Petrology, geochemistry and zirconology of impure calcite marbles from the Precambrian metamorphic basement at the southeastern margin of the North China Craton

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ABSTRACT

Impure calcite marbles from the Precambrian metamorphic basement of the Wuhe Complex, southeastern margin of the North China Craton, provide an exceptional opportunity to understand the depositional processes during the Late Archean and the subsequent Palaeoproterozoic metamorphic evolution of one of the oldest cratons in the world. The studied marbles are characterized by the assemblage calcite + clinopyroxene + plagioclase + K-feldspar + quartz + rutile ± biotite ± white mica. Based on petrography and geochemistry, the marbles can be broadly divided into two main types. The first type (type 1) is rich in REE with a negative Eu anomaly, whereas the second type (type 2) is relatively poor in REE with a positive Eu anomaly. Notably, all marbles exhibit remarkably uniform REE patterns with moderate LREE/HREE fractionation, suggesting a close genetic relationship.

Cathodoluminescence imaging, trace elements and mineral inclusions reveal that most zircons from two dated samples display distinct core-rim structures. Zircon cores show typical igneous features with oscillatory growth zoning and high Th/U ratios (mostly in the range 0.3–0.7) and give ages of 2.53−2.48 Ga, thus dating the maximum age of deposition of the protolith. Zircon rims overgrew during granulite-facies metamorphism, as evidenced by calcite + clinopyroxene + rutile + plagioclase + quartz inclusions, by Ti-in-zircon temperatures in the range 660-743 °C and by the low Th/U (mostly < 0.1) and Lu/Hf (<0.001) ratios. Zircon rims from two samples yield ages of 1839 ± 7 Ma and 1848 ± 23 Ma, respectively, suggesting a Palaeoproterozoic age for the granulite-facies metamorphic event. These ages are consistent with those found in other Precambrian basement rocks and lower-crustal xenoliths in the region, and are critical for the understanding of the tectonic history of the Wuhe Complex.

Positive Eu anomalies and high Sr and Ba contents in type 2 marbles are ascribed to syn-depositional felsic hydrothermal activity which occurred at 2.53−2.48 Ga. Our results, together with other published data and the inferred tectonic setting, suggest that the marbles protolith is an impure limestone, rich in detrital silicates of igneous origin, deposited in a back-arc basin within an active continental margin during the late Archean and affected by synchronous high-*T* hydrothermalism at the southeastern margin of the North China Craton.

Keywords: Zircon; impure calcite marble; partial melting; granulite-facies metamorphism; North China Craton.

1. Introduction

Marbles have been widely used to characterize metamorphic *P-T* evolution and fluid regime in metamorphic terrains (e.g., Boulvais et al., 2000; Castelli et al., 2007; Proyer et al., 2014). Nevertheless, it is often difficult to constrain their timing of formation and age of metamorphism because of the lack of appropriate geochronometers and/or the failure of datable minerals to grow during diagenesis or metamorphism. Although detrital zircons are ubiquitous in continental clastic sediments, they are rare in marbles. Under certain circumstances, however, marbles may contain few zircons; for example, zircons may be deposited synchronously with carbonate-rocks or they may form due to magmatic hydrothermal activity coeval to the formation of the marble protoliths. Because U and Pb are less mobile in zircon than in carbonate rocks, U-Pb dating on zircon can provide reliable geochronological constrains on the deposition timing of impure carbonate rocks. Furthermore, zircon rims of metamorphic origin (e.g., Rubatto et al., 2001; Möller et al., 2002; Rubatto, 2002; Whitehouse & Platt, 2003; Liu et al., 2004a, 2006, 2007a,b, 2009b) allow *in situ* U-Pb dating of metamorphic events as defined and characterized by inclusions of metamorphic minerals in zircon.

The North China Craton (NCC) is one of the oldest cratons in the world and there are numerous U-Pb zircon geochronological data on its Precambrian metamorphic basement. These data show that, except for minor >3.6 Ga components (Liu et al., 1992; Zheng et al., 2004; Wu et al., 2008), basement rocks have U–Pb zircon ages mainly clustering around 1.8–1.9 and ~2.5 Ga (e.g., Zhao et al., 2000, 2001, 2005; Wilde et al., 2002; Zheng et al., 2004; Guo et al., 2005; Wan et al., 2006; Tang et al., 2007; Liu et al., 2009a,b, 2011a, 2013; Tam et al., 2011; Zhai & Santosh, 2011; Zhang et al., 2012; Wang et al., 2012, 2013). The 2.5 Ga age was considered to coincide with a stage of major crustal growth of the NCC (Liu et al., 2009a, 2013). In addition, the basement rocks show a large range of Nd and Hf model ages with a peak at ~2.7 Ga, which is also considered to be a major crustal growth period in the NCC (Jiang et al., 2010). Based on Nd model ages, Wu et al. (2005) suggested that 2.8 Ga is the best estimate of the major mantle extraction age for the basement of the NCC. Zhai et al. (2005) considered that the 2.9–2.7 Ga age corresponds to the main crust-forming episode in the NCC, and that the ~2.5 Ga age reflects a high-grade metamorphic event. However, very few geochronological studies have focused on the Precambrian of the southeastern margin of the NCC.

