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Geochemical and Sr-Nd-Pb-Hf Isotopic Characteristics of Muchen Pluton in Southeast China, Constrain the Petrogenesis of Alkaline A-Type Magma

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Received: 2 December 2019; Accepted: 15 January 2020; Published: 19 January 2020

Abstract: We present comprehensive petrological, major-trace element, in situ zircon U-Pb dating and Sr-Nd-Pb isotopic data for Muchen granitoid (western Zhejiang Province, Southeast China), to constrain the petrogenesis of alkaline A-type granites and the geodynamic setting of Southeast China in the Early Cretaceous. The Early Cretaceous Muchen quartz monzonite yielded zircon U-Pb crystallization ages of 111.3 ± 0.7 Ma and is metaluminous to weakly peraluminous with SiO_2 contents ranging from 59 to 69 wt.%, and can be classified as alkaline A-type granitoid. The quartz monzonites have low $(^{87}\text{Sr}/^{86}\text{Sr})_i$ values (0.7052 to 0.7061) and high $\epsilon_{\text{Nd}}(t)$ values (-2.6 to -2.0), similar to nearby coeval mafic rocks that have been proposed to be derived from the enriched lithospheric mantle. The high Nb/Ta ratios (16.7 to 30.1, average 21.8) and low Nb/U ratios (as low as 3.5) indicate the involvement of slab-derived melt and fluids in this mantle. These geochemical properties of the Muchen quartz monzonites indicated that they might be from a phlogopite-bearing and rutile-rich subduction-modified subcontinental lithospheric mantle, and underwent strong fractional crystallization of olivine + orthopyroxene + plagioclase during magma ascent. The low Mg# values of these alkaline rocks (<30 mostly) may indicate a low-pressure source in a back-arc setting. The early Cretaceous alkaline granitoids in Southeast China are related to the continental back-arc setting caused by deep angle subduction of the paleo-Pacific plate.

Keywords: subducted melts/fluids; alkaline A-type magma; deep angle subduction; high Nb/Ta; paleo-Pacific plate; SE China

1. Introduction

Widespread Mesozoic igneous rocks in Southeast China [1,2], were mainly emplaced in the Jurassic and Cretaceous periods [3,4]. The majority of the Cretaceous igneous rocks are calc-alkaline [5–8], but some Cretaceous A-type granites or alkaline intrusions also occur [2,9–13]. A-type granites or alkaline intrusions generally develop during continental extension in post-orogenic or intraplate settings [14–17], and can be used to investigate lithospheric sources and magma evolution of these rocks, and geodynamic processes. Previous studies have provided petrological, geochemical, and isotopic constraints on the origin and evolution of A-type granites, leading to several models such as a low degree of partial melting of dry granulitic residue depleted by the prior extraction of granitic melt [18,19], partial melting

of tholeiitic rock derived from underplated mafic magma in the crust [20,21], re-melting metaluminous and peraluminous tonalite or granodiorite [22,23], fractional crystallization from mafic magmas with or without crustal assimilation [24–27], and magma mixing between mantle-derived and crust-derived magma [28–32]. Essentially, these models fall into three categories: crustal source, mantle source, and mixing source between crustal and mantle. However, previous studies show that A-type granites in SE China are generally high-silica ($\text{SiO}_2 > 70$ wt.%) rocks [9,13,33–36], making it difficult to determine whether mantle materials have been involved in their formation. Therefore, understanding the features of low- SiO_2 alkaline rocks can provide important insights into the petrogenesis of the A-type granitoids.

In this paper, we collected 9 samples from Muchen pluton in Zhejiang Province, SE China (GPS: $28^\circ 50' 22.4''\text{N}$, $119^\circ 09' 10.1''\text{E}$). These samples are alkaline granitoids, with $\text{SiO}_2 \approx 60\text{--}70$ wt.%. Previous paper considered that these rocks were derived from a hybrid magma produced by mixing between depleted mantle-derived mafic magmas and felsic magmas generated by partial melting of crustal materials, and were classified into I-type granitoids [30]. Here, we propose a counter-argument that these rocks are not a hybrid origin between the depleted mantle and crustal materials, and not I-type granitoids.

2. Geological Background and Petrography

South China, located on the eastern margin of Eurasia, consists of the Yangtze Block and Cathaysia Block. The specific location of South China is the south of the North China Craton, northeast of the Indochina Block, east of the Tibetan Plateau, and west of the Philippine Sea Plate (Figure 1; [37–41]). There is a consensus that the Yangtze Block and Cathaysia Block collided during the Neoproterozoic to form the South China Block. Subsequently, the South China Block began to collide with the Indochina Block and North China Block during the Triassic. Finally, the Yanshanian orogeny events of the South China Block produced widely distributed Mesozoic igneous rocks, including the widespread granitoids province in SE China (Figure 1). Early and Late Yanshanian granitic rocks are mainly distributed in inland and coastal areas of SE China, respectively. Generally, the Cretaceous magmatism along the coastal area was produced under an active continental margin setting that is related to the subduction of the paleo-Pacific plate [42,43].

Figure 1. Simplified geological map of South China showing the distribution of Mesozoic granitoid and volcanic rocks (modified after Liu et al. [30]).

Muchen pluton is located in Longyou County, Zhejiang Province, Southeast China (Figures 1 and 2). The north of this pluton is hosted in the Proterozoic metamorphic and igneous rocks and the south is the Late Jurassic igneous and sedimentary rocks. The area stretches over ~60 km² along NE to NNE trending. Moreover, small elliptical plutons of granite or granodiorite crop out near the Muchen pluton (Figure 2).

Figure 2. Simplified geological map of Muchen pluton (Modified after Liu et al. [30]). 1. Quartz monzonite; 2. Quartz syenite; 3. Quartz diorite; 4. Granite; 5. Late Yanshanian rhyolite porphyry; 6. Quaternary system; 7. Xishantou Formation; 8. Gaowu Formation; 9. metamorphic rocks of the Longou Group; 10. Faults (① Changle–Nan’ao fault; ② Zhenghe–Dapu fault; ③ Jiangshan–Shaoxing fault).

The Muchen pluton is mainly quartz monzonite, which consists of plagioclase (~30%), alkali feldspar (~35%), quartz (~15%), biotite (~10%), hornblende (~5%) and minor accessory minerals such as zircon and apatite (Figure 3). The main minerals in quartz monzonites are medium- to fine-grained in size. The oscillatory zones can be found in the euhedral to subhedral plagioclase. Anhedral alkali feldspars grow at the interstices of other minerals. Biotite and hornblende occur as euhedral to subhedral crystals. Some MMEs (mafic microgranular enclaves) were found in field. They usually show ellipse, strip shape in quartz monzonite (Figure 3b). The main minerals in MME are similar to host rocks, but the biotite and hornblendes contents are higher than those in the host rock. The size of the biotite, hornblendes in MMEs are about 100–200 µm, quietly smaller than those from the quartz monazite (500–2000 µm) (Figure 3g).

Figure 3. (a,b) Field photographs of quartz monzonite and MME (mafic microgranular enclave) in Muchen pluton; (c–f) are thin section photographs of the host quartz monzonite; (g) is the mineral assemblage between MME and host quartz monzonite; (h) is the minerals assemblage of MME. All the thin section photographs (c,d) are cross-polarised light. (Pl = plagioclase, Afs = alkali-feldspar, Qtz = quartz, Bt = biotite, Amp = amphibole, Ap = apatite).

3. Analytical Methods

Nine representative fresh samples from the Muchen pluton were selected for petrographic observations, major and trace element, and Sr-Nd-Pb analysis. Zircon crystals were separated from the sample LY-8 for in situ U-Pb dating and subsequent Hf isotopic analysis.

3.1. Zircon U-Pb Dating and Hf Isotope Analysis

Zircon crystals were separated from a representative quartz monzonite (LY-8) by conventional techniques, including crushing, sieving, and magnetic and heavy liquid separation, and final hand picking under a binocular microscope. Zircon grains were then mounted in epoxy resin and polished to expose crystal centers. Prior to analysis, transmitted and reflected light photomicrographs and cathodoluminescence (CL) images were taken to reveal any internal zoning and inheritance, and to select target sites for U-Pb dating and Hf isotope analyses. CL images of zircon grains were obtained using a Tescan MIRA3 LMH FESEM at Nanjing Hongchuang Exploration Technology Service Co., Ltd., Nanjing, China.

