

# Yangshan A-Type Granites in the Lower Yangtze River Belt Formed by Ridge Subduction: Radiogenic Ca and Nd Isotopic Constraints

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**ABSTRACT:** The Early Cretaceous aluminous A-type granites in the Lower Yangtze River belt (LYRB) can provide important insights into the Mesozoic magmatism in eastern China, but their origin remains highly controversial. In this study, radiogenic Ca-Nd isotopic analysis was performed for syenite porphyry and alkali-feldspar granite porphyry of the Yangshan pluton, a typical aluminous A-type granitic intrusion in the LYRB, to constrain its source and geodynamic setting. The results show that  $\varepsilon_{Ca}(126\text{ Ma})$ ,  $\varepsilon_{Nd}(126\text{ Ma})$  and  $K/Ca_{\text{source}}$  of the syenite porphyry range from -0.24 to +0.96, -7.2 to -6.0, and 0.31 to 1.26, respectively. The corresponding values for the alkali-feldspar granite porphyry range from 0.26 to 0.84, -8.0 to -6.1, and 0.79 to 1.08, respectively. Binary mixing modeling indicates that they were originated from the same sources with different proportion, namely, a mixing of 50% to 75% Neoproterozoic crust and 50% to 25% asthenospheric mantle. Together with previous works, we propose that the Early Cretaceous subduction of the ridge between the Pacific and Izanagi plates was responsible for the formation of the aluminous A-type granites in the LYRB.

**KEY WORDS:** Lower Yangtze River belt (LYRB), aluminous A-type granite, Yangshan pluton, radiogenic Ca-Nd isotopes, ridge subduction, geochemistry.

## 0 INTRODUCTION

The Early Cretaceous aluminous A-type granites distributed along the Lower Yangtze River belt (LYRB) are critical for elucidating the geodynamic mechanism in eastern China. However, their genesis remains controversial. Several petrogenesis models have been proposed, including (1) crustal anatexis with or without mixing of juvenile materials (Zhang et al., 2018; Gu et al., 2017; Xu et al., 2010); (2) mixing between asthenospheric

and enriched lithospheric mantle, and subsequent crystal fractionation (Yang et al., 2017); (3) upwelling of the asthenospheric mantle for A<sub>1</sub>-type granites, and partial melting of metasomatized lithospheric mantle for the A<sub>2</sub>-type (Li et al., 2014, 2012, 2011); (4) metasomatized mantle for A<sub>1</sub>-type granites, and reworking of Mesoproterozoic crust for A<sub>2</sub>-type granites (Yan et al., 2015); (5) partial melting of residual lower continental crust (Jiang et al., 2018a; Wang et al., 2018); and (6) generation from enriched lithospheric mantle with crustal contamination (Cao et al., 2008; Du et al., 2007). One reason for the controversy on the aluminous A-type granites may be the difficulty in distinguishing the contribution of different mantle components to granitic formation based on conventional radiogenic isotopes (e.g., Sr, Nd, Pb and Hf). As an example, only radiogenic Nd isotopic data often make it difficult to discern lithospheric

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ic mantle from juvenile crust (Mills et al., 2018), and the inconsistent  $\lambda^{176}\text{Lu}$  values result in contradictory interpretation of the same Hf isotopic data (Kreissig and Elliott, 2005; Bizzarro et al., 2003; Scherer et al., 2001). To overcome this deficiency, a novel tool, radiogenic  $^{40}\text{Ca}$  isotope, was explored in this study to provide new constraints on the petrogenesis of A-type granitic magmas.

Calcium (Ca), a major constituent element of the Earth, plays a critical role in geological processes (e.g., Lu et al., 2020; Zhu et al., 2020; Chen et al., 2018; Kang et al., 2017; Liu et al., 2017a). It has six stable isotopes, with mass number of 40, 42, 43, 44, 46, and 48, and typical natural abundances of 96.98%, 0.642%, 0.133%, 2.056%, 0.003%, and 0.182%, respectively (DePaolo, 2004). The most abundant isotope,  $^{40}\text{Ca}$ , has both non-radiogenic and radiogenic Ca isotopic variations in terrestrial materials. The latter is the daughter product of radioactive  $^{40}\text{K}$ . Approximately 89.5% of  $^{40}\text{K}$  produces  $^{40}\text{Ca}$  by  $\beta$  emission with a half-life of 1.25 Ga (DePaolo, 2004; Steiger and Jager, 1977). The short half-life of  $^{40}\text{K}$ , relative to the age of the Earth, means that radiogenic  $^{40}\text{Ca}$  is more sensitive to the contribution of pre-existing continental crust than other long-lived decay system such as Rb-Sr methods (the half-life of  $^{87}\text{Rb}$  is ~49 Ga) (Mills et al., 2018; Kreissig and Elliott, 2005). Moreover, potassium (K) and Ca are strongly differentiated during the formation of continental crust (Caro et al., 2010), which would result in granite with K/Ca ratios two to four orders of magnitude higher than those of the mantle. The mantle typically has a K/Ca ratio of 0.01 (Salters and Stracke, 2004), with a  $^{40}\text{K}/^{44}\text{Ca}$  ratio of 0.000 06, and an overall variation in  $^{40}\text{Ca}/^{44}\text{Ca}$  ratios through geological time of 0.000 6. Simon et al. (2009) showed that the  $\epsilon_{\text{Ca}}$  value of bulk silicate earth relative to NIST SRM 915a range from  $-0.68 \pm 2.28$  to  $-0.93 \pm 0.61$ , suggesting that the NIST SRM 915a may possess radiogenic  $^{40}\text{Ca}$  excesses. The similar conclusion was obtained by He et al. (2017). However, Caro et al. (2010) concluded that no resolvable difference in radiogenic Ca isotopic between the mantle and this standard were observed by measuring eight mafic rocks. Combining these data with the new (ultra)mafic rocks, Mills et al. (2018) found that the mantle is  $0.7\epsilon$  lower than SRM 915a.

