_{\text{Sn}^{4+}}^{\text{crystal/melt}}$, and that crystals include tin-bearing biotite, hornblende, sphene, ilmenite, and magnetite (Ishihara, 1981). If the oxygen fugacity is higher, the $\text{Sn}^{4+}/\text{Sn}^{2+}$ ratio value in the melt will increase (Linnen et al. 1995, 1996; Farges et al. 2006), accompanied by a higher bulk $D_{\text{Sn}}^{\text{crystal/melt}}$. As a result, tin in the residual melt will be relatively depleted. Low oxygen fugacity is also a favorable factor for enriching tin in residual magma by decreasing bulk $D_{\text{Sn}}^{\text{crystal/melt}}$, as observed in the many tin ore deposits associated with highly differential low oxygen fugacity granite (Ishihara 1981; Lehmann 1990).

It is speculated that tin tends to partition into the residual magma in differential fractional crystallization processes,

when the initial magma is characterized as peraluminous (crustal sources) with lower contents of Ti^{4+} , Fe^{3+} , and Mg^{2+} ; peralkaline; volatile-rich; and having low oxygen fugacity. Such magmas probably serve as favorable reservoirs or as an important transport media for tin ore formation.

2.2 Tin partition between granitic melt and aqueous fluid phase

Experimental results of tin partition coefficients $D_{\text{Sn}}^{\text{aq.fl./melt}}$ between granitic melt and coexisting aqueous fluid show that $D_{\text{Sn}}^{\text{aq.fl./melt}}$ is influenced by oxygen fugacity, temperature, pressure, and chemical compositions of melt and coexisting aqueous fluid (Wang et al. 1986; Li 1989; Webster 1990; Keppler and Wyllie 1991; Chen and Peng 1994; Xiong et al. 1998; Villemant and Boudon 1999; Hu et al. 2008).

Previous experimental results imply that tin favors partitioning into aqueous fluids with abundant Cl^- and F^- ligands (Wang et al. 1986; Li 1989; Keppler and Wyllie 1991; Chen and Peng 1994; Hu et al. 2008). The geochemistry of tin in aqueous fluids indicates that Sn^{2+} complexes with Cl^- more easily than with other complex ions, and divalent tin chloride compounds are stable in reducing acid media (Jackson and Helgeson 1985; Chen 1986; Li 1989; Wilson and Eugster 1990; Taylor and Wall 1993; Barnes 1997; Sherman et al. 2000; Müller and Seward 2001). An experimental study (Hu et al. 2008) conducted at 850 °C, 100 MPa and f_{O_2} near NNO revealed that $D_{\text{Sn}}^{\text{aq.fl./melt}}$ increases with increasing HCl content in aqueous fluid in which Sn^{2+} is the dominant species. Additionally, the aluminum saturation index (ASI) of the melts after equilibrium with high HCl concentration in the aqueous fluid phase will increase due to the transport of alkalis in the melt to the aqueous fluid phase. The presence of fluorine in the starting fluid does not significantly influence $D_{\text{Sn}}^{\text{aq.fl./melt}}$ because fluorine is inclined to partitioning into the melt phase (Webster 1990; Xiong et al. 1998; Villemant and Boudon 1999). Furthermore, compounds of Sn^{4+} and F⁻ could play an important role for tin transport in aqueous fluids when Sn^{4+} is the dominant species at higher oxygen fugacity conditions (Liu and Chen 1986).

Tin partition coefficients ($D_{\text{Sn}}^{\text{aq.fl./melt}}$) are also constrained by melt composition. According to our previous experimental data studied at 850 °C, 100 MPa, and f_{O_2} near NNO (Hu et al. 2008), $D_{\text{Sn}}^{\text{aq.fl./melt}}$ decreases with increasing alkali content in the granitic melt and increases with increasing ASI in the granitic melt. The relationship is described by $D_{\text{Sn}} = -0.0489 \times M_{\text{Alk}} + 0.4516$, $R^2 = 0.98$ (where M_{Alk} is the $\text{Na}_2\text{O} + \text{K}_2\text{O}$ mole content in the melt), and $D_{\text{Sn}} = 0.1886 \times \text{ASI} - 0.1256$, $R^2 = 0.99$. Tin

partition coefficients are correlated negatively with the Na/K molar ratio in peraluminous granitic melt when alkalinity and other component concentrations are relatively constant; the relationship is described as $D_{Sn} = -0.0314 \times R_{Na/K} + 0.0483$, $R^2 = 0.82$ (where $R_{Na/K}$ is the Na/K molar ratio in melt). These relationships imply that Na-rich alkaline granitic melt is favorable for tin partitioning in the melt phase, and that K-rich peraluminous granitic melt is advantageous for tin distribution in the coexisting aqueous fluids phase.

