

Article

Coupled U–Pb Geochronology of Monazite and Zircon for the Bozhushan Batholith, Southeast Yunnan Province, China: Implications for Regional Metallogeny

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Abstract: Constraining the duration of magmatism is of vital importance to the understanding of the magmatic-hydrothermal mineral system. The Bozhushan batholith, located in the middle section of the southeastern Yunnan ore district, mainly consists of biotite monzogranite and monzogranite. Many Sn–W–polymetallic deposits are developed around the Bozhushan batholith, but their temporal and genetic relationships remain controversial. LA-ICP-MS U–Pb zircon and monazite dating were respectively conducted on the same two samples, yielding weighted mean $^{206}\text{Pb}/^{238}\text{U}$ zircon ages of 85.1 ± 0.7 and 85.6 ± 0.9 Ma, and weighted mean $^{206}\text{Pb}/^{238}\text{U}$ monazite ages of 87.1 ± 0.9 and 88.1 ± 1.1 Ma. The crystallization ages of S-type granites obtained from the zircon U–Th–Pb system and monazite U–Th–Pb system are consistent within the analytical errors. After combining the new ages obtained in this study with recently published U–Pb zircon and cassiterite ages from the giant Baniuchang Ag–Sn–Pb–Zn deposit in the north, and U–Pb zircon and Re–Os molybdenite ages from the large Guanfang W deposit in the south, a temporal framework of magmatism-mineralization in the Bozhushan region has been established. The duration of magmatic activity at Bozhushan is about 7 Ma, with W mineralization occurring at ca. 92 Ma and Sn mineralization at 88–87 Ma.

Keywords: monazite; zircon; LA-ICP-MS U–Pb; Bozhushan batholith; southeastern Yunnan ore district

1. Introduction

The southeastern Yunnan ore district, in the western margin of the Cathaysia Block, is famous for hosting abundant Sn, W, Ag, Pb, Zn, and In resources [1–6]. Several world-class Sn–W–polymetallic deposits, such as Gejiu Sn–Cu deposit, Baniuchang Ag–Sn–Pb–Zn deposit and Dulong Sn–Zn deposit, as well as a series of large deposits to small occurrences, are spatially and genetically associated with Late Mesozoic magmatic activity [1–5]. All of these polymetallic deposits are developed around three Late Cretaceous S-type granitic batholiths that are exposed in the southeastern Yunnan ore district, including Gejiu, Bozhushan, and Laojunshan, which have been proven to be economically important (Figure 1). Among them, the Gejiu and Laojunshan batholiths have been widely investigated and proven to be causative intrusions for the giant Gejiu and Dulong deposit, respectively [7,8]. The giant Baniuchang deposit is about 15 km northwest of the Bozhushan batholith (Figure 1). This batholith did not attract enough attention until the genetic relationship between recently revealed

biotite monzogranite underneath the Bainiuchang deposit and the Bozhushan batholith had been identified [9,10]. However, the duration of magmatic activity in the Bozhushan region remained unclear due to the large discrepancies between previously published age data (whole-rock Rb-Sr: ~115 to 97 Ma [1]; single grain U–Pb age of zircon: 48 Ma [1]; zircon laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) U–Pb ages: 88 to 85 Ma [4]). Additionally, the large Guanfang W deposit and several Sn–W deposits developed around the Bozhushan batholith [6]. Therefore, more precise ages and a temporal framework of magmatic evolution and associated polymetallic mineralization for the Bozhushan region are required.

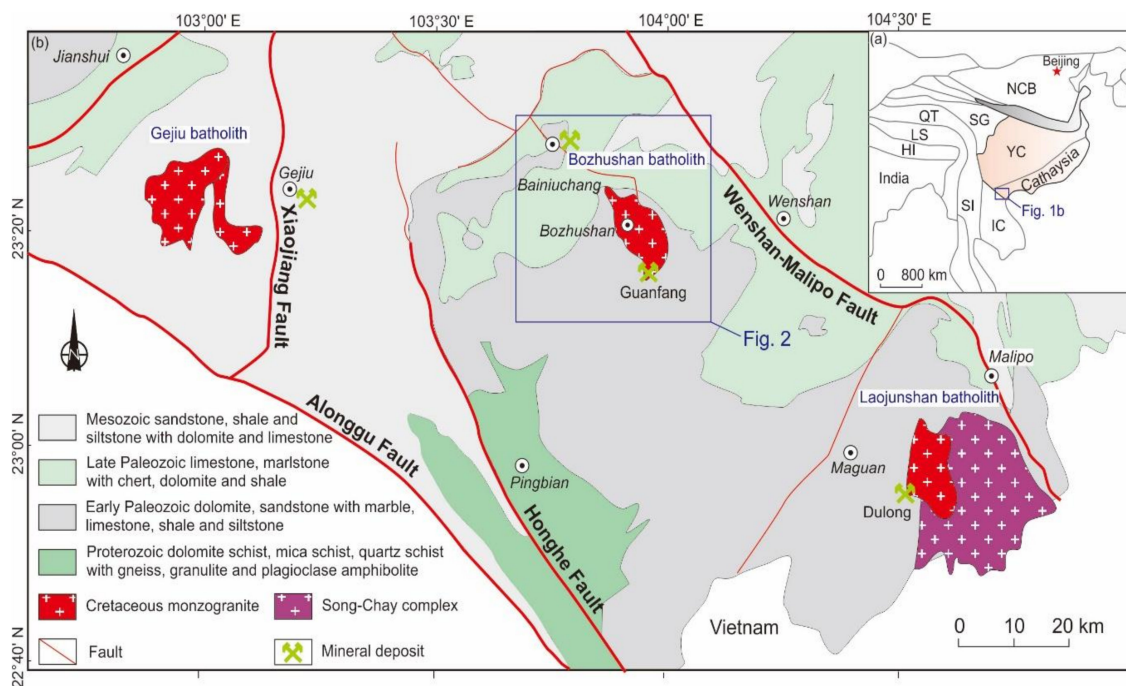


Figure 1. (a) Geological location of the studied area; (b) schematic map of southeastern Yunnan ore district, showing the distribution of Cretaceous batholiths and associated mineral deposits. Abbreviations: HI = High Himalaya Terrane; IC = IndoChina Terrane; LS = Lhasa Terrane; NCB = North China Block; QT = Qiangtang Terrane; SG = Songpan-Ganzi Terrane; SI = Sibumasu Terrane; YC = Yangtze Craton.