Previous studies have also clearly demonstrated that radiogenic  $^{40}\text{Ca}$  is a robust tracer in igneous petrogenesis (Mills et al., 2018; Marshall and DePaolo, 1989, 1982), early crust-mantle evolution (Kreissig and Elliott, 2005), the oceanic Ca cycle (Antonelli et al., 2021; Caro et al., 2010) and post-formation K depletion of the lower continental crust (Antonelli et al., 2019).

In this contribution, we report new radiogenic Ca-Nd isotopes for the aluminous A-type granites in the LYRB, coupled with compilation of the geochemical data in literature, in order to (1) constrain the radiogenic Ca isotopic composition of the aluminous A-type granites in the LYRB and their petrogenesis, and (2) elucidate the Early Cretaceous geodynamic evolution in the LYRB in eastern China.

## 1 GEOLOGICAL SETTING AND SAMPLES

The Yangtze Block lies between the Dabie-Sulu orogenic belt to the north and the Cathaysia Block to the south (Fig. 1). It comprises the Archean crystalline basement (the Kongling Group) composed of tonalitic, trondhjemitic and granitic (TTG) gneisses, metasedimentary and amphibolite rocks (Ren

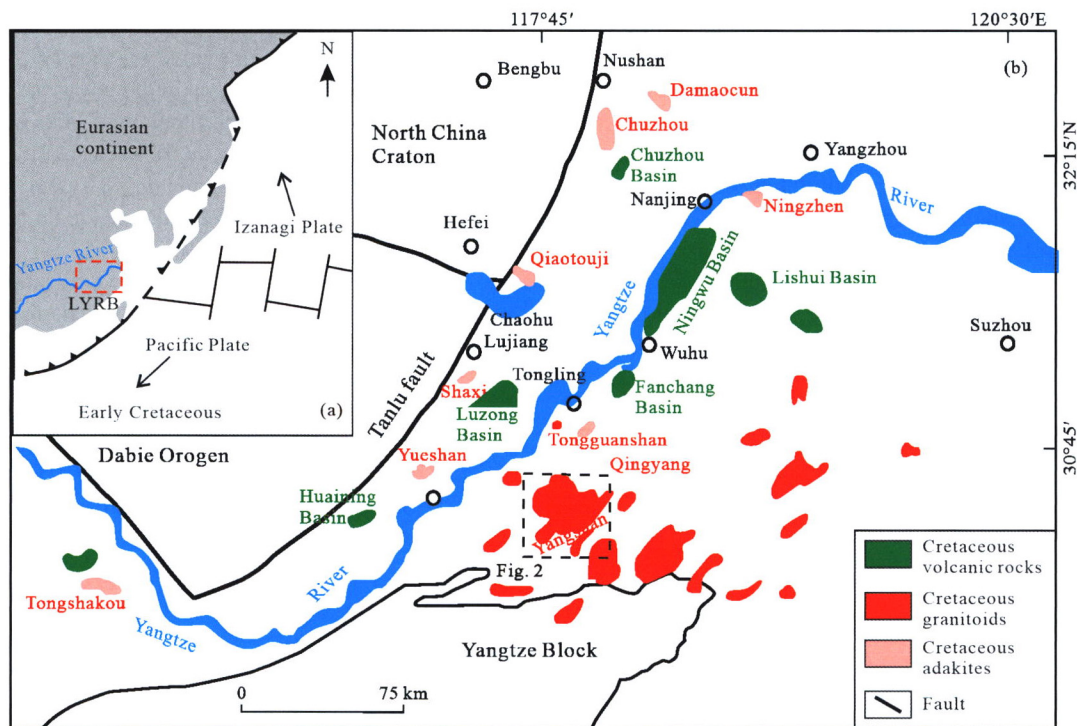
et al., 2020; Qiu et al., 2000; Gao et al., 1999). The basement is unconformably overlain by the Paleoproterozoic metasedimentary rocks, Cambrian to Silurian chert nodules, limestones and clastic rocks, and Devonian to Triassic sandstone, shale and argillaceous clastic rocks (Fan et al., 2016; Yan et al., 2015). The LYRB refers to the northern segment of the Yangtze Block (Fig. 1), which extends from Hubei Province in the west to the Jiangsu Province in the east (Ling et al., 2009). It primarily consists of the Late Precambrian metasedimentary and metavolcanic rocks, as well as Early Paleozoic clastic rocks, and Neoproterozoic and Mesozoic igneous rocks (Qian et al., 2019; Jiang et al., 2018b; Wu et al., 2012). In particular, Late Mesozoic igneous rocks are extensively exposed and are closely associated with polymetallic deposits (e.g., Liu G X et al., 2021; Liu S S et al., 2020), thus attracting widespread attention from geologists (Sun et al., 2010; Ling et al., 2009; Mao et al., 2006; Chen et al., 2001; Chang et al., 1991). The Mesozoic rocks were previously divided into two stages: (1) the 150 to 136 Ma rocks mainly comprise I-type granite, including granodiorite and monzogranite rocks; (2) the 136 to 120 Ma rocks consist of A-type granite and syenite as well as their volcanic counterparts (Wu et al., 2012). However, recent U-Pb, Rb-Sr and Ar-Ar ages indicate three stages: granodiorite from 152 to 136 Ma, monzogranite from 136 to 130 Ma, and K-feldspar granite from 130 to 120 Ma (Zhang et al., 2018).

