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Key Points:

- Distinct Sn isotope fractionation behaviors distinguish mineralized (Yanbei) from barren (Xiaoxiong) granites effectively
- Sn isotopes effectively trace fractional crystallization and fluid activity in granitic systems
- Reduced, F-rich magmas and late-stage fluids are key to Sn deposit formation

Supporting Information:

Supporting Information may be found in the online version of this article.

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The Distinction Between Sn-Mineralized and Sn-Barren Granites in Sn Isotopes

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Abstract Tin mineralization is commonly associated with highly evolved granites. However, not all highly evolved granitic rocks are mineralized with Sn. Comparative studies of Sn-fertile and Sn-barren granites can deepen our understanding of the key processes that lead to Sn enrichment in magmatic-hydrothermal systems. Here, we present Sn isotope data of two representative granitic suites in South China: the barren Xiaoxiong volcanic-intrusive complex and the Sn-mineralized Yanbei granite porphyry. The Xiaoxiong complex exhibit limited Sn isotope variation with $\delta^{122/118}\text{Sn}_{3161a}$ values ranging from 0.14 to 0.26‰ in the second-stage rocks and from 0.19 to 0.33‰ in the third-stage rocks, consistent with the baseline of the upper continental crust. In contrast, the Yanbei granite porphyry display a broad $\delta^{122/118}\text{Sn}_{3161a}$ range (0.05–0.48‰), reflecting the combined effects of fractional crystallization under relatively low oxygen fugacity conditions and subsequent fluid activity. Fractional crystallization of plagioclase with minor biotite, and Fe-Ti oxides under an oxygen fugacity of $\Delta\text{FMQ}\sim 0$ can account for the initial increase in $\delta^{122/118}\text{Sn}_{3161a}$, but only elevates Sn content by a factor of six, which is insufficient for economic mineralization. This suggests that magmatic fluid exsolution and fluid-melt interaction are crucial for substantial Sn enrichment. Modeling results show that exsolution of a small amount of fluid (2%–6%) from highly evolved melt (with $\Delta^{122/118}\text{Sn}_{\text{fluid-melt}}$ of -0.4 to -0.5 ‰) and that subsequent fluid-melt interaction can explain the observed low and variable $\delta^{122/118}\text{Sn}_{3161a}$ values and high Sn content in late-stage samples. This study demonstrates that Sn isotopes are effective in tracing Sn behavior during magmatic-hydrothermal evolution in granite-related systems.

Plain Language Summary Tin deposits are often found in highly evolved granites, yet not all such granites contain Sn. To understand what makes the difference, we studied two granite suites in South China: one barren (Xiaoxiong) and one fertile (Yanbei). Using Sn isotopes as a tracer, we found that fractional crystallization under reduced conditions can enrich Sn somewhat, but not enough to form a deposit. The key step is the release of Sn-rich fluids from the highly evolved melt. A small amount of this fluid (2%–6%) can dramatically concentrate Sn and leave a distinct isotopic fingerprint. Thus, Sn isotopes can offer a new way to evaluate the Sn metallogenic potential of granite-based systems.

1. Introduction

Tin (Sn) is a critical metal for modern electronics, renewable energy infrastructure, and high-performance alloys. The growing demand for Sn, coupled with potential supply constraints, drives the need for better understanding the formation mechanisms of Sn deposits. Tin exhibits complex geochemical behaviors during magmatic processes, showing moderately incompatible, lithophile, siderophile, and chalcophile characteristics, while becoming fluid-mobile during the magmatic-hydrothermal transition stages (Jochum et al., 1993; Lee, 2018). Most primary Sn deposits are closely related to highly fractionated granitic magmas (Heinrich, 1990; Lehmann, 2021; Lehmann et al., 1990). However, it is important to note that not all highly evolved granites are related to Sn mineralization. The enrichment of Sn to industrial ore grades is argued to be controlled by a combination of processes during granitic magma formation and evolution, including the partial melting of Sn-enriched source rocks (Yuan et al., 2019; Zhao, Chu, et al., 2022) extensive fractional crystallization within silicate melts (Lehmann, 1982, 2021), and the efficient extraction (Zhao, Zajacz, et al., 2022) and transport of Sn by exsolution of fluids (Lehmann, 2021; Zhao, Zajacz, et al., 2022). Therefore, it is essential to assess the contribution of various process, and important insights could be gained by comparing the barren granites and fertile granites that directly linked to Sn mineralization.

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New development in high-precision Sn isotope analysis (She, Li, An, & Cai, 2023; She, Li, An, Yang, & Zhang, 2023) offers a novel approach of direct isotopic tracing Sn enrichment mechanisms in magmatic-hydrothermal processes (She et al., 2024; K.-K. Sun et al., 2024). Early applications of Sn isotopes focused on mafic magma evolution, revealing Sn isotope fractionation during partial melting and the crystallization of ilmenite (Badullovich et al., 2017; X. Wang et al., 2018). However, studies of Sn isotope behaviors during crustal magmatic-hydrothermal processes relevant to granite-related Sn mineralization remain scarce. Recently, She et al. (2024) established the Sn isotope baseline for the average upper continental crust, laying a foundation for investigating magmatic-hydrothermal processes in granitic systems. K.-K. Sun et al. (2024) further demonstrated significant Sn isotope variations in Gejiu and Laochang mineralized granites, ascribing them to fractional crystallization (e.g., of biotite, feldspar, and Fe-Ti oxides) and fluid-mediated processes. Furthermore, recent studies of Sn isotopes in Sn-bearing minerals, such as cassiterite and stannite, have provided new insight into the mechanisms of Sn transport and precipitation, and the physicochemical conditions of ore-forming fluids (P. Liu, Mao, Lehmann, Weyer, et al., 2021; P. Liu et al., 2025; Mathur et al., 2025; M. Sun et al., 2024; Wu et al., 2023; Z.-H. Zhou et al., 2022). Despite these advances, it remains unclear whether Sn isotopes fractionate during crystal-melt separation within silicic crystal mushes, which is recognized as a fundamental mechanism in the formation of volcanic-plutonic complexes and the chemical differentiation of the upper crust (Bachmann & Bergantz, 2004; Bachmann & Huber, 2016; Laurent et al., 2020). Moreover, it is necessary to distinguish between the isotopic signatures of fractional crystallization and hydrothermal activity in Sn mineralization.

This study presents high-precision Sn isotope data on two representative Late Mesozoic granitic suites from South China with contrasting geochemical features and mineralization outcomes: the Xiaoxiong volcanic-intrusive complex and the Yanbei granite porphyry. The Xiaoxiong complex represents a barren suite that experienced crystal-melt separation and lacked fluid activity. In contrast, the Yanbei granite porphyry is a well-characterized, highly evolved melt product genetically linked to Sn mineralization. This comparative study aims to: (a) quantify the extent of Sn isotope fractionation during crystal-melt separation in silicic magmatic systems; (b) decipher the effects of fluid exsolution and fluid-melt interaction on Sn isotope signatures and Sn enrichment; (c) evaluate the applicability of Sn isotopes in assessing the Sn metallogenic potential of granitic systems.

2. Geological Setting and Samples

The Xiaoxiong and Yanbei complex are located in the Cathaysia Block of South China (Figure 1) and both were formed during the Late Mesozoic period (142–67 Ma) (X. M. Zhou et al., 2006). During this period, the Paleo-Pacific Plate underwent a complex tectonic transition of low-angle rapid subduction to high-angle rollback (He & Xu, 2012; Uyeda, 1982; X. M. Zhou & Li, 2000), which triggered multiple magmatic events and the formation of volcanic-intrusive complexes including the Xiaoxiong and Yanbei complexes (Li et al., 2021; P. Liu, Mao, Lehmann, Peng, et al., 2021; X. Xu et al., 2024).

2.1. The Xiaoxiong Complex

The Xiaoxiong complex is situated in Linhai, Zhejiang Province, southeast China (Figures 1a and 1c). It exhibits a typical ring-shaped structure with circumferential and radial faults, indicative of caldera collapse (Weng & Yu, 1999). The volcanic-plutonic assemblage formed in three stages: the lower Cretaceous formation (K_2x^1 , 98–96 Ma) dominated by basaltic trachyandesite and rhyolitic tuffs (RT-I), the middle formation (K_2x^2 , 95–92 Ma) featuring rhyolite (R-II), and the upper formation (K_2x^3 , ~88 Ma) composed of rhyolite (R-III) and quartz trachyte (QT-III). Spatially associated intrusive rocks include granite porphyry (GP-II, ~90 Ma) and syenite porphyry (SP-III, ~88 Ma), collectively representing a shallow crustal magma chamber system. The calc-alkaline to high-K calc-alkaline volcanic rocks and felsic plutons demonstrate a multistage evolution, with synchronous eruptions and intrusions reflecting fractional crystallization and crystal-melt segregation processes in a transient magmatic reservoir. Zircon U-Pb ages and Hf-Nd isotope data confirm the temporal overlap and genetic linkage between volcanic and plutonic phases, marking the terminal stage of the magmatism in the region (Zheng & Xu, 2021). This study selected volcanic-intrusive rock pairs from the second and third stages of the Xiaoxiong complex, which have been extensively documented and widely recognized as representative of melt extraction processes in the “mush model.” Tin isotope analyses were performed on rhyolites (R-II and R-III), granite porphyry (GP-II) and syenite porphyry (SP-III) that had been studied in detail by Zheng and Xu (2021).