Zircon is a highly refractory mineral with relatively low diffusion rates for many elements [11]. It contains relatively high Th and U contents and low common Pb abundances, thus it has a unique U–Th–Pb system and is often used as a mineral to trace magmatism and crustal growth history. Recent studies have shown that monazite also has an effective U–Th–Pb system, which can also be used for dating magmatism, metamorphism and mineralization events [12,13]. Monazite is also characterized by relatively high closure temperatures (700–750 °C) but is significantly more resistant to radiation damage compared with the zircon U–Th–Pb system [14–16]. Notably, monazite is a common mineral phase within S-type granites that crystallizes from metaluminous to peraluminous felsic melts generated by the melting of crustal pelitic composition under a relatively low temperature [17]. Inherited zircons from the host rocks are commonly captured within these granites, making it complex the interpretation of U–Pb zircon ages. In such cases, combining U–Pb monazite ages with zircon ages has been considered as a robust way to constrain the crystallization age of S-type granites [18].

In this study, zircon and monazite U–Pb dating were carried out on the same samples collected from the Bozhushan batholith. These new data were then integrated with recently published geochronological data (U–Pb zircon, Re–Os molybdenite and U–Pb cassiterite) to characterize the specific magmatic processes that led to extensive Sn–W–polymetallic mineralization in the Bozhushan region.

2. Geological Setting

2.1. Regional Geology

The Bozhushan batholith occurs in the middle section of southeastern Yunnan ore district, adjacent to the Yangtze Craton in the north and to the Sanjiang Tethys Domain to the west (Figure 1). The sedimentary host rocks are dominated by Paleozoic marine-sedimentary rocks consisting of Early Paleozoic siltstone, shale, limestone, and dolomite in the south and Late Paleozoic limestone, marlstone intercalated with chert, dolomite and shale in the northwest. The Mesozoic sedimentary sequence is restricted to the northeast and composed of sandstone, shale, and siltstone intercalated with dolomite and limestone (Figure 2) [19,20]. The most predominant structures in the Bozhushan region are NW-trending and NE-trending faults (Figure 2). The NW-trending faults might have provided conduits for the ascent of magmas, while the NE-trending faults cut the earlier NW-trending faults and the Bozhushan batholith.

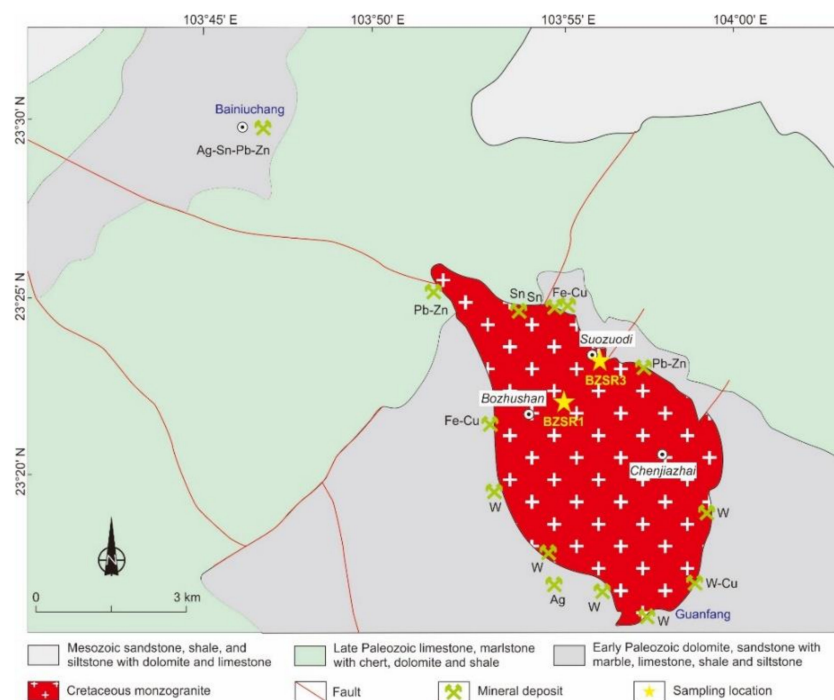


Figure 2. Simplified geological map of the Bozhushan Sn-W polymetallic ore district.

Many Sn-W-polymetallic ore deposits/occurrences are distributed around the Bozhushan granitic batholith, such as the Bainiuchang giant skarn Ag–Sn–Pb–Zn deposit, with resources of Ag 6470 t @ 95 g/t, Zn 172 Mt @ 2.46%, Pb 109 Mt @ 1.56% and Sn 8.6 Mt @ 0.12% [21], and the Guanfang skarn W deposit, with resources of W 10 Mt @ 0.5% [6]. The ore-related intrusions of the Bainiuchang deposit, revealed by recent drilling at depths from 1250 to 1420 m, were interpreted to be a branch of the Bozhushan batholith [22,23]. The Bozhushan intrusion was once divided into two-stage phases, including the earlier Chenjiazhai and later Bozhushan phase [1,4], but they have consistent LA-ICP-MS U–Pb zircon ages of 87–86 Ma [4,5], indicating that these granites from the Bozhushan batholith were products of a single magmatic system. The Bozhushan Late Cretaceous granites are alkali-rich, with $K_2O/Na_2O > 1$, $A/CNK = \text{molar } [Al_2O_3/(CaO + Na_2O + K_2O)] > 1$, obvious negative Eu anomalies and relatively high whole-rock ($^{87}Sr/^{86}Sr$) ratios of 0.7126 to 0.7257, which are typical values for S-type granites [24]. These S-type granites were formed during the oblique strike-slip motion (89–83 Ma) following the collision between the Okhotomorsk Block and the eastern Eurasia continental margin (100–89 Ma) [5]. The collision was driven by the NW-warding immigration of Paleo-Pacific Plate along

the eastern Eurasia continental margin [5,25]. These continuing processes may be responsible for the intense NW-trending faulting and magmatism-mineralization activities in the Bozhushan region [5].

2.2. Petrography of Bozhushan Batholith

The Bozhushan batholith is located about 30 km westward away from Wenshan County, Yunnan Province, covering an area of $\sim 120 \text{ km}^2$. The rock type is dominated by biotite monzogranite, intruding into the Paleozoic marine-sedimentary rocks along conjunction zone between the NW-trending faults and NE-trending folds (Figure 2). The Bozhushan biotite monzogranite are fine- to medium-grained, with 25–30 vol. % of K-feldspar, 25–30 vol. % of plagioclase, 25–30 vol. % of quartz, and 8–10 vol. % of biotite (Figure 3). Accessory minerals include apatite, zircon, monazite and ilmenite. Samples BZSR1 and BZSR3 were respectively collected from the Bozhushan and Suozuodi area and were used for monazite and zircon LA-ICP-MS U–Pb dating.

