The latest Yanshanian magmatic and metallogenic events in the middle-lower Yangtze River belt: Evidence from the Ningzhen region

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The Ningzhen region in Jiangsu Province represents the easternmost magmatic region in the middle-lower Yangtze River belt. The formation of the polymetallic deposits has close genetic relationships with Early Cretaceous intermediate-acid intrusions. In this study, LA-ICP-MS zircon geochronology of two Mesozoic intermediate-acid intrusive rocks (including the Shima porphyritic granodiorite and Gaozi quartz diorite porphyry) in the Ningzhen region were systematically investigated. These new geochronological data demonstrate that the intermediate-acid magmatism in the Ningzhen region dates to approximately between 109 and 101 Ma. We present new ⁴⁰Ar-³⁹Ar phlogopite ages for the Cishantou skarn iron deposits that constrain the timing of the mineralisation in the Ningzhen region. The phlogopite in the Cishantou skarn deposits yielded a ⁴⁰Ar-³⁹Ar plateau age of 104±1 Ma. This result coincides with the ages of the Anjishan and Tongshan Cu (Mo) deposits in the Ningzhen region. Our high-precision geochronological data together with recent high-precision geochronological studies (such as zircon LA-ICP-MS U-Pb, zircon SHRIMP U-Pb, molybdenite Re-Os and single-mineral ⁴⁰Ar-³⁹Ar dates) reveal that there were four periods (152–135 Ma, 135–127 Ma, 127–121 Ma, 109–101 Ma) of magmatism and ore formation in the middle-lower Yangtze River metallogenic belt. The Mesozoic intermediate-acid magmatism and mineralisation in the Ningzhen region belong to the latest episode in the middle-lower Yangtze River metallogenic belt.

Mesozoic intrusive rocks, LA-ICP-MS zircon geochronology, skarn iron deposit, ⁴⁰Ar-³⁹Ar age, Ningzhen region

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The middle-lower Yangtze River belt, where the ore deposits are genetically associated with the Late Mesozoic intrusive rocks, is one of the most important metallogenic belts in China. This belt is located along the northern margin of the Yangtze Block and the southeast part of the North China Block and the Dabie orogenic belt. Most deposits and intrusive rocks in the middle-lower Yangtze River belt are clustered in seven districts where the Yanshanian magmatism is particularly extensive. These districts, listed in succession from west to east, are the Edong, Jiurui, Anqing, Luzong, Tongling, Ningwu and Ningzhen districts (Figure 1) [1].

Precise and accurate isotopic age determinations for the diagenesis and mineralisation is crucial for understanding the spatial and temporal distribution of the igneous rocks and deposits in the middle-lower Yangtze River metallogenic belt and related tectonic events. Over the past decade, isotopic age data using the SHRIMP (Sensitive High Resolution Ion Microprobe) and/or LA-ICP-MS (laser ablation inductively coupled plasma mass spectrometer) zircon U-Pb, mica ⁴⁰Ar-³⁹Ar and sulfide Re-Os methods on igneous rocks and mineral deposits in the middle-lower Yangtze River metallogenic belt have rapidly accumulated in the literature [4]. Among these studies, it is widely acknowledged that the igneous rocks in the middle-lower Yangtze River belt show

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Figure 1 Schematic illustration of the seven magmatic and metallogenic districts of the middle-lower Yangtze River metallogenic belt (modified after [2,3]). Magma region: 1, Edong; 2, Jiurui; 3, Anqing; 4, Luzong; 5, Tongling; 6, Ningwu; 7, Ningzhen.

geochemical characteristics of temporal and spatial evolution [5,6]. The geochronological data indicate that magmatism and metallogenesis in the middle-lower Yangtze River metallogenic belt primarily occurred between 145 and 120 Ma [7,8]. From 145 to approximately 135 Ma, the main phase of high-K calc-alkaline magmatism and associated Cu-Au mineralisation were concentrated in areas of uplift (e.g. the Tongling district). Igneous activity from 135 to 127 Ma occurred primarily in rift areas, such as the Luzong and Ningwu basins, and this activity was contemporaneous with the main period of Fe mineralisation [4]. The Ningzhen region is the easternmost region in the middle-lower Yangtze River belt. Compared to the large radiometric dataset for the magmatic rocks and orebodies along the lower reaches of the Yangtze River, such as those from the Edong, Jiurui, Tongling, and Luzong regions, high-precision geochronological data from the intrusive rocks and ore deposits in the Ningzhen region are relatively scarce. Although previous studies have accumulated abundant geological data [9–14], the ages of the granitoids in the Ningzhen region have been poorly constrained using whole-rock K-Ar and Rb-Sr methods. These ages provide a loose constraint on the timing of the magmatism in the Ningzhen region. Recently, the Anjishan pluton in the Ningzhen region has been dated using the SHRIMP zircon U-Pb method [15]. Despite this technical advance, the age distribution of the Late Mesozoic igneous intrusions in this region remains unclear due to the low density of sampling. In addition, because of the complexity and multiple periods of mineralisation and the limitation of the isotopic dating methods, the metallogenic event in the Ningzhen region appears to be short lived. Consider-

ing this situation, it would appear unproductive to study the relationship between the magmatism and metallogenesis. Meanwhile this complexity hinders an understanding of the magmatic-metallogenic space-time framework in the middle-lower Yangtze River metallogenic belt.