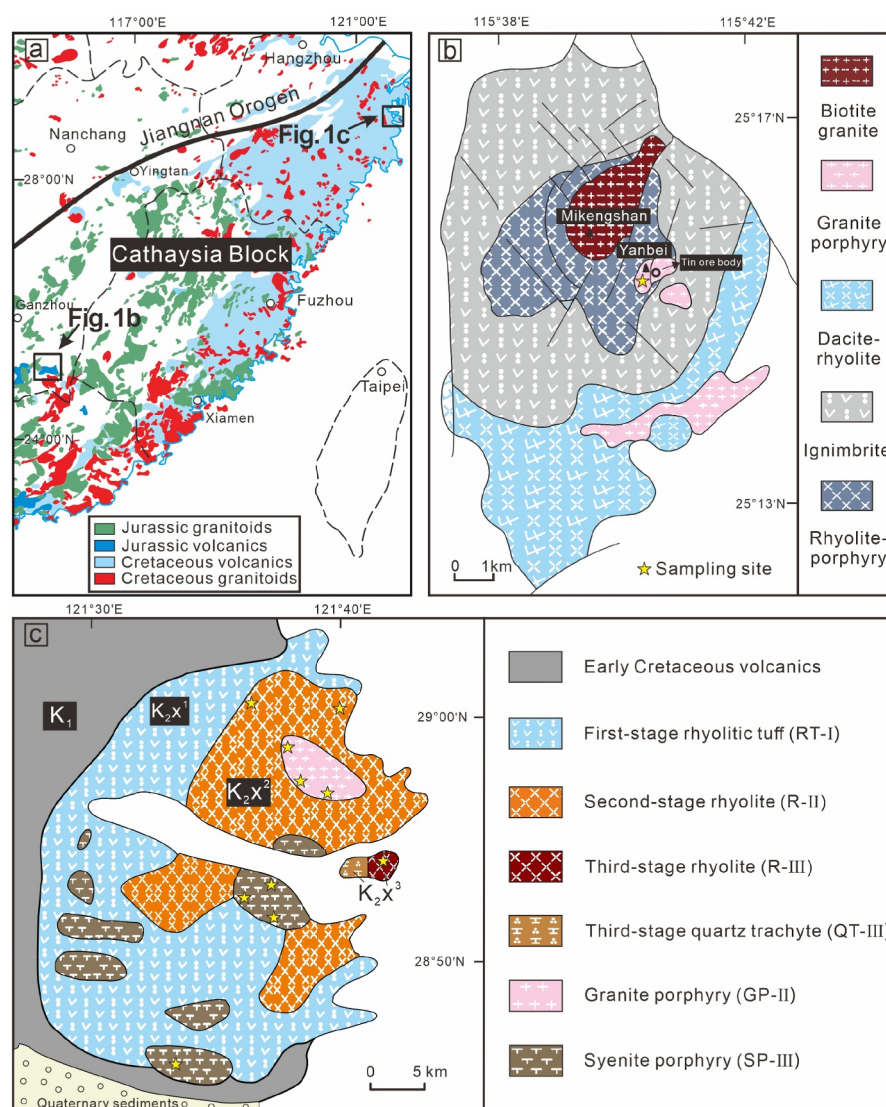


Figure 1. (a) Simplified geological map of SE China showing the distribution of Late Mesozoic intrusive-volcanic rocks (modified after X. M. Zhou et al., 2006). (b) Geologic sketch map of the Yanbei complex (modified after C.-S. Liu et al., 1999). (c) Geologic map of the Xiaoxiong complex (modified after Zheng & Xu, 2021). Sample locations are marked by yellow stars; detailed sample information can be found in Li et al. (2024) and Zheng and Xu (2021), respectively.

2.2. The Yanbei Complex

The Yanbei complex is located in land of southeastern China, within the Nanling W-Sn metallogenic province and the Early Cretaceous volcanic basin (Figures 1a and 1b). It hosts the Yanbei porphyry Sn deposit and comprises a volcanic-intrusive assemblage. The lithology comprises dacitic to rhyolitic volcanic rocks (including ignimbrites, rhyolite porphyry, and tuffaceous lavas) and highly fractionated granitic intrusions, such as granite porphyry and biotite granite. These rocks are peraluminous, with elevated SiO₂ (>75 wt%), F, and incompatible trace elements (e.g., Rb, Zr, Sn). The Sn ores occur as disseminated to veinlet-disseminated cassiterite at the contact between subvolcanic rhyolite porphyry and intrusive granite porphyry (C.-S. Liu et al., 1999). High-precision cassiterite U-Pb dating constrains the timing of Sn mineralization to ~130.4–136.7 Ma (P. Liu, Mao, Lehmann, Peng, et al., 2021). Building on the comprehensive petrological, geochronological, and geochemical characterization of the Yanbei complex by Li et al. (2021), this study presents new Sn isotope data for the Sn-mineralized granite porphyry.

3. Analytical Methods

The Sn isotope measurements were conducted at the State Key Laboratory of Critical Earth Material Cycling and Mineral Deposits, Nanjing University. Powdered sample that contained approximately 0.5 μg Sn was mixed with ^{117}Sn – ^{122}Sn double spike solution for a sample/spike ratio of $\sim 40:60$ prior to digestion. The sample was dissolved using a mixed acid solution (5 mL HNO_3 + 2 mL HCl + 1 mL HF) at 130°C for 24 hr on a hotplate. After complete digestion, the solution was evaporated to dryness at 90°C . The sample was then re-dissolved in 4 mL 3 M HCl and stored for subsequent Sn purification.

A two-stage column chromatography procedure reported by Qu et al. (2024) was employed for Sn purification. The first column (2 mL AG 1-X8 resin, 200–400 mesh) was conditioned with 10 mL 3 M HCl . After loading the sample, matrix elements were eluted with 30 mL of 0.5 M HCl followed by the selective elution of Sn, along with residual Cd, Zn, and Sb using 10 mL 2 M HNO_3 . The collected solution was evaporated at 90°C with 50 μL HF to inhibit hydrolysis and was finally re-dissolved in 8 mL 0.5 M HNO_3 for the second purification. The second column (2 mL AG 50W-X12 resin, 200–400 mesh) was preconditioned with 8 mL 0.5 M HNO_3 . The Sn fraction from the first column was loaded and matrix interferences (e.g., Mo and Sb) were removed with 8 mL 0.5 M HNO_3 . Tin was recovered by eluting with 10 mL 0.5 M HF . To ensure quantitative recovery, 2 mL HNO_3 was then added to the eluate. The final eluate was evaporated to dryness at 90°C and the sample was dissolved in 3 mL mixed acid of 0.3 M HNO_3 –0.006 M HF for Sn isotopic analysis.

Tin isotope analyses were performed on a Nu Sapphire multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) at Nanjing University, following the method of She, Li, An, and Cai (2023). The concentration of all Sn solutions was adjusted to 100 ng/mL before mass spectrometry. The typical signal intensity for ^{120}Sn was ~ 14 V per 100 ng/mL. During analysis, each sample was bracketed by a spiked NIST 3161a standard at the same concentration. All isotopic results are expressed in the $\delta^{122/118}\text{Sn}$ notation relative to the primary Sn isotopic reference solution NIST 3161a (Lot#140917; values consistent with Meister et al. (2026)): $\delta^{122/118}\text{Sn}_{3161a} (\text{‰}) = [({}^{122}\text{Sn}/{}^{118}\text{Sn})_{\text{sample}}/({}^{122}\text{Sn}/{}^{118}\text{Sn})_{3161a} - 1] \times 1,000$. The intermediate (2SD external) precision is better than $\pm 0.07\text{‰}$ based on repeated analysis of GSP-2 ($n = 12$) at Nanjing University (She, Li, An, & Cai, 2023). The accuracy of Sn isotope analysis was verified by analyzing geological reference materials along with samples (GSP-2 and BCR-2), which yielded $\delta^{122/118}\text{Sn}_{3161a}$ values of 0.25 ± 0.05 and 0.30 ± 0.03 (2SD, $n = 3$ for all), respectively (Table S2 in Supporting Information S1), in agreement with those reported by recently studies (Meister et al., 2026; She, Li, An, & Cai, 2023).

4. Results

The whole-rock Sn isotope compositions and related geochemical data of Xiaoxiong volcanic-intrusive complex and Yanbei granite porphyry are tabulated in Table 1 and Table S1 and Table S2 in Supporting Information S1.

The Xiaoxiong volcanic-intrusive complex display relatively homogenous Sn contents, with second-stage rhyolites (R-II), granite porphyry (GP-II), third-stage rhyolites (R-III) and syenite porphyry, containing 1.27–1.46 ppm, 0.85–1.13 ppm, 1.36–3.57 ppm, and 1.42–1.60 ppm, respectively (Table 1). These values are close to the Sn concentration of 2.1 ppm estimated for upper continental crust (Rudnick & Gao, 2003). The Sn isotope compositions are also uniform across volcanic and intrusive rocks (Figure 2), with the average $\delta^{122/118}\text{Sn}_{3161a}$ of $0.23\text{‰} \pm 0.04\text{‰}$ (1σ , $n = 3$), $0.22\text{‰} \pm 0.05\text{‰}$ (1σ , $n = 3$), $0.24\text{‰} \pm 0.05\text{‰}$ (1σ , $n = 5$) and $0.27\text{‰} \pm 0.05\text{‰}$ (1σ , $n = 6$), for R-II, GP-II, R-III, and SP-III, respectively. These results are consistent with the Sn isotope composition of $0.23 \pm 0.09\text{‰}$ for the estimated average continental upper crust (She et al., 2024).