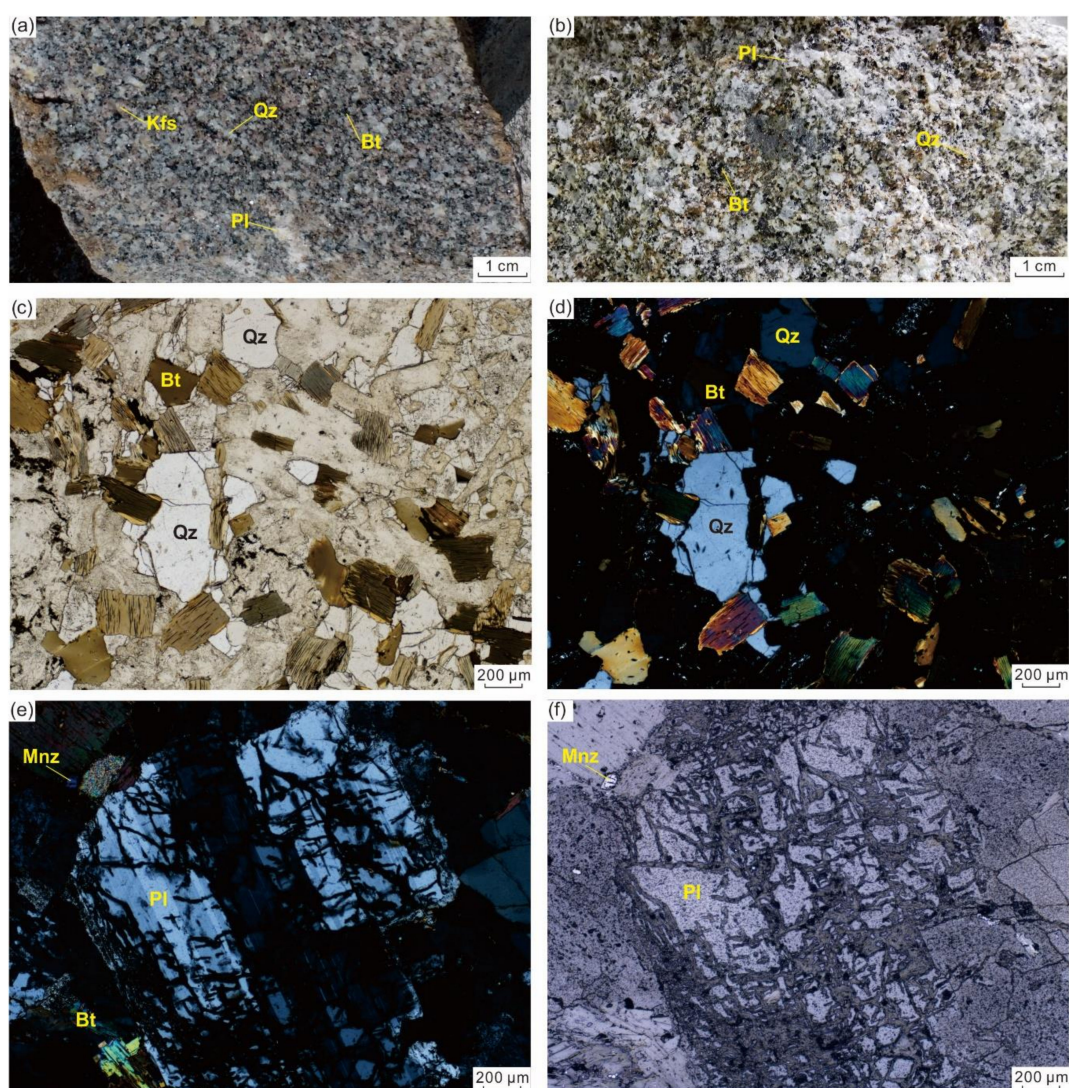


Figure 3. (a,b) representative photographs of hand-specimens from the Bozhushan batholith, showing the fine-medium grained texture of biotite monzogranite. (c,d) microphotographs of sheeted biotite and paragenetic quartz under plane-polarized light and cross-polarized light. (e–f) microphotographs of cataclastic plagioclase and intergrown quartz, with interstitial sparse monazite in quartz. Mineral abbreviations: Bt = Biotite; Kfs = K-feldspar; Mnz = monazite; Pl = Plagioclase; Qz = Quartz.

3. Analytical Methods

3.1. Separation and Cathodoluminescence Images of Zircon and Monazite

Zircon and monazite grains were separated by using heavy liquid and magnetic separation techniques at the Langfang Regional Geological Survey, Hebei Province, China. These separated grains were then handpicked under a binocular microscope and examined under transmitted and reflected light in a petrographic microscope. Handpicked zircons were placed on an epoxy mount of 2.5 cm in diameter and polished down to equatorial sections. In order to reveal their internal structures, zircon, and monazite Cathodoluminescence (CL) images were completed using an Analytical Scanning Electron Microscope (JSM-IT100) connected to a GATAN MINICL system at the Wuhan SampleSolution Analytical Technology Co., Ltd., Wuhan, China (SSAT). The imaging condition for zircon was 10 kV voltage of electric field and 80 μ A current of tungsten filament, while the imaging condition for monazite was 20 kV voltage and 160 μ A current.

3.2. In-Situ Zircon LA-ICP-MS U–Pb Dating

Zircon U–Pb dating and trace element analysis were simultaneously conducted by LA-ICP-MS at the SSAT. For detailed instrument parameters, operating conditions and analysis procedures, as well as data reduction software, please refer to Zong et al. [26]. Laser sampling was performed using a GeolasPro laser ablation system that consists of a COMPexPro 102 ArF excimer laser (Coherent, Santa Clara, CA, USA) (wavelength of 193 nm and maximum energy of 200 mJ) and a MicroLas optical system (Coherent). An Agilent 7700e ICP-MS instrument (Agilent, Santa Clara, CA, USA) was used to acquire ion-signal intensities. During the laser ablation process, helium was used as the carrier gas and argon was used as the compensation gas to adjust the sensitivity. Helium and argon were mixed through a T-connector before entering the ICP. The spot size and frequency of the laser were set to 32 μ m and 5 Hz, respectively. Zircon standard 91500 (LA-ICP-MS U–Pb age: 1062 ± 4.0 Ma [27]) and glass NIST610 were applied as external standards for isotopic and trace element fractionation correction, respectively. Eighteen analyses on 91500 collected during sample running returned a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 1062 ± 5.3 Ma (1σ , 95% confidence). The GJ-1 standard (LA-ICP-MS U–Pb age: 603.2 ± 2.4 Ma [28]) was used as a secondary standard to monitor data quality. Six analyses on GJ-1 during the laser session provided $^{206}\text{Pb}/^{238}\text{U}$ ages varying from 601 to 600 Ma, suggesting that the analytical error is less than 1%. Each time-resolved analysis data includes approximately 20–30 s blank signal and a 50 s sample signal. The off-line processing of analysis data (including the selection of samples and blank signals, the correction for instrument sensitivity drift, element content, U–Pb isotope ratio, and age calculation) was performed using software ICPMSDataCal 11.8 (China University of Geosciences, Wuhan, China) [29,30]. Concordia diagrams and weighted mean calculations of U–Pb zircon ages were made using Isoplot/Ex_ver3 [31]. Common-Pb corrections were made using the method of Anderson [32].