In this paper, on the basis of detailed field observation, we present LA-ICP-MS zircon U-Pb ages of the Shima and Gaozi intrusive rocks in the Ningzhen region. In addition, we also measured the ^{40}Ar - ^{39}Ar age of phlogopite in the Cishantou skarn iron deposits. Our new geochronological data shed new light on the magmatic-metallogenic evolution of the middle-lower Yangtze River metallogenic belt.

1 Geological setting

The middle-lower Yangtze River metallogenic belt is located on the northern margin of the Yangtze Block and in the southeast part of the North China Block and Dabie orogenic belt [1]. The middle-lower Yangtze River metallogenic belt is bounded by the Xiangfan-Guangji Fault on the northwest, the regional strike-slip Tancheng-Lujiang Fault on the northeast, and the Yangxin-Changzhou Fault on the south (Figure 1). This metallogenic belt generally displays a “V” shape, with the narrow end on the northwest and the wide end on the northeast [16,17]. The belt’s primary internal geologic structures include NW-striking faults and a fault zone along the Yangtze River.

The middle-lower Yangtze River metallogenic belt belongs to a part of the Neoproterozoic Jiangnan orogenic belt. However, there are two opinions regarding the timing of the

amalgamation of the Yangtze Block and the Cathaysia Block. One opinion is that this amalgamation occurred in the middle Neoproterozoic approximately 0.9 Ga [18,19], whereas the other opinion is that this event occurred in the middle Neoproterozoic approximately 0.81–0.83 Ga [20,21]. In either case, the middle Neoproterozoic (740–780 Ma) geology of the South China Block was characterised by continental rifting [22]. Since the Sinian, the middle-lower Yangtze River belt entered a period of sedimentary deposition on a stable platform. Starting in the Middle Triassic, the belt entered a stage of strong tectonic deformation. In the Middle Triassic, the belt was influenced by Indosinian movement: the belt constituted the foreland belt along the zone of collision between the South China and North China blocks and was dominated primarily by a restricted sea in which gypsum-bearing carbonate sediments were deposited [23]. After the Middle Triassic, large-scale folding associated with uplift began. Up until the Middle Jurassic, a series of continental basins developed in the belt. From the Late Jurassic to the Cretaceous, large-scale tectonism and magmatism, including emplacement of large volumes of plutonic rocks and large-scale mineralisation, were widespread and gave the middle-lower Yangtze River belt its dominant aspects [24]. The mineralisation provides examples of the “strata” and “multi-position in one” rules [16,25]. Late Jurassic–Early Cretaceous magmatic rocks sharing geochemical affinities with adakites are widespread in the middle-lower Yangtze River belt. These adakitic rocks likely played an important role in the polymetallic mineralisation.

The Ningzhen region in Jiangsu Province represents the easternmost magmatism in the middle-lower Yangtze River belt and is an important component of this magmatic rock belt. Extensive Mesozoic intrusive rocks were emplaced in the Ningzhen region. Major plutons in the Ningzhen region include, listed from west to the east, the Bancang, Qilinmen, Anjishan, Gaozi, Xinqiao, Shima and Jianbi intrusive bodies (Figure 2). Mafic to felsic intrusive rocks are present in the Ningzhen region, of which intermediate-acidic intrusive rocks account for approximately 80% and are the most widely distributed [10]. The Ningzhen area is rich in endogenous minerals, including copper, iron and zinc. The

types of ore deposits are primarily skarn, porphyry and hydrothermal infillings. The ore deposits are primarily distributed along the nearly east-west-trending anticline and faults, which dominate the geologic structure of the approximately east-west-trending mineralisation belt and all of which are spatially associated with the Late Mesozoic intermediate-acid intrusive rocks of the Ningzhen region.

