



Tin-carrier minerals in metaluminous granites of the western Nanling Range (southern China): Constraints on processes of tin mineralization in oxidized granites



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ABSTRACT

Huashan, Guposhan and Qitianling are three similar and representative metaluminous A-type tin granites in the western Nanling Range, China. They all have a high oxidization state with magnetite as the dominant Fe–Ti oxide. This study presents an understanding of systematic mineralogy of Sn-bearing minerals (biotite, titanite, magnetite and cassiterite) in the three granites. Biotite has an annite composition and both electron-microprobe and LA-ICP-MS analyses indicate trace amounts of tin in biotite (approximately 100–20 ppm). Chloritization of biotite is accompanied by formation of Sn-rich rutile and cassiterite. Titanite has a long history of crystallization from the early-magmatic stage through the late-magmatic stage to the hydrothermal stage. Owing to its solid-solution relationship with malayaite (CaSnSiO₅), titanite always contains tin to various extents. Early-magmatic titanite contains about 0.5 wt.% SnO₂, while the late-magmatic titanite is markedly enriched in tin (on average 14.8 and 3.4 SnO₂ in titanite from the Qitianling and Huashan granites, respectively). Magnetite grains typically display a trellis structure with ilmenite lamellae, where microinclusions of cassiterite (<1 μm in size) are present. This is likely consistent with features of the “oxy-exsolution” process of Sn-bearing titanomagnetite precursor. Cassiterite may be observed as late-magmatic phase, but most commonly appears as an alteration product of other primary minerals. All tin-bearing minerals in the three granites record a complete process of tin mineralization in granite. The features of tin in primary biotite, titanite and magnetite reflect an initial enrichment during the early stage of magmatic crystallization of the Huashan, Guposhan and Qitianling granites. Association of interstitial Sn-titanite and cassiterite suggests further tin enrichment related to fractional crystallization of granitic magmas. Fluids and alteration of primary minerals play an important role in the leaching, concentration and transportation of Sn during hydrothermal processes, which favors vein-type Sn mineralization.

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1. Introduction

Most primary tin deposits are closely related, in time and space, to granitic rocks, which display a distinct geochemical enrichment in Sn, as well as in other incompatible elements (e.g., F, Li, B, Cs, etc.). Tin granites are generally peraluminous and ilmenite-bearing (Lehmann and Mahawat, 1989; Linnen and Cuney, 2005). However, granites related to tin mineralization in the western Nanling Range (South China) are distinctly metaluminous and contain magnetite as the dominant Fe–Ti oxide phase. It is well known that tin can have two different valences, Sn²⁺ and Sn⁴⁺, at geologically relevant redox conditions. The behavior of tin in silicic melts and its effect on mineralization has been the subject of many experimental studies (e.g., Stemprok, 1990; Taylor and Wall, 1992; Linnen et al., 1995, 1996; Farges et al., 2006). Tin is dissolved in

H₂O-saturated subaluminous to peraluminous melts dominantly as Sn²⁺ under log fO₂ conditions more reduced than ~FMQ (fayalite + magnetite + quartz) + 2.5. By contrast, in oxidized granitic melts Sn⁴⁺ is the dominant oxidation state of tin dissolved in the melt (Linnen et al., 1996). In these cases, tin may enter into Ti-bearing minerals such as biotite, titanite and magnetite by isomorphous substitution of Sn⁴⁺ for Ti⁴⁺. Magmatic crystallization and the subsequent hydrothermal behavior of these minerals may be related to the environments of the granites, and reflect the behavior of tin during mineralization.

The Nanling Range in southern China is a district with extensive granitic magmatic activity and significantly deposits of W, Sn and rare metals. Qitianling, Huashan and Guposhan are three similar and representative metaluminous A-type tin granites (Zhu et al., 2008; Jiang et al., 2008). The aim of this study is to document a series of Sn-bearing minerals in three metaluminous granites, to record their re-equilibration during magmatic-to-hydrothermal processes, and finally to assess the potential role of such minerals in constraining tin mineralization in oxidized granites.

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2. Geological descriptions of the Nanling Range

The Nanling Range is a geographical term, traditionally defining all the mountains on the Guangxi–Guangdong and Hunan–Jianxi borders (approximately longitude 110.0–116.5°E, latitude 23.5–26.5°N); the range extends from west to east for more than 1000 km and from north to south for more than 200 km. Because it consists of the Yuechengling, Dupangling, Mengzhuling, Qitianling and Dayuling Mountains, the Nanling Range is also called the Five Mountains. Geologically, the Nanling Range is located within the South China Block (SCB). It is known for the wide-spread magmatic activity of the Yanshanian (Cretaceous–Jurassic) granitic intrusions, which have a surface exposure of about $64 \times 10^3 \text{ km}^2$ (Zhou et al. 2006), and for its associated W, Sn, Nb, and U mineralization (Xu et al. 1982; Hua et al. 2003).

A Sn/W (including other non-ferrous and rare-metal)-bearing granite belt occurs in the western part of the Nanling Range. This belt extends along a NE-trend for more than 250 km. The total exposure area is over 3000 km² (Fig. 1b, Zhu et al. 2008). Coeval granitic and basic-intermediate magmatic activities are widely distributed. The Nanling Range formed in a post-orogenic, intracontinental tectonic environment that experienced significant lithospheric extension and thinning. The crust–mantle interaction played an important role in the formation of granitic rocks in this region (Li et al. 2009). Moreover, these granitic bodies are typically multi-stage intrusions. Tin–tungsten mineralization developed during emplacement and evolution from the major intrusive stage to the post-magmatic-hydrothermal stage.