3.3. In-Situ Monazite LA-ICP-MS U–Pb Dating

U–Pb dating and trace element analysis of monazite were also conducted by LA-ICP-MS at the SSAT by using the same laser system. For minerals with relatively high U abundances, a “wire” signal smoothing device was included in the laser ablation system, by which smooth signals are produced, even at very low laser repetition rates down to 1 Hz [33]. It is very useful for in-situ U–Pb dating of high-U mineral [34]. The spot size and frequency of the laser were set to 16 μ m and 2 Hz, respectively. Monazite standard 44069 and glass NIST610 were used as external standards for U–Pb dating and trace element calibration, respectively. Reference standard material 44069 (SIMS U–Pb age: 424.9 ± 0.4 Ma [35]) was analyzed after every five unknowns under identical conditions. Sixteen analyses on 44069 collected during sample running defined a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 425.0 ± 2.1 Ma (1σ , 95% confidence). The Trebilcock standard (LA-ICP-MS U–Pb age: 272 ± 2 Ma [36]) was used as a secondary standard to monitor data quality. Six analyses on Trebilcock during laser

session have $^{206}\text{Pb}/^{238}\text{U}$ ages varying from 280 to 274 Ma, indicating that the analytical error is less than 3%. Each analysis incorporated a background acquisition of approximately 20–30 s followed by 50 s of data acquisition from the sample. The $^{207}\text{Pb}/^{206}\text{Pb}$, $^{206}\text{Pb}/^{238}\text{U}$, $^{207}\text{Pb}/^{235}\text{U}$, and $^{208}\text{Pb}/^{232}\text{Th}$ ratios were calculated from measured ion intensities using ICPMSDataCal 11.8 [28,29]. Concordia diagrams and weighted mean U–Pb ages were processed using Isoplot/Ex_ver3 [29]. Common-Pb corrections were made using the method of Anderson [32].

4. Results

4.1. Morphology and CL Signatures of Zircon and Monazite

Zircon grains from two samples (BZSR1 and BZSR3) selected for LA-ICP-MS U–Pb dating are shown in Figure 4a. These zircon crystals are colorless, transparent, and mostly euhedral long-columnar, with lengths of 100–300 μm and length/width ratios of 2:1 to 4:1. Most grains show oscillatory zoning patterns, representing typical features of magmatic zircons. Inherited zircon grains or cores were not found in the samples.

Monazite grains from the same two samples (BZSR1 and BZSR3) selected for LA-ICP-MS U–Pb dating are shown in Figure 4b. The monazite crystals are light-yellow, euhedral to subhedral short-columnar, with lengths of 50–100 μm and length/width ratios of 1:1 to 2:1. Most of monazite grains show homogenous structures and lack oscillatory zoning. Some monazite grains develop corrosion pores within the grains and corrosion rims. In order to obtain more reliable ages for the magmatic evolution, all the analyzed spots in this study avoided these corroded sections.

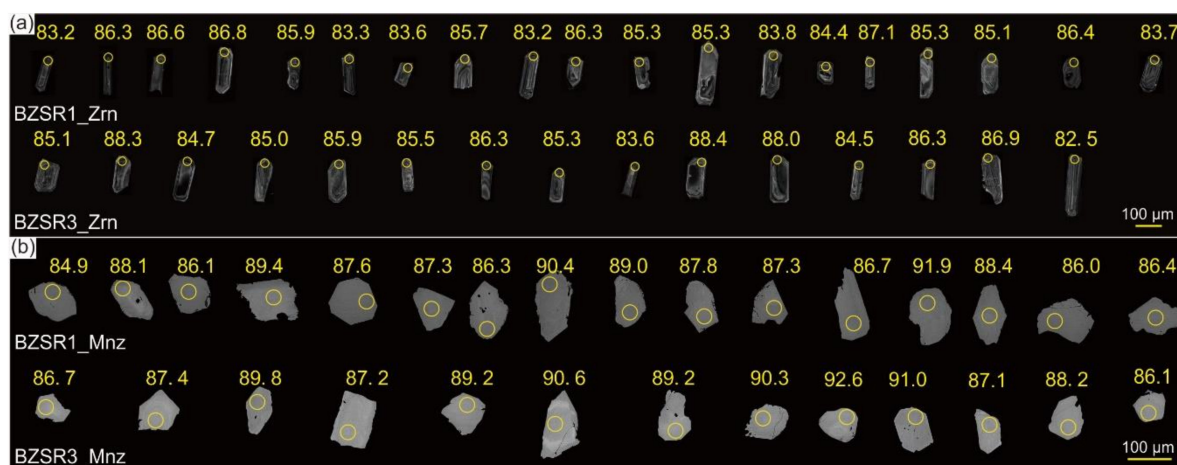


Figure 4. Cathodoluminescence (CL) images of analyzed zircons (a) and monazites (b) from the Bozhushan batholith. Yellow circles and numbers represent the spots selected for laser ablation and the calculated $^{206}\text{Pb}/^{238}\text{U}$ ages (Ma), respectively.

4.2. U–Pb Geochronology of Zircon

The analyzed U–Pb zircon ages of the Bozhushan batholith are listed in Table 1. Zircon grains from BZSR1 have variable Th (248–1520 ppm) and U (440–2118 ppm) contents, with wide-ranging Th/U ratios of 0.2 to 1.1, suggesting a magmatic origin [37]. Nineteen analyses yielded $^{206}\text{Pb}/^{238}\text{U}$ ages of 87.1 to 83.2 Ma, with a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 85.1 ± 0.7 Ma (1σ , MSWD = 2.1; Figure 5a). Zircon grains from BZSR3 have relatively high Th (888–3051 ppm) and U (2843–5270 ppm) contents, with variable Th/U ratios of 0.3 to 1.0. Fifteen analyses yielded $^{206}\text{Pb}/^{238}\text{U}$ ages ranging from 88.3 to 82.5 Ma, with a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 85.6 ± 0.9 Ma (1σ , MSWD = 3.0; Figure 5b).