In the southeastern margin of the NCC, the Precambrian metamorphic basement is exposed in the Bengbu and neighboring areas (Xu et al., 2006b; Guo and Li, 2009; Liu et al., 2009b; Wan et al., 2010; Yang et al., 2012; Wang et al., 2013) (Fig. 1), and mainly includes the Huoqiu Complex and the Wuhe Complex. The Huoqiu Complex consists mainly of biotite-plagioclase gneiss, quartzite, mica schist, marble, banded iron formation and amphibolite, and the meta-sedimentary rocks contain abundant ~3.0 and ~2.7 Ga detrital zircons with metamorphic overgrowths at ~1.85 Ga (Wan et al., 2010). The Wuhe Complex consists of Precambrian metamorphic mafic and felsic rocks of igneous origin and supracrustal rocks intruded by Mesozoic granitoids (Fig. 1). The intrusive contacts between the Mesozoic granitoids and the country rocks of the Wuhe Complex are still observable in the field, and the Mesozoic granitoids have been extensively investigated (Xu et al., 2005; Wang et al. 2009; Yang et al., 2010; Liu et al., 2012; Li et al., 2014).

The main rock types in the Wuhe Complex are garnet-granulite, garnet-amphibolite, mica schist, quartzite, meta-sandstone, marble and various gneisses; this rock association is similar to that of the Houqiu Complex, west of Bengbu (Wan et al., 2010). Due to the poor outcrop exposure, the Wuhe Complex has not received much attention as concerning its geochronology and petrogenesis, and only sparse geochronological data have been published so far. The formation time of the Wuhe Complex was previously considered to be late Archean on the 1:200000 regional geological map of the Bureau of Geology and Mineral Resources of Anhui Province (1979). Tu (1994) obtained zircon U-Pb ages of 2408 ± 13 – 2455 ± 10 Ma by conventional isotope dilution multigrain or single zircon analysis for biotite-plagioclase gneisses, and considered these ages as representative of the protolith age. Recently, several precise U-Pb geochronological data were reported for the Wuhe Complex. Xu et al. (2006b) reported LA-ICP-MS zircon U-Pb ages from a garnet-plagioclase pyroxenite and interpreted the obtained 1833 ± 8 Ma age to represent the timing of formation of the Wuhe Complex; they further proposed that the Wuhe Complex experienced metamorphism shortly after its formation. Guo and Li (2009) reported a metamorphic age of 1870 ± 10 Ma for the granulite-facies stage from a garnet-amphibolite by zircon SHRIMP dating. Liu et al. (2009b) and Wang et al. (2013) yielded 1839 ± 31 Ma and 1876 ± 18 Ma ages through SHRIMP zircon dating of a garnet-amphibolite and a garnet-granulite, respectively, and interpreted these ages as representative of the timing of the high-pressure (HP) granulite-facies metamorphism, in combination with zircon trace-element, mineral inclusion and petrological evidence.

Altogether, these studies suggest that the Wuhe Complex experienced granulite-facies metamorphism at 1.83−1.88 Ga, defined by a homogeneous metamorphic zircon population devoid of igneous core relics in most of the meta-basic rocks. However, the timing of protoliths formation is still a matter of debate.

In this paper, a successful SHRIMP U-Pb dating coupled with CL imaging, trace elements and mineral inclusions study and thermodynamic modeling, was conducted for the first time on zircons of two samples of impure marble from the Wuhe Complex. Our aim is to provide new insights on the age and tectonic setting of the Precambrian metamorphic basement at the southeastern margin of the NCC, with special emphasis on the protolith's nature and age. The results yield tight constraints on the maximum depositional age of the marble's protolith, as well as on the minimum (or retrograde) age of the granulite-facies metamorphic event. This study also provides evidence supporting the use of refractory zircons as provenance indicators, and provides insight into the petrogenesis and element mobility of the marbles.

2. Geological setting

The NCC is one of the largest and oldest cratonic blocks in the world, as evidenced by the presence of >3.6 Ga ancient crustal remnants occurring as metamorphic terrains or lower crustal xenoliths (Liu et al., 1992; Song et al., 1996; Zheng et al., 2004; Wu et al., 2008; Zhang et al., 2012). The NCC is bounded by faults and younger orogenic belts (Fig. 1): the early Palaeozoic Qilianshan orogen and the late Palaeozoic Tianshan–Inner Mongolia–Daxinganling orogen bound the NCC to the west and to the north, respectively, whereas to the south the Mesozoic Qinling–Dabie–Sulu high- to ultrahigh-pressure belt separates the NCC from the Yangtze Craton. The NCC underwent a series of tectonothermal events in the late Archean and Paleoproterozoic (e.g., Zhai et al., 2000; Zhao et al., 2000, 2001; Wilde et al., 2002; Kusky and Li, 2003; Zhai and Liu, 2003; Guo et al., 2005; Kröner et al., 2005; Wan et al., 2006, 2011, 2014; Hou et al., 2006, 2008; Tang et al., 2007; Guo and

Li, 2009; Liu et al., 2009a,b, 2011a, 2013; Jiang et al., 2010; Tam et al., 2011; Zhai and Santosh, 2011; Zhang et al., 2012; Wang et al., 2012, 2013), and was stabilized during the late Paleoproterozoic (e.g., Zhai et al., 2000).