Zircon U-Pb isotopic analyses were conducted by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) at the Mineral Laboratory of the School of Resources and Environmental Engineering, Hefei University of Technology, Hefei China, using an Agilent 7900 ICP-MS Coupled to a Teledyne Cetac Technologies Analyte Excite laser-ablation system with a 193 nm ArF excimer laser. The ablated material was transported in helium carrier gas and combined with argon complementary gas prior to entering the plasma source of the ICP-MS. Analyses were carried out with a laser beam diameter of 30 μm and repetition rate of 7 Hz. Data acquisition for each analysis took 80 s (40 s on background; 40 s on signal). Offline processing of data includes selection of background signal, correction of sensitivity drift and analysis of major and trace element concentration through ICP-MS DataCal [44]. Detailed data processing methods are described in the literature [45,46]. A homogeneous standard zircon (GEMOC GJ-1; $^{207}\text{Pb}/^{206}\text{Pb}$ age of 608.5 ± 1.5 Ma; [47]) was used to correct for the mass discrimination of the mass spectrometer and any elemental fractionation. A near-concordant standard zircon, 91500 (1065 Ma), was used as an internal standard to assess the reproducibility and instrument stability. The U-Th-Pb isotope ratio of zircon 91500 is recommended by Wiedenbeck [48]. Mean age calculations and plotting of Concordia diagrams were performed using Isoplot/Ex_ver3.0 [49].

Hafnium isotopic compositions of zircon were measured by the LA-MC-ICP-MS at the Isotope Laboratory at the School of Resources and Environmental Engineering, Hefei University of Technology. A Teledyne Cetac Technologies Analyte Excite laser-ablation system and ThermoFisher Neptune Plus MC-ICP-MS were combined for the experiments. A 193 nm ArF excimer laser was focused on the zircon surface with fluence of $\sim 3.0 \text{ J cm}^{-2}$. Ablation protocol employed a spot diameter of 55 μm at an 8 Hz repetition rate for 30 s (equating to 240 pulses). A mix gas of helium ($\sim 0.9 \text{ L/min}$) and argon ($\sim 0.9 \text{ L/min}$) was applied as the carrier gas to transport the aerosol to the MC-ICP-MS. Standard zircons (including Qinghu, Plešovice, and Penglai) were treated as quality control during the analytical process. All the data were reduced off-line with LAZrHf-Calculator@HFUT [50]. Analytical results of $^{176}\text{Hf}/^{177}\text{Hf}$ ratios for the three standard zircons Penglai, Plešovice and Qinghu measured in one batch experiment are 0.282915 ± 0.000019 , 0.282484 ± 0.000007 and 0.282997 ± 0.000009 , respectively, which agree very well with the reference values (reference ratios of $^{176}\text{Hf}/^{177}\text{Hf}$ for Penglai, Plešovice and Qinghu are 0.282906 ± 0.000016 , 0.282482 ± 0.000013 and 0.282996 ± 0.000044 , respectively; [51–53]). The long-term monitoring of standard zircons initial $^{176}\text{Hf}/^{177}\text{Hf}$ values were calculated based on a Lu decay constant of 1.865E^{-11} [54]. The model ages were calculated under the assumption that the $^{176}\text{Lu}/^{177}\text{Hf}$ of average crust is 0.015, and the $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{176}\text{Lu}/^{177}\text{Hf}$ ratios of chondrite and depleted mantle at present are, respectively, 0.282772 and 0.0332, and 0.28325 and 0.0384 [55].

3.2. Whole-Rock Elemental and Sr-Nd-Pb Isotope Analysis

Whole-rock major and trace element analyses were performed at Guizhou Tongwei Analytical Technology Co., Ltd. (Guiyang, China) using a Panalytical Axios PW4400 XRF and Thermal X series 2 (ICP-MS) equipped with a Cetac ASX-510 Autosampler. Instrument drift was corrected with internal spikes and external monitors. The ICP-MS procedure for trace element analysis follows the protocol of Eggins et al. [56] with modifications as described in Kamber et al. [57] and Li et al. [58].

For Sr-Nd-Pb isotope analysis ~50–100 mg of rock powder was dissolved with a mixture of concentrated nitric and hydrofluoric acid in bomb at 185 °C in an oven for 3 days, and dried down on a hot plate at 80 °C. After converting any fluoride to nitrate, the dried residue was taken up with 3 mL 2N nitric acid and passed through column chemistry to separate Sr, Pb, Nd from the matrix, using a modified procedure following [59–61]. Typical procedural blanks are ca. 65, 50, 60 pg for Sr, Pb, Nd, respectively.

Strontium isotopes were analyzed on a VG Sector 54 thermal ionization mass spectrometer system at University of Queensland, using a three-sequence dynamic procedure. Fractionation was corrected assuming $^{86}\text{Sr}/^{88}\text{Sr}$ ratio = 0.1194. NBS-9987 was used as a monitor of instrument status. The standard NBS-987 was used during the run, in which the value 0.710252 ± 0.000008 (2σ , $n = 4$) for $^{87}\text{Sr}/^{86}\text{Sr}$ was obtained.

The Nd and Pb isotopes were analyzed on the Nu Plasma HR MC-ICP-MS at University of Queensland. Instrument bias and mass fractionation for Nd isotopes was corrected by normalizing raw ratios to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$. Standards (W-2a, BHVO2) were measured during the run (0.512533 ± 0.000009 , $0.512,982 \pm 0.000007$, respectively), which are within the range of recommended values (<http://georem.mpch-mainz.gwdg.de/>). All errors are 2σ . Instrument bias and mass fractionation for Pb isotope was corrected by Tl, which with $^{205}\text{Tl}/^{203}\text{Tl} = 0.23875$. BHVO2 in the same batch as the unknown samples, yielded average ratios, with 2σ as below: $^{208}\text{Pb}/^{204}\text{Pb} = 38.2464 \pm 24$; $^{207}\text{Pb}/^{204}\text{Pb} = 15.5385 \pm 9$; $^{206}\text{Pb}/^{204}\text{Pb} = 18.6463 \pm 9$. The ratios were similar to the values from [62].

4. Results

4.1. Zircon U-Pb Ages and Hf Isotopic Compositions

Cathodoluminescence (CL) images from representative zircons from the Muchen quartz monzonite are shown in Figure 4. The results of LA-ICP-MS U-Pb isotopic analysis for this sample was listed in Supplementary S1 and shown in Figure 5. The Lu-Hf isotopic results are given in Supplementary S2.

Figure 4. Cathodoluminescence (CL) images of selected zircon crystals from representative Muchen quartz monzonite and granite. The morphology of zircon grains, $^{206}\text{Pb}/^{238}\text{U}$ ages, $\epsilon_{\text{Hf}}(t)$ values are shown. Small white spots indicate U-Pb dating positions of laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), and large yellow spots indicate the sites of Hf isotope analyses of LA-MC-ICP-MS, with spot diameters showing the approximate laser spot sizes.

Figure 5. Zircon U-Pb Concordia diagrams for representative quartz monzonite and granite from the Muchen pluton.

Zircon grains separated from quartz monzonite (LY-8) are euhedral and prismatic, and approximately 150–250 μm in length with length/width ratios of 1:1 to 3:1 and show well-developed oscillatory zoning in CL images (Figure 4). Thirty-nine U-Pb analyses show high Th/U ratios (0.53 to 1.16), indicating a magmatic origin for these zircons [63]. The $^{206}\text{Pb}/^{238}\text{U}$ ages range from 106 ± 2 Ma (1 sigma) to 118 ± 2 Ma (1 sigma) with a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 111.3 ± 0.7 Ma ($\text{MSWD} = 1.5$, 2 sigma; Figure 5), which is consistent with previous study (112 Ma; [30]). These same zircon grains yielded a narrow range of initial $^{176}\text{Hf}/^{177}\text{Hf}$ values (0.282655 to 0.282778) and $\epsilon_{\text{Hf}}(t)$ values (-1.7 to $+2.6$; Figure 6), corresponding to two-stage Hf model ages ($T_{\text{DM2}}(\text{Hf})$) of 1.00 to 1.28 Ga (Supplementary S2).