3. Analytical methods

Whole-rock major-element compositions of the Huashan, Guposhan and Qitianling granites were measured using an ARL 9800XP + X-ray fluorescence spectrometer in the Modern Analytical Center, Nanjing University, following procedures described by Franzini et al. (1972) and Xie et al. (2010). The samples were prepared in Pt–Au crucibles with the LiBr flux (40 mg/ml, 0.6 mL) using the fusion technique. The calcination temperature of loss on ignition was 960 °C. The analytical absolute deviation of SiO₂ and Al₂O₃ are less than 0.5% and 0.3% respectively. Relative deviation of CaO, K₂O, Fe₂O₃ and TiO₂ are less than 5%, and of MgO, Na₂O, P₂O₅, MnO are less than 10%.

Trace- and rare-earth elements (REE) were analyzed by Finnigan Element II inductively coupled plasma mass spectrometry

(ICP-MS) at the State Key Laboratory for Mineral Deposits Research, Nanjing University. Details of the analytical methods are described in Gao et al. (2003) and Zhou et al. (2004). Precisely weighed 50 mg sample powders were digested within 1 mL of HF and 0.5 mL of HNO₃ in screw high-pressure PTFE-stainless steel bombs at 190 °C. The residues were dissolved at 140 °C using 5 mL 30% (v/v) HNO₃. International granitic standard GSR-1 was used to monitor the quality of the analyses throughout the analytical processes. Rhodium was used as an internal standard to correct the groundmass effects and instrument drift. The precision is better than 10% for most of the elements analyzed.

Backscattered electron (BSE) images and quantitative analyses of polished thin sections were analyzed using a JEOL JXA-8100M electron microprobe (EMP) at the State Key Laboratory for Mineral Deposits Research. The operating conditions were an accelerating voltage of 15 kV, and a probe current of 20 nA for most elements. The counting time on peaks was 80 s for W and Sn, and 20 s for other major elements. The diameter of the electron beam was 1 μm. All data were corrected following standard ZAF correction procedures. Natural minerals and synthetic glasses were used as standards.

In situ analysis of tin contents in biotite were also determined using an Agilent 7500a ICPMS equipped with a 193-nm ArF Excimer laser ablation (LA) system (Geolas CQ) at the Institute of Geology and Geophysics (Chinese Academy of Sciences). The details of the analytical procedures of trace elements compositions determinations are provided in Xie et al. (2010) and Wu et al. (2010). Polished thin sections were ultrasonically cleaned with ethanol. The laser spot size was 70 μm with a laser repetition rate of 9 Hz. During laser ablation, helium gas was flushed into the sample cell to minimize aerosol deposition around the ablation pit and argon gas was then used to improve transport efficiency. NIST SRM610 and 612 silicate glasses were used as calibration standards, and ²⁹Si was used as an internal standard. All of the trace element levels were calculated by using the GLITTER (ver 4.0) program. The precision is better than 10% for most of elements analyzed.

4. Petrology of the Huashan, Guposhan and Qitianling granites

The Huashan, Guposhan and Qitianling A-type granites are all ring-shaped bodies and have similar petrographic features. The Huashan granite crops out with an area of approximately 500 km². It consists of a core of medium-grained biotite granite with some fine-grained granite dikes and is surrounded by

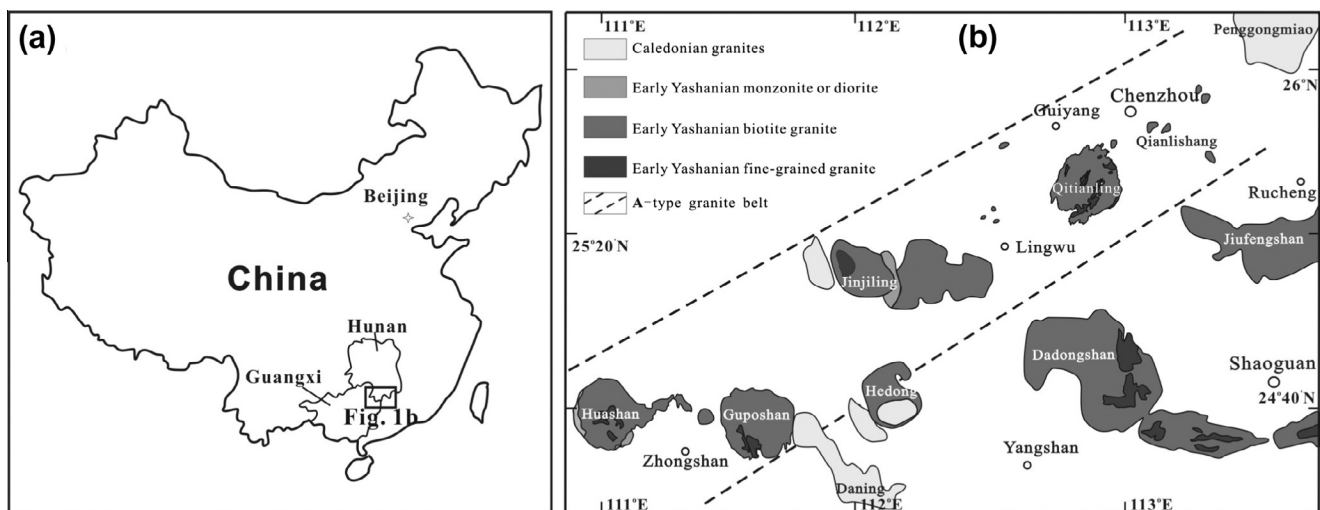


Fig. 1. Distribution of granites in the western Nanling Range, South China (After Zhu et al. 2006).

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