Based on ages, lithological assemblages, tectonic evolution and P–T–t paths, the NCC can be divided in the Eastern Block, the Western Block and the Trans-North China Orogen or Central Orogenic Zone in between (e.g., Zhao et al., 2000, 2001; Kusky and Li, 2003; Zhai and Liu, 2003). The study area is located in the Eastern Block along the southeastern margin of the NCC, which is bounded by the Tan-Lu fault zone to the east and the Dabie orogen to the south (Fig. 1).

As briefly stated before, the Precambrian metamorphic basement exposed here consists predominantly of the Huoqiu Complex (Wan et al., 2010) and the Wuhe Complex (Xu et al., 2006b; Liu et al., 2009b; Wang et al., 2013). The deformed Neoproterozoic to late Paleozoic cover and the late Archean to Paleoproterozoic metamorphic basement are intruded by small Mesozoic intrusions (Fig. 1b), composed mainly of granite and dioritic porphyry. The Precambrian metamorphic basement in the study area is mainly located around Bengbu (Xu et al., 2006b; Liu et al., 2009b; Wan et al., 2010; Wang et al., 2013) (Fig. 1a); in contrast, the Precambrian metamorphic basement is not exposed in the Xuzhou-Suzhou area, where abundant deep-seated enclaves or xenoliths occur within the Mesozoic intrusions (Xu et al., 2006a; Liu et al., 2009b, 2013; Wang et al., 2012).

The Wuhe Complex comprises a variety of lithologies, among which the most studied are meta-basic rocks. Previous studies documented that meta-basic rocks in the region have experienced HP granulite- and amphibolite-facies metamorphic events (Liu et al., 2009b; Wang et al., 2013). Metamorphic peak conditions have been preliminary estimated in the range 670–850 °C, 1.0–1.2 GPa on the basis of conventional thermobarometry applied to mineral assemblages observed in garnet-amphibolite (Liu et al., 2009b). Metamorphic peak has been inferred at 1839 ± 31 Ma on the basis of zircon geochronology on the same lithology (Liu et al., 2009b). This study focuses on impure calcite marbles enclosing these meta-basic rocks; the samples were collected at Fengyang near Bengbu (Figs. 1 and 2).

3. Petrography of samples

Five marble samples from the Precambrian basement of the Wuhe Complex were selected for this study. All the samples are impure calcite marbles with similar paragenesis but different mineral modes. Beside calcite, they contain variable amounts of silicates and accessory minerals, in particular clinopyroxene, plagioclase, K-feldspar, quartz, hornblende, white mica, biotite, epidote, titanite, magnetite (partially replaced by limonite), apatite, tourmaline, barite and rare rutile (Figs. 3 and 4; Table 1). The impure marbles host lenses or boudins of garnet-amphibolite and garnet-granulite, variable in size from a few centimeters to several tens of meters (Fig. 2a) (Liu et al., 2009b; Wang et al., 2013; this study). Except for Wm (white mica), other mineral abbreviations in figures and tables are after Whitney and Evans (2010).

The studied samples can be classified into two main types: silicate-rich (Type 1) and silicate-poor (Type 2) marbles. Type 1 is weakly deformed or undeformed (Fig. 3a–d), whereas Type 2 is strongly foliated (Fig. 3e–h).

3.1. Type 1 marble

The silicate-rich Type 1 marble (samples 12FY1-1 and 12FY1-2) consists mainly of calcite, quartz, clinopyroxene and minor biotite, plagioclase and K-feldspar (Fig. 3a-c); hornblende and epidote are secondary phases. Titanite, rutile, apatite, opaque minerals (magnetite, replaced by limonite), and barite occur as accessory minerals (Figs 3a–d & 4a,b). Plagioclase locally occurs as inclusion in clinopyroxene (Fig. 3c & 4a) and it is preserved in the overgrowth rim domains of zircon; it locally shows a discontinuous rim of K-feldspar (Fig. 4a). K-feldspar is mostly microcline; it locally contains few vermicular quartz inclusions (Fig. 3b), this microstructure being compatible with partial melting (Zhou et al., 2004). Hornblende partially replaces clinopyroxene at its rim (Fig. 3d). White mica is lacking in the matrix, but it has been observed as inclusion in the zircon metamorphic rims, thus suggesting that it was a stable phase during the prograde metamorphic evolution of this marble type.

3.2. Type 2 marble

The silicate-poor Type 2 marble (samples 12FY2, 12FY3-1 and 12FY4) consists mainly of calcite and white mica, minor plagioclase, K-feldspar and quartz and rare biotite and clinopyroxene. Hornblende and epidote are secondary minerals. Titanite, rutile, opaque minerals, tourmaline and apatite occur as accessory phases (Figs. 3e–h and 4c–f). Porphyroblastic K-feldspar is locally partially replaced at its rim by late

Ba-rich K-feldspar associated with quartz and plagioclase (Fig. 4c–e). Plagioclase porphyroblasts are sometimes replaced by K-feldspar, epidote and calcite (Fig. 4f).