In contrast, the Yanbei granite porphyry exhibits significant geochemical variations, with Sn contents ranging from 7 to 217 ppm, F contents varying from 4,070 to 17,000 ppm, and Rb/Sr ratios spanning from 22 to 46 (Table 1; Table S1). The $\delta^{122/118}\text{Sn}_{3161a}$ values also display considerable variations (0.05 – 0.48‰), which increase with rising Sn content, F content, and Rb/Sr ratios, then decrease after reaching the heaviest value (Figures 2, 3b, and 3d).

Table 1
Whole-Rock Sn Isotope Compositions and Other Geochemical Characteristics for the Xiaoxiong Volcanic-Intrusive Complex and the Yanbei Granite Porphyry

Sample	Type	$\delta^{122/118}\text{Sn}_{3161.6}$ (‰)	2 σ	SiO ₂ (%) ^a	CaO (%) ^a	K ₂ O (%) ^a	MgO (%) ^a	TiO ₂ (%) ^a	FeO ^T (%) ^a	Sn (ppm) ^a	Ba (ppm) ^a	Rb (ppm) ^a	Sr (ppm) ^a	F (ppm) ^a	Eu/ Eu ³⁺	$\epsilon_{\text{Nd}}(t)^a$	CIW	CIA	A/ CNK	A/ NK	Qtz-Ab-Or	Location
Xiaoxiong																						
10xx-10	Rhyolite (R-II)	0.18	0.06	80.74	0.05	3.55	0.01	0.1	0.36	1.29	1.31	98.38	95.07	49	–	0.34	–	64	52	1.08	1.09	0.47-0.31-0.22 6° E121° 37°56″
19xx-09		0.26	0.05	75.08	0.37	5.02	0.38	0.13	0.64	1.46	1.49	243.94	159.91	21.6	–	0.38	–5.5	63	49	0.97	1.03	0.31-0.38-0.31 N28°59′ 36.70″ E121°35′ 10.80″
19xx-10		0.24	0.07	79.15	0.18	5.28	0.04	0.11	0.26	1.27	1.37	274.08	180.8	28.38	–	0.4	–5.8	70	52	1.06	1.1	0.44-0.24-0.32 N28°59′ 34.07″ E121° 35°11″
19xx-48	Rhyolite (R-III)	0.19	0.07	76.95	0.09	5.48	0.38	0.16	1.25	3.46	3.65	76.54	267.12	24.37	–	0.28	–3.9	69	50	1.02	1.03	0.39-0.27-0.34 N28°54′ 641″ E121°41′ 38.51″
19xx-50		0.23	0.07	77.06	0.34	5.1	0.35	0.16	1.25	3.92	4.02	38.07	254.79	19.05	–	0.25	–4	65	48	0.94	0.99	0.38-0.30-0.32 N28°54′ 13.55″ E121° 41°47.8″
19xx-58-1		0.29	0.03	75	0.66	4.84	0.37	0.12	0.68	1.45	1.44	186.43	159.62	56.37	–	0.39	–	65	51	1.05	1.16	0.37-0.32-0.31 N28°58′ 16.93″ E121°37′ 33.24″
19xx54-1	Granite porphyry (GP-II)	0.25	0.06	67.97	1.22	5.06	0.69	0.27	1.52	1	1.05	2075.78	113.46	270.9	–	1	–	59	49	0.95	1.09	0.15-0.51-0.34 N28°56′ 42.54″ E121°40′ 17.62″
19xx-55		0.21	0.08	69.21	1.2	5.19	0.49	0.31	1.69	1.12	1.1	2224.12	122.41	298.71	–	0.99	–5.2	63	50	1.02	1.19	0.22-0.41-0.37 N28°56′ 35.23″ E121°39′ 25.05″
19xx-56		0.14	0.07	67.21	2.49	4.48	0.82	0.25	1.49	0.85	1.01	1751.56	111.29	200.79	–	1.02	–	55	47	0.87	1.17	0.18-0.50-0.32 N28°56′ 54.60″ E121°39′ 20.39″
19xx-59		0.26	0.08	69.01	1	4.61	0.7	0.26	1.54	0.93	1.01	1790.06	113.22	196.45	–	0.97	–	61	51	1.02	1.16	0.19-0.50-0.31 N28°59′ 1.35″ E121°38′ 44.49″
19xx-60		0.26	0.08	69.76	1.19	4.45	0.52	0.31	1.73	1.13	1.12	2045.23	107.16	237.78	–	1.01	–5.4	60	50	0.99	1.15	0.22-0.48-0.30 N28°58′ 32.11″ E121°38′ 57.09″
19xx-29	Syenite porphyry (SP-III)	0.22	0.03	61.03	2.06	5.71	1.77	0.97	3.56	1.6	1.62	1701.02	81.76	187.54	–	0.99	–	62	49	0.95	1.2	0.06-0.51-0.43 N28°45′ 41.36″ E121°35′ 33.68″
19xx-33		0.2	0.05	60.82	2.61	5.7	1.28	0.79	3.74	1.55	1.63	1633.74	90.49	161.65	–	0.99	–3	59	47	0.88	1.18	0.06-0.50-0.43 N28°45′ 59.87″ E121°35′ 43.19″
19xx-42		0.33	0.04	63.39	1.39	6.32	1.19	0.78	2.89	1.42	1.52	2083.89	75.27	168.57	–	1.09	–	61	48	0.92	1.06	0.02-0.55-0.43 N28°55′ 39.45″ E121°38′ 42.67″

Table 1
Continued

Sample	Type	$\delta^{222/18}\text{Sn}_{3161a}$ (‰)	2σ	SiO_2 (%) ^a	CaO (%) ^a	K_2O (%) ^a	MgO (%) ^a	TiO_2 (%) ^a	FeO^T (%) ^a	Sn (ppm) ^a	Ba (ppm) ^a	Rb (ppm) ^a	Sr (ppm) ^a	F (ppm) ^a	Eu^a Eu^b	$\epsilon_{\text{Nd}}(t)^a$	CIW	CIA	A/CNK	A/NK	Qtz-Ab-Or	Location
19xx-43-1		0.32	0.06	64.23	1.61	6.45	1.1	0.87	2.84	1.5	2069.11	93.51	149.65	—	1.07	−3.2	59	47	0.87	1.03	0.01-0.56-0.43	N28°55′ 20.69″ E121°38′ 18.20″
19xx-44-1		0.28	0.03	61.92	2.01	6.05	1.37	1.1	3.29	1.56	1858.97	74.61	186.81	—	0.99	—	58	46	0.85	1	0.01-0.57-0.43	N28°55′ 14.86″ E121°38′ 54.38″
19xx-65		0.26	0.05	61.2	2.04	7.36	1.92	0.08	4.36	1.49	1994.07	239.9	289.89	—	1.04	−3.2	63	46	0.85	1.06	0.02-0.44-0.54	N28°52′ 27.82″ E121°36′ 39.40″
Yanbei																						
15HC-9	Granite porphyry (GP)	0.05	0.05	77.25	0.62	4.87	0.1	0.08	0.7	7	58	651	29.3	4,070	0.06	−3.5	66	51	1.05	1.17	0.42-0.27-0.31	N 25°15′ 45.38″ E 115°40′ 10.93″
15HC-10		0.48	0.06	76.98	0.69	4.82	0.07	0.09	0.78	39	54.6	670	29.3	6,090	0.06	—	67	52	1.07	1.2	0.43-0.26-0.31	
15HC-11		0.38	0.02	77.1	0.62	5.14	0.04	0.08	0.47	26	52.5	598	24.4	4,160	0.05	−3.5	65	50	1	1.1	0.38-0.30-0.32	
15HC-12		0.17	0.05	77.42	0.72	5	0.07	0.07	0.66	11	53.1	681	30.9	4,950	0.05	—	67	52	1.06	1.2	0.43-0.26-0.32	
15HC-13		0.21	0.06	77.26	0.65	4.86	0.07	0.08	0.76	8	49.7	630	27.7	4,760	0.06	−3.5	67	52	1.07	1.19	0.43-0.26-0.31	
15HC-14		0.2	0.08	76.14	0.61	5.37	0.07	0.08	0.69	8	71	702	30.3	4,320	0.06	—	67	51	1.05	1.16	0.40-0.25-0.35	
15HC-15		0.27	0.03	78.42	0.6	4.76	0.06	0.08	0.64	13	46.2	656	28.3	5,380	0.05	−3.5	68	52	1.1	1.23	0.46-0.24-0.30	
15HC-16		0.26	0.06	76.11	0.7	5.39	0.05	0.07	0.34	25	57.2	607	26.3	4,660	0.07	—	65	50	1	1.11	0.36-0.30-0.34	
17HC-52		0.27	0.02	75.06	0.83	4.42	0.04	0.05	1.92	79	26.2	998	28	11,000	0.04	−3.4	76	59	1.44	1.73	0.53-0.16-0.31	N 25°15′ 23.28″ E 115°40′ 36.94″
17HC-54		0.15	0.01	74.51	0.68	3.46	<0.01	0.02	2.16	217	19.5	956	20.8	17,000	0.04	−3.7	78	64	1.79	2.14	0.59-0.16-0.25	

Note. CIA is defined as molar $\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O}) \times 100$, and CIW as $\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O}) \times 100$, where CaO^* refers to CaO in silicate (Harnois, 1988; Nesbitt & Young, 1982). A/NK = molar $\text{Al}_2\text{O}_3/(\text{Na}_2\text{O} + \text{K}_2\text{O})$; A/CNK = molar $\text{Al}_2\text{O}_3/(\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO})$. Qtz-Ab-Or represents the CIPW-normative proportions of quartz, albite and orthoclase. ^aData sources: the Xiaoxiong volcanic-intrusive complex, Zheng and Xu (2021); the Yanbei granite porphyry, Li et al. (2021, 2024). ^bTin content was calculated inversely via the double-spike method for comparison (Stracke et al., 2014).