The Yangshan pluton ( $30^{\circ}17'N$  to  $30^{\circ}18'30''N$ ,  $117^{\circ}42'28''E$  to  $117^{\circ}46'28''E$ ) located in the northeast of Shitai County, Anhui Province, is a part of the Jiuhuashan Complex (Fig. 2). It is tectonically part of the Shitai dome fold, which is situated in the northern margin of the Lower Yangtze Block (Gu et al., 2017). The unit also comprises Late Neoproterozoic low-grade metasedimentary and metavolcanic rocks, and Paleozoic marine clastic sediments and carbonates (Jiang et al., 2018b; Wang, 2009). Rock types of the Yangshan pluton mainly include alkali-feldspar granite porphyry and syenite porphyry, both of which belong to aluminous A-type granites. The alkali-feldspar granite porphyry comprises phenocrysts and groundmass. The phenocrysts are comprised of quartz, K-feldspar, biotite and hornblende as well as accessory zircon and apatite, making up 40 vol.% to 50 vol.% of whole rocks. The groundmass is comprised of feldspar and quartz (Gu, 2017). The syenite porphyry is composed of 10 vol.% to 20 vol.% phenocrysts including quartz, K-feldspar, plagioclase and biotite, as well as accessory zircon and apatite (Gu, 2017).

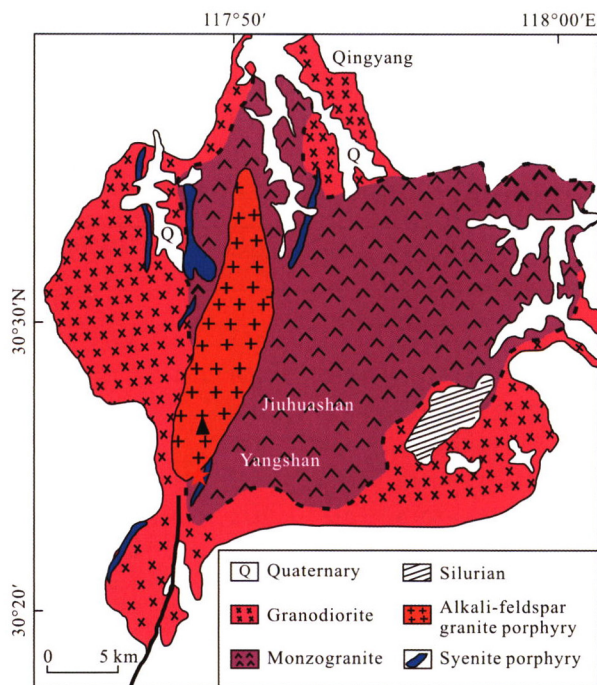
## 2 ANALYTICAL METHODS

Radiogenic Ca-Nd isotopic analysis was conducted in a class 100 hood at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (SKLaBIG-GIGCAS) and described in the following two subsections.

The separation of Ca follows the procedures described by Zhu et al. (2016) and Liu et al. (2017b) with minor modifications (Table S1). Whole rock powder samples were dissolved in a mixture of concentrated HF and HNO<sub>3</sub> (3 : 1) for 5 days at 120 °C. Once in solution, the samples were evaporated to dryness at 100 °C and redissolved in 2 mL of 6 M HCl to remove insoluble fluoride compounds. The samples were finally dis-



**Figure 1.** Geological map of the Lower Yangtze River belt. (a) Sketch map showing the ridge subduction between the Izanagi and Pacific plates; (b) geological sketch map showing the Early Cretaceous igneous rocks in the LYRB (modified after Jiang et al., 2018b; Su et al., 2013; Ling et al., 2009; Sun et al., 2007).



**Figure 2.** Geological map of the Yangshan intrusion, displaying the rock types and sample localities (modified after Jiang et al., 2018b; Gu et al., 2017; Xu et al., 2010).

solved in 0.05 mL of 1.6 M HCl to obtain a clear solution for column separation. The completely digested samples without addition of the double spike were loaded on the Teflon column containing 1 mL AG MP 50 (100 to 200 meshes) resin to purify Ca. Given that the samples analyzed here have the high K/Ca ratios (4 to 19), it is necessary to add two chemical separations as high-K samples could lead to drifting of the Ca elution peaks.

In the first chemical separation, we collected solutions from 17 to 45 mL to ensure the 100% recovery of Ca. It is likely that the residual K was presented in the Ca cuts. According, 18 to 44 mL solutions in the second purification of Ca following the methods of Zhu et al. (2016) and Liu et al. (2017b) were applied to further remove residual K. Using the modified purification procedure, a perfect separation of K and Ca with nearly 100% Ca recovery for these samples was achieved well (Table S1).

Radiogenic Ca isotopic ratio was determined by thermal ionization mass spectrometry (TIMS). Purified Ca (~3 µg) was loaded on a single Ta filament with 5% phosphoric acid as an activator. A single-sequence Faraday cup of L2, C, H1, H2 and H3 was used to collect <sup>40</sup>Ca, <sup>41</sup>K, <sup>42</sup>Ca, <sup>43</sup>Ca and <sup>44</sup>Ca, simultaneously. The <sup>42</sup>Ca/<sup>44</sup>Ca ratio of 0.312 21 was employed to calibrate the instrumental mass discrimination (Russell et al., 1987). The <sup>41</sup>K signal was monitored to correct isobaric interference of <sup>40</sup>K on <sup>40</sup>Ca using <sup>40</sup>K/<sup>41</sup>K = 0.001 738. Two or three unspiked NIST SRM 915a were carried out per analysis batch, each bath consisting of 21 samples, to assess the stability of the instrument. Triplicate analyses were performed for each sample, and means ±2SD was reported (Table 1). The NIST SRM 915a without the double spike yields a <sup>40</sup>Ca/<sup>44</sup>Ca ratio of 47.166 7 ± 0.004 9 (2σ, N = 7). The radiogenic Ca isotopic ratio is reported as the ε<sup>40/44</sup>Ca value relative to the unspiked NIST SRM 915a.