All the investigated marbles show a consistent peak assemblage of calcite + clinopyroxene + quartz + plagioclase + K-feldspar ± biotite (type 1) ± white mica (type 2), with accessory rutile and titanite. In addition, based on petrographic observations, at least two generations of retrograde mineral assemblages can be locally recognized: (i) calcite + plagioclase + hornblende + white mica + biotite + titanite ± ilmenite; (ii) epidote + chlorite + calcite + magnetite. These assemblages are representative of amphibolite- and greenschist-facies metamorphism, respectively.

Following the metamorphic pressure peak (>1.0 GPa; Liu et al., 2009b), fluid access must have been very limited thus explaining the lack of complete retrograde reactions and the preservation of small-scale compositional gradients in feldspar. Furthermore, early K-feldspar porphyroblasts are often rimmed by late Ba-rich fine-grained K-feldspar together with quartz and plagioclase (Fig. 4c,e) or replaced by Ba-rich K-feldspar (Fig. 4d; Table 1). These microstructures are compatible with late K-feldspar being formed from a melt (Vernon and Collins, 1988; Holness and Sawyer, 2008; Sawyer, 2010; Holness et al., 2011).

4. Analytical methods

Zircons were extracted from two samples (12FY1-1 and 12FY4) by crushing and sieving, followed by magnetic and heavy liquid separation and hand-picking under binoculars. The zircon grains were mounted in epoxy, together with a zircon U–Pb standard TEM (417 Ma) (Black et al., 2003). The mount was then polished until all zircon grains were approximately cut in half. The internal zoning patterns of the crystals were observed by CL imaging at Beijing SHRIMP Center, Chinese Academy of Geological Sciences (CAGS).

Zircon was dated using a SHRIMP II at the Beijing SHRIMP Center. Uncertainties in ages are quoted at the 95% confidence level (2σ). A spot size of about 30μm was used. Common Pb corrections were made using measured ^{204}Pb. The SHRIMP analyses followed the procedures described by Williams (1998). Both optical photomicrographs and CL images were taken as a guide to select the U–Pb dating spots. Five scans through the mass stations were made for each age determination. Standards used were SL13, with an age of 572 Ma and U content of

238 ppm, and TEM, with an age of 417 Ma (Williams, 1998; Black et al., 2003). The U-Pb isotope data were treated following Compston et al. (1992) with the ISOPLOT program of Ludwig (2001). The representative CL images for the studied zircons are presented in Figs. 5 and 6. The U-Pb data for zircon dating are listed in Table 2.

Zircon trace element analyses were conducted by the laser ablation ICP-MS at the State Key Laboratory of Continental Dynamics, Northwest University in Xi'an, China. The Geolas Pro laser-ablation system was used for the laser ablation experiments. The Laser wavelength is 193 nm and ablation spot size is 32 μm. The laser frequency and beam energy are 10 Hz and 140 mJ respectively. The ICP-MS used was an Elan DRCII from PerkinElmer Sciex. Detailed analytical procedure was reported by Yuan et al. (2004). Element concentrations of zircons were calculated using Pepita software with the zircon SiO_2 contents as internal standard and the NIST610 as external standard. The simultaneous analysis data on NIST612 show that the accuracy and precision of trace elements are better than 10%. The limit of detection for the different REE varied from 0.02 to 0.09 ppm. The analytical data are listed in Table 3 and chondrite-normalized REE patterns are presented in Fig. 7.

Mineral inclusions in zircon were identified by a Nicolet FT Raman 960-ESP spectrometer with a 532 nm Ar laser excitation at CAS Key Laboratory of Crust–Mantle Materials and Environments at University of Science and Technology of China, Hefei. The beam size for Raman spectroscopy was 1~3 μm. Monocrystalline silicon was analyzed during the analytical session to monitor the precision and accuracy of the Raman data. The representative Raman spectra of mineral inclusions in zircon are shown in Figs. 8 and 9. Furthermore, minerals relevant for this study were analyzed with a JEOL JXA-8800R EMPA at the Institute of Mineral Resources, Chinese Academy of Geological Sciences (CAGS) in Beijing (operating conditions: 15 kV accelerating voltage; 20 nA beam current; 50 s counting time).

Whole-rock major and trace elements were determined by X-ray fluorescence spectrometry (XRF) and by ICP-MS, respectively, at the Langfang Laboratory, Hebei Bureau of Geology and Mineral Resources. Analytical uncertainties range from ±1 to ±5% for major elements and ±5% to ±10% for trace elements. Whole-rock analytical data are given in Table 4.

5. Results

5.1. CL images, trace elements and mineral inclusions in zircon

On the basis of CL images, mineral inclusions and trace elements, core-rim domains with sharp boundaries have been clearly recognized in zircons from the dated samples 12FY1-1 (Type 1) and 12FY4 (Type 2) (Figs. 5–9). Most of the cores exhibit oscillatory growth zoning with high Th/U ratios (mostly in the range 0.3–0.7), which is typical of igneous zircon (e.g., Hanchar and Rudnick, 1995; Gebauer et al., 1997; Corfu et al., 2003). Rare older inherited/xenocrystic zircons were occasionally found (Fig. 5j). However, some cores are truncated, embayed or irregularly shaped (Figs. 5a, h, l and 6a, c, e, h), suggesting that they were partially or completely resorbed, probably in the presence of a hydrous melt or fluid (e.g., Corfu et al., 2003). As shown in Fig. 7 and Tables 2 & 3, the igneous cores and overgrowth domains of zircons are characterized by distinctly high and low REE contents, and high (> 0.3) and low (< 0.2, mostly < 0.1) Th/U ratios, respectively. Generally, metamorphic zircons have Th/U ratio < 0.1–0.2, whereas igneous zircons have high Th/U ratio (> 0.2) (e.g. Rubatto et al., 1999; Hoskin and Schaltegger, 2003). Hence, the rim domains of the zircons are interpreted as metamorphic overgrowths on detrital igneous cores. This interpretation is supported by the clinopyroxene, plagioclase, white mica, rutile and quartz inclusions preserved within metamorphic zircon domains (Figs. 5c, h, i and 6b, g, i), compatible with medium- to high-grade metamorphic conditions (e.g., Indares, 2003; Pattison, 2003 and see the following Section 5.2).