2.3 Tin partition influenced by F and Cl

Volatile elements, particularly F and Cl, play important roles in the evolution of magmas and hydrothermal ore-forming fluid (Webster and Holloway 1988; Webster 1990). The halogens affect intrusion properties such as viscosity, diffusibility, and vapor saturation. Fluorine and chlorine in silicate melt can improve diffusibility of cations by reducing cation activation energies for diffusion (Baker and Watson 1988). Therefore, diffusibility and solubility of tin in melt increase with increasing F and Cl contents in the melt (Bhalla et al. 2005), and high-F and high-Cl content melt could extract tin during magma evolution before the magma is water-saturated. By complexing with metals, they exert strong controls over the compositional variations and the style of mineralization in hydrothermal ore deposits.

According to previous studies (Webster 1990; Xiong et al. 1998; Villemant and Boudon 1999), F is preferentially partitioning into the melt phase, and the partition coefficients of F between aqueous fluid and silicate melt at high pressure and temperature conditions are generally less than 1. As a result, F should be enriched in those kinds of melts through granitic crystallization and differentiation. In contrast to F, Cl prefers partitioning into aqueous fluids with a wide range of partition coefficients from 2 to 117 (Webster 1992b, c, 1997; Bureau et al. 2000). Mg, Ca, Fe, Si, and F clearly influence Cl partitioning behavior between aqueous fluids and silicate melts. Chlorine partition coefficients increase with decreasing molar ratios of $(Al+Na+Ca+Mg)/Si$ and F content in silicate melts; increasing $H_2O/(H_2O+CO_2)$ molar ratios and Cl content in the system are also favorable for chlorine partitioning into the aqueous fluid phase (Webster and Holloway 1988; Webster 1992a; Signorelli and Carroll 2000; Mathez and Webster 2005).

Experimental studies on tin partitioning behavior between the aqueous fluid and granitic melt phases in systems with coexisting F and Cl at 850 °C, 100 MPa, and f_{O_2} near NNO show that $D_{Sn}^{aq.fl./melt}$ is generally less than 0.1, with a little variation when F content in the melt is

more than about 1 wt%. However, $D_{Sn}^{aq.fl./melt}$ increases rapidly when F content in the melt is less than about 1 wt%—i.e. decreasing F content in the melt phase is favorable for tin partitioning into the aqueous fluid phase (Hu et al. 2009). In other words, granitic silicate melt with high F content (more than about 1 wt%) could extract tin, becoming enriched in tin in the melt phase. This is consistent with the fact that a lot of granites associated with tin deposits have a relatively high F content. Increasing $D_{Sn}^{aq.fl./melt}$ values can be caused by increasing Cl partition coefficients, especially in a water-saturated magma system with high HCl content but low F content. Stronger partitioning of Cl into the fluid phase also may cause the partitioning of major elements such as Na and K into the aqueous fluid phase, while the concentrations of SiO_2 and Al_2O_3 in the melt phase are evidently unaffected by increasing HCl concentrations (Frank et al. 2003; Hu et al. 2008). Additionally, Na and K will lead to increased ASI in the melts. It is also implied that increasing $D_{Sn}^{aq.fl./melt}$ is a result of decreasing F content in the melt phase, which could be caused by a great deal of F-bearing minerals crystallizing from tin-rich melt or F degassing into the aqueous fluid phase when pressure is abruptly lowered through fractures or faults, or near the edge of the magma chamber. Furthermore, lower F content in the melt also could decrease tin saturated solubility in the melt (Bhalla et al. 2005), contributing to disseminated cassiterite crystallization in the melt accompanied by F-bearing minerals. Noticeably, chlorine and fluorine begin to exsolve at respective pressures of ~ 100 MPa and ≤ 10 MPa and degas at the rates of 22–55 %, and 0–15 %, respectively, upon eruption (Spilliaert et al. 2006). In shallow magma degassing processes, the aqueous fluids generated by the different degassing paths are deficient in F but enriched in Cl (Villemant and Boudon 1999), which apparently is favorable for Cl-rich aqueous fluid extraction of tin from the melt phase, as well as water–rock interactions.