$$\epsilon_{Ca} = \left[ \frac{({}^{40}\text{Ca}/{}^{44}\text{Ca})_{\text{sample}}}{({}^{40}\text{Ca}/{}^{44}\text{Ca})_{\text{SRM 915a}}} - 1 \right] \times 10\,000 \quad (1)$$

Another method on assessing instrument stability is to measure the NIST SRM 915a and IAPSO seawater with the ad-

dition of a  $^{42}\text{Ca}$ - $^{43}\text{Ca}$  double spike. Their results are both consistent with our laboratory long-term standard values within the analytical uncertainty. One duplicated sample (13CZYS-07) exhibited satisfactory reproducibility within uncertainty (Table 1). The procedural blank was 23.6 ng, which is insignificant compared to the  $\sim 50$   $\mu\text{g}$  Ca column loadings. Additional details of Ca isotopic analysis are documented by Bai et al. (2020), Zhu et al. (2016) and Liu Y F et al. (2015).

Chemical separation of Nd follows the procedures reported by Ma et al. (2013). Approximately 200 ppb Nd solutions were measured on multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS, Nu Plasma 1700).  $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$  was applied to correct instrumental mass fractionation, and the JNdi-1 standard was used to monitor instrument stability. Three replicate measurements of this standard were performed during sample analysis and an average  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios of  $0.512124 \pm 0.000025$  ( $2\sigma$ ,  $N = 3$ ) was obtained (Table 1), consistent with the certified value within error. In addition, two standards, GSP-2 and JG-2, were used for quality-control purposes during sample purification, yielding  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios of  $0.511340 \pm 0.000004$  ( $2\sigma$ ) and  $0.512227 \pm 0.000003$  ( $2\sigma$ ), respectively (Table 1), which agree well with published values (Weis et al., 2006). Whole-procedure blanks for Nd were  $< 1$  ng.

### 3 RESULTS

Whole-rock major and trace elements have been reported in Gu et al. (2017), thus we only summarize it briefly. The alkali-feldspar granite porphyry has  $\text{SiO}_2$  from 76.3 wt.% to 77.4 wt.%,  $\text{K}_2\text{O}$  from 4.22 wt.% to 4.80 wt.%,  $\text{Al}_2\text{O}_3$  from 11.95 wt.% to 12.26 wt.%, CaO from 0.17 wt.% to 0.97 wt.%, total

REE concentrations from 118.5 ppm to 135.7 ppm,  $(\text{La}/\text{Yb})_N$  ratios from 4.9 to 5.9 and negative Eu-anomaly from 0.07 to 0.10 (Gu et al., 2017). The syenite porphyry has  $\text{SiO}_2$ , CaO,  $\text{Al}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ , and total REE concentrations of 74.91 wt.% to 75.58 wt.%, 0.30 wt.% to 0.58 wt.%, 12.32 wt.% to 12.53 wt.%, 4.99 wt.% to 5.85 wt.%, and 230.6 ppm to 251.7 ppm, respectively, with  $(\text{La}/\text{Yb})_N$  ratio of 7.5 to 8.2 and negative Eu-anomaly ( $\text{Eu}/\text{Eu}^* = 0.14$  to 0.17) (Gu et al., 2017).

Nd isotopic data for the Early Cretaceous Yangshan aluminous A-type granites from the LYRB are reported in Table 1. Whole rock  $\epsilon_{\text{Nd}}(126 \text{ Ma})$  values of syenite porphyry range from -7.2 to -6.0 and those of alkali-feldspar granite porphyry are from -8.0 to -6.1, respectively, agreeing well with the literature values (Jiang et al., 2018b; Wang et al., 2018; Zhang et al., 2018; Gu et al., 2017; Wu et al., 2012; Xu et al., 2010). The  $\epsilon_{\text{Ca}}(126 \text{ Ma})$  values for syenite porphyry and alkali-feldspar granite porphyry were first reported in this study ranging from -0.24 to +0.96 and 0.26 to 0.84, respectively (Table 1).

## 4 DISCUSSION

### 4.1 Magma Source of Aluminous A-Type Granites in the LYRB

The radiogenic Ca isotope geochemistry is still in its infancy. To better understanding the evolutionary process of radiogenic Ca isotope, we employed an evolution model of radiogenic Ca isotope in Yangtze Craton (Fig. 3). In this model, the evolutionary pathways of radiogenic Ca isotopic compositions are derived from different reservoirs with geological time. The three reservoirs with  $\text{K}/\text{Ca} = 0.01$  in the mantle (Salters and Stracke, 2004),  $\text{K}/\text{Ca} = 0.05$  in the basaltic lower crust (Rudnick and Gao, 2003),

**Table 1** Radiogenic Ca-Nd isotopic compositions of the Yangshan aluminous A-type granites in the Lower Yangtze River belt

