# SHRIMP dating of volcanic rocks from Ningwu area and its geological implications

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Abstract The SHRIMP U-Pb ages are reported for two volcanic rocks from the Longwangshan and the Dawangshan formations respectively, Ningwu area, Jiangsu Province. The Dawangshan formation (NB-01) is dated at (127  $\pm$  3) Ma, and the Longwangshan formation (NL-01), (131  $\pm$  4) Ma. Besides, a few Archean zircons are also found in the Longwangshan formation, which suggests a possible Archean basement in the region.

Keywords: volcanic rocks, Ningwu area, SHRIMP dating, Early Cretaceous, Archean.

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Precisely dating of volcanic rocks is fundamental to the understanding of the geological evolution of a basin. However, in volcanic rocks, particularly in the case of intermediate-mafic rocks, the zircon populations are complicated because of the common occurrence of inheritance (or cores) and/or exotic zircons incorporated during eruption, except for the magmatic zircons. So, in zircon geochronology of volcanic rocks, it is the key to distinguish zircons of different origins and sources. At present, Cathodoluminescence (CL) directed SHRIMP dating serves as the best way out.

Volcanic rocks from the Ningwu Basin are intermediate-mafic, and mostly, shoshonites, with minor high-potassic calc-alkaline series<sup>[1–7]</sup>. The ages of the volcanic rocks are still open to debate. In the past, most volcanic rocks were considered to be in the late Jurassic, but the recent 1:50000 mapping has attributed the Longwangshan formation to the late Jurassic, and the other parts are revised to the Cretaceous<sup>[6, 8]</sup>. In order to precisely define the ages of the volcanic rocks in the region, two samples from the Dawangshan and Longwangshan formations respectively are dated using Beijing SHRIMPII. This work confirms that the volcanic rocks were formed at the early Cretaceous.

#### **1** Geological setting and sample description

The Ningwu Basin lies between Nanjing and Wuhu (fig. 1), where volcanic rocks (~1000 km<sup>2</sup>) erupted in the depression that developed since Sinian, belonging to a successive Mesozoic intra-continental basin. The strata of the area are the upper Triassic Huangmaqing, lower Jurassic Xiangshan and upper Jurassic Xihengshan formations, with minor upper Cretaceous Pukou formation and Tertiary sandy conglomerate that overlie the volcanic rocks. The volcanic rocks of the

Ningwu area comprise predominantly the Longwangshan formation (20%) and the Dawangshan formation  $(75\%)^{[9]}$ , and the less Gushan and Niangniangshan formations (less than 5%). The lower part of the Longformation is wangshan composed of light-grayed tuffite, silty mudstone, volcanic conglomerate, and the upper, mostly lavas of benmoreite, mugearite, and hornblende with volcanic breccia intercalation. The Dawangshan formation is over 300 m thick. The lower part of the formation is pyroxene latite, with minor volcanic conglomerate, breccia, tuff, tuffite and tuffaceous silt, the middle, purple andersite, with locally tuffaceous silt lens, and the upper, gray-reddish, lightgraved trachyte and trachy-ignimbrite. The Gushan formation is less distributed, containing black andesite and dacite in the upper part, pyroclastic rocks and sedimentary rocks in the lower part. The Niangniangshan formation is only found in the west of Niangniang hill, where the lower part of the for-



Fig. 1. The sketch map of the Ningwu Basin showing the distribution of volcanic rock and sampling sites (simplified after Ningwu research Project<sup>[10]</sup>). 1, Niangniangshan formation; 2, Gushan formation; 3, Dawangshan formation; 4, Longwangshan formation; 5, gabbro-diorite porphyrite; 6, andesite porphyrite, latitic porphyrite and trachyporphyry; 7, monzonite and quartz diorite; 8, granite; 9, gabbro; 10, presumed faults; 11, faults; 12, sampling sites.

mation is conglomerate, breccia, pseudoleucite phonolite and ignimbrite, and the upper, phonolitic welded breccia and hauyne phonolite. The samples SHRIMP dated were collected from the middle of Longwangshan (NL-01) and the top of the Dawangshan formations (NB-01). The sampling sites are shown in fig. 1.