3 The Furong tin deposit and the Qitianling intrusion

3.1 Geological characteristics

As a new-found superlarge tin deposit, the Furong deposit is located in the largest Nanling Mountains' tungsten-tin polymetallic metallogenic belt in Hunan Province, south-east China (Xu et al. 2000; Wei et al. 2002). The deposit is closely associated with the Qitianling granite intrusion spatially, temporally, and metallogenically (Wang et al. 2003a; Cai et al. 2004; Wang et al. 2004; Jiang et al. 2006;

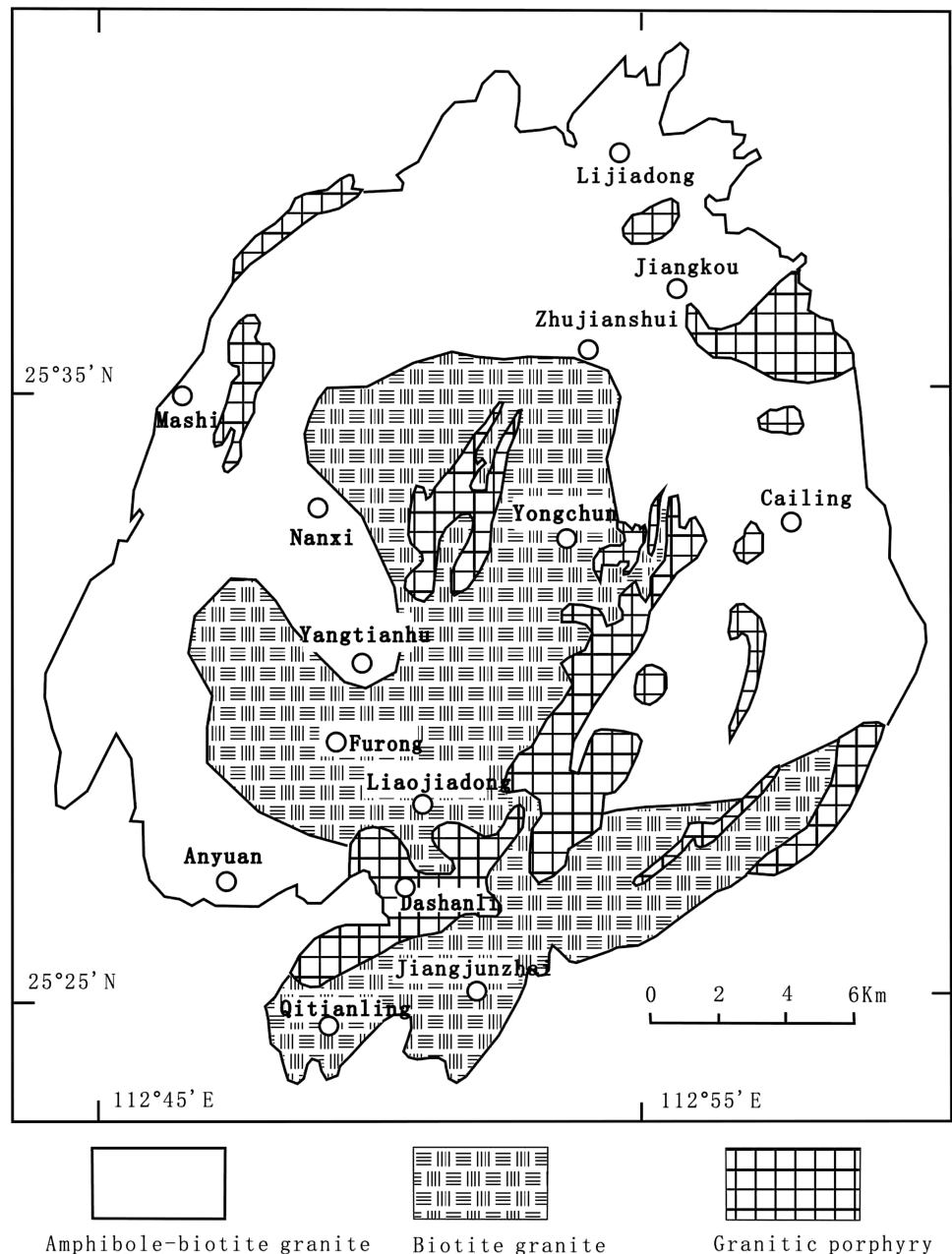
Li 2006; Shuang 2007; Peng et al. 2008). The tin ore bodies of the deposit occur in the Qitianling granite complex or along its contacts with the wall rocks (Wei et al. 2002). The host mineral is cassiterite with accessory minerals such as pyrite, chalcopyrite, magnetite, galena, sphalerite, arsenopyrite, etc. Located at the intersection of the NE-trending Yanling-Chenzhou-Lanshan and the NW-trending Chenzhou-Shaoyang tectonomagmatic belts, the Qitianling granite complex crops out over an area of about 520 km² and includes the Qiguling, Wuliqiao, Goutouling, Maziping, Nanxi, and Lijiadong units (Fig. 1). According to ⁴⁰Ar-³⁹Ar isotopic dating, the ages of the granites associated with the deposit are in the range of 151–160 Ma and the