In type 1 sample 12FY1-1, igneous cores in zoned zircons contain quartz + calcite + plagioclase + apatite + white mica, whereas white mica, calcite, quartz, clinopyroxene, rutile and plagioclase are included in metamorphic rims (Figs 5 & 8). In type 2 sample 12FY4, igneous zircon cores contain quartz + plagioclase + white mica + graphite + apatite, whereas white mica, calcite, quartz, graphite, clinopyroxene, rutile, plagioclase and biotite are included in metamorphic rims (Figs. 6 and 9).

5.2. P-T-X(CO_2) metamorphic evolution

The P-T-X(CO_2) evolution of the studied marbles has been qualitatively constrained by calculating two isobaric T-X(CO_2) pseudosections, using the bulk compositions of samples 12FY1-1 (Type 1) and 12FY3 (Type 2) (Table 4), because of their highest SiO_2 content (i.e. these are the most "impure" marbles) among the studied samples for each marble type. Pressure was fixed at 15 kbar, following previous estimate on meta-basic rocks associated to the marbles (Liu et al., 2009); results obtained at lower pressures are briefly discussed in the following. The two pseudosections allow to broadly interpret the prograde- to peak nature of the observed mineral assemblages, and to qualitatively discuss the fluid composition evolution. A more quantitative reconstruction of the P-T-X(CO_2) evolution of the studied marbles is beyond the aim of this work.

Isochemical phase diagrams in the NKCFMAST–HC (Na_2O-K_2O-CaO-FeO-MgO-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2) system were calculated using Perple_X (version 6.7.1, Connolly 1990, 2009) and the thermodynamic dataset and equation of state for H_2O–CO_2 fluid of Holland and Powell (1998, revised 2004). The following solid solution models were used: dolomite (Holland and Powell, 1998), garnet (Holland and Powell, 1998), amphibole (Wei and Powell, 2003; White et al., 2003), biotite (Tajcmanova et al., 2009), white mica (Coggon & Holland, 2002; Auzanneau *et al*., 2010), clinopyroxene (Holland and Powell, 1996), plagioclase (Newton et al., 1980) and scapolite (Kuhn, 2004), in addition to the binary H_2O-CO_2 fluid. Calcite, quartz, microcline, zoisite, rutile and titanite were considered as pure end-members.

The T-X(CO_2) pseudosection for Type 1 marbles is dominated by tri- and four-variant fields, with few five-variant fields. The most relevant features of the pseudosection are (Fig. 10): (i) calcite-bearing, dolomite-absent, mineral assemblages are limited to relatively high-T (> 700 °C), except for low X(CO_2) values; (ii) quartz is completely consumed at T > 800 °C; (iii) the clinopyroxene + K-feldspar assemblage is only stable in dolomite-absent fields, i.e. at T > 700 °C for X(CO_2) > 0.2; (iv) plagioclase is stable in the whole T-X(CO_2) region of interest; (v) biotite mainly occurs in a narrow stability field at 700–800 °C, together with calcite, quartz and clinopyroxene, whereas white mica is stable at T < 750 °C; (vi) garnet occurs at relatively high-T, only for low X(CO_2) values; zoisite and amphibole stability fields are also limited to low X(CO_2) values; (vii) rutile is stable up to T of 700–800°C, depending on X(CO_2), whereas titanite appears at higher T. The observed mineral assemblage in Type 1 marbles (Cal + Cpx + Pl + Kfs + Qz + Bt) is modeled by a narrow four-variant field at 775–820 °C and 0.4 < X(CO_2) < 0.8.

The P-T pseudosection for Type 2 marbles is dominated by tri-, four- and five-variant fields. The most relevant features of this pseudosection (Fig. 11) are similar to those described for Type 1 marbles as concerning the stability of carbonate minerals, clinopyroxene, quartz and white mica. A small amount of K-feldspar is stable at low-T conditions, biotite is stable at T > 700–750 °C, and the stability field of titanite is limited to very low or very high $X(CO_2)$ values. The observed mineral assemblage in Type 2 marbles (Cal + Wm + Cpx + Pl + Kfs + Qz + Bt) is modeled by a very narrow four-variant field at 730–750 °C and $0.25 < X(CO_2) < 0.42$, limited toward high-T by the disappearance of white mica.