Samples	Age (Ma) <sup>a</sup>	Sm/Nd <sup>a</sup>	$^{143}\text{Nd}/^{144}\text{Nd}$	$\epsilon_{\text{Nd}}(t)$	$T_{2\text{DM}}$ (Ma)	K/Ca <sup>a</sup>	$^{40}\text{Ca}/^{44}\text{Ca}^b$	$\epsilon_{40/44\text{Ca}}^c$	$\epsilon_{40/44\text{Ca}}(t)^d$	N	2SD	K/Ca <sub>source</sub>
Syenite porphyry												
13CZYS-07	127	0.20	$0.512262 \pm 0.000003$	-6.1	1418	12.2	$47.1724 \pm 0.0044$	1.21	0.24	3	0.93	0.78
13CZYS-07-R <sup>e</sup>			$0.512265 \pm 0.000003$	-6.0	1413		47.1712	0.95	-0.01	1		
13YS-g1	127.6	0.20	$0.512222 \pm 0.000003$	-6.9	1487	4.4	$47.1672 \pm 0.0036$	0.11	-0.24	3	0.76	0.35
13YS-g2	127.6	0.21	$0.512219 \pm 0.000005$	-7.0	1492	5.3	$47.1732 \pm 0.0041$	1.38	0.96	3	0.86	1.26
13YS-g3	127.6	0.21	$0.512210 \pm 0.000004$	-7.2	1507	5.6	$47.1676 \pm 0.0047$	0.19	-0.25	3	1.00	0.33
13YS-g4	127.6	0.20	$0.512246 \pm 0.000003$	-6.4	1445	6.0	$47.1698 \pm 0.0043$	0.66	0.18	4	0.91	0.71
13YS-g5	127.6	0.19	$0.512243 \pm 0.000004$	-6.4	1440	9.8	$47.1689 \pm 0.0038$	0.47	-0.31	3	0.81	0.31
13YS-g6	127.6	0.21	$0.512243 \pm 0.000004$	-6.6	1459	7.1	$47.1720 \pm 0.0049$	1.12	0.56	3	1.04	0.99
Alkali-feldspar granite porphyry												
13CZYS-12	126	0.14	$0.512132 \pm 0.000001$	-8.0	1575	18.8	$47.1776 \pm 0.0037$	2.31	0.84	3	0.78	1.08
13CZYS-13	126	0.13	$0.512231 \pm 0.000005$	-6.1	1416	15.9	$47.1738 \pm 0.0048$	1.51	0.26	3	1.03	0.79
Neoproterozoic granitic gneiss												
14FC11	803					3.1	$47.1787 \pm 0.0051$	2.54		3	1.08	
References												
JNdi-1			$0.512124 \pm 0.000025$									
NIST SRM 915a							$47.1667 \pm 0.0049$			8	1.03	
GSP-2			$0.511340 \pm 0.000004$									
JG-2			$0.512227 \pm 0.000003$									

<sup>a</sup>. After Gu (2017) and Liu L et al. (2015); <sup>b</sup>. normalized to  $^{42}\text{Ca}/^{44}\text{Ca} = 0.31221$  using the exponential fractionation law (Russell et al., 1978); <sup>c</sup>. relative to unspiked NIST SRM 915a; <sup>d</sup>.  $t = 126$  Ma, age-corrected values; <sup>e</sup>. full-procedure duplicate.

and  $K/Ca = 0.35$  in average continental crust are assumed to have formed at 3 800 Ma ago, giving three different evolutionary pathways. From these three evolutionary pathways, it can be concluded that the higher the time-integrated  $K/Ca$  ratio, the greater enrichment in radiogenic  $^{40}Ca$ . Moreover, this is indistinguishable radiogenic Ca compositions between lower crust and the mantle within the analytical uncertainties. Therefore, the values of  $\epsilon_{Ca} < 1$  indicate that these magma mainly involved mantle compositions in their genesis, or were generated by partial melting of mafic lower crust. The  $K/Ca$  ratios of 0.35, the highest value formed from the upper mantle, was applied to simulate the evolutionary pathways of radiogenic Ca isotopes from the Nd model age (1 500 Ma) to remelting. It is quite clear that remelting occurred at 126 Ma based on the U-Pb ages. Subsequently, the  $K/Ca$  ratio was revised to 9.5 (the average value of these samples) and evolved to the present day (green line). Another evolutionary pathway also suggests that even when highest  $K/Ca$  ratio (0.35) in crust-mantle separation was used, its results were still lower than measured data (brown line) (Fig. 3). Other evolutionary paths did not evolve to match the measurements (Fig. 3). The contradiction between theoretical and experimental studies could be best explained by changes in sources compositions, which may have added new materials to its source.

There appear to be only one published report on radiogenic Ca isotopic compositions of Dabie granitoids in China (Wang et al., 2019). The Dabie granitoids display age-corrected  $\epsilon_{Ca}(126\text{ Ma})$  values from 0.01 to 1.15, while the Early Cretaceous aluminous A-type granites range from -0.31 to 0.96, all of which are broadly identical to the mantle value within error (Table 1). In order to further distinguish their source compositions, we estimated source  $K/Ca$  ratio of Dabie granitoids and LYRB aluminous A-type granites using Eq. (2) and followed the method of Marshall and Depaolo (1989).

$$\left(\frac{K}{Ca}\right)_{\text{source}} = \frac{\epsilon_{Ca}(T) - \epsilon_{Ca}(T_0)}{Q_{Ca}(e^{\lambda_K T_0} - e^{\lambda_K T})} \quad (2)$$

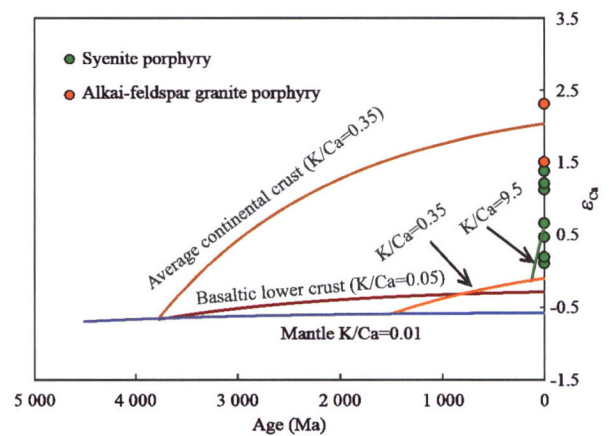
where

$$Q_{Ca} = \frac{R_p(Ab^{40}K/Ab^{44}Ca)}{(^{40}Ca/^{44}Ca)_{\text{mantle}}} \times 10\,000$$