Qitianling granite intrusion occurred in Yanshanian (Liu et al. 2003). The results of further studies suggest that the main geological period of mineralization occurred between 150 and 160 Ma (Mao et al. 1997). This implies that the intrusion of the Qitianling granite and the mineralization of the Furong tin deposit occurred in the same geological period.

3.2 Petrological and geochemical characteristics of the Qitianling granite complex

The Qitianling granite complex is primarily composed of amphibole-biotite granite and biotite granite. Generally,

Fig. 1 Geological sketch map of the Qitianling granite (modified from Zhu et al. 2007)



both are peralkaline, K-rich, and have high volatiles contents mainly in the form of biotite and fluorite. Crystallization temperatures of the amphibole-biotite granite are in the range of 680–740 °C, which is higher than that of the later biotite granite with crystallization temperatures of 530–650 °C (Li et al. 2007a). The oxygen fugacities of the amphibole-biotite granite and biotite granite range from –16.00 to –15.31 and –19.20 to –17.50, respectively (Li et al. 2007a). The oxygen fugacities of both granites are relatively low, especially those of the biotite granites which approach NNO (Zhao et al. 2005). The chemical compositions of the two granites are shown in Tables 2 and 3.

The geologic age of the early stage amphibole-biotite granite is in the range of 158.6 to 162.9 ± 0.4 Ma (Bi et al. 2008). It has a porphyritic texture with phenocrysts of quartz, K-feldspar, plagioclase, biotite, hornblende, etc., and its accessory minerals are apatite, sphene, zircon, magnetite, etc. The contents of SiO₂, alkalis (K₂O+Na₂O), FeO_{total}, and TiO₂ in the amphibole-biotite granite have weight percentages in the range of 68.59–69.96, 7.45–7.97, 4.04–4.12, and 0.49–0.59, respectively. The ASI is in the range of 1.27–13.7 and the differentiation index (DI) is in the range of 82.40–84.71. Tin concentrations in the amphibole-biotite granite range from 14.90 to 95.80 µg/g.

The biotite granite is the later intrusion with a geologic age of 156.7–153.5 ± 0.4 Ma (Bi et al. 2008). The contents of SiO₂, alkalis (K₂O+Na₂O), FeO_{total}, and TiO₂ in

Table 3 Volatiles F and Cl contents of biotite in the amphibole-biotite granite and biotite granite

Lithology	F (wt%)	Cl (wt%)	F/Cl
Amphibole-biotite granite	0.00–0.11	0.41–0.60	0.00–0.21
Biotite granite	0.23–0.99	0.23–0.48	1.02–2.92

Data from Bi et al. (2008)

the granite have weight percentages in the range of 75.07–76.49, 7.95–8.59, 1.64–1.87, and 0.09–0.12, respectively. Tin concentrations in the biotite granite are less than 12.80 µg/g. The ASI of the biotite granite is higher than that of the early stage amphibole-biotite granite, as is the DI value of the biotite granite with a range of 92.80–93.93. In contrast to the early amphibole-biotite granite, the biotite granite is characterized by its enrichment in silicon and potassium, peraluminous categorization, and high degrees of differentiation.