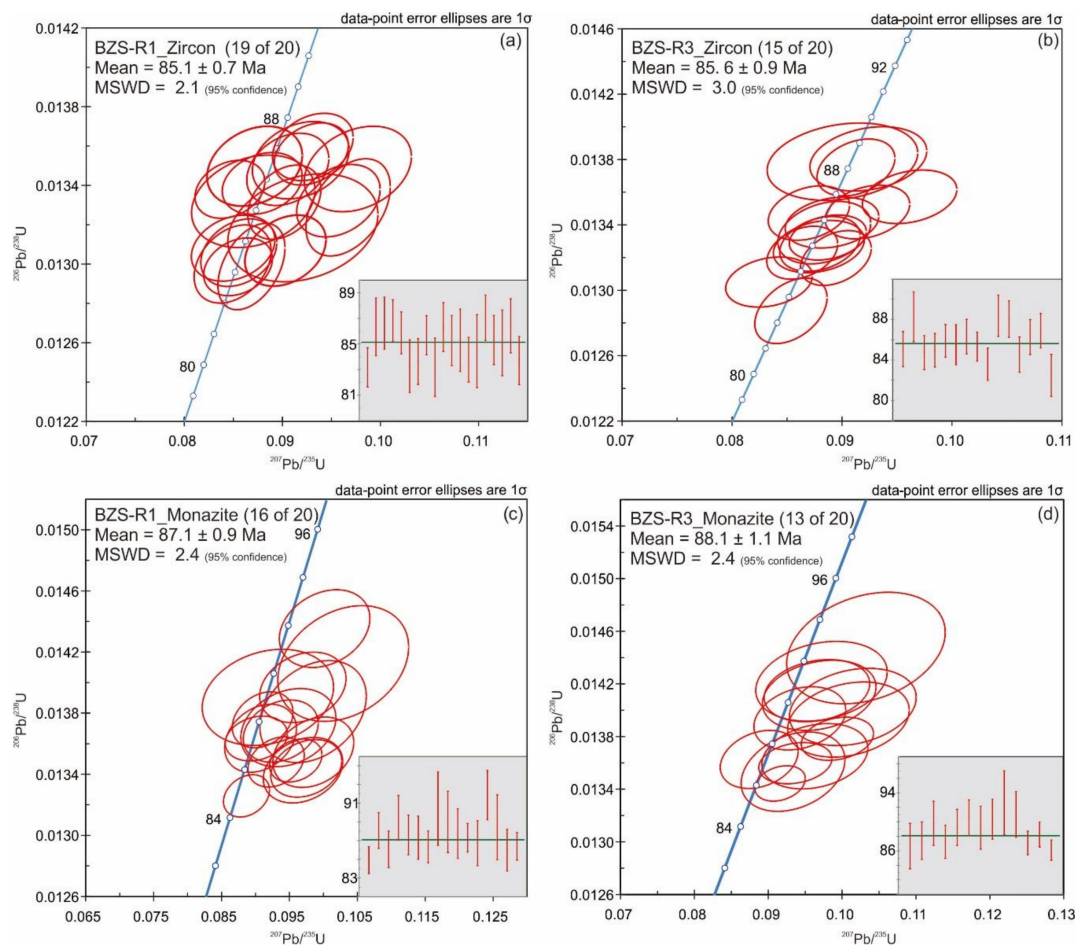


Figure 5. (a,b) LA-ICP-MS zircon U–Pb concordia diagrams for the Bozhushan batholith. (c,d) LA-ICP-MS monazite U–Pb concordia diagrams for the Bozhushan batholith. The age data and concordia plots were reported at 1σ error, whereas the uncertainties for weighted mean ages are given at a 95% confidence level.

Table 1. LA-ICP-MS zircon U–Pb isotopic data of the Bozhushan batholith.

Spot No.	Th	U	Th/U	Isotopic Ratios					Age (Ma)			
	(ppm)	(ppm)		²⁰⁷ Pb/ ²³⁵ U	1σ	²⁰⁶ Pb/ ²³⁸ U	1σ	RHO	²⁰⁷ Pb/ ²³⁵ U	1σ	²⁰⁶ Pb/ ²³⁸ U	1σ
BZSR1-01	286	1597	0.2	0.0855	0.0029	0.0130	0.0001	0.2764	83.3	2.7	83.2	0.8
BZSR1-02	1204	1057	1.1	0.0977	0.0045	0.0135	0.0002	0.2883	94.6	4.1	86.3	1.1
BZSR1-03	329	906	0.4	0.0919	0.0040	0.0135	0.0002	0.2707	89.2	3.7	86.6	1.0
BZSR1-04	506	1682	0.3	0.0929	0.0031	0.0136	0.0001	0.2864	90.2	2.9	86.8	0.8
BZSR1-06	596	1641	0.4	0.0879	0.0033	0.0134	0.0001	0.2526	85.6	3.1	85.9	0.8
BZSR1-07	469	1692	0.3	0.0849	0.0032	0.0130	0.0002	0.3305	82.8	3.0	83.3	1.0
BZSR1-08	303	1144	0.3	0.0856	0.0032	0.0131	0.0001	0.2908	83.4	3.0	83.6	0.9
BZSR1-09	581	1484	0.4	0.0847	0.0029	0.0134	0.0001	0.2619	82.5	2.7	85.7	0.8
BZSR1-10	1520	2118	0.7	0.0868	0.0028	0.0130	0.0002	0.4301	84.6	2.6	83.2	1.1
BZSR1-11	603	1256	0.5	0.0905	0.0034	0.0135	0.0002	0.2955	88.0	3.2	86.3	1.0
BZSR1-12	1015	1644	0.6	0.0902	0.0030	0.0133	0.0002	0.3432	87.7	2.8	85.3	1.0
BZSR1-13	248	1005	0.2	0.0870	0.0051	0.0133	0.0002	0.2440	84.7	4.8	85.3	1.2
BZSR1-14	525	1185	0.4	0.0850	0.0035	0.0131	0.0001	0.2554	82.8	3.3	83.8	0.9
BZSR1-15	306	440	0.7	0.0921	0.0063	0.0132	0.0002	0.2504	89.5	5.8	84.4	1.4
BZSR1-16	508	1507	0.3	0.0931	0.0034	0.0136	0.0001	0.2852	90.4	3.1	87.1	0.9
BZSR1-17	682	1346	0.5	0.0957	0.0035	0.0133	0.0002	0.3112	92.8	3.2	85.3	1.0
BZSR1-18	944	2050	0.5	0.0967	0.0035	0.0133	0.0002	0.4183	93.7	3.3	85.1	1.3
BZSR1-19	397	857	0.5	0.0872	0.0040	0.0135	0.0002	0.2697	84.9	3.7	86.4	1.1
BZSR1-20	677	1284	0.5	0.0903	0.0034	0.0131	0.0001	0.3021	87.8	3.1	83.7	0.9
BZSR3-01	1234	3950	0.3	0.0880	0.0030	0.0133	0.0001	0.3038	85.6	2.8	85.1	0.9

Table 1. Cont.