2 Samples and petrography

The Shima pluton is located 12 km southwest of the city of Zhenjiang. The exposed area of the pluton measures 34 km². This pluton can be divided into three parts, the Tiaozhuangshan, Xuwan and Donglinchang intrusions, whose primary rock types are diorite porphyry, granodiorite and syenogranite, respectively. A porphyritic granodiorite (sample 09NZ09-1) was collected from the Zhangjiazhuang quarry within the Xuwan intrusion. The sample is gray to pink and displays a massive structure and a porphyritic texture, with a phenocryst content of approximately 30% to 40%. The phenocrysts consist of plagioclase, quartz, K-feldspar, amphibole and biotite. The plagioclase phenocrysts measure 0.5×1 mm–1.2×2 mm and are the most common mineral phase. These phenocrysts display euhedral or subhedral tabular forms and sometimes exhibit polysynthetic twinning and zoning texture. Some plagioclase phenocrysts have been altered to sericite. The quartz phenocrysts (0.3–0.8 mm) are present as xenomorphic granular crystals and interstitial fill between other minerals. Undulatory extinction of some of the quartz is observed. The K-feldspar phenocrysts (0.3–0.8 mm) are present as xenomorphic granular crystals. The biotite phenocrysts (0.5–1.2 mm) are present either as mineral aggregates or as euhedral sheets. In many places, the biotite has been altered to chlorite and typically contains small inclusions of magnetite and sphene. The amphibole phenocrysts (0.4×0.8 mm–0.7×1.5 mm) are present as euhedral or subhedral columnar crystals consisting of hornblende, some of which displays simple twinning. The groundmasses with phanerocrystalline texture are composed of plagioclase (20%), quartz (20%), K-feldspar

Figure 2 The distribution of Mesozoic intrusive rocks in the Ningzhen region (modified after [13]).

(15%), biotite (4%) and amphibole (3%). The accessory minerals include apatite, sphene, zircon and Fe-Ti oxides.

The Gaozi pluton controlled by regional longitudinal fracture, is situated in an east-west direction in the northern part of the central segment of Ningzhen region. This pluton can be divided into two parts: Xiashu and Leixiang intrusions. The Xiashu intrusion with main rock types of monzonitic granite, granodiorite, quartz monzonite, quartz diorite and quartz diorite porphyry, crops out in an area of 120 km². We collected a sample of quartz diorite porphyry (09NZ17-1) from the Xiashu intrusion near the Tongshan copper deposit. The sample is gray to celadon, showing massive structure and porphyritic texture with phenocryst contents of 20%–30%. The phenocrysts consist of plagioclase, amphibole, biotite and quartz. Plagioclase phenocrysts (0.3×0.5 mm–0.8×1.5 mm), occurring as euhedral or subhedral tabular are the most common mineral phase and sometimes show polysynthetic twin and zoning texture. Amphibole phenocrysts (0.2×0.4 mm–0.5×1.0 mm), occurring as euhedral to subhedral columnar or nearly rhombic transverse section, are hornblende. Quartz phenocrysts (0.2–0.5 mm) occurring as xenomorphic granular, partially corroded into a rounded shape. Biotite phenocrysts (0.3–0.6 mm) occur sheet. The groundmass is fine grained, with hypautomorphic to xenomorphic texture, and consists predominantly of plagioclase, amphibole, quartz and biotite with minor accessory apatite, sphene, zircon and Fe-Ti oxides.

3 Geological characteristics of the deposits

In this paper, we selected the Cishantou skarn iron deposit in the Ningzhen region for investigating the timing of the metallogenesis. The Cishantou iron deposit is a small contact-metasomatism skarn deposit located in the southern Xiashu area. The orebody is hosted primarily in the skarn developed along the contact between the limestone of the Qixia Formation and the intermediate-acid intrusive rocks. The mineralisation in the Cishantou iron deposit is associ-

ated with the quartz diorite porphyry. Most of the orebodies are vein, capsular, or lenticular in shape. The ore body strikes almost NE and dips SE at an angle of 50° to 90°.

The ore minerals form skarn deposits with a massive, disseminated, veined-network, banded and brecciated structure and include primary magnetite, hematite, limonite, specularite, pyrite and chalcopyrite. The ore has a variety of textures, including a xenomorphic granular texture, poikilitic texture and metasomatic texture. The gangue minerals include phlogopite, diopside, garnet, chlorite, actinolite, apatite and calcite. The wall-rock alteration in the Cishantou iron deposit is well developed (Figure 3(a)) and is characterised by chloritisation, phlogopite mineralisation, carbonation, marbleisation and pyritisation. A magnetite rock was collected from the Cishantou iron deposit. The phlogopite in the deposit is closely associated with the mineralisation processes. The phlogopite is dark green, mostly euhedral and flaky, and is closely associated with magnetite (Figure 3(b)).