Furthermore, a series of studies on the Qitianling granite provide important information on the tectonic background of the formation (Zheng and Jia 2001; Shuang et al. 2006; Li et al. 2007b; Bi et al. 2008). The Qitianling granite is characterized as peralkaline granite, having characteristic levels of rare earth elements, trace elements, and major elements, as well as Sr, He, Pb, S, H, and O isotope geochemistry characteristics of a peralkaline granite. Peralkaline granite may derive from crustal melting triggered by

Table 2 Chemical compositions of the Qitianling granite (wt%)

Lithology	Amphibole-biotite granite				Biotite granite				
	Qiguling		Wuliqiao		Goutouling		Maziping		
	Sample	QGL2-21	P-12-2	WLQ-2	WLQ-3	GTL-12	GTL-18	MZP-8	MZP-10
SiO ₂	69.96	69.36	68.59	68.93	75.70	76.49	75.15	75.07	
TiO ₂	0.59	0.49	0.49	0.49	0.12	0.10	0.09	0.09	
Al ₂ O ₃	13.40	13.37	12.90	14.00	12.41	12.16	12.30	12.59	
Fe ₂ O ₃	4.12	4.04	4.12	4.07	1.87	1.84	1.64	1.78	
MnO	0.08	0.09	0.09	0.11	0.08	0.07	0.04	0.05	
MgO	0.72	0.64	0.77	0.68	0.19	0.21	0.05	0.09	
CaO	2.36	1.97	2.24	2.46	0.83	0.70	0.77	0.80	
Na ₂ O	3.13	3.11	2.66	3.01	3.18	3.29	2.87	3.37	
K ₂ O	4.33	4.86	5.25	4.71	4.76	4.71	5.31	5.21	
P ₂ O ₅	0.19	0.17	0.16	0.18	0.02	0.02	0.01	0.01	
LOI	0.94	1.06	1.42	0.76	0.50	0.26	1.09	0.85	
Total	99.80	99.16	98.70	99.39	99.66	99.87	99.32	99.92	
CIPW norms									
Quartz	30.08	28.62	28.81	28.05	37.31	37.74	37.11	34.07	
K-feldspar	25.90	29.30	31.92	28.23	28.39	27.97	31.97	31.11	
Albite	26.75	26.79	23.11	25.82	27.10	27.92	24.69	28.75	
DI	82.73	84.71	83.84	82.10	92.80	93.63	93.77	93.93	
Sn ^a	30.10	16.40	95.80	14.90	12.80	6.30		5.70	

LOI loss on ignition, DI differentiation index

^a The unit of Sn content is µg/g (after Bi et al. 2008)

heat from the upwelling mantle. The two-stage granites of the Qitianling intrusion have a common magmatic origin and are assigned to A-type granite. It is implied that the Qitianling intrusion occurred under the geodynamic setting of lithospheric thinning of South China and post-orogenic crustal extension during the Mesozoic.

4 Discussion

As above mentioned, the Qitianling peralkaline granite derived mainly from crustal resources with some mantle material incorporated. Tin content in the early-stage amphibole-biotite granite varies from 14.90 to 95.80 $\mu\text{g/g}$ (average 39.3 $\mu\text{g/g}$), and volatile content of the whole rock is rather high, especially Cl content as compared to the later stage biotite granite (Table 3). The early tin-rich and volatile-rich magma could have derived from tin-rich crustal strata melted by upwelling mantle heat. Additionally, the Qitianling granite is characterized as peralkaline and volatile-rich with lower oxygen fugacity near NNO, all of which are advantages for tin enrichment in residual magma during early-stage crystallization and differentiation processes under high pressure and closed conditions. As a result, the later stage peralkaline silicate magma would be a favorable reservoir with higher tin and volatile contents. The Cl-rich and tin-bearing hydrothermal fluid could be derived from the residual magma because of the higher $D_{\text{Sn}}^{\text{aq.fl./melt}}$ and $D_{\text{Cl}}^{\text{aq.fl./melt}}$ achieved by higher silicon and water contents in the system. Average SiO_2 content in the late-stage biotite granite is 75.60 wt%, which is higher than that in the amphibole-biotite granite (69.21 wt%). Higher $D_{\text{Sn}}^{\text{aq.fl./melt}}$ and $\text{Cl}_{\text{Sn}}^{\text{aq.fl./melt}}$ could also be caused by a great deal of F-bearing minerals such as fluorite and topaz crystallizing from tin-rich melt during magma cooling or by F degassing into the aqueous fluid phase when pressure is lower around fractures and faults and at the top of the magma chamber. The combination of the above favorable factors enhances $D_{\text{Sn}}^{\text{aq.fl./melt}}$ and $D_{\text{Cl}}^{\text{aq.fl./melt}}$ greatly, which enhances tin partitioning in the aqueous fluids.