Sample NB-01 is a latite from the Dawangshan formation, which contains SiO<sub>2</sub> (56.33%),  $K_2O$  (3.02%),  $Na_2O$  (2.30%), with  $K_2O/Na_2O$  (1.3), and a relatively low total alkaline content of

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 $5.3\%^{[7]}$ . The rock is porphyritic, with phenocryst consisting of clinopyroxene, plagioclase and K-feldspar, and matrix, tiny needle-like plagioclase filled with pyroxene that mostly altered to chlorite shows an interlocking texture. The sample weighs about 10kg. Zircon varies from 100  $\mu$ m to 200  $\mu$ m in size. Most zircons are light-yellow, transparent, euhedral prismatic-idiomorphic, representing typical magmatic morphology. Several grains are subhedral-anhedral with rounded surface, highly fractured inside, that is obviously distinct from the majority.

The sample NL-01 is a latite from the Longwangshan formation, with compositions  $SiO_2$  (56%),  $K_2O$  (30%),  $Na_2O$  (45%) and  $K_2O/Na_2O$  (1.2), with relatively high total alkaline content of 9.75%<sup>[7]</sup>. It is also porphyritic. The phenocryst is made up of plagioclase, K-feldspar, and hornblende with reaction rim, and less magnetite. The matrix is predominantly trachytic microplagioclase. Carbonization and chloritization are found common in the sample. The sample weighs about 10kg. Zircons are rare, only 20 grains, which vary from 30µm to 200µm. Most of them are anhedral, with rounded surfaces, and only a few euhedral prismatic grains. This extremely heterogeneous zircon population reflects a variety of origins.

# 2 Analytical procedures

Zircon was extracted by conventional techniques including handpicking under a microscope. Zircons from each sample, together with a piece of RSES reference zircon SL13 and several grains of TEM, were mounted in epoxy and polished nearly half to expose their centers. It was used for CL imaging and later SHRIMP U-Pb dating. CL imaging was used to guide the SHRIMP dating. The CL study was undertaken on an electron microprobe at the Institute of Mineral Resources, Chinese Academy of Geological Sciences.

The SHRIMP U-Pb analyses were performed on the newly installed Beijing SHRIMP II in the Chinese Academy of Geological Sciences. Details of the procedure for the analysis of zircons using SHRIMP have been given by Compston et al.<sup>[11]</sup> and Williams et al.<sup>[12]</sup>. For the zircon analyses, nine ion species of  $Zr_2O^+$ , <sup>204</sup>Pb<sup>+</sup>, background, <sup>207</sup>Pb<sup>+</sup>, <sup>208</sup>Pb<sup>+</sup>, U<sup>+</sup>, Th<sup>+</sup>, ThO<sup>+</sup> and UO<sup>+</sup> were measured on a single electron multiplier by cyclic stepping of the magnetic field, recording the mean ion counts of every 7 scans. A primary ion beam of ~4.5 nA, 10 kV O<sup>-2</sup> and ~25–30 µm spot diameter were used. Mass was analyzed at a mass resolution of ~5400 (1% peak height). Interelement fractionation in ion emission of zircon was corrected by referring to the RSES references, using SL13 (572 Ma, 238ppm) at the first and TEM (417 Ma)for the final. The reproducibility of TEM was repeatedly measured to be ~2%. The software of Ludwig SQUID1.0<sup>[13]</sup> and attached ISOPLT<sup>[14]</sup> were used for data processing. The ages are calculated using the constants recommended by IUGS (1977). The uncertainties in ages listed in table 1 are cited as 1 $\sigma$ , and the weighted mean ages are quoted at 95% confidence level.