4 Analytical methods

4.1 LA-ICP-MS zircon U-Pb geochronology

Representative zircon grains were extracted by heavy-liquid and magnetic methods and were further purified by hand-picking under a binocular microscope. The zircons were set in an epoxy mount that was polished to expose zircons in section. Before the *in situ* U-Pb isotope analyses, the morphology and internal structure of these zircons were studied using a binocular microscope and cathodoluminescence (CL) imaging to find appropriate spots for the isotope analyses. The CL images were obtained using a JEOL JXA-8900RL microprobe housed at the Chinese Academy of Geological Sciences, Beijing, and set at 15 kV.

The U-Pb zircon dating was performed using a LA-ICP-MS on an Agilent 7500 equipped with a 193-nm ArF excimer laser housed at the State Key Laboratory of Geological Processes and Mineral Resources of China, University of Geosciences, Wuhan. A GeoLas 200 M equipped with a

Figure 3 (a) The intense alteration of wall rocks and (b) the phlogopite coexisting with magnetite in the Cishantou skarn iron deposit.

193-nm ArF-excimer laser (32- μm beam diameter) with a homogenising, imaging optical system was used for the laser-ablation experiments. Zircon 91500 was used as an external standard to normalise isotopic discrimination during analysis, and this external standard was analysed twice every five analyses. NIST610 was used to optimise the machine. The off-line selection and integration of the background and analyte signals and time-drift correction and quantitative calibration for U-Pb dating were performed using the program ICPMSDataCal [26]. Common lead correction was performed using the EXCEL program CompCorr#3_151 [27]. The weighted mean ages were calculated and the concordia were plotted using the program ISOPLOT (ver 3.0) [28]. The detailed analytical procedure follows reference [29].

4.2 Phlogopite ^{40}Ar - ^{39}Ar dating method

The phlogopite coexisting with magnetite in the Cishantou iron deposit was dated using the ^{40}Ar - ^{39}Ar isotope method. The samples were collected from the open mining pit in the Cishantou iron deposit. All samples were crushed and purified using magnetic methods and rinsing to remove the magnetite and other minerals. After sieving, samples with grain sizes of 60 to 80 mesh were cleaned and dried. Phlogopite grains were carefully selected under a binocular microscope to reach a purity up to 99.9%. After cleaning by ultrasonic treatment in ethanol, the samples were sealed in a quartz bottle for irradiation in a nuclear reactor (The Swimming Pool Reactor, Chinese Institute of Atomic Energy, Beijing). The standard sample (The Free University of Holland, ZBH-2506), whose age is 132.7 ± 0.1 Ma, was also

irradiated. The total time of irradiation was 54 h.

After irradiation and 3 months of cooling, incremental step-heating ^{40}Ar - ^{39}Ar analyses were performed using a laser step-heating method at the Key Laboratory of Isotope Geochronology and Geochemistry in the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. A gas-sourced mass spectrometer (GV Instruments-5400Ar) and a laser gun (COHERENT-50W) were used for the isotope measurements. The decay constant used was $\lambda = 5.543 \times 10^{-10} \text{ a}^{-1}$ [30]. The correction factors for interfering isotopes generated during irradiation were determined by analysis of irradiated pure K_2SO_4 and CaF_4 , yielding the following ratios: $(^{36}\text{Ar}/^{37}\text{Ar})\text{Ca} = (2.64 \pm 0.02) \times 10^{-4}$, $(^{39}\text{Ar}/^{37}\text{Ar})\text{Ca} = (7.04 \pm 0.06) \times 10^{-4}$, $(^{40}\text{Ar}/^{39}\text{Ar})\text{K} = (8 \pm 3) \times 10^{-4}$. The program ArArCALC (ver. 2.2c) was used to calculate the plateau age and isochron [31]. The operation and data processing procedures were similar to those described by references [32,33]. The uncertainty of the plateau age is 2σ .

5 Results

5.1 Shima pluton

The zircons from the Shima porphyritic granodiorite (sample 09NZ09-1) are euhedral, colourless to grey and 100–200 μm in length with an elongation ratio of 1:1–3:1. The typical CL images of the zircons (Figure 4) show that most zircons display clear internal structure and well-developed oscillatory zoning.

The zircon U-Pb data from the Shima porphyritic granodiorite are presented in Table 1. The uranium and thorium concentrations vary from 431 to 806 ppm and 370 to 1142

Figure 4 Cathodoluminescence (CL) images with U-Pb ages (in Ma) for representative zircons from the Shima porphyritic granodiorite (sample 09NZ09-1).