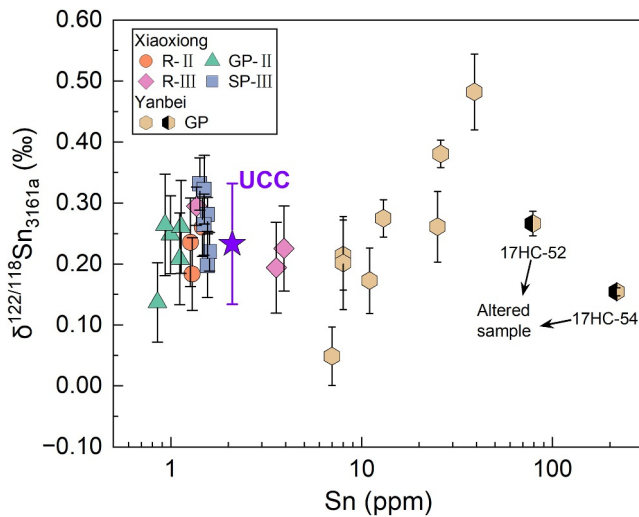


Figure 2. Plot of $\delta^{122/118}\text{Sn}_{3161a}$ versus Sn contents for the Xiaoxiong intrusive-volcanic complex and Yanbei granite porphyry. The upper continental crust, with a Sn content of 2.1 ppm (Rudnick & Gao, 2003) and a $\delta^{122/118}\text{Sn}$ value of $0.233 \pm 0.099\text{‰}$ (She et al., 2024), is shown for comparison. The two Yanbei samples (17HC-52 and 17HC-54) that underwent fluid alteration are represented by half-filled symbols in this and all subsequent figures for consistency.

5. Discussion

5.1. Effects of Chemical Weathering, Hydrothermal Alteration, and Source Heterogeneity

Chemical weathering, source heterogeneity, and hydrothermal alteration are common geological processes that can potentially modify Sn isotope signatures. In this study, chemical weathering can be excluded as the main cause of Sn isotope variation in these two complexes since all samples analyzed in this study have low Chemical Index of Alteration (CIA: defined as molar $\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O}) \times 100$) and Chemical Index of Weathering (CIW: defined as molar $\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O}) \times 100$) values, with the exception of two Yanbei granite porphyry (17HC-52 and 17HC-54; Figure 4a). The absence of correlation between $\delta^{122/118}\text{Sn}_{3161a}$ and CIA values further indicates that chemical weathering did not cause the Sn isotope variability for the Xiaoxiong and Yanbei samples (Figure 4b).

Actually, the two high CIA (and CIW) Yanbei granite porphyry (17HC-52 and 17HC-54) show evidence of hydrothermal alteration. As illustrated in Figure 5a, they exhibit anomalously high A/CNK (molar ratio $\text{Al}_2\text{O}_3/(\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO})$) values compared to other Yanbei granite porphyries, which indicates significant alkali loss resulting from interaction with late-stage fluid (Li et al., 2021). Furthermore, in the CIPW (Cross et al., 1902) normative Qtz-Ab-Or (Quartz-Albite-Orthoclase) diagram (Figure 5b), these

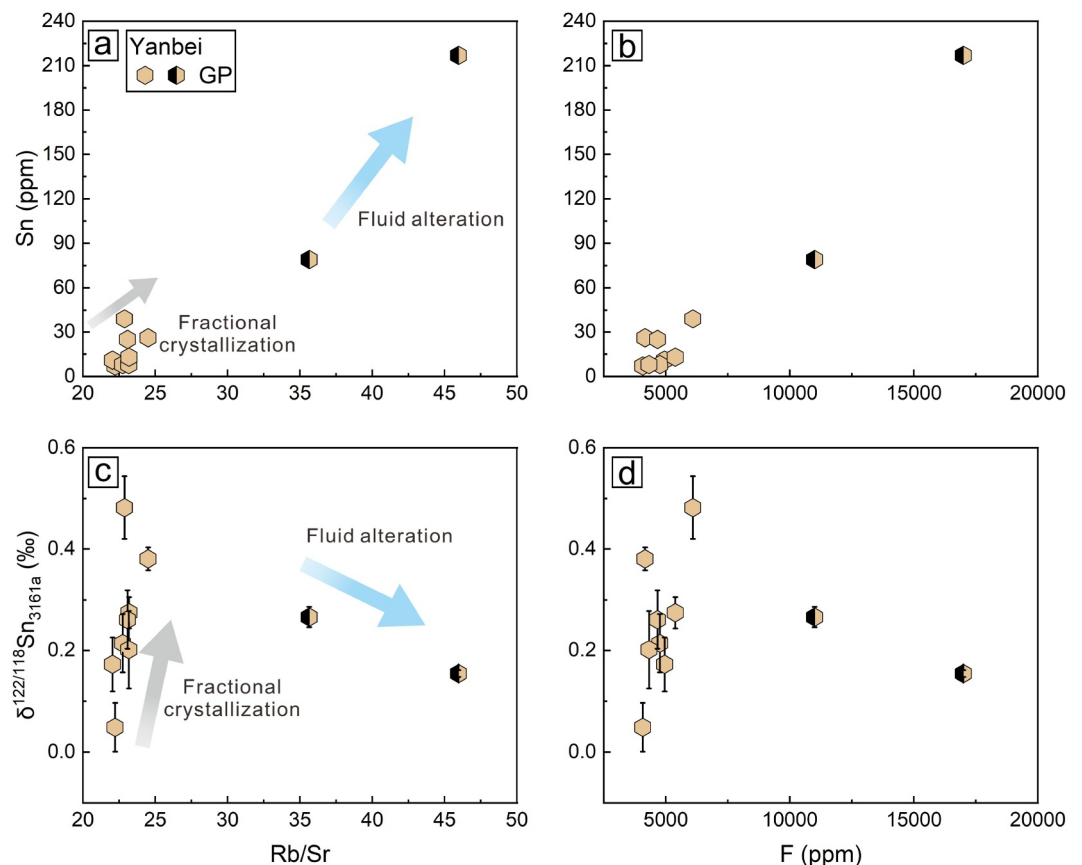


Figure 3. Relationships between Sn geochemistry and selected element ratios/abundances: (a, b) Sn content and $\delta^{122/118}\text{Sn}$ versus Rb/Sr ratio; (c, d) Sn content and $\delta^{122/118}\text{Sn}$ versus F content.