Spot No.	Th	U	Th/U	Isotopic Ratios					Age (Ma)			
	(ppm)	(ppm)		²⁰⁷ Pb/ ²³⁵ U	1σ	²⁰⁶ Pb/ ²³⁸ U	1σ	RHO	²⁰⁷ Pb/ ²³⁵ U	1σ	²⁰⁶ Pb/ ²³⁸ U	1σ
BZSR3-03	2160	2843	0.8	0.0900	0.0056	0.0138	0.0002	0.2252	87.5	5.2	88.3	1.2
BZSR3-05	1469	4784	0.3	0.0864	0.0026	0.0132	0.0001	0.3281	84.1	2.5	84.7	0.8
BZSR3-06	888	3270	0.3	0.0879	0.0034	0.0133	0.0001	0.2562	85.5	3.2	85.0	0.8
BZSR3-07	1692	3668	0.5	0.0891	0.0035	0.0134	0.0001	0.2425	86.7	3.2	85.9	0.8
BZSR3-08	1693	2968	0.6	0.0884	0.0035	0.0134	0.0002	0.2991	86.0	3.2	85.5	1.0
BZSR3-10	1333	3830	0.3	0.0923	0.0031	0.0135	0.0001	0.2922	89.7	2.9	86.3	0.9
BZSR3-11	1111	3525	0.3	0.0887	0.0029	0.0133	0.0001	0.2616	86.3	2.7	85.3	0.7
BZSR3-13	1890	3086	0.6	0.0834	0.0032	0.0131	0.0001	0.2481	81.3	3.0	83.6	0.8
BZSR3-14	3051	3065	1.0	0.0924	0.0043	0.0138	0.0002	0.2476	89.7	4.0	88.4	1.0
BZSR3-15	1384	3628	0.4	0.0913	0.0029	0.0138	0.0001	0.3271	88.7	2.7	88.0	0.9
BZSR3-16	1712	4042	0.4	0.0894	0.0026	0.0132	0.0001	0.3535	87.0	2.5	84.5	0.9
BZSR3-17	1355	4096	0.3	0.0870	0.0030	0.0135	0.0001	0.2906	84.7	2.8	86.3	0.9
BZSR3-18	1102	4553	0.2	0.0962	0.0035	0.0136	0.0001	0.2706	93.2	3.2	86.9	0.9
BZSR3-19	1890	5270	0.4	0.0854	0.0027	0.0129	0.0002	0.4030	83.2	2.5	82.5	1.0

4.3. U–Pb Geochronology of Monazite

The analyzed U–Pb monazite ages of the Bozhushan batholith are listed in Table 2. All the monazites are characterized by relatively high Th (1.54–10.43 wt. %) and U (754–9033 ppm) abundances. Sixteen monazites from sample BZSR1 yielded $^{206}\text{Pb}/^{238}\text{U}$ ages varying from 91.9 to 84.9 Ma, with a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 87.1 ± 0.9 Ma (1σ , MSWD = 2.1; Figure 5c). Thirteen monazites from sample BZSR3 yielded $^{206}\text{Pb}/^{238}\text{U}$ ages varying from 92.6 to 86.1 Ma, with a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 88.1 ± 1.1 Ma (1σ , MSWD = 2.1; Figure 5c).

Table 2. LA-ICP-MS monazite U–Pb isotopic data of the Bozhushan batholith.

Spot No.	Th (wt. %)	U (ppm)	Isotopic Ratios					Age (Ma)			
			$^{207}\text{Pb}/^{235}\text{U}$	1 σ	$^{206}\text{Pb}/^{238}\text{U}$	1 σ	RHO	$^{207}\text{Pb}/^{235}\text{U}$	1 σ	$^{206}\text{Pb}/^{238}\text{U}$	1 σ
BZSR1(MZ)-01	4.89	7565	0.0887	0.0028	0.0133	0.0001	0.2734	86.3	2.6	84.9	0.7
BZSR1(MZ)-02	10.43	4086	0.0911	0.0037	0.0138	0.0001	0.2710	88.5	3.4	88.1	1.0
BZSR1(MZ)-03	6.24	4503	0.0975	0.0043	0.0134	0.0002	0.2616	94.5	4.0	86.1	1.0
BZSR1(MZ)-04	10.11	1879	0.0970	0.0052	0.0140	0.0002	0.2514	94.0	4.8	89.4	1.2
BZSR1(MZ)-05	4.20	3046	0.0937	0.0045	0.0137	0.0002	0.2529	91.0	4.2	87.6	1.1
BZSR1(MZ)-06	6.20	2452	0.0907	0.0043	0.0136	0.0002	0.2801	88.2	4.0	87.3	1.2
BZSR1(MZ)-07	6.09	9033	0.0930	0.0034	0.0135	0.0001	0.2729	90.3	3.1	86.3	0.9
BZSR1(MZ)-08	7.38	795	0.1029	0.0079	0.0141	0.0003	0.2863	99.5	7.2	90.4	2.0
BZSR1(MZ)-09	4.67	953	0.0918	0.0079	0.0139	0.0003	0.2148	89.2	7.3	89.0	1.6
BZSR1(MZ)-10	8.32	3022	0.0948	0.0057	0.0137	0.0002	0.2528	92.0	5.3	87.8	1.3
BZSR1(MZ)-11	6.84	4041	0.0901	0.0037	0.0136	0.0001	0.2117	87.6	3.5	87.3	0.8
BZSR1(MZ)-15	5.24	2147	0.0985	0.0049	0.0135	0.0002	0.2813	95.4	4.5	86.7	1.2
BZSR1(MZ)-16	6.39	1915	0.1002	0.0055	0.0144	0.0002	0.2659	96.9	5.0	91.9	1.3
BZSR1(MZ)-17	5.25	867	0.0985	0.0064	0.0138	0.0003	0.3040	95.4	5.9	88.4	1.7
BZSR1(MZ)-18	5.46	3824	0.0970	0.0048	0.0134	0.0002	0.2650	94.0	4.4	86.0	1.1
BZSR1(MZ)-19	7.67	6793	0.0959	0.0032	0.0135	0.0001	0.2596	93.0	2.9	86.4	0.7
BZSR3(MZ)-01	7.03	1344	0.0934	0.0057	0.0135	0.0002	0.2961	90.6	5.3	86.7	1.6
BZSR3(MZ)-02	1.54	2107	0.0963	0.0059	0.0137	0.0002	0.2437	93.4	5.4	87.4	1.3
BZSR3(MZ)-03	7.48	1207	0.1015	0.0070	0.0140	0.0002	0.2471	98.1	6.5	89.8	1.5
BZSR3(MZ)-04	4.90	2304	0.0888	0.0043	0.0136	0.0002	0.2724	86.4	4.0	87.2	1.1
BZSR3(MZ)-06	4.49	1717	0.0943	0.0051	0.0139	0.0002	0.2611	91.5	4.7	89.2	1.2
BZSR3(MZ)-08	7.21	2345	0.0966	0.0058	0.0141	0.0002	0.2257	93.6	5.4	90.6	1.2
BZSR3(MZ)-10	7.57	1561	0.1009	0.0067	0.0139	0.0002	0.2510	97.6	6.2	89.2	1.5
BZSR3(MZ)-11	5.08	1423	0.0969	0.0063	0.0141	0.0002	0.2378	93.9	5.8	90.3	1.4
BZSR3(MZ)-12	6.86	754	0.1032	0.0088	0.0145	0.0003	0.2814	99.8	8.1	92.6	2.2
BZSR3(MZ)-13	4.25	1572	0.0972	0.0073	0.0142	0.0002	0.2327	94.2	6.7	91.0	1.6
BZSR3(MZ)-16	4.87	4464	0.0937	0.0040	0.0136	0.0001	0.2175	90.9	3.8	87.1	0.8
BZSR3(MZ)-18	8.32	5060	0.0994	0.0040	0.0138	0.0001	0.2421	96.2	3.7	88.2	0.9
BZSR3(MZ)-19	5.10	7020	0.0916	0.0028	0.0134	0.0001	0.2682	89.0	2.6	86.1	0.7

4.4. Rare Earth Element Patterns of Zircon and Monazite

Zircons from the Bozhushan batholith exhibit enrichment of heavy rare earth elements (HREEs) relative to light rare earth elements (LREEs), significant positive Ce anomalies and negative Eu anomalies (Figure 6a,b). Monazites are characterized by enriched LREEs and depleted HREEs, with negative Eu anomalies (Figure 6c,d).