Table 1 LA-ICP-MS zircon U-Pb data of the Shima and Gaozi plutons in the Ningzhen region

Spot	Element (ppm)				Isotopic ratios								Age (Ma)			
	Th	U	Total Pb	Th/U	$^{207}\text{Pb}/^{206}\text{Pb}$	1 σ	$^{207}\text{Pb}/^{235}\text{U}$	1 σ	$^{206}\text{Pb}/^{238}\text{U}$	1 σ	$^{208}\text{Pb}/^{232}\text{Th}$	1 σ	$^{207}\text{Pb}/^{235}\text{U}$	1 σ	$^{206}\text{Pb}/^{238}\text{U}$	1 σ
09NZ09-1 Shima porphyritic granodiorite																
1	756	619	14.14	1.22	0.06481	0.00335	0.14342	0.00764	0.01612	0.00024	0.00505	0.00013	136	7	103	1
2	741	593	13.24	1.25	0.05656	0.00338	0.12039	0.00665	0.01587	0.00023	0.00475	0.00015	115	6	102	1
3	390	414	9.04	0.94	0.05882	0.00401	0.13020	0.00887	0.01647	0.00029	0.00527	0.00019	124	8	105	2
4	1142	806	18.48	1.42	0.04796	0.00266	0.10255	0.00546	0.01564	0.00022	0.00471	0.00013	99	5	100	1
5	478	520	11.19	0.92	0.05426	0.00351	0.11955	0.00752	0.01612	0.00026	0.00524	0.00020	115	7	103	2
6	466	448	9.74	1.04	0.05021	0.00390	0.10632	0.00802	0.01566	0.00027	0.00556	0.00022	103	7	100	2
7	681	605	13.78	1.13	0.06319	0.00438	0.13391	0.00878	0.01578	0.00025	0.00561	0.00017	128	8	101	2
8	626	575	12.43	1.09	0.06143	0.00425	0.12768	0.00805	0.01567	0.00024	0.00508	0.00015	122	7	100	1
9	414	446	9.27	0.93	0.05225	0.00373	0.11414	0.00808	0.01595	0.00026	0.00509	0.00019	110	7	102	2
10	646	577	13.01	1.12	0.05391	0.00327	0.11914	0.00686	0.01630	0.00022	0.00558	0.00017	114	6	104	1
11	370	431	9.19	0.86	0.06016	0.00412	0.13019	0.00872	0.01586	0.00028	0.00552	0.00018	124	8	101	2
12	863	690	15.70	1.25	0.05123	0.00386	0.10885	0.00799	0.01556	0.00026	0.00489	0.00015	105	7	100	2
13	1037	783	19.43	1.32	0.06388	0.00419	0.14013	0.00895	0.01606	0.00026	0.00560	0.00019	133	8	103	2
14	521	551	11.56	0.95	0.05323	0.00350	0.11345	0.00751	0.01532	0.00024	0.00499	0.00017	109	7	98	2
15	697	583	13.61	1.20	0.04947	0.00356	0.10764	0.00726	0.01618	0.00024	0.00519	0.00014	104	7	103	2
09NZ17-1 Gaozi quartz diorite porphyry																
1	497	460	10.91	1.08	0.07097	0.00589	0.15345	0.01005	0.01709	0.00049	0.00517	0.00026	145	9	109	3
2	483	470	11.08	1.03	0.07843	0.00787	0.17871	0.01630	0.01730	0.00048	0.00499	0.00029	167	14	111	3
3	571	496	11.59	1.15	0.06150	0.00654	0.13395	0.01222	0.01689	0.00057	0.00493	0.00033	128	11	108	4
4	564	461	11.18	1.22	0.08205	0.00689	0.18394	0.01369	0.01725	0.00050	0.00479	0.00025	171	12	110	3
5	753	606	15.18	1.24	0.06751	0.00568	0.15699	0.01270	0.01753	0.00045	0.00527	0.00025	148	11	112	3
6	466	522	11.92	0.89	0.06991	0.00473	0.16223	0.01104	0.01719	0.00042	0.00548	0.00033	153	10	110	3
7	552	567	12.67	0.97	0.06892	0.00593	0.15460	0.01202	0.01653	0.00047	0.00485	0.00029	146	11	106	3
8	466	529	12.61	0.88	0.05817	0.00423	0.13986	0.00959	0.01778	0.00045	0.00552	0.00030	133	9	114	3
9	688	577	14.57	1.19	0.07560	0.00592	0.17472	0.01190	0.01740	0.00040	0.00512	0.00027	164	10	111	3
10	722	594	14.21	1.22	0.05793	0.00458	0.12217	0.00987	0.01618	0.00040	0.00517	0.00025	117	9	103	3
11	459	425	10.13	1.08	0.06826	0.00666	0.14995	0.01265	0.01714	0.00064	0.00513	0.00035	142	11	110	4
12	748	590	14.24	1.27	0.06696	0.00661	0.14621	0.01286	0.01610	0.00040	0.00514	0.00026	139	11	103	3
13	602	586	14.35	1.03	0.06707	0.00578	0.14772	0.01147	0.01712	0.00042	0.00561	0.00028	140	10	109	3
14	625	589	14.03	1.06	0.06274	0.00478	0.14208	0.01043	0.01724	0.00045	0.00492	0.00031	135	9	110	3
15	934	759	19.14	1.23	0.06448	0.00609	0.14423	0.01014	0.01768	0.00049	0.00506	0.00024	137	9	113	3

ppm, respectively, and the Th/U ratios vary between 0.86 and 1.42, typical of magmatic zircons. Fifteen spot analyses from 15 grains yield concordant results with a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 101.6 ± 1.1 Ma (Figure 5(a)), which is interpreted as the crystallisation age of the Shima porphyritic granodiorite. There is a systematic shift toward higher $^{207}\text{Pb}/^{235}\text{U}$ ages from the ICP-MS data because of the extremely low levels of ^{207}Pb .