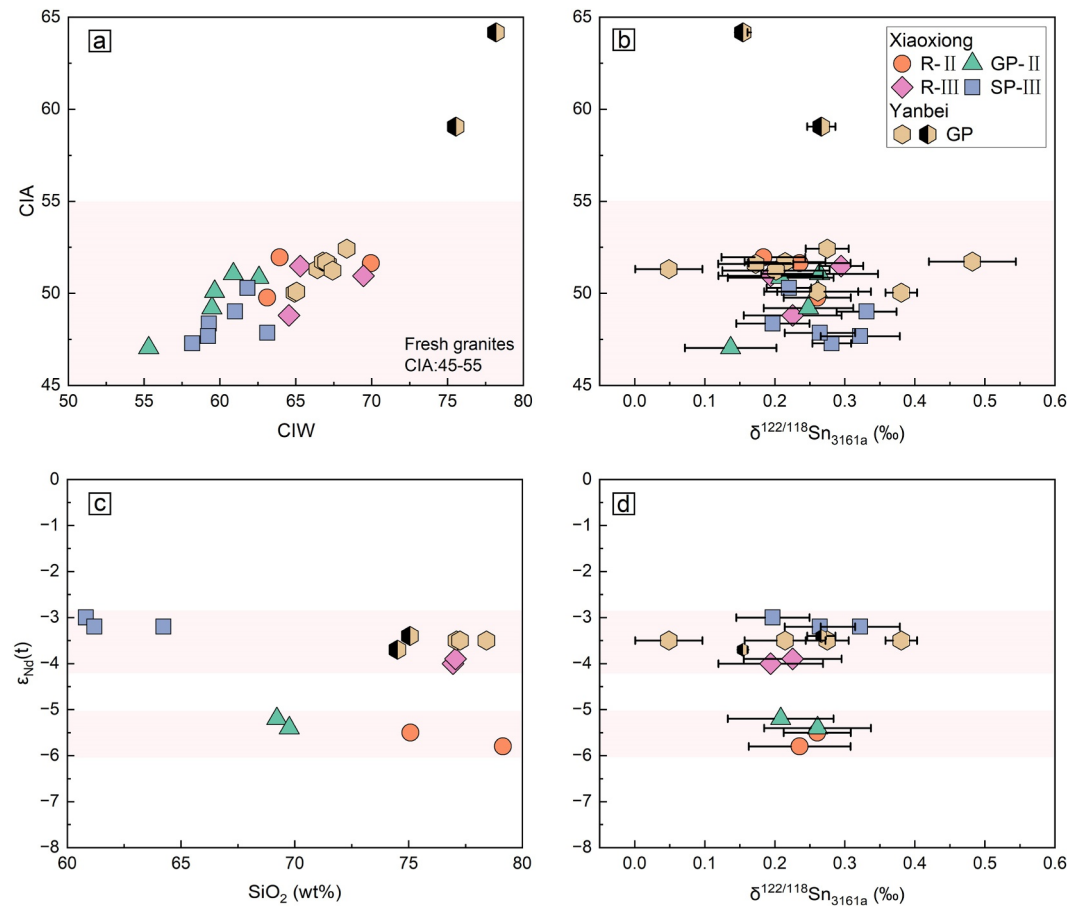


Figure 4. Geochemical relationships for the Xiaoxiong volcanic-intrusive complex and the Yanbei granite porphyry. (a, b) Plots of chemical index of alteration (CIA) versus (a) chemical index of weathering (CIW) and (b) $\delta^{122/118}\text{Sn}_{3161a}$. CIA is defined as molar $\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O}) \times 100$, and CIW as $\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O}) \times 100$, where CaO^* refers to CaO in silicate (Harnois, 1988; Nesbitt & Young, 1982). The colored area represents fresh granites with CIA ranging from 45 to 55 (Nesbitt & Young, 1982). (c, d) Plots of whole-rock $\epsilon_{\text{Nd}}(t)$ versus (c) SiO_2 (wt. %) and (d) $\delta^{122/118}\text{Sn}_{3161a}$.

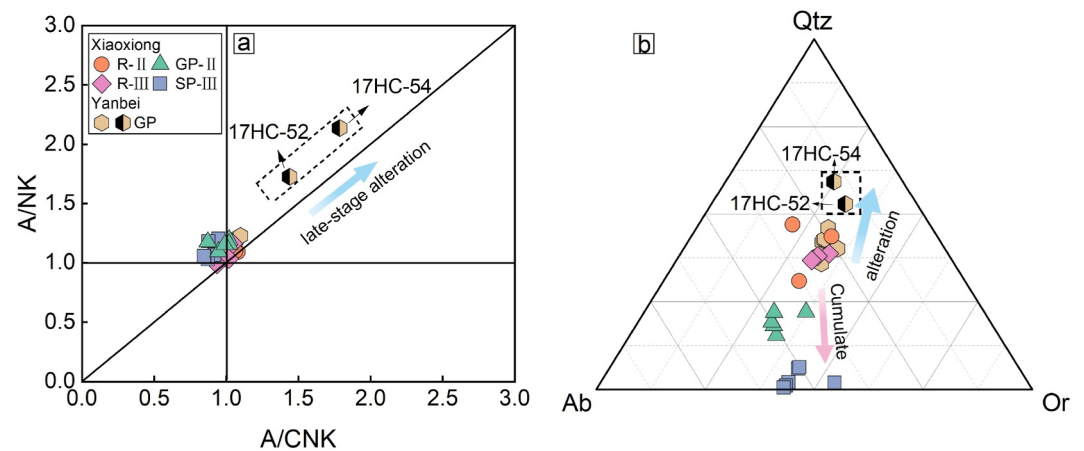


Figure 5. (a) A/NK (molar ratio $\text{Al}_2\text{O}_3/(\text{Na}_2\text{O} + \text{K}_2\text{O})$) versus A/CNK (molar ratio $\text{Al}_2\text{O}_3/(\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO})$) and (b) CIPW (Cross et al., 1902) normative Qtz–Ab–Or (Quartz-Albite-Orthoclase) diagrams for the Xiaoxiong volcanic-intrusive complex and Yanbei granite porphyry, showing the distinct geochemical signature of altered samples (17HC-52 and 17HC-54).

two samples display compositional trends consistent with sericitization and silicification (Miroslav, 1979). This hydrothermal alteration resulted in distinct Sn isotope fractionation, which will be discussed in detail in Section 5.3.

In addition, the Sn isotope variations observed in this study are unlikely to have been influenced by source heterogeneity. First, both the Xiaoxiong volcanic-intrusive complex and Yanbei granite porphyry exhibit homogeneous Nd isotope compositions ($\epsilon_{\text{Nd}}(t)$), that show no correlation with SiO_2 or $\delta^{122/118}\text{Sn}_{3161\text{a}}$ values (Figures 4c and 4d). Moreover, the third-stage rocks from Xiaoxiong exhibit higher $\epsilon_{\text{Nd}}(t)$ and $\epsilon_{\text{Hf}}(t)$ values and crystallization temperatures compared to the second-stage rocks, implying the recharge of mantle-derived melts (X. Xu et al., 2024), but no systematic Sn isotope fractionation is observed between the samples. Therefore, the contrasting Sn isotopic features of the Xiaoxiong and Yanbei samples should be caused by magmatic and hydrothermal processes.

5.2. Sn Isotope Variation During Fractional Crystallization

Sn isotope fractionation during magma evolution can be controlled by fractional crystallization (Badullovich et al., 2017; She et al., 2024; K.-K. Sun et al., 2024). The Xiaoxiong samples show remarkably homogeneous Sn isotope compositions, while Yanbei displays significant $\delta^{122/118}\text{Sn}$ variations (0.05–0.48‰). This contrast can stem from differences in their crystallization histories.

5.2.1. Difference in Fractional Crystallization Process in Xiaoxiong Volcanic-Intrusive Complex and Yanbei Granite Porphyry

The Xiaoxiong intrusive rocks (GP-II and SP-III) exhibit a distinct compositional gap relative to their volcanic counterparts, characterized by systematic enrichment of Al_2O_3 , CaO , MgO , TiO_2 , FeO^{T} , Ba , and Eu in volcanic rocks (Figure 6). This geochemical feature aligns with crystal-melt separation in a magma mush system (Gelman et al., 2014; Lee & Morton, 2015). The Xiaoxiong granite porphyry and syenite porphyry represent crystal accumulation phases dominated by K-feldspar and plagioclase, while the Xiaoxiong volcanic rocks and the Yanbei granite porphyry correspond to the differentiated melt phase.

To quantitatively assess the effects of fractional crystallization processes, we performed trace element modeling on the Xiaoxiong volcanic-intrusive complex and the Yanbei granite porphyry with Sr due to its strong partitioning into plagioclase, the primary fractionation phase in granitic systems. The Sr-Rb/Sr evolution of the Xiaoxiong volcanic-intrusive complex and the Yanbei granite porphyry were reconstructed using mass balance calculations and Rayleigh fractional crystallization modelling:

$$C_{\text{initial melt}}^{\text{Sr}} = F \times C_{\text{melt}}^{\text{Sr}} + (1 - F) \times C_{\text{cumulate}}^{\text{Sr}} \quad (1)$$

where F is the melt fraction, $C_{\text{initial melt}}^{\text{Sr}}$, $C_{\text{melt}}^{\text{Sr}}$ and $C_{\text{cumulate}}^{\text{Sr}}$ are the Sr concentration in the initial melt, residual melt and cumulate, respectively. The concentration of Sr in the residual melt is given by:

$$C_{\text{melt}}^{\text{Sr}} = C_{\text{initial melt}}^{\text{Sr}} \times F^{D_{\text{crystal-melt}}^{\text{Sr}} - 1} \quad (2)$$

where $D_{\text{crystal-melt}}^{\text{Sr}}$ is the bulk partition coefficient, defined as:

$$\sum_{i=1}^n X_i \times K_{di} \quad (3)$$

where X_i is the mass fraction of mineral i in the modal mineral assemblage (Table S3.1 in Supporting Information S1) and K_{di} is the mineral-melt partition coefficient. Initial melt compositions were estimated via linear regression equation of the geochemical gap between volcanic and intrusive rocks (See Table S3.2 in Supporting Information S1). The crystallization sequence and mineral proportions were constrained using Rhyolite-MELTS (Gualda et al., 2012) simulations at a pressure of 2–3 kbar, oxygen fugacity of FMQ to FMQ+3, 3–4 wt.% initial H_2O , with temperature decreasing from the liquidus in 5°C increments. Several conditions were tested (Table S3.3 in Supporting Information S1), and showed no significant effect on the final mineral assemblage.