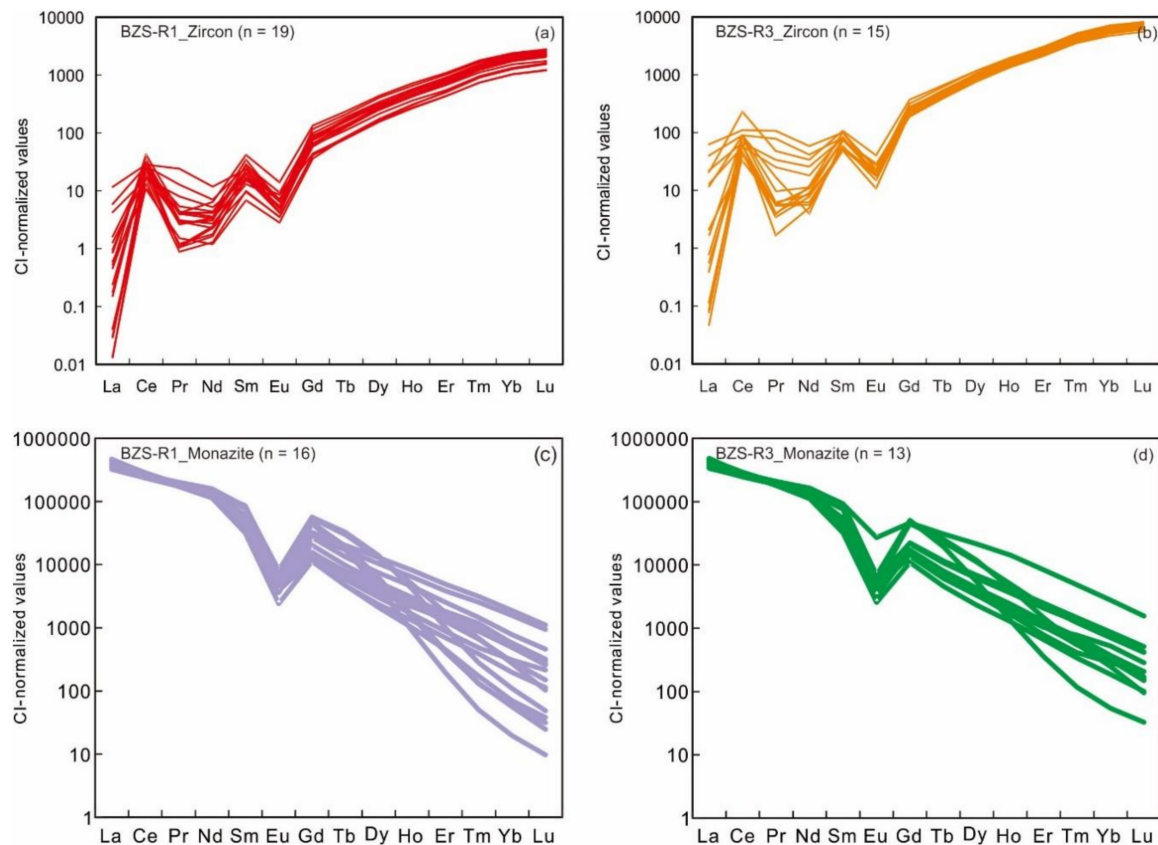


Figure 6. (a,b) Chondrite (C1)-normalized REE distribution patterns of zircon grains from the Bozhushan batholith. (c,d) C1-normalized REE distribution patterns of monazite grains from the Bozhushan batholith. The elemental abundances of C1 were from [38].

5. Discussion

Several Sn–W–polymetallic deposits represented by the giant Bainiuchang Ag–Sn–Pb–Zn deposit and large Guanfang W deposit are spatially and genetically related to the Bozhushan batholith (Figure 2). Previous whole-rock Rb–Sr and single zircon grain U–Pb age data have shown that the Bozhushan batholith was emplaced during the Early Cretaceous to Late Eocene (115–48 Ma) [1]. However, several works reported Late Cretaceous crystallization ages for the Bozhushan batholith and coincident Late Cretaceous mineralization ages (Table 3; Figure 7). Li [20] and Chen et al. [25] reported zircon LA-ICP-MS U–Pb ages of 91 to 86 Ma for granite porphyry and biotite monzogranites obtained from drill holes made in the Bainiuchang deposit, which are consistent with the age spectrum of 92 to 84 Ma yielded by cassiterite LA-ICP-MS U–Pb dating [21]. Biotite monzogranite samples collected from the Bozhushan, Chenjiazhai and Suozuodi batholiths have similar weighted mean zircon $^{206}\text{Pb}/^{238}\text{U}$ ages varying from 87.8 ± 0.4 to 85.1 ± 0.7 Ma, corresponding to their U–Pb monazite ages of 88–87 Ma obtained in this study. The Guanfang W deposit, hosted at the contacts between the southernmost Bozhushan batholith and a Middle Cambrian marble, has provided a Re–Os molybdenite isochron age of 91.6 ± 1.3 Ma [6]. These molybdenite grains used for dating coexist with scheelite, thus the isochron age could represent the timing of W-dominated mineralization in the Bozhushan region.

Monzogranite and biotite monzogranite samples from the Guanfang area (i.e., the southernmost of Bozhushan batholith) have weighted mean zircon $^{206}\text{Pb}/^{238}\text{U}$ ages of 91.6 ± 1.0 Ma and 88.6 ± 0.8 Ma, respectively [6,20]. Additionally, Li [20] reported that the SHRIMP U–Pb zircon ages of porphyritic biotite monzogranites in the Guanfang area varies from 89.5 ± 0.4 to 87.3 ± 0.3 Ma, which is consistent with the ages of W-dominated mineralization. The compilation of geochronological data for the Bozhushan batholith and representative deposits demonstrates that both the emplacement of granitic magmas and the extensive Sn–W–polymetallic mineralization occurred during the Late Cretaceous (92–85 Ma). The duration of granitic magmatism in the Bozhushan region revealed by compiled U–Pb zircon and monazite ages is about 7 Ma, with the earlier W-mineralization occurring at ca. 92 Ma and the later Sn-mineralization occurring at ca. 88–87 Ma (Figure 6). The temporal discrepancy between W-mineralization and Sn-mineralization might be a product of a long-lived fertile magmatic-hydrothermal systems that lasted for several million years, in which the highly evolved magmas would be much more favorable to the enrichment in Sn [39].