5.2 Gaozi pluton

The zircons from the Gaozi quartz diorite porphyry (sample 09NZ17-1) are euhedral, colourless to grey and 80–150 μm in length with an elongation ratio of 1:1–3:1. The typical CL images of the zircons (Figure 6) show that most of the zircons display clear internal structure and well-developed

oscillatory zoning.

Fifteen spot analyses were conducted on 15 zircons from the Gaozi quartz diorite porphyry (09NZ17-1). The zircon U-Pb data for the Gaozi quartz diorite porphyry are presented in Table 1. The uranium and thorium concentrations vary from 425 to 759 ppm and 459 to 934 ppm, respectively, and the Th/U ratios vary between 0.88 and 1.27, typical of magmatic zircons. In the zircon U-Pb concordia diagrams (Figure 5(b)), there is a deviation toward concordant curves for some samples because of the small variation in the zircon $^{206}\text{Pb}/^{238}\text{U}$ ages and the wide range of the zircon $^{207}\text{Pb}/^{235}\text{U}$ ages, which may be due to the extremely low concentrations of young radiogenic ^{207}Pb in the zircon and the low test accuracy. In summation, a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 109.1 ± 1.9 Ma is interpreted as the crystallisation age of the Gaozi quartz diorite porphyry.

Figure 5 LA-ICP-MS zircon U-Pb concordia diagrams for (a) porphyritic granodiorite (sample 09NZ09-1) and (b) quartz diorite porphyry (sample 09NZ17-1).

Figure 6 Cathodoluminescence (CL) images with U-Pb ages (Ma) of the representative zircons from Gaozi quartz diorite porphyry (sample 09NZ17-1).

5.3 The timing of metallogenesis in the Cishantou iron deposit

Analytical results from the phlogopite coexisting with magnetite in the Cishantou iron deposit are listed in Table 2. The plateau and isochron ^{40}Ar - ^{39}Ar ages of the phlogopite are shown in Figure 7. Eleven consequent steps, with apparent ages between 94.6 and 104.1 Ma for the phlogopite (sample 09NZ33), define a plateau age of 104 ± 1 Ma (Figure 7). An isochron age of 104.2 ± 1.2 Ma (MSWD=0.2), calculated from all steps, is in good agreement with the plateau age. The ^{40}Ar - ^{36}Ar intercept of 241 ± 30 is distinguishable from the air $^{40}\text{Ar}/^{36}\text{Ar}$ ratio (295.5 ± 5) to some extent, probably due to excess ^{40}Ar (mostly $>90\%$) [34]. The data yielded a generally flat ^{40}Ar - ^{39}Ar age spectrum, suggesting a closed system behaviour. Therefore, the plateau age of the phlogopite (104 ± 1 Ma) has geological significance and may represent the cooling age for the formation of phlogopite.

6 Discussion

6.1 Timing of diagenesis

Precise and accurate isotopic age determinations of the intrusive rocks are crucial for understanding the geodynamic background. Previously, the ages of the Yanshanian intrusive rocks in the Ningzhen region have been poorly constrained using whole-rock K-Ar and Rb-Sr methods. These age data provide a loose constraint on the timing of the magmatism in the Ningzhen area. For example, previous mineral K-Ar, zircon U-Pb and whole-rock K-Ar age data indicated that the Shima pluton in the Ningzhen region was emplaced between 109.6 and 82.8 Ma [35]. Ye [36] reported that the granodiorite porphyry in the Funiushan pluton in the Ningzhen region formed 111 ± 1 Ma ago, based on whole-rock Rb-Sr methods. The spread of these ages suggests that they cannot provide precise constraints on the timing of magmatism in the Ningzhen region.