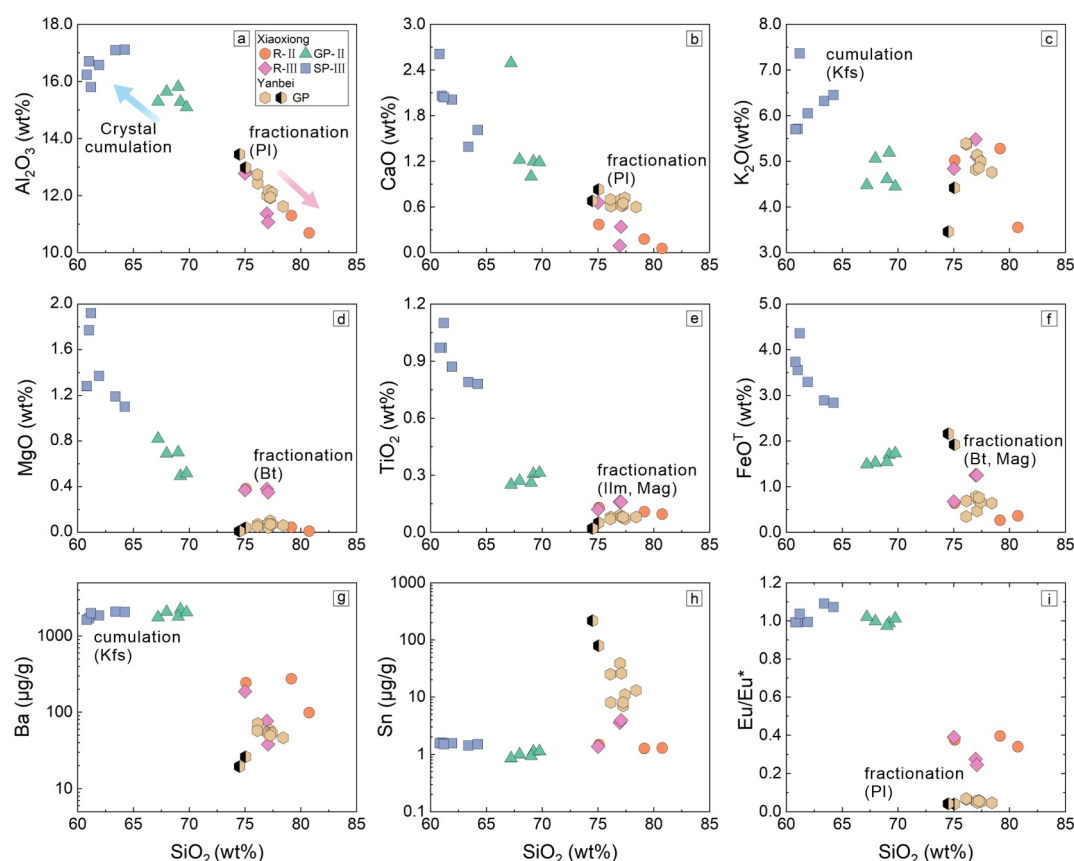


Figure 6. Compositional variations versus SiO_2 for the Xiaoxiong volcanic-intrusive complex and Yanbei granite porphyry: (a–f) major elements and (g–i) trace-element contents/ratios. Abbreviations: Pl = plagioclase, Kfs = K-feldspar, Bt = biotite, Ilm = ilmenite, Mag = magnetite.

The modelling results are shown in Figures 7a–7c and consistent with petrographic observations (Li et al., 2021; Zheng & Xu, 2021). Specifically, in the second-stage Xiaoxiong magma, cumulates comprise plagioclase, quartz, alkali feldspar and minor biotite and Fe-Ti oxides (Figure 7a). The third-stage magma cumulates are dominated by alkali feldspar and plagioclase, with minor quartz, biotite and Fe-Ti oxides (Figure 7b). In contrast, the Yanbei granite porphyry crystallize an extracted melt assemblage of plagioclase, quartz, alkali feldspar with minor biotite and Fe-Ti oxides (Figure 7c). The modelled mineral abundances in these three systems align with the elemental geochemistry (Figure 6) and the modeled compositional evolution of Sr and Rb/Sr ratios fits the observed data (Figures 7d–7f). These consistencies support the reliability of our model and a genetic link for the Xiaoxiong volcanic-intrusive rocks through crystal-melt separation.

The difference in mineral abundances and mineral/melt partition coefficient of Sn, which are governed by magma oxygen fugacity, leads to the contrasting Sn isotope fractionation behaviors will be discussed below (Section 5.2.2).

5.2.2. Contrasting Sn Isotope Behaviors in the Xiaoxiong Volcanic-Intrusive Complex and Yanbei Granite Porphyry

The Xiaoxiong volcanic-intrusive complex exhibits negligible Sn isotope fractionation, with $\delta^{122/118}\text{Sn}$ values ranging from 0.14 to 0.26‰ in its second-stage rocks and from 0.19 to 0.33‰ in the third-stage rocks, consistent with the baseline of the upper continental crust ($0.233 \pm 0.099\%$, She et al. (2024)). In contrast, the Yanbei granite porphyry displays systematic and significant $\delta^{122/118}\text{Sn}$ variations (0.05–0.48‰) that correlate with magmatic differentiation indices (Rb/Sr and F content, Figure 3), despite sharing similar mineral assemblages with Xiaoxiong.

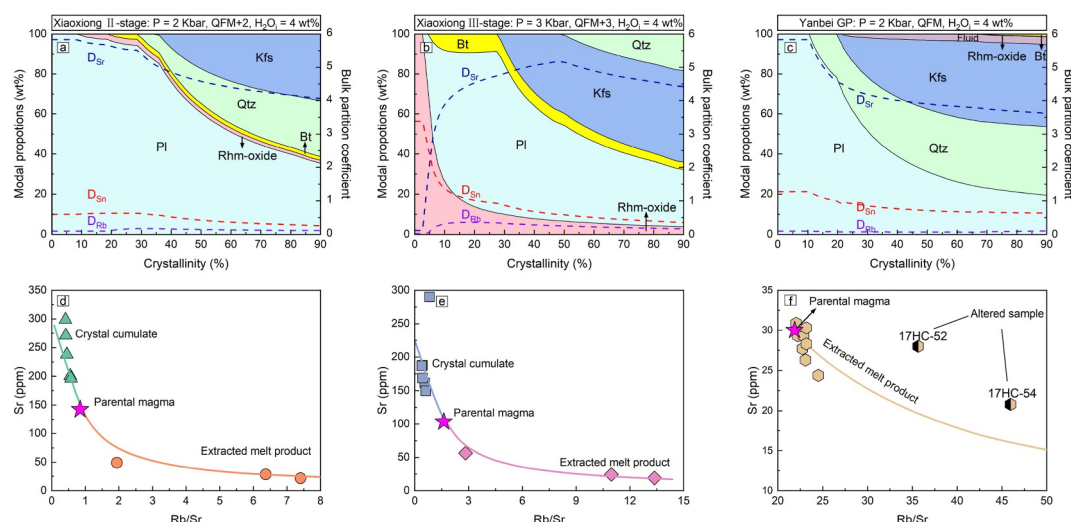


Figure 7. Results of Rhyolite-MELTS modelling and mass-balance calculation for three magmatic systems: (a) and (d) the second-stage Xiaoxiong rocks; (b) and (e) the third-stage Xiaoxiong rocks; and (c) and (f) Yanbei granite porphyry. Panels (a–c) modal mineral proportions and the calculated bulk partition coefficients of Rb, Sr, and Sn (dashed lines); (d–f) Plots of Sr versus Rb/Sr ratios for the Xiaoxiong volcanic-intrusive complex and Yanbei granite porphyry. The colored lines show the compositional evolution for the crystal cumulate and extracted melt calculated by Rayleigh fractionation and mass-balance.

The distinct Sn isotope behaviors between the two complexes can be affected by magma oxygen fugacity (fO_2), which controls the partition of Sn between minerals and melt. Minerals such as biotite and Fe-Ti oxides preferentially incorporate heavy Sn isotopes, as they readily accommodate Sn^{4+} through substitution for Ti^{4+} , Fe^{3+} , and Al^{3+} (Badullovich et al., 2017; Roskosz et al., 2020). In contrast, plagioclase would incorporate light Sn isotopes due to the greater compatibility of Sn^{2+} than Sn^{4+} (Badullovich et al., 2017). Based on zircon trace-element oxybarometry (Loucks et al., 2020), the initial magmatic fO_2 of the Yanbei granite porphyry had ΔFMQ values ranging from -1 to 0 , whereas the Xiaoxiong volcanic-intrusive complex was more oxidized ($\Delta FMQ > +2$; Table S4 in Supporting Information S1).

At the oxidizing conditions of the Xiaoxiong volcanic-intrusive complex, the crystallization of biotite, Fe-Ti oxides and plagioclase collectively influenced Sn isotope fractionation. Because recent experimental studies confirm that the compatibility of Sn in biotite and Fe-Ti oxides increases under higher fO_2 conditions (Huang et al., 2024; Wei et al., 2024), resulting in all three minerals become effective hosts for Sn under the oxidized conditions of Xiaoxiong. Monte Carlo simulations using partition coefficients appropriate for the fO_2 of Xiaoxiong (Figure S1 in Supporting Information S1) show that a mineral assemblage dominated by plagioclase (60%–85%), with subordinate biotite (3%–20%) and Fe-Ti oxides (<12%), can produce near-zero net Sn isotope fractionation. This occurs because the preference of plagioclase for light Sn isotopes is counterbalanced by the preference of biotite and Fe-Ti oxides for heavy Sn isotopes. This situation is similar to the Rb isotope system in the Qitianling granites (Hu et al., 2024). The calculated mineral proportions are consistent with observed modal abundances in Xiaoxiong volcanic-intrusive complex. Moreover, the insufficient separation of crystals and melt in granitic magma systems governed by the high viscosity of silicic melts and increasing crystallinity, producing both melt-rich cumulates and crystal-bearing residual melts (Lee & Morton, 2015; Wickham, 1987) can further prevent Sn isotope fractionation between intrusive and volcanic rocks.