Figure 6. Histograms of $\epsilon_{\text{Hf}}(t)$ values for zircons from representative Muchen alkaline quartz monzonite.

4.2. Major and Trace Element Geochemistry

Whole-rock major and trace element compositions for the Muchen pluton are given in Table 1. All the samples from the Muchen are silica-over-saturated rocks, containing quartz with various SiO_2 (59.45 to 68.61 wt.%), and plot in the alkaline series field on a total alkali-silica (TAS) diagram (Figure 7a). The Muchen samples have moderately high alkali contents ($\text{Na}_2\text{O} + \text{K}_2\text{O} = 8.64\text{--}10.46$ wt.%) and K contents ($\text{K}_2\text{O}/\text{Na}_2\text{O} = 0.73\text{--}1.45$, average 1.22; Figure 7b,c), similar to the shoshonites [64]. The Muchen samples are metaluminous ($\text{A}/\text{CNK} = 0.89\text{--}1.04$) to weakly peraluminous (Figure 7d). Although all the samples of the Muchen pluton have relatively lower $\text{TFe}_2\text{O}_3/\text{MgO}$ ratios (3.77–9.06, average 5.98) than those of general A-type granites ($\text{TFe}_2\text{O}_3/\text{MgO} = 13.4$; [16]), the high 10,000 Ga/Al ratios, Zr + Nb + Ce + Y and $\text{Na}_2\text{O} + \text{K}_2\text{O}$ contents suggests that Muchen pluton is A-type granitoids (Figure 8), which revises the conclusion of [30].

Figure 7. Chemical classification of rocks from the Muchen rocks. (a) Total alkali vs. silica (TAS) diagram [65]; with the thick solid line from Irvine and Baragar; [66]; (b) SiO_2 vs. alkalinity ratio (A.R.) diagram [67]; (c) K_2O vs. SiO_2 diagram (solid lines from [68]; dashed lines from [69]); (d) A/NK vs. A/CNK diagram [70,71]; Previous data of Muchen rocks from Liu et al. [30]. $\text{A}/\text{CNK} = \text{Al}_2\text{O}_3/(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$ (with molar ratio), $\text{A}/\text{NK} = \text{Al}_2\text{O}_3/(\text{Na}_2\text{O} + \text{K}_2\text{O})$ (with molar ratio).

All the samples are characterized by moderate to high REE contents (149–527 ppm) with lightly fractionated light rare earth elements (LREE; average $(\text{La}/\text{Sm})_{\text{N}} < 6$) and moderate heavy REE (HREE) fractionation (average $(\text{La}/\text{Yb})_{\text{N}} = 14.76$). Chondrite-normalized REE patterns have a relatively steep slope with variable negative Eu anomalies ($\delta\text{Eu} = 0.22\text{--}0.75$, average 0.46; Figure 9a). The samples are enriched in Rb, Th, U, K, Pb, Zr, and Hf and marked depleted in Nb, Ta, Sr, Ba, P, and Ti (Figure 9b).

Table 1. Chemical Composition of Muchen Pluton.

Sample	LY-2	LY-4	LY-6	LY-7	LY-8	LY-9	LY-11	LY-12	LY-14	MC-1(1) *	MC-2(3) *	MC-3 *	MC-4 *	MC-2(1) *	MC-2 *
Rock type	Quartz Monzonite									MMEs					
Major elements (in wt.%)															
SiO ₂	65.89	65.60	59.45	62.18	64.50	63.68	68.28	68.61	65.81	64.76	63.98	67.08	63.79	55.35	54.84
Al ₂ O ₃	15.92	15.88	17.17	16.57	17.25	16.84	15.85	15.45	15.69	16.57	16.60	16.43	16.25	17.96	17.50
TFe ₂ O ₃	3.90	4.24	6.71	5.53	3.50	4.51	3.01	3.05	3.94	4.04	4.65	3.18	4.88	7.92	8.02
MgO	0.50	0.76	1.78	1.18	0.73	0.84	0.38	0.34	0.80	1.12	1.02	0.46	1.43	2.43	2.38
CaO	1.34	1.76	3.76	2.86	1.85	2.18	1.01	1.22	2.08	1.96	1.70	1.29	3.26	4.90	5.54
Na ₂ O	4.12	4.29	4.99	4.77	4.51	4.53	4.47	4.73	4.12	4.54	4.75	5.17	4.29	4.86	5.10
K ₂ O	5.96	5.89	3.65	5.20	5.95	5.72	5.63	5.36	5.49	5.48	5.84	5.82	5.01	4.27	2.35
P ₂ O ₅	0.11	0.14	0.40	0.23	0.16	0.18	0.08	0.07	0.16	0.22	0.20	0.12	0.31	0.59	0.54
TiO ₂	0.23	0.34	0.64	0.46	0.32	0.36	0.18	0.20	0.34	0.36	0.39	0.22	0.50	0.74	0.91
MnO	0.07	0.18	0.29	0.23	0.16	0.16	0.07	0.14	0.13	0.16	0.17	0.15	0.10	0.26	0.41
LOI	1.70	0.59	0.93	0.43	0.74	0.66	0.81	0.56	1.19	1.40	1.04	0.74	0.88	1.28	3.60
Totle	98.05	99.08	98.84	99.22	98.94	99.02	98.97	99.16	98.57	99.21	99.30	99.92	99.82	99.28	97.59
Mg#	20.40	26.20	34.43	29.79	29.15	26.99	20.06	17.94	28.75	35.45	30.29	22.27	36.73	37.80	37.02
A.R.	2.82	2.89	2.41	2.93	2.79	2.82	3.26	3.63	2.73	2.92	3.16	3.80	2.57		
A/CNK	1.02	0.95	0.90	0.89	1.00	0.95	1.04	0.98	0.95	0.98	0.96	0.96	0.88	0.83	0.83
A/NK	1.20	1.18	1.41	1.23	1.24	1.23	1.18	1.14	1.23	1.24	1.17	1.11	1.30	1.42	1.60
K ₂ O/Na ₂ O	1.45	1.37	0.73	1.09	1.32	1.26	1.26	1.13	1.33	1.21	1.23	1.13	1.17	0.88	0.46
Na ₂ O+K ₂ O	10.08	10.18	8.64	9.97	10.46	10.25	10.10	10.09	9.61	10.02	10.59	10.99	9.30	9.13	7.45
TFe ₂ O ₃ /MgO	7.73	5.58	3.77	4.67	4.81	5.36	7.89	9.06	4.91	3.61	4.56	6.91	3.41	3.26	3.37
Trace Element (in ppm)															
Li	12.4	9.07	11.9	4.66	9.85	9.34	7.17	2.89	30.6						
Be	4.03	3.07	7.22	3.44	3.44	4.16	4.06	5.10	4.88						
Sc	2.75	3.23	6.50	5.78	2.63	3.57	1.58	1.60	3.28	3.81	4.35	2.83	6.75	7.45	13.75
Ti	1640	1930	3730	2640	1820	2020	1000	1080	1960						
V	20.9	22.3	63.2	35.2	25.3	26.4	9.20	7.79	33.0	38.80	29.30	10.10	70.20	115.60	136.40
Cr	5.35	5.82	5.55	5.22	2.90	5.45	5.63	4.80	7.13	3.26	4.14	1.58	2.74	2.25	2.00
Mn	704	1380	2260	1760	1080	1240	475	868	1070						
Co	3.67	4.17	7.91	5.91	3.46	3.90	1.42	1.52	5.07	6.38	5.68	2.26	7.94	16.41	15.76
Ni	2.00	1.71	2.83	1.65	1.01	1.49	1.46	1.04	2.15						
Cu	7.03	8.67	13.3	12.9	23.6	28.5	14.6	9.10	6.53	5.13	5.32	1.96	3.99	12.32	12.56
Zn	59.3	81.7	123	102	64.2	63.6	72.8	52.4	107	83.60	116.50	70.80	51.50	178.60	204.40
Ga	20.1	17.0	19.5	19.4	18.0	19.1	17.7	18.7	17.5	17.45	19.79	18.86	18.47	18.80	20.71
Ge	1.78	1.66	1.91	1.88	1.69	1.80	1.63	2.02	1.61						
Rb	279	174	157	156	186	180	174	162	233	126.70	180.60	183.80	142.50	131.60	93.10

Table 1. Cont.