Based on the data of the fluid inclusion study on the Furong tin deposits (Shuang 2007), the temperature and pressure of the deposits at formation are mainly in the ranges of 300–450 °C and 17.9–180 MPa. The physicochemical conditions are favorable for F-bearing crystals crystallizing and Cl-rich volatiles degassing. So, the later stage magma of the Qitianling intrusion possessed advantageous physicochemical conditions to produce Cl-rich fluid. The Cl-rich fluid reacted with the melt, leading to increased $D_{\text{Sn}}^{\text{aq.fl./melt}}$ that is a factor in deriving high tin-bearing aqueous fluids. At the same time, the Cl-rich fluid also reacted with tin-bearing minerals, such

as biotite and magnetite, thus extracting more tin from these minerals to the aqueous fluid phase.

As shown in Tables 2 and 3, Sn and Cl contents in the later stage biotite granite are less than those in the amphibole-biotite granite, which may be the result of Sn and Cl partitioning into the aqueous fluid phase. In contrast with Cl distribution behavior, F is inclined to partition into the melt phase, with a degassing pressure and degassing rate of 10 MPa and 15 %, respectively, which are lower than those of Cl at 100 MPa and 22–55 %, respectively (Spilliaert et al. 2006). F content in the melt phase increases with the evolution of magma in a closed, high-pressure system; F mainly remains in the late-stage biotite granite because the ore-forming pressure of the Furong deposit is more than 10 MPa. Therefore, the F/Cl ratio (1.02–2.92) in biotite of the later stage biotite granite is evidently higher than that of the amphibole-biotite granite (0–0.21). Furthermore, the ASI of biotite granite is higher than that of amphibole-biotite granite, which may be related to the abstraction of alkalis by the Cl-rich aqueous fluid phase derived from the residual melt phase.

The evidence from the fluid inclusion study on the Furong deposit shows that the physical chemistry of the ore-forming fluid is characterized by mid-to-high temperature and salinity, and by a Cl-bearing fluid solution with the composition of $\text{CO}_2\text{-CH}_4\text{-CaCl}_2\text{-NaCl-KCl-H}_2\text{O}$ (Shuang 2007; Bi et al. 2008). Research on the minerals (Li et al. 2007a) has revealed that the values of $\log(f_{\text{H}_2\text{O}}/f_{\text{HF}})^{\text{fluid}}$, $\log(f_{\text{H}_2\text{O}}/f_{\text{HCl}})^{\text{fluid}}$, and $\log(f_{\text{HF}}/f_{\text{HCl}})^{\text{fluid}}$ in the aqueous fluids coexisting with the amphibole-biotite granite are 4.22–4.39, 2.78–3.24, and –1.82 to –1.73, respectively. The parallel values of the aqueous fluid coexisting with the late-stage biotite granite are 3.27–3.53, 2.85–3.22, and –0.75 to –0.02, respectively. Evidently, the magmatic hydrothermal fluids derived from the magma in the later stage of the Qitianling intrusion bear higher levels of Cl, which is a favorable condition for tin partitioning into the aqueous fluid phase.

According to Sn, F, and Cl partition behavior and the petrological geochemical characteristics of the Qitianling granite mentioned above, the later stage magma of the Qitianling intrusion possesses favorable physicochemical conditions for deriving a Sn-rich aqueous fluid phase as part of tin ore formation. It can be deduced that tin-bearing ore-forming hydrothermal fluid could be derived from peralkaline, peraluminous, volatile-rich intrusions under favorable physicochemical conditions.

5 Conclusion

Based on the behavior of tin mineralization associated with granitic magmatism and on tin partition coefficients between the minerals and the different melts, we conclude

that tin is likely to be concentrated in residual granitic melt and in the aqueous fluid phase during crystallization and differentiation processes when the granitic magma is peralkaline, high in volatiles, and low in Ca, Fe, and Mg. The highly evolved residual peralkaline granitic magmas could have silicate melts enriched in tin, and thus serve as favorable tin ore reservoirs for later-magmatic hydrothermal tin deposit formation. Tin-rich aqueous fluid could be derived from later peralkaline granitic magma with decreasing F content, increasing water saturation and silica content, under favorable lower pressure and temperature physical conditions. Acidic, Cl-rich aqueous fluids are particularly likely to scavenge abundant tin from highly evolved K-rich, peralkaline, granitic silicate melts, as well as from the high tin-bearing minerals such as biotite, hornblende, titanite, etc. They are favorable for hydrothermal tin metallization. Therefore, the Qitianling peralkaline intrusion could have produced tin-bearing mineralized hydrothermal aqueous fluid for the Furong tin deposit formation.

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