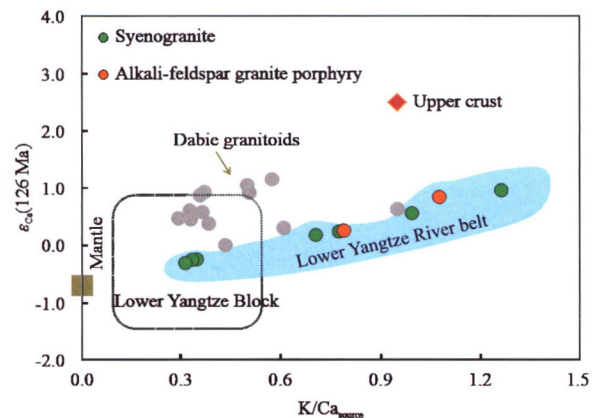
Ab is isotopic abundance;  $K/Ca$  indicates the atomic ratio (Marshall and Depaolo, 1989);  $\lambda_K$  and  $R_p$  are the total decay constant of  $^{40}K$  and the branching ratio, respectively (DePaolo, 2004; Steiger and Jager, 1977);  $\epsilon_{Ca}(T)$  and  $\epsilon_{Ca}(T_0)$  denote  $\epsilon_{Ca}$  values the time  $T$  (zircon U-Pb age) and  $T_0$  (Nd model age), respectively.  $\epsilon_{Ca}(T)$  can be calculated from measured  $^{40}Ca/^{44}Ca$ ,  $K/Ca$  ratios and U-Pb ages, while  $\epsilon_{Ca}(T_0)$  is -0.70 (Mills et al., 2018), assuming that the crustal reservoir derived from the upper mantle that time.

Combining Nd isotopic data with zircon U-Pb ages (Wang et al., 2019; He et al., 2013), the source  $K/Ca$  ratios could be calculated. The results show that the source  $K/Ca$  ratios (126 Ma) for Dabie granitoids range from 0.33 to 0.61 and are plotted in the lower continental crust field in an  $\epsilon_{Ca}(126\text{ Ma})$ - $K/Ca_{\text{source}}(126\text{ Ma})$  diagram (Fig. 4). This observation indicates that Dabie granitoids originated from the middle-lower continental crust, consistent with previous studies (He et al., 2013; Ling et al., 2011; Huang et al., 2008; Wang et al., 2007), which supports the

reliability of the radiogenic Ca isotope geochemical index. Also, the source  $K/Ca$  ratios of all samples in the LYRB ranging from 0.31 to 1.26 were obtained (Table 1). It appears that the source  $K/Ca$  ratios of the LYRB samples are, on average, higher than those of the Dabie granitoids (Fig. 4), indicating that they have different source compositions. More specifically, the Early Cretaceous aluminous A-type granites source clearly has higher  $K/Ca$  materials than Dabie granitoids. In additions, the vast majority of the LYRB samples are substantially higher than that of middle-lower crust (0.1 to 0.5) (Rudnick and Gao, 2003), and tend to cluster around the value for average upper crust value (0.95) (Taylor and McLennan, 1995). Sedimentary and metasedimentary rocks are highly variable in  $K/Ca$  ratios (Marshall and Depaolo, 1982), and are lower (0.1) in the mafic lower crust (Rudnick and Gao, 2003), both of which are different from source  $K/Ca$  ratios of these samples. The  $\epsilon_{Ca}(126\text{ Ma})$  values of Yangshan aluminous A-type granites are consistent with the middle-lower continental crust or mantle value at our current level of analytical precision (1  $\epsilon$  unit), but their source  $K/Ca$  ra-



**Figure 3.** The evolutionary path of the radiogenic Ca isotope of the different geological reservoirs from 3 800 Ma to the present day. The oldest crustal component in the Lower Yangtze Block (Zhang et al., 2006), 3 800 Ma, was taken as the starting point. The mantle evolved throughout the geological time.



**Figure 4.**  $\epsilon_{Ca}(126\text{ Ma})$  vs.  $K/Ca_{\text{source}}$  diagram (Dabie data from Wang et al. (2019), and radiogenic Ca isotopic data and  $K/Ca$  ratios from DePaolo (2004) and Rudnick and Gao (2003)). The lower continental crust field was represented by amphibolites from the Luzhenguan Complex in the Dabie-Sulu Orogen (Lu et al., 2020).

tios are substantially higher than the latter (Fig. 4), implying that their magma source may be a mixture of the upper-crust materials and mantle, rather than from the K-poor and Ca-rich mafic lower crust materials.

The extremely low radiogenic Hf and Nd isotopic compositions of the lower crust of the Yangtze Block and the relatively high aluminous A-type granites of the LYRB further suggest that the lower crustal material does not represent the main source component of aluminous A-type granites (Guo et al., 2014; Zhang and Zheng, 2013; Gao et al., 1999). Moreover, the lower continental crust has low K, Th and U contents, so rocks formed from it should have low K contents and Pb isotopic ratios, which is inconsistent with the geochemical characteristics of aluminous A-type granites in the region (Yang et al., 2017; Yan et al., 2015). Previous studies have also shown no obvious heavy rare earth elements (HREEs) differentiation, which apart from the possibility of the residues garnet in their magma source (Gu et al., 2017). The depletion of Sr and negative Eu anomalies indicate a plagioclase-rich source and reflect their shallow-crust origin (Yan et al., 2015). Zircon saturation temperatures exhibit that the formation temperature for the aluminous A-type granites in the LYRB is relatively higher (760–782 °C, with average of 772 °C) than that of the early I-type granites (667–720 °C with average of 694 °C) (Wang et al., 2018; Gu et al., 2017; Yan et al., 2015).