Sample	LY-2	LY-4	LY-6	LY-7	LY-8	LY-9	LY-11	LY-12	LY-14	MC-1(1) *	MC-2(3) *	MC-3 *	MC-4 *	MC-2(1) *	MC-2 *
Rock type	Quartz Monzonite									MMEs					
Sr	303	266	405	454	344	390	106	99.4	351	463.00	386.00	130.00	473.00	893.00	480.00
Y	22.1	27.1	45.2	44.0	28.9	32.7	24.5	32.3	31.1	26.04	41.28	28.21	37.76	25.52	42.23
Zr	307	324	302	399	363	287	326	394	286	294.00	431.00	389.00	277.00	156.00	189.00
Nb	14.7	20.6	35.5	26.0	20.8	22.5	20.5	27.0	25.7	20.42	28.54	26.76	25.31	13.63	23.99
Mo	5.63	6.48	5.48	3.72	10.3	2.25	2.07	2.21	1.45						
Sn	2.62	2.30	3.42	2.84	2.26	2.45	2.34	2.49	2.30						
Sb	0.146	0.154	0.468	0.131	0.158	0.129	0.189	0.160	0.160						
Cs	7.60	3.50	5.40	3.14	4.50	3.68	4.52	3.21	5.22	6.87	5.01	4.20	1.76	13.88	7.18
Ba	605	501	381	612	545	684	200	156	528	565.00	602.00	177.00	474.00	809.00	233.00
La	39.7	39.3	67.8	52.1	58.5	89.0	66.1	167.00	28.3	56.90	69.00	52.80	48.90	46.50	67.10
Ce	71.4	73.3	144	108	85.7	165	93.1	222	59.1	111.20	144.80	98.20	94.20	86.30	153.80
Pr	8.22	9.38	17.0	13.8	10.8	16.1	12.6	25.6	7.35	12.09	16.89	11.58	10.71	10.58	16.00
Nd	29.5	35.0	63.5	53.0	37.5	54.0	41.9	78.5	28.2	43.37	64.70	41.96	40.67	42.72	57.59
Sm	5.43	6.66	11.7	10.4	6.75	8.89	6.77	10.6	5.87	7.13	11.55	7.49	7.84	8.24	9.97
Eu	1.19	0.967	1.12	1.32	1.15	1.24	0.641	0.624	1.04	1.19	1.20	0.64	1.46	2.32	1.32
Gd	4.36	5.49	9.35	8.59	5.57	6.90	5.18	7.20	5.10	6.22	9.82	6.59	7.08	7.07	8.80
Tb	0.670	0.856	1.40	1.32	0.856	1.04	0.788	1.07	0.828	0.95	1.57	1.04	1.11	1.03	1.34
Dy	3.76	4.78	7.61	7.37	4.79	5.65	4.37	5.72	4.78	5.36	8.73	5.87	6.28	5.22	7.49
Ho	0.764	0.969	1.50	1.46	0.965	1.13	0.886	1.14	0.996	1.04	1.63	1.11	1.27	0.95	1.42
Er	2.23	2.79	4.24	4.12	2.76	3.21	2.59	3.31	2.94	3.08	4.77	3.45	3.76	2.66	4.20
Tm	0.365	0.447	0.663	0.646	0.441	0.512	0.422	0.543	0.489	0.48	0.70	0.53	0.56	0.37	0.65
Yb	2.40	2.90	4.23	4.10	2.85	3.34	2.80	3.57	3.22	3.20	4.44	3.62	3.78	2.43	4.22
Lu	0.384	0.456	0.643	0.635	0.447	0.515	0.442	0.562	0.503	0.50	0.70	0.55	0.60	0.38	0.63
Hf	7.48	7.64	6.58	9.02	8.28	6.91	8.14	9.69	7.27	8.31	11.59	11.21	7.70	4.38	5.09
Ta	0.883	0.881	1.18	0.951	0.813	0.960	0.988	1.34	1.42	1.48	1.66	1.54	2.08	1.12	1.21
Tl	1.91	1.27	1.07	0.909	1.30	1.10	1.23	1.05	1.10						
Pb	24.9	28.7	17.9	20.2	17.8	16.2	13.8	14.8	21.4	16.19	21.89	16.01	11.86	22.39	14.97
Th	19.8	11.7	8.40	10.4	13.2	16.7	26.6	36.0	23.3	18.53	18.76	17.03	24.94	12.71	12.20
U	4.23	2.47	2.24	2.21	2.53	2.82	4.38	4.85	5.02	3.28	2.36	3.25	3.20	2.28	2.75
ΣERR	170	183	335	267	219	357	239	527	149	252.71	340.50	235.43	228.22	216.77	334.53
(La/Yb) _N	11.87	9.72	11.50	9.11	14.72	19.11	16.93	33.55	6.30	12.75	11.15	10.46	9.28	13.73	11.41
δEu	0.75	0.49	0.33	0.43	0.57	0.48	0.33	0.22	0.58	0.55	0.34	0.28	0.60	0.93	0.43
Nb/Ta	16.65	23.38	30.08	27.34	25.58	23.44	20.75	20.15	18.10	13.80	17.19	17.38	12.17	12.17	19.83
Nb/U	3.48	8.34	15.85	11.76	8.22	7.98	4.68	5.57	5.12	6.23	12.09	8.23	7.91	5.98	8.72
Zr + Nb + Ce + Y	415	445	527	577	498	507	464	675	402	451.66	645.62	542.17	434.27	281.45	409.02
10,000 Ga/Al	2.39	2.02	2.15	2.21	1.97	2.14	2.11	2.29	2.11	1.99	2.25	2.17	2.15	1.98	2.24
Y/Nb	1.50	1.32	1.27	1.69	1.39	1.45	1.20	1.20	1.21	1.28	1.45	1.05	1.49	1.87	1.76
Yb/Ta	2.72	3.29	3.58	4.31	3.51	3.48	2.83	2.66	2.27	2.16	2.67	2.35	1.82	2.17	3.49

LOI: loss on ignition; TFe₂O₃: Total Fe calculated as Fe₂O₃; Mg# = 100 × MgO/(TFe₂O₃ + MgO) (molecular proportion); M = (Na + K + 2Ca)/(Al × Si) (cation ratio); A.R. (alkalinity ratio) = (Al₂O₃ + CaO + ALK)/(Al₂O₃ + CaO − ALK) (wt.%), ALK value is twice wt.% content of the Na₂O, when SiO₂ > 50 wt.%, 2.5 > K₂O/Na₂O > 1; A/CNK = Al₂O₃/[CaO + Na₂O + K₂O] (mol%); A/NK = Al₂O₃/[Na₂O + K₂O] (mol%); δEu = 2 × Eu_N/(Sm_N + Gd_N). N is chondrite normalized. Data with * are from Liu et al. [30].

Figure 8. Chemical classification of rocks from the Muchen rocks. (a) 10,000 Ga/Al versus $\text{Na}_2\text{O} + \text{K}_2\text{O}$ (wt.%) diagram [16]. (b) $(\text{Zr} + \text{Nb} + \text{Ce} + \text{Y})$ (ppm) versus $\text{TFe}_2\text{O}_3/\text{MgO}$ diagram [16]. (c) Y/Nb versus Yb/Ta diagram, gray fields represent A₁- and A₂-type granites of [72]. (d) Y-Ce-Nb diagram, dashed line corresponds to Y/Nb ratio of 1.2 [73]. Previous data of Muchen rocks from Liu et al. [30].