Table 2 ^{40}Ar - ^{39}Ar data of phlogopite in the Cishantou skarn iron deposit, Ningzhen region

Sample and step	Laser power (W)	$^{40}\text{Ar}/^{39}\text{Ar}$	$^{37}\text{Ar}/^{39}\text{Ar}$	$^{36}\text{Ar}/^{39}\text{Ar}$	$^{40}\text{Ar}/^{39}\text{Ar}_K$	$^{40}\text{Ar}^*(\%)$	$^{39}\text{Ar}_K(\%)$	K/Ca	Age (Ma)	$\pm 2\sigma$ (Ma)
09NZ33 ($J=0.0081871\pm0.0000409$)										
11G2033B	4.50	9.43699	0.04745	0.00967	6.57667	69.69	0.00408	0.43	94.610	0.86
11G2033C	5.00	8.04693	0.02045	0.00274	7.23507	89.91	0.00909	0.43	103.82	0.78
11G2033D	5.30	8.34939	0.02198	0.00377	7.23417	86.64	0.00861	0.43	103.81	0.52
11G2033E	5.60	7.93758	0.01276	0.00230	7.25609	91.41	0.00933	0.43	104.11	0.48
11G2033F	6.00	7.80293	0.00558	0.00189	7.24410	92.84	0.01893	0.43	103.94	0.50
11G2033G	6.40	7.77830	0.00930	0.00177	7.25468	93.27	0.01520	0.43	104.09	0.49
11G2033H	6.90	7.73487	0.01488	0.00164	7.24902	93.72	0.00997	0.43	104.01	0.48
11G2033L	7.60	7.69309	0.01159	0.00150	7.24960	94.24	0.01202	0.43	104.02	0.47
11G2033I	8.50	7.86385	0.04245	0.00215	7.22776	91.91	0.00350	0.43	103.72	0.68
11G2033J	10.00	8.00079	0.11983	0.00271	7.19757	89.96	0.00140	0.43	103.29	1.23
11G2033K	15.00	7.87279	0.07930	0.00229	7.19504	91.39	0.00173	0.43	103.26	1.81

Figure 7 (a) Plateau and (b) isochron ^{40}Ar - ^{39}Ar ages of phlogopite in the Cishantou iron deposit, Ningzhen region.

In this paper, we report new LA-ICP-MS zircon U-Pb ages of the Shima porphyritic granodiorite and the Gaozi quartz diorite porphyry in the Ningzhen region, which yielded ages of 101.6 ± 1.1 Ma and 109.1 ± 1.9 Ma, respectively. The Anjishan granodiorite porphyry was dated at 106.9 ± 0.9 Ma using the SHRIMP zircon U-Pb method [15]. All these newly obtained, precise U-Pb ages demonstrate that the Mesozoic intermediate-acid magmatism in the Ningzhen region dates to approximately 109–101 Ma, clearly younger than the time of the Mesozoic magmatism in other regions of the middle-lower Yangtze River belt. Therefore, the Mesozoic intermediate-acid magmatism in the Ningzhen region may represent a separate period of diagenesis in the middle-lower Yangtze River belt.

6.2 Timing of metallogenesis

The precise dating of the deposits is the foundation for a model of metallogenic geodynamics. It has been demonstrated in many studies that ^{40}Ar - ^{39}Ar dating of phlogopite can be used to reliably date ore deposits [37,38]. Mineral assemblage studies show that the phlogopite is intergrown with magnetite in the Cishantou iron deposit. These miner-

als are both products of the same stage of mineralisation. Consequently, we assume that the well-defined plateau ages of phlogopite constrain the ages of the Cishantou iron deposit. As shown in this paper, the phlogopite samples display excellent agreement between their plateau and isochron ages within the analytical uncertainty. Therefore, the well-defined plateau age of 104 ± 1 Ma of phlogopite is accurate and considered to be a reliable estimate for the time of mineralisation of the Cishantou iron deposits. At present, a few ages of the mineralisation in the Ningzhen region have been obtained. For instance, molybdenite Re-Os isochron ages of 108 ± 2 Ma and 106 ± 3 Ma were reported in the Anjishan and Tongshan deposits, respectively [12]. The zircon U-Pb dates indicate that Mesozoic intermediate-acid intrusive rocks in the Ningzhen region were emplaced in the Early Cretaceous, ranging from 109 Ma to 101 Ma ago. These ages suggest that crystallisation of the intermediate-acid intrusive rocks and initiation of the mineralisation are temporally and possibly also genetically related. The phlogopite in the Cishantou skarn deposits yielded an ^{40}Ar - ^{39}Ar plateau age of 104 ± 1 Ma, coinciding with the ages of the Anjishan and Tongshan porphyry-skarn copper and iron polymetallic deposits in the Ningzhen region.

Consequently, these deposits in the Ningzhen region belong to one set of the Early Cretaceous polymetallic metallogenic events in the middle-lower Yangtze River metallogenic belt.