The observed mineral assemblages in both marble types thus define granulite-facies high-T conditions of 730–800°C (at 15 kbar), and relatively high $X(CO_2)$ values of the coexisting fluid. These peak P-T conditions are in agreement with those estimated for the associated garnet-amphibolite using conventional thermobarometry (670-850 °C, 10-12 kbar; Liu et al., 2009b). The occurrence of Rt (and Wm for Type 1 marbles) included in zircon rims suggest that these zircon domains grew at T slightly lower than peak-T conditions (because these phases are not stable at peak-T conditions); on the other hand, the Cpx included in the same domains point to T > 700°C. Microstructural evidence thus constrains the growth of zircon rims at 700–750°C, for P = 15 kbar. However, neither micro-structural evidence nor the results of thermodynamic modeling allow to clarify if the zircon rims grew before or after the peak of metamorphism (i.e. if zircon rims are prograde or retrograde). In fact, any prograde T-$X(CO_2)$ internally buffered path crossing the Cpx-in and Dol-out curves (Figs. 10 and 11) may explain the mineral inclusions preserved in the overgrowth rims of zircon, as well as any retrograde path in the opposite direction.

It is worth noting that the results of pseudosection modelling (i.e. growth of zircon rims at 700–750°C, for P = 15 kbar) are in very good agreement with the independently estimated Ti-in-zircon temperatures obtained from the zircon rims (i.e. 660–743 °C; see the following section 5.3; Figs. 10b and 11b), thus confirming that 15 kbar is a reliable estimate for peak P conditions. Conversely, pseudosections modelled at lower pressures (i.e. 10 kbar; Supplementary Figs. 1 and 2) for the same bulk compositions yielded results not compatible with: (i) the independently estimated Ti-in-zircon temperatures: at P = 10 kbar, in fact, white mica is predicted to be stable at T < 630-640°C, and this is not compatible with the occurrence of white mica inclusions in zircon rims yielding Ti-in-zircon temperatures of 660-743°C; (ii) the peak P-T conditions inferred for the associated metabasic rocks: at P = 10 kbar, in fact, the observed peak mineral assemblages are modeled at 600-730°C, whereas peak-T for the garnet-amphibolite coexisting with marbles were constrained at 670–850 °C using conventional thermometers (Liu et al., 2009) and at 700–739 °C using the Ti-in-zircon thermometer (Wang et al., 2013).

5.3. Ti-in-zircon temperatures

Ti-in-zircon temperatures were calculated following the revised calibration of Ferry and Watson (2007) at α_{TiO2} = 0.6 and 1, respectively. Quartz is present in all the studied samples; the activity of SiO_2 thus was considered as 1. The activity of TiO_2 for zircons coexisting with rutile inclusions was set to be 1 whereas for the others it was considered as 0.6 as suggested by Watson and Harrison (2005). The Ti contents in zircons and the corresponding calculated temperatures are listed in Table 3 (using minimum temperature estimations at α_{TiO2} = 1 for discussion in the text). Core and rim domains in the analyzed zircons have Ti contents of 4.67–43.5 ppm and 3.69–9.73 ppm respectively (Table 3), yielding Ti-in-zircon temperatures of 679–906 °C (detrital igneous cores) and 660–743 °C (metamorphic rims), respectively.

Concerning zircon cores, recent studies (Liu et al., 2010, 2015; Timms et al., 2011) suggest that the highest temperature values defined by Ti-in-zircon and Zr-in-rutile may be the closest to the real temperatures, indicating the condition of zircon growth/crystallization, whereas the lower temperatures might be the consequence of re-equilibration. Hence, the higher temperatures (such as 906 °C estimated from one zircon igneous core domain) may represent the formation temperature of igneous zircon, while the lower ones probably represent the late re-equilibration temperature.

Concerning zircon rims, similar metamorphic temperatures of 700–739 °C have been estimated by Ti contents in zircons from the garnet-amphibolite coexisting with marbles (Wang et al., 2013). Moreover, these Ti-in-zircon temperatures are in very good agreement with the results of thermodynamic modeling (see Section 5.2), which suggest a T of 700–750 °C for the growth of metamorphic zircon rims. These temperatures are lower than those estimated for the peak assemblages based on the T-X(CO_2) pseudosections (i.e. 730-820°C) as well as the temperatures of 670–850 °C estimated for the HP granulite-facies metamorphism on the basis of garnet-clinopyroxene pairs and Zr-in-rutile thermometers for the garnet-amphibolite coexisting with marbles (Liu et al., 2009b). Both microstructural and thermo-barometric data thus suggest that zircon rims grew at temperatures slightly lower than peak-T conditions, most likely during early retrograde evolution of the studied marbles (see also Section 6.1). In this regard, the ages obtained from the overgrowth rims of zircon should therefore be considered as minimum-peak ages at granulite-facies conditions (Liu et al., 2016) (see the following Discussion).