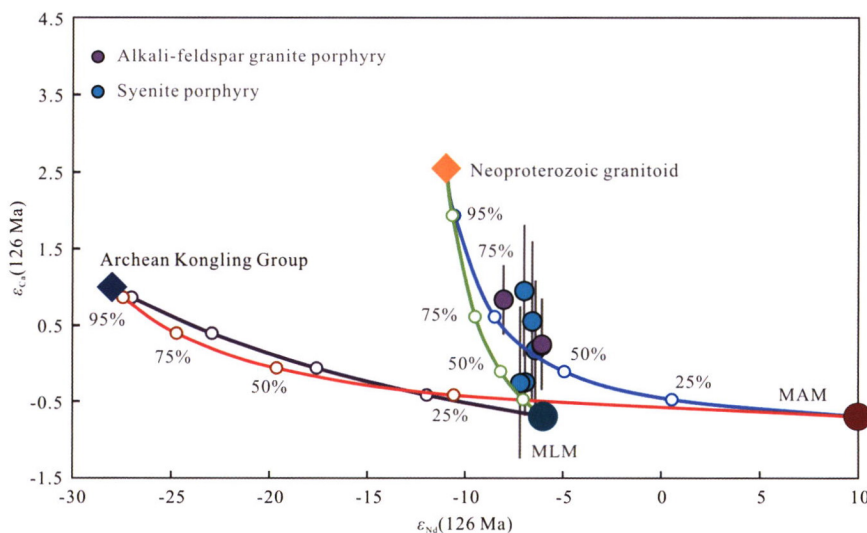
Thus on balance, traditional geochemical signatures and the new radiogenic  $^{40}\text{Ca}$  data with the source K/Ca ratio (126 Ma) are best explained by a mixing of the mantle and upper crustal materials in the source of aluminous A-type granites, rather than by simple crust or mantle composition alone.

#### 4.2 Assessing Crustal and Mantle Contributions in Aluminous A-Type Granites

To quantitatively evaluate the relative contributions of the crustal and mantle materials, a two end-member mixing model

using the radiogenic  $^{40}\text{Ca}$  and Nd isotopic for aluminous A-type granites was developed in this study. In these modeling calculations, the melts of asthenospheric mantle, the melts of lithospheric mantle, the Archean crust and Neoproterozoic crust were used as isotopic end-members (Fig. 5). The  $\epsilon_{\text{Ca}}$  values and CaO contents for the melt derived asthenospheric and lithospheric mantle both do not differ, being  $-0.7\epsilon$  and 11.3 wt.% (Mills et al., 2018; Hofmann, 1988), respectively. The  $\epsilon_{\text{Nd}}$  values and Nd contents for the asthenospheric melts are +10 and 11 ppm, respectively (Chen et al., 1994; Hofmann, 1988), while the lithospheric melts are  $-6$  and 35 ppm (Yan et al., 2015, 2005), respectively. Among the crustal end-members, the Archean crust was represented by the Kongling Group in the Yangtze Block with a CaO content of 9.59 wt.%, the  $\epsilon_{\text{Nd}}$  values of  $-28$ , and the Nd concentration of 39 ppm (Rudnick and Gao, 2003; Gao et al., 1999). No radiogenic  $^{40}\text{Ca}$  data have been reported for the Archean Kongling Group, but its  $\epsilon_{\text{Ca}}$  value should be difficult to discern within the current precision range because of its low K/Ca ratio of 0.05. This conclusion is also supported by  $\epsilon_{\text{Ca}}$  value for granitoids in the Dabie Orogen (Wang et al., 2019), which are considered as derived from ancient lower crust. In this view, an estimated  $\epsilon_{\text{Ca}}$  value for the Archean Kongling Group of 1 was used. Neoproterozoic crust is represented by the Fuchashan Complex in southern Anhui Province with CaO and Nd contents of 3.59 wt.% and 27 ppm (Liu L et al., 2015), and an  $\epsilon_{\text{Ca}}$  (126 Ma) value of 2.54 measured here, respectively. Modeling calculations using the above parameters indicate that the magmatic source for the aluminous A-type granites of the LYRB is composed of 50% to 75% Neoproterozoic crust and 50% to 25% asthenospheric mantle materials (Fig. 5).

In summary, we consider that the mantle compositions are important in the petrogenesis of aluminous A-type granites of the LYRB. It not only provides an indispensable heat source for the melting of the upper continental crust, but also injects materials into their magma source. Binary mixing model using



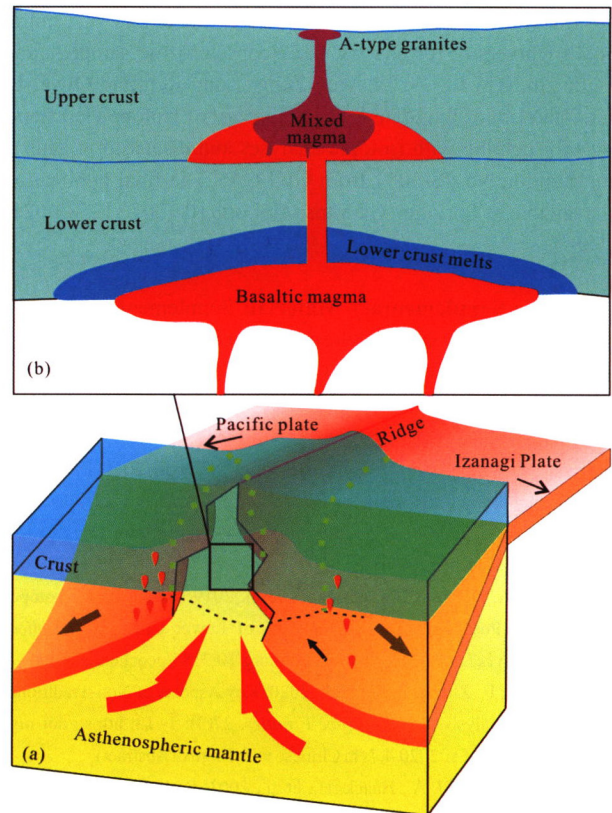
**Figure 5.**  $\epsilon_{\text{Ca}}$ (126 Ma) vs.  $\epsilon_{\text{Nd}}$ (126 Ma) diagram for the four end members mixing models. MAM is the melts of asthenospheric mantle: Nd = 11 ppm;  $\epsilon_{\text{Nd}}$  = +10; CaO = 11.3 wt.%;  $\epsilon_{\text{Ca}}$  =  $-0.7$  (Mills et al., 2018; Chen et al., 1994; Hofmann, 1988). MLM is the melts of lithospheric mantle: Nd = 35 ppm;  $\epsilon_{\text{Nd}}$  =  $-6$ ; CaO = 11.3 wt.%;  $\epsilon_{\text{Ca}}$  =  $-0.7$  (Mills et al., 2018; Yan et al., 2015, 2005). The Archean crust was represented by the Kongling Group: Nd = 39 ppm;  $\epsilon_{\text{Nd}}$  =  $-28$ ; CaO = 9.59 wt.%;  $\epsilon_{\text{Ca}}$  = 1 (Rudnick and Gao, 2003; Gao et al., 1999). Neoproterozoic crust was represented by Neoproterozoic granitoid: Nd = 27 ppm;  $\epsilon_{\text{Nd}}$  =  $-11$ ; CaO = 3.56 wt.% (Liu L et al., 2015), and  $\epsilon_{\text{Ca}}$ (126 Ma) = 2.54 (Table 1).