6.3 Geochronological significance of diagenesis and metallogenesis

The middle-lower Yangtze River belt, which exhibits the characteristics of multistage igneous diagenesis and metallogenesis, is an important area of large-scale Mesozoic diagenesis and metallogenesis in eastern China [2,39]. Beginning in the early 1970s, a large number of radiometric age dates have been reported for the Mesozoic igneous rocks in the middle-lower Yangtze River metallogenic belt. According to our high-precision geochronological data together with recent high-precision geochronological studies (such as zircon LA-ICP-MS U-Pb, zircon SHRIMP U-Pb, molybdenite Re-Os and single-mineral Ar-Ar radiometric dates) of the Mesozoic intrusive rocks and deposits in the middle-lower Yangtze River belt, the Late Mesozoic intrusive magmatism ranges in age from 152 to 101 Ma, with a peak at approximately 140–135 Ma. Similar ages of mineralisation ages were obtained for the deposits, showing a close relationship between the mineralisation and Late Mesozoic intrusive magmatism in the middle-lower Yangtze River metallogenic belt.

The ages of the Mesozoic intrusive magmatism and mineralisation in the middle-lower Yangtze River metallogenic belt show a clear evolutionary trend from west to east (Figure 8). The earliest intrusive magmatism in this belt was recorded by the Yinzu diorite-gabbro complex (151.8 ± 2.7 Ma), in the Edong region [40], and the Shatanjiao quartz monzonite (151.8 ± 2.6 Ma), in the Tongling region [41]. Notably, the Shima intrusion (101 Ma), in the Ningzhen region, is younger than any of the other intrusions in the middle-lower Yangtze River belt.

Based on an analysis of published high-precision zircon U-Pb ages, molybdenite Re-Os ages, and phlogopite ^{40}Ar - ^{39}Ar ages for the Late Mesozoic intrusions and associated mineralisation together with our high-precision geo-

chronological data from the Ningzhen region, we recognise four periods of magmatism and ore formation in the middle-lower Yangtze River metallogenic belt.

The first period occurred 152–135 Ma ago. The main phase of emplacement of the high-K calc-alkaline diorites in the Edong, Tongling and Luzong regions was associated with the porphyry, skarn and stratabound Cu-Au mineralisation and represented a significant magmatic event in the middle-lower Yangtze River belt [42,43]. These diorites are I-type, and previous workers have argued that they are adakitic rocks.

The second period occurred 135–127 Ma ago. During this period, the main phase of emplacement of K-rich alkaline volcanic rocks (including trachyandesite, trachyte, andesite and basalt) was associated with U-Au mineralisation and was concentrated in the basins of Fanchang, Luzong, Ningwu and Lishui [7,44–46].

The third period occurred 127–121 Ma ago. During this period, the main phase of emplacement of A-type granites and Na-rich basic rocks was related to Fe mineralisation and was concentrated in the basins of Fanchang and Ningwu [7,47].

The fourth period occurred 109–101 Ma ago. During this period, the main phase of emplacement of the high-K calc-alkaline granitoids and associated Cu-Fe mineralisation was concentrated in the Ningzhen region. The Mesozoic intermediate-acid magmatism and mineralisation in this region belonged to the latest episode in the middle-lower Yangtze River metallogenic belt, which is of great significance in understanding the tectonic-magmatic-metallogenic evolution of the middle-lower Yangtze River belt.

7 Conclusion

(1) The zircon U-Pb dates presented results in this paper indicate that the intermediate-acid intrusive rocks in the Ningzhen region were emplaced in the Early Cretaceous, between 109 and 101 Ma.

(2) Phlogopite in the Cishantou skarn deposits yielded an

Figure 8 Age distribution of Mesozoic (a) intrusive rocks and (b) mineral deposits in the middle-lower Yangtze River metallogenic belt. For the corresponding age data and references, see Tables S1 and S2.

^{40}Ar - ^{39}Ar plateau age of 104 ± 1 Ma, coinciding with the ages of the Anjishan and Tongshan porphyry-skarn deposits in the Ningzhen region. Consequently, these deposits in the Ningzhen region are one part of the Early Cretaceous polymetallic metallogenic events in the middle-lower Yangtze River metallogenic belt.

(3) There were four periods (152–135 Ma, 135–127 Ma, 127–121 Ma, 109–101 Ma) of magmatism and ore formation in the middle-lower Yangtze River metallogenic belt. The Mesozoic intermediate-acid magmatism and mineralization in the Ningzhen region are the products of the latest diagenesis and metallogenesis in the middle-lower Yangtze River metallogenic belt.

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Supporting Information

- Table S1** List of representative Mesozoic intrusive rocks in the Middle-Lower Yangtze River metallogenic belt (Age data used for constructing charts in Figure 8(a))
- Table S2** List of representative Mesozoic mineral deposits in the Middle-Lower Yangtze River metallogenic belt (Age data used for constructing charts in Figure 8(b))

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