For comparison, in the more reduced Yanbei granite porphyry, the low fO_2 conditions limited the incorporation of Sn into biotite and Fe-Ti oxides. As a result, the crystallization of these minerals was suppressed as a major process for Sn isotope fractionation. Consequently, plagioclase crystallization became the dominant factor controlling Sn isotope behavior, driving the residual melt toward heavier Sn isotope compositions during fractional crystallization. A similar trend is observed in the Laochang granite of the Gejiu Sn deposit (K.-K. Sun et al., 2024). Despite a higher proportion of biotite crystallization (5%–15%) in their Rayleigh fractionation model, the more reduced conditions ($\Delta FMQ = -2.5 \sim 0$, K.-K. Sun et al. (2023)) rendered biotite ineffective for

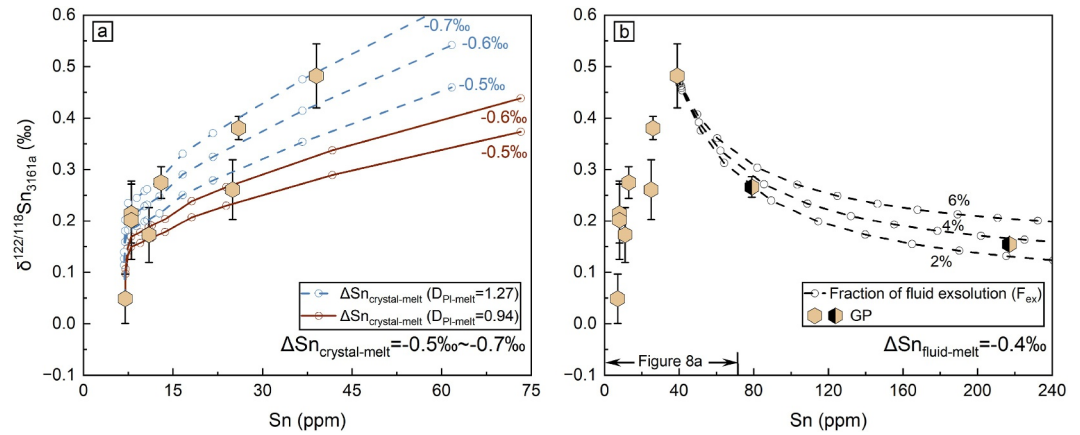


Figure 8. (a) Rayleigh fractionation models for the co-evolution of whole-rock Sn contents and $\delta^{122/118}\text{Sn}$ values during fractional crystallization. Model curves are labeled with $\Delta^{122/118}\text{Sn}_{\text{crystal-melt}}$ and calculated using mineral proportions from Rhyolite-Melts simulation, with blue and red curves denoting the partition coefficient of Sn between plagioclase and melt ($\text{DSn}_{\text{Pl-melt}}$) equal to 1.27 and 0.94, respectively (Badullovich et al., 2017) (Table S3.1 in Supporting Information S1). Plagioclase is one of the most abundant fractionating minerals in felsic magmas and may exert a significant control on Sn isotope fractionation. (b) The results of the binary mixing model (Deng et al., 2022; Ranta et al., 2021), combined with Rayleigh fractionation equations, simulating fluid exsolution and subsequent fluid-melt interaction as a function of the proportion of exsolved fluid (the percentages on curves). The models were calculated with a $\Delta^{122/118}\text{Sn}_{\text{fluid-melt}}$ of $-0.4‰$.

Sn isotope fractionation. As a result, plagioclase remained the dominant control, driving the residue melt toward heavier Sn isotope compositions.

We use Rayleigh model to quantify Sn isotope fractionation during fractional crystallization of the Yanbei granite porphyry:

$$C_{\text{melt}}^{\text{Sn}} = C_{\text{initial melt}}^{\text{Sn}} \times F^{D_{\text{crystal-melt}}^{\text{Sn}} - 1} \quad (4)$$

where $C_{\text{melt}}^{\text{Sn}}$ and $C_{\text{initial melt}}^{\text{Sn}}$ are the Sn content in the evolved and initial melt, respectively; F is the fraction of melt; $D_{\text{crystal-melt}}^{\text{Sn}}$ is bulk partition coefficient of Sn between crystal and melt. This equation is the same as Equation 2.

$$\text{and } \delta^{122/118}\text{Sn} = (\delta^{122/118}\text{Sn}_i + 1000) \times f^{(\alpha-1)} - 1000 \quad (5)$$

where $\delta^{122/118}\text{Sn}$ and $\delta^{122/118}\text{Sn}_i$ are Sn isotope composition of the evolved melt and initial melt, respectively; f is the fraction of Sn remaining in the melt and α is Sn isotope fractionation factor between crystal and melt (Table S5.1 in Supporting Information S1). Sample 15HC-9 that has the lowest F content was used to represent the initial melt ($\delta^{122/118}\text{Sn}_i = 0.05‰$). Modeling results (Figure 8a) reveal that a fractionation factor $\Delta^{122/118}\text{Sn}_{\text{crystal-melt}}$ of -0.5 to $-0.7‰$ can explain the initial rising trend of Sn isotope compositions in the Yanbei granite porphyry. Combining the fractionation factors obtained from Rayleigh fractional crystallization with Monte Carlo simulations of Xiaoxiong volcanic-intrusive complex, together with the constraints on the fractionation factors of the KI sample from Badullovich et al. (2017), the Sn isotope fractionation factors for biotite, plagioclase, and Fe-Ti oxides are estimated as $0.6 \pm 0.4‰$, $-0.7 \pm 0.2‰$, and $0.7 \pm 0.2‰$ (2σ), respectively (see details in Text S1 in Supporting Information S1).

The Yanbei granite porphyry is estimated to have undergone 45%–90% fractional crystallization, leading to a six-fold enrichment in Sn. It is important to note that fractional crystallization alone is still insufficient to account for economic Sn grades, implying the involvement of additional enrichment mechanisms, such as hydrothermal activity. The pronounced Sn isotope fractionation in the Yanbei granite porphyry, compared to Xiaoxiong, reflects its more reduced magmatic conditions and higher initial Sn content, which collectively promoted effective Sn enrichment during magmatic evolution.

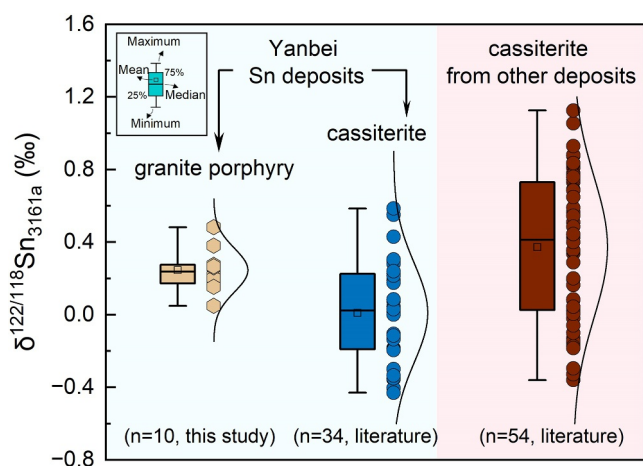


Figure 9. Tin isotope composition of the Yanbei granite porphyry (this contribution) compared with that of cassiterite from Yanbei (P. Liu et al., 2025; Yamazaki et al., 2013) and of cassiterite from global porphyry-type Sn deposits or grown within granites (P. Liu et al., 2025; Mathur et al., 2025; Wu et al., 2023).

5.3. Sn Isotopes as an Effective Tracer of Fluid-Melt Interaction

Beyond fractional crystallization, fluid activity can also influence the Sn isotope systematics (She et al., 2024; K.-K. Sun et al., 2024). At Yanbei, two granite porphyry samples (17HC-52 and 17HC-54) exhibit geochemical evidence of fluid alteration (Figure 5), and show decreased $\delta^{122/118}\text{Sn}$ values with elevated Rb/Sr (>35) and F content (>10,000 ppm) (Figure 3).

Cassiterite precipitation has also been invoked to explain low $\delta^{122/118}\text{Sn}$ values in whole-rock samples (K.-K. Sun et al., 2024). Figure 9 compares the whole-rock Sn isotope compositions of the Yanbei granite porphyry with data for cassiterite from Yanbei (dark blue in Figure 9, data from Yamazaki et al. (2013); P. Liu et al. (2025)) and global porphyry-type or granite-hosted deposits (dark red in Figure 9, data from Wu et al. (2023); Mathur et al. (2025)). The Sn isotope composition of cassiterite is highly heterogeneous globally, reflecting the isotopic signature of its parent magma, the extent of magmatic evolution, and the influence of fluid activity or precipitation sequences (Figure 9). At Yanbei, the $\delta^{122/118}\text{Sn}$ values of cassiterite are generally lower than those of the most evolved granite porphyry samples. This indicates that the light Sn isotope signatures observed in two altered samples could partially result from minor cassiterite incorporation. However, this minor mineralogical contribution does not alter the primary interpreta-

tion. The extremely high F contents (>10,000 ppm) and elevated Rb/Sr ratios are definitive signatures of fluid-rock interaction, not features introduced by cassiterite. Furthermore, cassiterite itself is a product of magmatic-hydrothermal transition, and its presence underscores that hydrothermal activity has occurred. Therefore, while cassiterite incorporation, the coupled light Sn isotopes, extreme F enrichment, and high Rb/Sr ratios predominantly record alteration by F-rich fluids, which remains the dominant process. This interpretation is further corroborated by the fact that our dissolution technique (using common acids) cannot attack cassiterite, which is highly resistant to dissolution (e.g., requiring KCN or prolonged treatment in an autoclave; She, Li, An, Yang, and Zhang (2023)).