Table 1 SHRIMP U-Pb data of zircons from two volcanic rocks, Ningwu area

Spots	<sup>206</sup> Pb <sub>c</sub>	U/	Th/	<sup>232</sup> Th/	$^{206}\text{Pb}^{*}/$	$^{206}\text{Pb}/^{238}\text{U}$	207Pb/206U	<sup>207</sup> Pb*/	<b>⊥</b> 0⁄₀	<sup>207</sup> Pb*/	<b>⊥</b> 0⁄₀	<sup>206</sup> Pb*/	⊥0⁄⊲
spors	(%)	$10^{-6}$	$10^{-6}$	<sup>238</sup> U	$10^{-6}$	Age/Ma	Age/Ma	<sup>206</sup> Pb*	± 70	<sup>235</sup> U	± 70	<sup>238</sup> U	± 70
NB-01													
1.1	7.05	68	39	0.59	1.20	121 ±4	$-1650 \pm 2900$	0.0260	85	0.0680	85	0.0191	3.6
2.2	2.01	134	72	0.55	4.65	$251 \pm 5$	$-198 \pm 230$	0.0425	9.0	0.2320	9.3	0.0397	2.1
3.1	2.00	167	123	0.76	2.93	$128 \pm 3$	$-325 \pm 320$	0.0404	13	0.1110	13	0.0200	2.2
4.1	1.76	111	75	0.70	3.38	$220\ \pm 5$	$-271 \pm 410$	0.0413	16	0.1970	16	0.0347	2.4
4.2	2.72	98	82	0.86	2.89	$212 \pm 5$	$-339 \pm 660$	0.0400	26	0.1850	26	0.0335	2.5
5.1	2.45	104	71	0.71	1.73	$120 \pm 4$	$-327 \pm 680$	0.0400	26	0.1050	26	0.0188	3.2
6.1	2.35	126	78	0.63	2.13	$123 \pm 3$	$-346 \pm 690$	0.0400	27	0.1060	27	0.0192	2.8
7.1	2.23	120	78	0.67	2.13	$129 \pm 4$	$-248 \pm 480$	0.0416	19	0.1160	19	0.0202	3.1
8.1	1.95	120	122	1.06	2.06	125 ±3	$195 \pm 550$	0.0500	24	0.1350	24	0.0197	2.6
9.1	3.14	126	96	0.79	2.23	127 ±4	$-453 \pm 460$	0.0385	17	0.1060	18	0.0200	2.7
10.1	1.23	266	216	0.84	4.55	126 ±3	-211 ±360	0.0423	14	0.1150	14	0.0197	2.2
11.1	4.01	124	88	0.73	2.08	120 ±3	$-1490 \pm 1500$	0.0270	46	0.0700	46	0.0189	2.7
12.1	0.13	182	125	0.71	3.11	127 ±3	539 ±170	0.0582	7.9	0.1590	8.2	0.0199	2.2
13.1	1.10	163	108	0.69	2.92	132 ±3	$-247 \pm 200$	0.0417	7.8	0.1190	8.1	0.0207	2.2
15.1	1.09	96	71	0.76	1.71	131 ±3	219 ±130	0.0505	5.6	0.1440	6.0	0.0205	2.3
15.2	2.28	225	175	0.80	3.94	127 ±3	-829 ±420	0.0335	15	0.0920	15	0.0199	2.2
16.1	3.61	124	90	0.75	2.19	126 ±3	-535 ±580	0.0373	22	0.1020	22	0.0198	2.4
NL-01													
1-1	4.61	201	170	0.88	12.1	430 ±14	630 ±120	0.0605	5.7	0.5780	6.5	0.0690	3.4
1-2	9.89	58	27	0.48	4.55	507 ±19	-111 ±850	0.0420	37	0.5000	35	0.0819	4.0
3-1	0.03	182	58	0.33	72.8	2458 ±65	2485 ±9.1	0.1628	0.54	10.42	3.2	0.4640	3.2
4-1	0.60	461	232	0.52	15.8	$248\ \pm 8$	$-240 \pm 180$	0.0415	7.3	0.2260	7.7	0.0393	3.2
5-1	1.79	314	212	0.70	5.66	$129\ \pm 4$	-1251 ±730	0.0284	24	0.0810	23	0.0202	3.3
5-2	0.39	1449	859	0.61	25.6	131 ± 4	108 ±63	0.0481	2.7	0.1363	4.1	0.0205	3.1
5-3	0.39	1287	847	0.68	23.2	133 ± 4	-102 ±81	0.0440	3.4	0.1266	4.6	0.0208	3.2
6-1	_	138	130	0.98	77.5	3232 ±80	3098 ±1	0.2366	0.43	3 21.24	3.2	0.6510	3.1
7-1	0.07	634	87	0.14	190	1929 ±52	1839 ±6	0.1124	0.35	5 5.410	3.1	0.3490	3.1
8-1	0.72	276	127	0.47	13.8	360 ±11	396 ±100	0.0544	4.7	0.4330	5.6	0.0575	3.2
8-2	3.86	162	57	0.37	8.92	372 ±12	-1038 ±910	0.0299	33	0.2560	31	0.0594	3.4
9-1	_	99	63	0.66	38.6	2403 ±63	2421 ±22	0.1567	1.3	9.760	3.4	0.4520	3.2
9-2	0.02	179	90	0.52	77.4	2621 ±67	2592 ±10	0.1735	0.59	9 12.01	3.2	0.5020	3.1
11-1	1.15	1877	1827	1.01	34.0	132 ± 4	-103 ±120	0.0438	5.0	0.1257	5.8	0.0207	3.1
12-1	12.63	155	106	0.70	2.98	125 ± 5	-510 ±1400	0.0350	60	0.1010	54	0.0196	4.0
12-2	11.13	176	114	0.67	3.46	131 ± 5	445 ±710	0.0540	34	0.1580	32	0.0205	3.9
13-1	1.50	1248	888	0.73	23.0	$134\ \pm 4$	11 ±150	0.0455	6.5	0.1315	7.2	0.0210	3.2