Figure 9. (a) Chondrite-normalized rare earth elements (REE, chondrite values are from Sun and McDonough. [74]) and (b) primitive-mantle-normalized multi-element patterns (Primitive values are from McDonough and Sun. [75]) for Muchen rocks. Cretaceous basaltic rocks in the coastal region of Cathaysia Block are from Chen et al. [76] and Meng et al. [77]. Previous data of Muchen rocks are from Liu et al. [30].

4.3. Sr-Nd-Pb Isotopic Composition

The whole-rock Sr-Nd-Pb isotopic data are given in Tables 2 and 3. Initial ratios of isotopes ($(^{87}\text{Sr}/^{86}\text{Sr})_i$, $(^{206}\text{Pb}/^{204}\text{Pb})_i$, $(^{207}\text{Pb}/^{204}\text{Pb})_i$, $(^{208}\text{Pb}/^{204}\text{Pb})_i$ and $\epsilon_{\text{Nd}}(t)$) were calculated using the zircon U-Pb age (111 Ma) obtained in this study.

The Muchen pluton has homogeneous $(^{87}\text{Sr}/^{86}\text{Sr})_i$ values (0.7052 to 0.7061) and $\epsilon_{\text{Nd}}(t)$ values (−2.6 to −2.0), and corresponding two-stage Hf model ages (T_{DM2}) of 1.07–1.12 Ga. On the $(^{87}\text{Sr}/^{86}\text{Sr})_i$ vs. $\epsilon_{\text{Nd}}(t)$ diagram (Figure 10), all the samples plot near the chondritic uniform reservoir (CHUR) reference field. Lead isotope compositions are homogenous with $(^{206}\text{Pb}/^{204}\text{Pb})_i = 18.11$ –18.30, $(^{207}\text{Pb}/^{204}\text{Pb})_i = 15.59$ –15.60, $(^{208}\text{Pb}/^{204}\text{Pb})_i = 38.39$ –38.53. All the samples show high radiogenic Pb isotopic ratios that plot to the right of the Geochron and above the Northern Hemisphere Reference Line (NHRL; Figure 11; [78]). In addition, they plot between the DM (Depleted Mantle) and EM (Enriched Mantle) end-members (Figure 11) [79].

Figure 10. $(^{87}\text{Sr}/^{86}\text{Sr})_i$ versus $\epsilon_{\text{Nd}}(t)$ diagram for Muchen rocks. Data source: Previous data of Muchen rocks [30]; Pingtan mafic intrusion, Daiqianshan mafic intrusion and Quanzhou mafic intrusion [79]; Darongshan granite [1]; Qinghu monzonite [80]; Cretaceous basalts and rhyolites [81–83]; Lithospheric mantle-derived mafic rocks (111–77 Ma) [76,77].

Figure 11. (a) $^{207}\text{Pb}/^{204}\text{Pb}(t)$ vs. $^{206}\text{Pb}/^{204}\text{Pb}(t)$ and (b) $^{208}\text{Pb}/^{204}\text{Pb}(t)$ vs. $^{206}\text{Pb}/^{204}\text{Pb}(t)$ of Muchen rocks. The isotopic compositions of EM I, EM II and DMM are from Zindler and Hart [79], the Geochron line and NHRL (Northern Hemisphere Reference Line) are from Hart [78].

Table 2. Pb Isotopic Data for Muchen Pluton.

Sample No.	Locality	Rock type	Th	U	Pb	$^{206}\text{Pb}/^{204}\text{Pb}$	$\pm 2\sigma$	$^{207}\text{Pb}/^{204}\text{Pb}$	$\pm 2\sigma$	$^{208}\text{Pb}/^{204}\text{Pb}$	$\pm 2\sigma$	$(^{206}\text{Pb}/^{204}\text{Pb})_i$	$(^{207}\text{Pb}/^{204}\text{Pb})_i$	$(^{208}\text{Pb}/^{204}\text{Pb})_i$
LY-6	Muchen	quartz monzonite	8.40	2.24	17.9	18.1413	0.0008	15.5992	0.0008	38.6277	0.0022	18.13	15.59	38.47
LY-7	Muchen	quartz monzonite	10.4	2.21	20.2	18.1188	0.0007	15.5963	0.0008	38.6439	0.0022	18.11	15.59	38.47
LY-8	Muchen	quartz monzonite	13.2	2.53	17.8	18.1377	0.0010	15.6001	0.0009	38.6485	0.0024	18.12	15.59	38.39
LY-11	Muchen	quartz monzonite	26.6	4.38	13.8	18.3354	0.0009	15.6181	0.0008	39.0586	0.0023	18.30	15.60	38.39
LY-14	Muchen	quartz monzonite	23.3	5.02	21.4	18.2813	0.0009	15.6124	0.0009	38.9027	0.0036	18.26	15.60	38.53

Table 3. Rb-Sr and Sm-Nd Isotopic Data for Muchen Pluton.

Sample No.	Locality	Rock type	Rb	Sr	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$(^{87}\text{Sr}/^{86}\text{Sr})_i$	Sm	Nd	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$	$\epsilon_{\text{Nd}}(t)$	T _{DM2}	Age
			ppm	ppm				ppm	ppm				Ga	Ma
LY-6	Muchen	quartz monzonite	157.0	405.0	1.08	0.707844 ± 0.000008	0.7061	11.7	63.5	0.1138	0.512458 ± 0.000009	−2.3	1.10	111
LY-7	Muchen	quartz monzonite	156.0	454.0	0.96	0.707209 ± 0.000008	0.7057	10.4	53.0	0.1212	0.512474 ± 0.000007	−2.1	1.08	111
LY-8	Muchen	quartz monzonite	186.0	344.0	1.51	0.708055 ± 0.000011	0.7057	6.75	37.5	0.1111	0.512466 ± 0.000008	−2.1	1.08	111
LY-11	Muchen	quartz monzonite	174.0	106.0	4.58	0.712463 ± 0.000013	0.7052	6.77	41.9	0.0998	0.512435 ± 0.000008	−2.6	1.12	111
LY-14	Muchen	quartz monzonite	233.0	351.0	1.85	0.708788 ± 0.000009	0.7059	5.87	28.2	0.1285	0.512488 ± 0.000010	−2.0	1.07	111
MC-1-1 *	Muchen	quartz monzonite	126.7	463.2	0.79	0.708234 ± 0.000006	0.7070	7.13	43.37	0.0993	0.512442 ± 0.000014	−2.4	1.11	112
MC-4 *	Muchen	quartz monzonite	142.5	472.6	0.87	0.707230 ± 0.000008	0.7058	7.84	40.67	0.1165	0.512416 ± 0.000011	−3.2	1.17	112
MC-2-1 *	Muchen	MME	131.6	892.8	0.43	0.706889 ± 0.000008	0.7062	8.24	42.72	0.1166	0.512446 ± 0.000003	−2.6	1.12	112
MC-2 *	Muchen	MME	93.1	480.3	0.56	0.707353 ± 0.000007	0.7065	9.97	57.59	0.1046	0.512600 ± 0.000009	0.6	0.86	112

Note: $\epsilon_{\text{Nd}}(t)$ values are calculated by granitoid ages and based on ^{147}Sm decay constant of 6.54×10^{-12} , the $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ ratios of chondrite and depleted mantle at present day are 0.512638 and 0.1967, 0.513151 and 0.2136, respectively [84]. Rb, Sr and Sm, Nd contents was analysed by ICP-MS. $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ was calculated by Rb, Sr, Sm and Nd contents with following equation: $^{87}\text{Rb}/^{86}\text{Sr} = (\text{Rb} \times 0.2783/86.909)/(\text{Sr} \times 0.0986/85.90926)$; $^{147}\text{Sm}/^{144}\text{Nd} = (\text{Sm} \times 0.1500/146.9149)/(\text{Nd} \times 0.23798/143.9101)$. The isotopic abundance of Rb, Sr, Sm and Nd are from CIAAW (Commission on Isotopic Abundances and Atomic Weights; <https://www.ciaaw.org/>). T_{DM2} ages are calculated according to the two-stage model as presented by Wu et al. [85]. Data of * are from Liu et al. [30].