5.4. Zircon U-Pb ages

Twenty-six U-Pb spot analyses were made on 21 zircon grains from sample 12FY1-1 (Table 2 and Fig. 12a), including 2 inherited/xenocrystic, 12 detrital igneous cores and 12 rims. Except for 5 spot analyses, the remaining 21 analyses of both igneous cores (10 spots) and metamorphic rim domains (11 spots) define a discordia line with an upper intercept age of 2498 ± 86 Ma and a lower intercept age of 1780 ± 66 Ma, corresponding to the Neoarchean crystallization ages of detrital zircons and late Paleoproterozoic metamorphism, respectively (Fig. 12a). The upper intercept age of 2498 ± 86 Ma is in good agreement with one near-concordant igneous core age of 2489 ± 13 Ma within error. Eight metamorphic rim domains of zircon record $^{206}Pb/^{238}U$ concordant ages ranging from 1807 to 1878 Ma with a weighted mean age of 1835 ± 6 Ma, consistent with the upper intercept age of 1839 ± 7 Ma defined by 11 spot analyses of rim domains within error. In addition, one inherited igneous zircon with a Th/U ratio of 0.34 defines a $^{206}Pb/^{238}U$ concordant age of 2680 ± 13 Ma.

Twenty-eight U-Pb spot analyses were made on 15 zircon grains from sample 12FY4 (Table 2; Fig. 12b). Except for 4 spot analyses, the 24 analyses of both detrital igneous cores (13 spots) and metamorphic rim domains (11 spots) define a discordia line with an upper intercept age of 2407 ± 64 Ma and a lower intercept age of 1683 ± 67 Ma, corresponding to the Neoarchean crystallization and the late Paleoproterozoic metamorphism, respectively (Fig. 12b). One near-concordant igneous core age is 2533 ± 11 Ma. Three metamorphic rim domains of zircon record $^{206}Pb/^{238}U$ concordant ages ranging from 1843 to 1864 Ma with a weighted mean age of 1850 ± 28 Ma, consistent with the upper intercept age of 1848 ± 23 Ma defined by 12 spot analyses of rim domains within error.

In summary, zircon from the two dated samples exhibit clear core-rim patterns evidenced by CL images, trace elements and mineral inclusions, each one with a discrete age record. All the rim domains of zircon from the two dated samples define identical $^{206}Pb/^{238}U$ concordant ages within analytical uncertainty, i.e. 1835 ± 6 Ma (sample 12FY1-1, Type 1) and 1850 ± 28 Ma (sample 12FY4, Type 2), respectively. In addition, detrital igneous cores of zircon preserved in the samples record 2489 ± 13 Ma and 2533 ± 11 Ma concordant ages. Only two inherited zircon cores were found in sample 12FY1-1 and one of them records a ~ 2.7 Ga concordant age (Fig. 12a; Table 2). The inherited igneous zircon has a Th/U ratio of 0.34 and includes plagioclase (Fig. 5j, k), both features suggesting a felsic origin (Amelin, 1998; Fedo et al., 2003).

5.5. Whole-rock major and trace elements

Five impure marble samples have been analyzed in this study and the results show a broad range in major- and trace-element compositions (Table 4; Figs 13 & 14). To facilitate the identification and understanding of geochemical trends, the samples are divided into two groups based on SiO_2 contents and rare earth element (REE) concentrations. This subdivision is consistent with the aforementioned petrographic classification based on the silicate assemblages. The first group (Type 1, samples 12FY1-1 and 12FY1-2) has high SiO_2 (37.22–45.17 wt%), Na_2O (2.26–2.59 wt%) and Al_2O_3 (7.66–9.40 wt%) contents, and is rich in REE (ΣREE = 55.05~80.14 ppm) with a marked negative Eu anomaly (Eu/Eu*= 0.59–0.63). By contrast, the second group (Type 2, samples 12FY2, 12FY3-1 and 12FY4) has low SiO_2 (4.63–12.63 wt%), Na_2O (0.06–0.44 wt%) and Al_2O_3 (0.86–1.82 wt%) contents, and it is relatively poor in REE (ΣREE = 8.56–18.77 ppm) with a weak to strong positive Eu anomaly (Eu/Eu* = 1.05–1.71). Type 1 samples have relatively high Zr and Nb contents (135–161.4 ppm and 8.62–10.1 ppm, respectively), and low Sr contents (306.4–401.1 ppm) opposite to Type 2 (low Zr and Nb contents of 22.8–46.5 ppm and 0.38–0.87 ppm, respectively, and high Sr contents of 750.6–1276 ppm). These features reflect the silicate mineral assemblages, because Type 1 marbles contain more clinopyroxene, titanite, ilmenite and zircon than Type 2 marbles. However, the two marble types have similar Nb/Ta, Zr/Hf, Er/Nd, Y/Ho, Sc/Y and Th/U ratios (Table 4), and near-identical REE patterns with moderate LREE/HREE fractionation (La_N/Yb_N= 7.19–9.96 and 9.64–13.79) (Fig. 13). In addition, the samples have high Ba and Sr contents of 172.6–1062 ppm and 306.4–1276 ppm, respectively (Table 4) and mostly display primitive-mantle normalized negative Nb– Ta and Ti anomalies (Fig. 14).

6. Discussion

6.1. Protolith and metamorphic ages of impure marbles

Dating the unfossiliferous Precambrian sedimentary rocks is often a difficult task (Nelson, 2001). The most reliable methods for directly determining depositional sedimentary ages are: (i) dating the interstratified volcanic rocks, such as those near the Precambrian–Cambrian boundary (e.g., Bowring et al., 1993; Bowring and Schmitz, 2003), or (ii) dating the time-of-deposition of authigenic xenotime overgrowths on detrital zircon grains (e.g., McNaughton et al., 1999).