1, Errors are 1-sigma; Pbc and Pb\* indicate the common and radiogenic portions, respectively; 2, error in standard calibration was 0.79% and 1.07% for NB01 and NL01 respectively (not included in the above errors but required when comparing data from different mounts; 3 common Pb corrected using measured <sup>204</sup>Pb.

## **3** Results and interpretation

SHRIMP U-Pb data (NB-01 and NL-01) are listed in table 1.The ages of NB-01 and representatives of NL01 are denoted on their corresponding CL images (fig. 2(a)—(h)).



Fig. 2. CL images of zircons from the volcanic rocks, Ningwu area. (a)—(h), NB-01; (i)—(l), NL-01. Circle and number denote the spot center and age (Ma).

# 3.1 The Dawangshan formation (NB-01)

Zircons from the sample NB-01 are relatively homogeneous. As shown in CL images, most dated grains have rhythmic zoning (i.e. grain3, fig. 2(c); grain 1, 6, fig. 2(a); grain 7, 8, 9, fig. 2(e), grain10, 12, 13, fig. 2(f); grain16, fig. 2(h)), which indicates their magmatic origins. The  ${}^{206}$ Pb/ ${}^{238}$ U age ranges from 120 Ma to 132 Ma (table 1) with weighted mean at (127 ± 3) Ma (fig. 3), that reflects the formation age of the rock.

One grain shows clearly core-overgrowth relation (i. e., grain 2, fig. 2(b)) where the core is dated at 251 Ma. On one anhedral grain with rhythmic zoning (grain 4, fig. 2(d)), two analyses give the ages of 212 Ma and 220 Ma respectively. These zircons might be attributed to inheritance or exotic during the volcanic eruption.



Fig. 3. U-Pb concordia diagram of zircons from NB-01.

## 3.2 The Longwangshan formation (NL-01)

Zircons of NL-01 are complicated as revealed by the CL images. A few grains are euhedral-subeuhedral (e. g., grain12, fig. 2(l)), with nearly perfect pyramid and prisms (e. g., grain5,

fig. 2(i)). Compared to NB-01, rhythmic zoning in zircons from NL-01 is less developed or totally absent, which might result from the volcanic eruption and rapid cooling. The  $^{206}$ Pb/ $^{238}$ U age varies from 125 Ma to 134 Ma, mostly in the narrow range of 129—134 Ma (table 1). In fig.4, seven data points are clustered together with weighted mean at (131 ± 4) Ma (fig. 4), interpreted as the formation age of the rock.