radiogenic Ca-Nd isotopes show that a mixture of 50% to 75% Neoproterozoic crust and 50% to 25% asthenospheric mantle constitutes the main source compositions of the aluminous A-type granites in the LYRB.

### 4.3 Geodynamic Setting

The geodynamic setting of Mesozoic igneous rocks in the LYRB remains controversial, and several genetic models have been recommended by previous researches, as follow: (1) lithospheric thinning triggered by delamination or thermodynamic erosion (Su et al., 2013; Li et al., 2009; Xue et al., 2009; Xie et al., 2008); (2) the low angle subduction of paleo-Pacific Plate and subsequent roll-back of basaltic slab, resulting in the partial melting of the lower crust (Wang et al., 2018), or Neoproterozoic crust (Gu et al., 2017; Yang et al., 2017; Yan et al., 2015) or highly fractional crystallization (Fan et al., 2016); (3) slab tearing induced by changes in the subduction angle of paleo-Pacific Plate (Wu et al., 2012); and (4) the ridge subduction between the Pacific and Izanagi plates during the Early Cretaceous (Zhang et al., 2020; Jiang et al., 2018b; Sun et al., 2018, 2010, 2007; Ling et al., 2011, 2009). Although the geodynamic evolution of the Early Cretaceous cannot be unambiguously elucidated through the current isotopic data of the LYRB Mesozoic igneous rocks, it is clear that the unradiogenic mantle-like  $\epsilon_{\text{Ca}}(126 \text{ Ma})$  values and upper crust-like source K/Ca ratios of the aluminous A-type granites can provide more details for the ridge subduction model.

Based on geological, geochemical, and geophysical evidence, Ling et al. (2009) proposed a ridge subduction model for the Mesozoic mineralization in the LYRB (Fig. 6). This model states that between 140 to 125 Ma, the Pacific Plate drifted southwestward and the Izanagi Plate drifted northwestward, resulting in ridge subduction. This model is favorable for the spatial distribution of adakitic and calc-alkaline rocks, Nb-enriched basalts, A-type granitoids, and ore deposits in the LYRB (Ling et al., 2009). During ridge subduction, oceanic crust near the mid-ocean ridge was hot and partially melted. As the melts ascended, they reacted with mantle peridotites and subsequent contaminated by the lower continental crust materials, forming the adakitic rocks. Oceanic crust away from the mid-ocean ridge is cold and has a high water content, which can cause dehydration of subducted slabs and generate calc-alkaline magmas. These processes clearly expound the origin of magmatic rocks in the LYRB between 150 and 136 Ma. The slab window opened and induced the upwelling of hot asthenosphere. The Nb-rich fluid released by the subducting slab led to partial melting of the metasomatized mantle, producing basaltic magma (Ling et al., 2009; Sun et al., 2008). A portion of basaltic magma rose and erupted to the surface, resulting in the formation Nb-rich basalts, while another portion intruded the crust-mantle boundary, inducing partial melting of the lower crustal materials (Fig. 6). The mixing of basaltic magma and lower crustal melts produced the intermediate-acid intrusive rocks. Besides, partial melting of the lithospheric mantle and lower continental crust led to the crustal thinning in narrow regions, creating cracks that as channels for magma to rise. Finally, the rise of hot asthenospheric melts into the shallow crustal levels induced partial melting of Neoproterozoic crust. Therefore, we propose that the series of



**Figure 6.** A simplified petrogenetic model of the Early Cretaceous aluminous A-type granites in the LYRB. (a) Modified after Luo et al. (2018), Jiang et al. (2018a) and Ling et al. (2009).

geological processes described above controlled the formation of aluminous A-type granites in the LYRB.

## 5 CONCLUSIONS

Radiogenic Ca isotope has the potential to distinguish the contribution of the mantle to granitic formation. The initial  $\epsilon_{\text{Ca}}(126 \text{ Ma})$  values for both syenite porphyry and alkali-feldspar granite porphyry in the Yangshan pluton range from -0.31 to 0.96, consistent with the mantle within error. In conjunction with the source K/Ca ratios, the results indicate that the parental magmas of these rocks are the result of crust-mantle interactions. Binary mixing model using radiogenic Ca-Nd isotopic compositions shows that a mixture of 50% to 75% Neoproterozoic crust and 50% to 25% asthenospheric mantle materials constitutes their magma sources. Integrating with previous works, we propose that Early Cretaceous ridge subduction of the Pacific and Izanagi plates was responsible for generation of aluminous A-type granites in the LYRB.

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