5. Discussion

5.1. Magma Temperature

Zircon saturation thermometry (T_{Zr} ; [86]) can provide a simple and robust means to estimate magma temperatures. Calculated zircon saturation temperatures of the Muchen quartz monzonite after Watson and Harrison [86] are 847 to 867 °C (average 859 °C; Figure 12a). Meanwhile, Ti-in-zircon thermometer ($T_{Ti-in-Zircon}$ [87]) can also be used to estimate magma temperatures. Calculated zircon crystal temperatures of Muchen quartz monzonite after Watson et al. [87] are 612 to 708 °C (average 654 °C; Figure 12c). The Ti-in-zircon temperatures ($T_{Ti-in-Zircon}$) are lower than zircon saturation thermometry (T_{Zr}) for the Muchen quartz monzonite. This is consistent with previous studies [88] because that the Ti-in-zircon thermometer ($T_{Ti-in-Zircon}$) records the crystallization temperature of zircon, and zircon saturation thermometry (T_{Zr}) records the melt temperature in an early stage. However, the nearly over 200 °C difference in Muchen quartz monzonite is rare.

Figure 12. Histograms of zircon saturation thermometry (T_{Zr}) and Ti-in-zircon thermometry ($T_{Ti-in-Zircon}$) for Muchen quartz monzonite (LY-8). (a) Calculated by Boehnke et al. [89]; (b) Calculated by Watson and Harrison [86]; (c) Calculated by Watson et al. [87]. (d) Calculated by Ferry and Watson [90].

Therefore, we re-calculate the magma temperature using the latest zircon saturation thermometry [89] and Ti-in-zircon thermometer [90]. The new calculated zircon saturation temperatures (T_{Zr}) are 802 to 825 °C (average 816 °C; Figure 12b) for the Muchen quartz monzonite. The latest Ti-in-zircon thermometer [90] is closely related with the activities of SiO_2 (named α_{SiO_2} in this paper) and TiO_2 (named α_{TiO_2} in this paper). Generally, the α_{SiO_2} is 0.5–1.0 in crustal rocks [91]. However, the presence of quartz suggests that the Muchen quartz monzonite was silica-saturated and would have α_{SiO_2} of 1. Similarly, the presence of zircon suggests that the α_{SiO_2} value is greater than 0.5 [91]. Therefore, the new calculated Ti-in-zircon temperatures [90] for the Muchen quartz monzonite are at most 660 to 775 °C (average 710 °C; Figure 12d), and the temperature might be overestimated by about 60 to 70 °C due to the variation of α_{TiO_2} . The obvious difference between zircon saturation temperature and Ti-in-zircon temperature for Muchen quartz monzonite is with over

~100 °C. The Ti-in-zircon thermometer is mainly affected by titanium content [91]. For the Muchen quartz monzonites, the titanium contents gradually decrease with the increasing SiO₂ (Figure 13a), suggesting that the lower Ti-in-zircon temperature should be attributed to the crystal fractionation of titanium-rich minerals (such as Fe-Ti oxide), which results in the decrease of titanium content in zircons. Calculated Ti-in-zircon temperature for the Muchen quartz monzonite may record the late stage temperature of melt. Previous studies concluded that hydrous magma has low Ti-in-zircon temperatures ($T_{\text{Ti-in-Zircon}}$) [6,92]. The existence of hydrous minerals (e.g., hornblende, biotite; Figure 3) suggests a water-rich environment in magma for the Muchen pluton. Therefore, the Ti-in-zircon thermometer is not robust relative to zircon saturation thermometry in the Muchen quartz monzonite. No correlation between zirconium and SiO₂ content in the Muchen quartz monzonites (Figure 13b) also suggests that zircon saturation thermometry is more robust than Ti-in-zircon thermometer to estimate magma temperature of the Muchen quartz monzonite.

Figure 13. (a) SiO₂ vs. Ti and (b) SiO₂ vs. Zr diagrams for Muchen quartz monzonites.

In summary, we proposed that the zircon saturation temperatures (above 800 °C; Figure 12a,b) can represent the melt temperature of the Muchen quartz monzonite, suggesting a high melting temperature in magma source.

5.2. Magma Sources

The homogenous Sr-Nd-Pb-Hf isotopic features (Figures 6, 10 and 11; Tables 2 and 3 and Supplementary S2) and uniform trace element patterns (Figure 9) indicate a stable origin for the Muchen pluton. All the samples of Muchen pluton have enriched Sr-Nd and Lu-Hf isotopic compositions ($(^{87}\text{Sr}/^{86}\text{Sr})_i = 0.7052\text{--}0.7061$, $\epsilon_{\text{Nd}}(t) = -2.6$ to -2.0 , $\epsilon_{\text{Hf}}(t) = -1.7$ to $+2.6$) in this study, similar to previous study ($(^{87}\text{Sr}/^{86}\text{Sr})_i = 0.7058\text{--}0.7070$, $\epsilon_{\text{Nd}}(t) = -3.3$ to -2.4 , $\epsilon_{\text{Hf}}(t) = -1.0$ to $+1.8$; [30]). Both Nd and Hf isotopes plot above the fields of Nd and Hf isotope evolutionary area for the Proterozoic crustal basement in the Cathaysia Block and close to the CHUR reference line (Figure 15), which preclude the involvement of crustal basement of Cathaysia Block, and suggests a significant mantle-derived contribution in the primary magma.

In addition, the Nb/Ta ratio also is a sensitive index for magma source due to follow reasons: (1) Nb and Ta have the same valency (+5) and very similar ionic radii (69 pm and 68 pm for Nb and Ta, respectively; [93]) and are not significantly fractionated by most geological processes; (2) Nb/Ta ratios are generally constant during magmatic processes such as partial melting and fractional crystallization unless a significant volume of rutile and/or low-Mg-number amphibole is involved in the mantle source [12,94–99].

The Muchen quartz monzonites have much higher Nb/Ta ratios (16.7 to 30.1, average 22.8) than those of continental crust (mean Nb/Ta = 13.4, 16.5, 8.3, 12.4 for upper crust, middle crust, lower crust and average crust, respectively; [100]), and primitive mantle (Nb/Ta = 17.65; [74]). Partition coefficients for rutile/melt from both natural and experimental systems suggest that rutile is a potential phase to fractionate Nb from Ta and produce super-chondritic Nb/Ta ratios in the melt [95,97,101]. Batch melting calculations using an N-MORB (normal-type mid-oceanic ridge basalt) starting composition (Nb = 2.33, Ta = 0.132, Nb/Ta = 17.7; [74]) and melt and phase proportions based on recent melting experiments [102] suggest that an increase in Nb/Ta ratio to about 25 is possible with ~1 wt.% rutile in the residue phases [103]. Partial melting of amphibole-bearing peridotites could also produce melts with high Nb/Ta ratios [101]. Therefore, the higher Nb/Ta ratios may indicate the presence of residual rutile or amphibole in the source of the Muchen quartz monzonites. However, the correlations between Rb/Sr and Ba/Rb ratios preclude the presence of amphibole in the source of the Muchen quartz monzonites (Figure 14a). Thus, a rutile-rich source is proposed for Muchen quartz monzonites in this study. The high Nb/Ta and moderate Zr/Hf ratios in the Muchen rocks also favor a rutile-rich metasomatized mantle (Figure 14b; [97]). Moreover, the characteristics of Rb/Sr and Ba/Rb of Muchen quartz monzonites suggest a phlogopite-rich source (Figure 14a). Phlogopite is a K-rich mineral. The high potassic features of Muchen quartz monzonites ($K_2O = 3.65\sim5.96$ wt.%, average 5.45 wt.%) may be derived from phlogopite. Stolz et al. [103] proposed that the mantle source of high potassic arc volcanic rocks, which have high Nb/Ta value, was modified by silicic melts derived from the subducted slab, whereas for the low potassic arc rocks involved a slab-derived fluid. So, the high Nb/Ta ratios of high potassic Muchen quartz monzonites may suggest a slab-derived melt metasomatized mantle. Similarly, Li et al. [12] proposed that the high Nb/Ta ratios (average 21.6) of the Late Mesozoic Jintonghu intrusive in SE China is also attributed to the modification of slab-derived fluid and melt by the subduction of the paleo-Pacific Plate. In addition, the low Ba/La and high Th/Yb ratios of Muchen quartz monzonites also favor a melt metasomatized mantle (Figure 14c; [104]). Ayers [105] suggested that fluids dehydrated from a subducted slab have very low Nb/U ratios (~0.22) that reflect the transfer of significant amounts of large ion lithophile elements (LILEs), but not high field-strength elements (HFSEs), into the slab-derived fluids. Muchen quartz monzonites have variable Nb/U ratios (3.48–15.85, average 7.89), with half Nb/U ratios below 8.00, especially for LY-2 (Nb/U = 3.48). Therefore, the source of Muchen quartz monzonites also included the slab-derived fluids.