Two fluid-mediated processes, namely fluid exsolution and fluid-melt interaction, may occur during magmatic-hydrothermal transition. Fluid exsolution refers to the release of volatile-rich fluids from shallow, crystallizing magma upon fluid saturation. Fluid-melt interaction involves chemical exchange between the fluid and the melt. Tin is a fluid-mobile element with fluid-melt partition coefficients can reach up to 22.8 (Keppler & Audétat, 2025). Previous studies have suggested that the exsolved fluids from granitic magmas would preferentially incorporate light Sn isotopes (M. Sun et al., 2024; T. Wang et al., 2021). If so, this process would drive the residual melts toward heavier isotopic compositions, which is inconsistent with the observation. An alternative explanation is fluid-melt interaction that can also induce Sn isotope fractionation.

Using Rayleigh fractionation equations and a binary mixing model (Deng et al., 2022; Ranta et al., 2021), we simulated fluid exsolution and subsequent fluid-melt interaction (Figure 8 and Table S5 in Supporting Information S1). We assumed that the alteration observed in samples 17HC-52 and 17HC-54 was caused by fluids derived from the exsolution of the highly fractionated granite porphyry melt. Deng et al. (2022) proposed that the fluids responsible for Sn enrichment in the Qitianling granite originated from deep magmatic fluids within a trans-crustal system. In contrast, we suggest that the fluids responsible for the fluid-melt interaction at Yanbei were exsolved from the granite porphyry itself. Because in F-rich magmatic systems like Yanbei, high F content increases the solubility of H_2O and Cl in silicate melts, lowers melt viscosity and liquidus temperature and delays fluid exsolution (Alferyeva et al., 2018; Aude' et al., 2000; Manning, 1981; Webster & Rebbert, 1998). This suppression of early fluid release can prevent premature scavenging of Sn from the melt by crystallizing phases, allowing Sn to be efficiently enriched in the evolving melt until extensive fractionation ultimately leads to Sn mineralization (Ma et al., 2024). Our results show that a Sn isotope fractionation factor ($\Delta\text{Sn}_{\text{fluid-melt}}$) of -0.4 to -0.5‰ during the exsolution of 2%–6% fluid can reproduce the observed isotopic and elemental data. This finding is also consistent with the theoretical predictions from first-principles calculations by T. Wang et al. (2023), who demonstrate that under equilibrium conditions, light Sn isotopes are preferentially partitioned into hydrothermal fluid species. Moreover, the efficacy of this limited degree of fluid exsolution (2%–6%) in

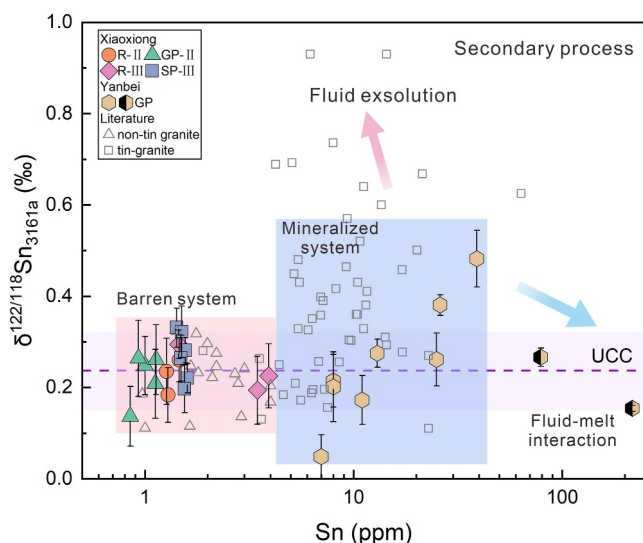


Figure 10. Whole-rock $\delta^{122/118}\text{Sn}$ values versus Sn contents, comparing data from this study with literature (She et al., 2024; K.-K. Sun et al., 2024). The pink field represents barren systems, and the blue field represents Sn-mineralized systems. The dashed line indicates the upper continental crust value of 0.23‰ (She et al., 2024).

effectively extracting Sn is further supported by the decompression model of Keppler and Audétat (2025), which demonstrates that the release of ~3.5% fluid accompanying 70% crystallinity can mobilize up to 32% of the initial Sn budget.

5.4. Implications for Sn Mineralization

Tin-productive granites are typically highly fractionated, reduced magmatic systems that are rich in volatiles like F, and they are suggested to originate from the partial melting of crustal rocks with the involvement of mantle-derived components (Blevin & Chappell, 1992; Chen et al., 2013; Lehmann, 1982, 2021; Linnen et al., 1996). These granites are chemically characterized by metaluminous to peraluminous signatures, and enriched high field strength elements (e.g. Nb, Zr, Ce, and Y) (Chen et al., 2013; Lehmann, 2021; Ni et al., 2023). Accessory minerals like cassiterite, titanite, and ilmenite are key proxies for Sn potential, and the Fe and Sn contents in micas also serve as useful indicators (H.-Y. Sun et al., 2024; R. Wang et al., 2017).

In addition to these well-established geochemical and mineralogical features indicators, Sn isotopes may also be sensitive for assessing the Sn mineralization potential of granites. The fundamental premise is that significant mass-dependent isotope fractionation occurs between different Sn valence states (Sn^{2+} and Sn^{4+}) and during the partitioning of Sn between minerals, melts, and hydrothermal fluids (Roskosz et al., 2020; M. Sun et al., 2022; T. Wang

et al., 2023). The comparative case study presented here shows that mineralized systems like Yanbei exhibit large, systematic variations in Sn isotope ratios, whereas barren systems like Xiaoxiong show compositions closely clustered near average crustal values (Figure 10). This clear distinction establishes Sn isotopes as an effective indicator for assessing the mineralization potential of a granitic system.

The contrasting Sn isotope behavior between mineralized and barren systems is primarily controlled by magmatic oxygen fugacity ($f\text{O}_2$). The predominant association of Sn mineralization with reduced (ilmenite-series) granites, as classified by Ishihara (1977), is a preference driven by redox-controlled processes. Under reduced conditions, Sn is stabilized as Sn^{2+} , which possesses high solubility and diffusivity (Linnen et al., 1996). Furthermore, these conditions facilitate the liberation of Sn from source minerals (e.g., biotite, titanite, magnetite) and prevent its scavenging by early-crystallizing minerals, thereby enabling its effective enrichment in highly evolved melts (Lehmann et al., 1990; Romer & Kroner, 2016).

However, although fractional crystallization under reduced conditions ($\Delta\text{FMQ} < 0$) can enrich Sn in the residual melt, this process alone is insufficient to achieve economic concentrations of Sn in granitic systems. Hydrothermal fluids, which exsolved from highly evolved, volatile-rich melts play an essential role in transporting and further concentrating Sn. The presence of F plays a key role in this process by increasing water and Cl solubility in the melt, delaying fluid exsolution (Holtz et al., 1993; Webster & Rebbert, 1998). Ultimately, fluids are released and focus metal deposition by degassing and decompression (Keppler & Audétat, 2025; Zhao, Zajacz, et al., 2022). Additionally, our Sn isotope evidence from the Yanbei deposit confirms that ore-forming fluids were derived from genetically related granite porphyry, consistent with findings from K.-K. Sun et al. (2024).

Thus, combination of extensive fractional crystallization under reduced and F-rich magma and late-stage fluid exsolved from highly evolved melt may provide the essential material for the formation of Sn deposits.

6. Conclusions

This study presents a systematic investigation of Sn isotope fractionation in two contrasting granitic suites from South China: the barren Xiaoxiong volcanic-intrusive complex and the mineralized Yanbei granite porphyry. Our results demonstrate distinct Sn isotope behaviors during magmatic-hydrothermal evolution and provide constraints on Sn enrichment mechanism:

1. The Yanbei granite porphyry associated with Sn mineralization exhibits significant Sn isotope fractionation (0.05–0.48‰), whereas the barren Xiaoxiong volcanic-intrusive complex shows a relatively homogeneous Sn

isotope composition with limited isotope variation. Although the absolute $\delta^{122/118}\text{Sn}$ values of the two systems partly overlap, their evolutionary behaviors are fundamentally different. The Yanbei system records progressive Sn isotope fractionation during magmatic differentiation, whereas the Xiaoxiong system shows little Sn isotope fractionation during magmatic evolution. This disparity is primarily governed by the mineral-melt partition of Sn, which is influenced by the magma oxygen fugacity.

2. Rayleigh fractionation modeling indicates that extensive crystallization ($\sim 45\%$ – 90%) of plagioclase, biotite, and Fe-Ti oxides, with a fractionation factor $\Delta^{122/118}\text{Sn}$ of -0.5 to -0.7% , can explain the initial enrichment of Sn and rise of $\delta^{122/118}\text{Sn}$ of Yanbei granite porphyry. However, this process alone produces moderate Sn enrichment (~ 6), insufficient for economic mineralization.
3. The formation of Yanbei Sn deposits required additional fluid-mediated processes. Fluid-melt interaction involving 2% – 6% fluid from highly evolved granitic melt, with $\Delta^{122/118}\text{Sn}_{\text{fluid-melt}} \approx -0.4$ to -0.5% , accounts for the decrease in $\delta^{122/118}\text{Sn}$, and high Sn, F contents in late-stage samples.

Tin isotopes can serve as a sensitive tracer for fractional crystallization efficiency, especially intensity of fluid activity in granite systems. The contrasting Sn isotope signatures between barren and mineralized granites provide a powerful tool for evaluating Sn metallogenic potential and understanding ore-forming processes.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Availability Statement

The Sn isotope data first reported in this study are available at the data repository Zenodo (C. Xu et al., 2025). The other geochemical data were obtained from Zheng and Xu (2021) and Li et al. (2021).

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