The majority of zircons from NL-01 vary from the late Paleozoic to Archean



Fig. 4. U-Pb concordia diagram of zircons from NL-01.

(table 1). These zircons are morphologically irregular, showing varieties of internal structures. Four analyses give Archean or early Proterozoic ages (table 1, grain 9, fig. 2(1); grain 3, fig. 2(i); grain 6, fig. 2(k)), and 3 other zircons give Paleozoic age (table 1, grain 4, fig. 2 (j); grain 1, 8, fig. 2 (i)). Some zircons are structureless, and the others with rhythmic zoning, which clearly reveals the heterogeneity of the population, and so indicates their different sources. One possible explanation is that these zircons are exotic during the volcanic eruption.

## 4 Discussions

4.1 Formation ages of the Ningwu volcanic rocks

There are a series of Mesozoic volcanic basins along the lower reach of the Yangtze River, such as Fanchang, Luzong, Ningwu, Lishui and Liyang basins, however, there exist debates for their timing. Previously, most of volcanic rocks were considered to be in the late Jurassic. But, in recent 1:50000 mapping, the lower part of the volcanic series (e.g., the Longwangshan and Dawangshan formations in the Ningwu and Liyang basins, the Longwangshan and Donglushan formations in the Lishui basin, the Longmenyuan and Zhuanqiao cycles in the Luzong basin) is considered to exist in the late Jurassic, and the others are revised to the early Cretaceous<sup>[8]</sup>. The published data have shown the Longwangshan formation of 136—125 Ma, the Dawangshan, 125—120 Ma, the Gushan, 117—110 Ma, and the Niangniangshan, a little younger, 106—91 Ma, generally, which are in the early Cretaceous<sup>[8,10]</sup>. Nevertheless, most data mentioned above are K-Ar or Ar-Ar ages, which should be treated as the cooling ages to Ar blocking temperature of the volcanic rocks.

Using SHRIMP method, the Longwangshan formation is dated at  $(131 \pm 4)$  Ma, and the top Dawangshan formation,  $(127 \pm 3)$  Ma, recording the formation ages of the volcanic rocks. It is suggested that the Ningwu volcanic rocks erupted during the early Cretaceous and lasted for a very short period. Accordingly, the volcanic rocks in the basins along the lower reach of the Yangtze River started eruption at the early Cretaceous. Also, the late Jurassic strata were probably predated.

## 4.2 Geochronological information of an Archean basement in Ningwu area

Some Archean and early Proterozoic zircons are found in the volcanic rock (NL01) from the Longwangshan formation. Three grains yield ages of 2403–2621 Ma, and one grain,3232 Ma. The Ningwu basin is situated in the east part of the Yangtze Block, where Gao et al.<sup>[15]</sup> geochronologically defined the emplacement age of 2.9 Ga for trondhjemites from the Kongling high-grade metamorphic terrain, and some detrital zircons of 3.3 Ga were found from the meta-sedimentary rocks, which proved an Archean continental basement occurring in the Yangtze Block. The present work also yields detrital zircon ages of 3.2Ga and 2.4—2.6 Ga in the volcanic rocks of the Longwangshan formation, suggesting there would be an Archean basement of lower crust in the region.

## 5 Conclusion

The SHRIMP ages of Ningwu volcanic rocks range from  $(131 \pm 4)$  Ma to  $(127 \pm 3)$  Ma, which suggests the volcanic rock in Ningwu and its relevant from the lower Yangtze area erupted in the early Cretaceous. The volcanic rocks from the Ningwu basin are shoshonite and high-K calc-alkaline series deriving from metasomatic enriched mantle<sup>[7]</sup>, indicating that an early Creta-

ceous basaltic underplating event might take place in the area, that is probably related to the intermediate to acid magmatic activities during Mesozoic in the middle and lower Yangtze areas.

The ages of 3.2 Ga and 2.4—2.6 Ga of the exotic zircons from the Niangua volcanic rock are similar to the oldest ages of the Yangtze Block reported by Gao et al.<sup>[15]</sup>. Therefore, it is concluded that there would also be an Archean basement of lower crust in the region.

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