Figure 14. (a) Rb/Sr vs. Ba/Rb; (b) Zr/Hf vs. Nb/Ta diagram (Guo et al., 2004); (c) Th/Yb vs. Ba/La diagram [104]; (d) SiO_2 vs. $(^{87}\text{Sr}/^{86}\text{Sr})_i$; (e) SiO_2 vs. $\epsilon_{\text{Nd}}(t)$; (f) SiO_2 vs. Sr. Data source: Primitive Mantle (PM) and mid-oceanic ridge basalt (MORB) [74]; Ocean Island Basalt (OIB) [101,108]; Depleted Mantle (DM) [109]. Previous data of Muchen [30].

Figure 15. Nd and Hf isotope diagram of Muchen pluton. (a) The Nd isotope evolution for Cathaysia crustal basement are from Chen and Jahn [37]. (b) Hf isotope evolution for Cathaysia crustal basement are from Xu et al. [106] and He et al. [107]).

In summary, we propose that partial melting of enriched mantle metasomatized by slab-derived melt (mainly) and fluids produced the primary magma of Muchen pluton.

5.3. Crustal Contamination and Fractional Crystallization

Muchen quartz monzonites have constant Sr and Nd isotopic ratios ($(^{87}\text{Sr}/^{86}\text{Sr})_i$ and $\epsilon_{\text{Nd}}(t)$ (0.7052 to 0.7061 and -2.6 to -2.0 , respectively) with the increasing of SiO_2 (59~69 wt.%) (Figure 14d,e), which is inconsistent with crustal contamination. Here, we suggest that crustal contamination play a negligible role in the formation of the Muchen host quartz monzonites.

The systematic variation trends of major elements (Figure 16) and the subparallel REE patterns (Figure 9) indicate an important role of fractionation crystallization (FC) during magma evolution. The rapid decrease in TFe_2O_3 and increase in SiO_2 with the decreasing MgO suggest that olivine is a major fractionated phase in the source for the Muchen quartz monzonites (Figure 16d,e). Pyroxene is also a significant fractionated phase causing positive correlations between CaO and MgO (Figure 16f). Crystal fractionation of plagioclase is also significant, as indicated by the negative correlations between SiO_2 and Al_2O_3 and Sr (Figures 14f and 16a). Crystal fractionation of plagioclase would cause significant negative anomalies of Eu in granitoids and/or zircons. Thus, the obvious negative Eu anomalies in both the quartz monzonites ($\delta\text{Eu} = 0.22$ to 0.75 , average 0.48) and zircons ($\delta\text{Eu} = 0.01$ – 0.22 , average 0.08) suggest significant fractionation of plagioclase. Fractionation of accessory minerals such as

apatite and Fe-Ti oxides likely accounts for the negative correlations between SiO_2 and P_2O_5 and TiO_2 (Figure 16b,c). Therefore, fractionation of a mineral assemblage of olivine + pyroxene + plagioclase can roughly explain the chemical variation trends in the alkaline Muchen quartz monzonites.

Figure 16. Bivariate plots of the Muchen alkaline rocks. Previous data of Muchen rocks are from [30]. The black arrow in figure (a–f) represents the fractional crystallization trend of Muchen magma.

5.4. Petrogenesis

In addition to host alkaline quartz monzonites, mafic microgranular enclaves (MMEs) also found in Muchen pluton (Figure 3). Liu et al., [30] proposed that Muchen quartz monzonites are derived from a hybrid magma produced by mixing between crustal materials and depleted mantle. In this study, we give a counter-argument that Muchen quartz monzonites are not formed by mixing between crustal-derived felsic magma and depleted mantle-derived mafic magma. We propose that MMEs are fragments of recrystallized or melt residues from the magma source, or early formed crystals from the host magma for follow reasons: (1) the geochemical features between the MMEs and host quartz

monzonites are almost the same, e.g., same spider, REE and Sr-Nd-Hf isotopes (Figure 9; Table 1); (2) the high K contents, high temperatures (above 800 °C; Figure 12), and distinct but high Nb/Ta ratios of the Muchen alkaline rocks are not simply explained by magma mixing between depleted mantle with continental crust melts.

Besides, Muchen alkaline quartz monzonites have similar Sr-Nd isotope signatures (~111 Ma, $(^{87}\text{Sr}/^{86}\text{Sr})_i = 0.7052\text{--}0.7061$, $\varepsilon_{\text{Nd}}(t) = -2.6$ to -2.0) with coeval mafic rocks from Pingtan (~116 Ma, $(^{87}\text{Sr}/^{86}\text{Sr})_i = 0.7054\text{--}0.7056$, $\varepsilon_{\text{Nd}}(t) = -0.4$ to -1.6), Quanzhou (~113 Ma, $(^{87}\text{Sr}/^{86}\text{Sr})_i = 0.7054\text{--}0.7060$, $\varepsilon_{\text{Nd}}(t) = -2.9$ to -2.4) and Daiqianshan (~113 Ma, $(^{87}\text{Sr}/^{86}\text{Sr})_i = 0.7059\text{--}0.7061$, $\varepsilon_{\text{Nd}}(t) = -3.1$ to -2.4) in SE China [6,104,110]. These mafic rocks are formed via 5%–20% melting of a depleted mantle source metasomatized by the addition of 3%–5% subducted sediment-derived melt [104]. Therefore, partial melting of metasomatized mantle may be the real origin of Muchen alkaline rocks, with significant fractional crystallization of olivine + orthopyroxene + plagioclase. In addition, the high $\varepsilon_{\text{Nd}}(t)$ value of MME (+0.6) suggests that a small proportion of mantle, which was not metasomatized by slab melts, may add to the primitive magma of Muchen pluton.

Normally, melts from the basaltic lower continental crust are characterized by low Mg# values (<40) regardless of the degree of melting, whereas those with higher Mg# values (>40) can only be generated by the involvement with a mantle component [111]. However, the Muchen quartz monzonite has low Mg# values (18 to 34, average 26; Table 1). Here, we proposed that the low Mg# character of the Muchen quartz monzonite is a real case for the pressure effect of Mg# for the following two reasons:

(1) Experimental petrology suggests that the pressure of melting is as important as source composition in generating an A-type melt [22]. The Mg# values of A-type granitic magma was affected by pressures (Mg# = 35~42 for 8 kbar and Mg# = 19~21 for 4 kbar) [22].

(2) MELTs simulation: MELTs is a perfect tool to simulate the process of magmatic evolution in different pressure conditions (<http://melts.ofm-research.org/>) [112]. The Cretaceous mafic rocks in SE China [40] were chosen to simulate the crystal fractionation process in different pressures setting (8~3 kbar) using MELTs. These mafic rocks have similar Sr-Nd isotopes ($(^{87}\text{Sr}/^{86}\text{Sr})_i = 0.7053\text{--}0.7070$, $\varepsilon_{\text{Nd}}(t) = -3.8$ to -1.2) to the Muchen alkaline quartz monzonite. The results confirm that mantle-derived magma could produce intermediate-acid magma with low Mg# values (<30) in relative low pressure (≤ 7 kbar) through crystallization of olivine, pyroxene, spinel and/or plagioclase (Figure 17; Supplementary S4). However, the magma could only evolve to low-silicic magma ($\text{SiO}_2 < 60$ wt.%) with relatively high Mg# values (Mg# >42) under 8 kbar pressure conditions (Figure 17; Supplementary S2). Therefore, the low Mg# features of Muchen quartz monzonites (<30 mostly) may be attributed to a low-pressure setting with the pressures below 7 kbar. Previous study also suggests that the rock-forming pressure of the Muchen pluton is low (~0.2 GPa) [30].