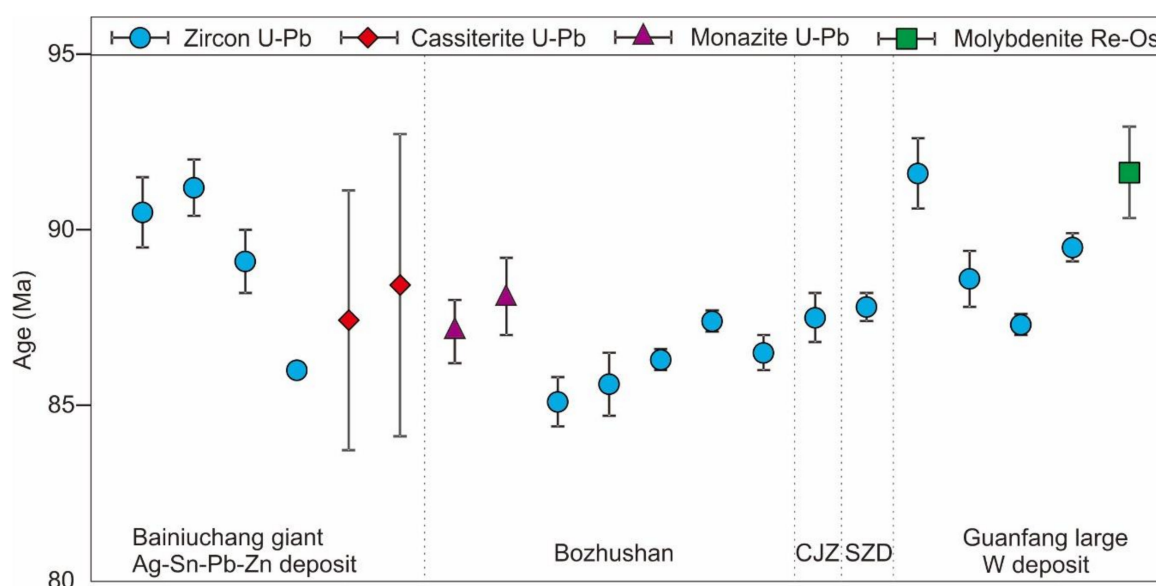


Figure 7. Compilation of geochronological data for the Bozhushan batholith and representative deposits, southeastern Yunnan district. Data sources: The Bainiuchang giant Ag–Sn–Pb–Zn deposit is from [20,21,25]; The Bozhushan area is from [4,25]; The Chenjiazhai (CJZ) area is from [4]; The Suozuodi (SZD) area is from [4]; The Guanfang large W deposit is from [6,20].

The Gejiu and Laojunshan batholiths in the southeastern Yunnan ore district have magmatism-mineralization age spectrums of 95–77 Ma [7,40,41] and 93–77 Ma [5,42,43], suggesting that the Late Cretaceous is a period of extensive magmatic activities and associated Sn–W–polymetallic mineralization in the southeastern Yunnan Province. Cheng et al. [5] compared the geological features and geochronological data of Sn–W mineralization in southeastern Yunnan Province with those in northeastern Vietnam, and concluded that they share many similarities and should have formed under the same lithospheric extensional setting in response to the subduction of the Palaeo-Pacific Plate. In summary, the Late Cretaceous granitic rocks in the southeastern Yunnan Province are closely related to Sn–W–polymetallic mineralization, especially at the contacts between these granites and Paleozoic marbles.

Table 3. Geochronological data for the Bozhushan batholith and representative deposits, southeastern Yunnan district.

Region	Rock Type	Sample No.	Method	Age (Ma)	Genetic Type	Metal	Tonnage	Age (Ma)	Method
Bainiuchang	Fine- to medium-grained biotite monzogranite	BN1380-01	Zircon LA-ICP-MS U-Pb	90.5 ± 1.0 [20]	Skarn	Ag-Sn-Pb-Zn	6470 t@95 g/t Ag, 172 Mt@2.46% Zn, 109 Mt@1.56% Pb, 8.6 Mt@0.12% Sn	87.4 ± 3.7 [21]	Cassiterite LA-ICP-MS U-Pb
	Fine- to medium-grained biotite monzogranite	ZK146-05	Zircon LA-ICP-MS U-Pb	91.2 ± 0.8 [20]				88.4 ± 4.3 [21]	Cassiterite LA-ICP-MS U-Pb
	Fine- to medium-grained biotite monzogranite	ZK146-N1	Zircon LA-ICP-MS U-Pb	89.1 ± 0.9 [20]					
	Granite porphyry	DMS	Zircon LA-ICP-MS U-Pb	86.0 ± 0.2 [25]					
Bozhushan	Fine- to medium-grained biotite monzogranite	BZS-R1	Monazite LA-ICP-MS U-Pb	87.1 ± 0.9					
	Fine- to medium-grained biotite monzogranite	BZS-R3	Monazite LA-ICP-MS U-Pb	88.1 ± 1.1					
	Fine- to medium-grained biotite monzogranite	BZS-R1	Zircon LA-ICP-MS U-Pb	85.1 ± 0.7					
	Fine- to medium-grained biotite monzogranite	BZS-R3	Zircon LA-ICP-MS U-Pb	85.6 ± 0.9					
	Medium- to coarse-grained biotite monzogranite	BZS-1	Zircon LA-ICP-MS U-Pb	86.3 ± 0.3 [25]					
	Medium- to coarse-grained biotite monzogranite	BZS-2	Zircon LA-ICP-MS U-Pb	87.4 ± 0.3 [25]					
	Fine- to medium-grained biotite monzogranite	CYB0807079	Zircon LA-ICP-MS U-Pb	86.5 ± 0.5 [4]					
Chenjiazhai	Porphyritic biotite monzogranite	CYB0807086	Zircon LA-ICP-MS U-Pb	87.8 ± 0.4 [4]					
Suozuodi	Porphyritic biotite monzogranite	CYB0807084	Zircon LA-ICP-MS U-Pb	87.5 ± 0.7 [4]					
Guanfang	Medium-grained biotite monzogranite	ZK8-234-01	Zircon LA-ICP-MS U-Pb	91.6 ± 1.0 [6]	Skarn	W	10 Mt@0.5% W	91.6 ± 1.3 [6]	Molybdenite Re-Os
	Fine- to medium-grained biotite monzogranite	HDPD06-01	Zircon LA-ICP-MS U-Pb	88.6 ± 0.8 [6]					
	Fine- to medium-grained porphyritic biotite monzogranite	YTS-01	Zircon SHRIMP U-Pb	87.3 ± 0.3 [20]					
	Fine- to medium-grained porphyritic biotite monzogranite	YTS-02	Zircon SHRIMP U-Pb	89.5 ± 0.4 [20]					

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