In summary, the geochemical characteristics of the Muchen monzonites suggest that they were derived from partial melting of enriched metasomatized mantle in a low-pressure setting (see in detail in Section 5.5).

Figure 17. SiO_2 vs. $\text{Mg\#}$ diagram for Muchen quartz monzonites and simulative magma. (a–f) represent the simulate results in different temperature (T) and pressure (P) condition. (a): T = 3 kbar, and T = 1500 °C, 1400 °C, 1300 °C, 1200 °C, 1100 °C, 1000 °C, 950 °C, 900 °C, 850 °C, 800 °C, 750 °C; (b): T = 4 kbar, and T = 1500 °C, 1400 °C, 1300 °C, 1200 °C, 1100 °C, 1000 °C, 950 °C, 900 °C, 850 °C; (c): T = 5 kbar, and T = 1500 °C, 1400 °C, 1300 °C, 1200 °C, 1100 °C, 1000 °C, 950 °C, 900 °C, 850 °C; (d): T = 6 kbar, and T = 1500 °C, 1400 °C, 1300 °C, 1200 °C, 1100 °C, 1000 °C, 950 °C, 900 °C; (e): T = 7 kbar, and T = 1500 °C, 1400 °C, 1300 °C, 1200 °C, 1100 °C, 1000 °C, 950 °C, 900 °C, 850 °C; (f): T = 8 kbar, and T = 1500 °C, 1400 °C, 1300 °C, 1200 °C, 1100 °C, 1000 °C. Mafic end member from Wang et al. [40].

5.5. Geodynamic Implications

Previous studies suggest that the formation ages of Mesozoic A-type granitoids or alkaline intrusions in South China become younger from west to east and are generally older than ~120 Ma in the west of the Zhenghe-Dapu fault (Figure 1) [8,113]. The Muchen pluton is metaluminous to weakly peraluminous A-type granitoids. However, the Muchen pluton has younger zircon U-Pb age (~111 Ma; Figure 5) than those A-type granitoids distributed in the west of the Zhenghe–Dapu fault, but older age than those these A-type granitoids distributed in coastal area (~100–90 Ma) [8,14,114,115], thus providing an opportunity to refine the model for the origin of A-type granitoids and further constrain the Cretaceous tectonic evolution of South China.

During the Late Yanshanian, large-scale and regional lithospheric extension has been identified due to the widespread A-type granites or alkaline rocks [8], intraplate basalts [3], bimodal volcanic rocks [116], and metamorphic core complexes [117] in Southeast China. A-type magmas are typically produced in an extensional tectonic setting (e.g., back-arc extension, continental arc, post-collisional extension, and within-plate settings; [72]). The Early Cretaceous A-type granitoids for the Muchen pluton distributed near the boundary between A₁-type magma and A₂-type magma (Figure 8d). Similarly, these rocks also plotting in both volcanic arc granite (VAG) and within-plate granite (WPG) field (Figure 18). Liu et al. [118] propose that SE China underwent an asynchronizing paleo-Pacific slab rollback process during the early-stage of early Cretaceous (145–110 Ma), then a back-arc tectonic setting occurred due to the subduction angle of paleo-Pacific plate become steeper. Other authors also suggest that the tectonic setting of SE China changed from a compressional subduction regime to an extensional regime during the Cretaceous time due to a progressive increase in the subduction angle of the paleo-Pacific plate, which corresponding transition time at approximately 110 Ma [14,119]. The Muchen pluton emplaced at 111 Ma, and all the samples are enriched in LILEs and LREE, but depleted in HFSEs, which suggesting a subduction-related environment [18,30,120–122]. Thus, a series of evidence show that the Muchen pluton most likely generated in a back-arc extensional setting due to the subduction angle of the paleo-Pacific slab become steeper during the Early Cretaceous. Meanwhile, the low Mg# values of Muchen rocks indicate a low-pressure feature, which is consistent with the extensional setting. Therefore, the extensional regime of SE China may be existence before 110 Ma, which gives a proper environment to produce the Muchen alkaline rocks.

Figure 18. Tectonic discrimination diagrams for the Muchen alkaline rocks [123]. The field for post-collision granite (post-COLG) from Pearce [120]. Abbreviations: syn-COLG: syn-collision granite; post COLG: post-collision granite; WPG: within-plate granite; ORG: ocean ridge granite; VAG: volcanic arc granite.

In summary, we propose a simplified genetic model for the Muchen quartz monzonite: (1) the normal subduction of the paleo-Pacific plate contributed subduction-related melts/fluids and trace elements such as Nb, Ta, U, K to the sub-continental lithospheric mantle; (2) the increasing subduction angle of the paleo-Pacific plate caused lithosphere extension and asthenospheric mantle upwelling; (3) and triggered partial melting of the enriched mantle induced by metasomatism of slab derived fluids and melts. (4) Subsequently, the primary basaltic magma experienced strongly fractional crystallization of olivine + pyroxene + spinel + plagioclase as it ascended, which produced the Muchen alkaline quartz monzonite.

6. Conclusions

(1) The Muchen rocks are mainly K-rich alkaline A-type quartz monzonites, generated in the Early Cretaceous (~111 Ma).

(2) The Muchen quartz monzonites have homogeneous isotopic compositions, with $(^{87}\text{Sr}/^{86}\text{Sr})_i = 0.7052$ to 0.7070 , $\varepsilon_{\text{Nd}}(t) = -3.2$ to -2.0 , $\varepsilon_{\text{Hf}}(t) = -1.7$ to $+2.6$. The primitive magma of the Muchen quartz monzonites was derived partial melting of slab derived melts (mainly) and fluids metasomatized mantle. This magma experienced strongly fractional crystallization of olivine + pyroxene + spinel + plagioclase as it ascended, which produced the Muchen alkaline quartz monzonite.

(3) The MMEs also have homogeneous isotopic compositions, with $(^{87}\text{Sr}/^{86}\text{Sr})_i = 0.7062$ to 0.7065 and $\varepsilon_{\text{Nd}}(t) = -2.6$ to $+0.6$. They are fragments of recrystallized or melt residues from the Muchen magma source, or early formed crystals.

(4) Low Mg# values of the Muchen alkaline rock were formed in a back-arc extension setting, due to deep angle subduction of the paleo-Pacific plate during the Early Cretaceous.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2075-163X/10/1/80/s1>: Supplementary S1: Zircon LA-ICP-MS U-Pb dating results of representative samples from Muchen pluton. Supplementary S2: Zircon in situ LA-MC-ICPMS Hf isotopic compositions of representative samples from Muchen pluton. Supplementary S3: Zircon LA-ICP-MS rare earth elements results of representative samples from Muchen pluton. Supplementary S4: Results of MELTs simulation.

Author Contributions: Conceptualization and Writing-Original Draft Preparation by H.Y. and F.W.; Hafnium isotopes analysis by H.-O.G. and H.S.; Data process by C.G.; All authors have read and agreed to the published version of the manuscript.

Funding: This worked was funded by National Key R&D Program of China (Grant number 2016YFC0600404 and 2016YFC0600206), Natural Science Foundation of China (Grant number 41873034), and the Fundamental Research Funds for the Central Universities (Grant number PA2018GDQT0020).

Acknowledgments: We thank Nengping Shen for whole rock major, trace and Sr-Nd-Pb isotope analysis. Thanks to Qiuyuan Yuan for zircon CL photograph. Especially thanks to Peter Hollings and Noel White for polishing the English for the English version.

Conflicts of Interest: The authors declare no conflict of interest.

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