Under certain circumstances, however, the age of the youngest detrital zircon in a population can approach the age of deposition (Nelson, 2001). Furthermore, the youngest U–Pb ages of zircon grains in a population of detrital zircons have been used to constrain maximum depositional ages of stratigraphic units (Rainbird et al., 2001; Brown and Gehrels, 2007; Dickinson and Gehrels, 2009). This approach is especially valuable for Precambrian strata lacking biostratigraphic age control (Jones et al., 2009) and for metamorphosed Phanerozoic strata lacking preserved fossils (Barbeau Jr et al., 2005). Therefore, U-Pb geochronology applied on detrital zircons may be a powerful method for constraining the depositional ages of carbonate rocks (Fedo et al., 2003; Tang et al., 2006). However, difficulties are often encountered in obtaining reasonable isochrones because the U-Pb isotopic system of carbonate rocks is prone to be disturbed by diagenesis or alteration.

Most of the zircons in the studied samples consist of a late-Archean core surrounded by a Palaeoproterozoic metamorphic rim (Figs. 5 and 6). The zircons in both dated samples define a discordia (Fig. 12):

- The two upper-intercept ages are similar (in the relatively narrow range of 2.53–2.48 Ga) and consistent (within analytical uncertainties) with the 2489 ± 13 Ma and 2533 ± 11 Ma ages obtained from concordant igneous zircon cores from the two samples. The two concordant ages have been obtained from the magmatic zircons that were not significantly subjected to Pb loss. In view of rare ~ 2.7 Ga inherited zircons (only two grains) in the dated samples, this is a good evidence that the zircons were predominantly derived from a single igneous source with or without rare contribution of terrigenous materials during deposition of the marble's protolith. The calcite, quartz and plagioclase inclusions within the igneous core domains of zircon and the tectonic setting mentioned above, both suggest that the 2.53–2.48 Ga igneous zircon grains should come from the adjacent arc (see below in detail), and are considered to represent the maximum age of deposition of the marble's protolith.

- The two lower-intercept ages are similar to the ages of 1835 ± 6 Ma and 1850 ± 28 Ma obtained from concordant metamorphic overgrowth rims of zircons from the two samples. In addition, granulite-facies mineral inclusions such as clinopyroxene, rutile, quartz and plagioclase (Figs. 5h, i and 6b, g, i) were found in the overgrowth rim domains. The zircon rims are further characterized by low REE contents, low Th/U and Lu/Hf ratios of < 0.2 and 0.001, and absent or slightly negative Eu anomalies (Tables 2 and 3; Fig. 7), indicating that they grew in the presence of garnet and plagioclase (e.g., Rubatto, 2002; Whitehouse and Platt, 2003; Liu et al., 2006, 2011b). Therefore, the ages of 1835 ± 6 Ma and 1850 ± 28 Ma should record the age of granulite-facies metamorphism. These results are very similar to the previously reported granulite-facies ages of 1839 ± 31 Ma from the garnet-amphibolite lenses associated to the marbles (Liu et al., 2009b); however, they are younger than the 1876 ± 18 Ma age from garnet-granulite in a nearby locality (Wang et al., 2013) and the 1.88–1.95 Ga age of peak metamorphism (Liu et al., 2016). This suggests that the 1.83–1.85 Ga ages should be interpreted as early-retrograde ages, and that zircon rims grew soon after the peak of metamorphism, still under granulite-facies conditions. This conclusion is also supported by mineral assemblages and compositions observed in zircon domains of both 1.88–1.95 Ga and 1.80–1.85 Ga from the garnet-amphibolites and garnet-granulites associated to the studied marbles (Wang et al., 2013; Liu et al., 2016). In these metabasic rocks, low-Na clinopyroxene (Na_2O < 0.7 wt%), plagioclase and garnet occur as common mineral inclusions with minor biotite within the 1.80–1.85 Ga metamorphic zircons, whereas garnet, rutile, quartz and plagioclase are occasionally discovered to be present in the 1.88–1.95 Ga metamorphic zircon domains. Based on thin-section observations and EMP analysis, the clinopyroxene inclusions in garnet contain high Na_2O contents (mostly 1.25–1.6 wt%), and generally coexist with rutile and quartz in the garnet amphibolite and garnet granulite, suggesting HP granulite metamorphism (Liu et al., 2009, 2013).

In addition, rare *c*. 2.7 Ga inherited zircons exhibit oscillatory zoning with Th/U ratios of 0.34–0.36 and plagioclase inclusions (Fig. 5j, k), probably suggesting a proximal earlier episode of felsic magmatism. This is in agreement with the zircon

U-Pb dating and Hf-isotope investigations of the lower-crustal xenoliths from the same region (Liu et al., 2013).

In summary, the zircon geochronological data combined with the petrological investigations in this study support a scenario in which the Wuhe Complex formed in the late Archean, consistent with data already obtained from the Precambrian granulite terrains and lower-crustal xenoliths in the NCC (Zhai and Santosh, 2011; Wang et al., 2012; Zhang et al., 2012; Liu et al., 2013). The Wuhe Complex subsequently experienced peak HP granulite-facies and early-retrograde metamorphism at 1.8–1.9 Ga, corresponding to the Paleoproterozoic collisional orogenic event along the Jiao-Liao-Ji belt (Liu et al., 2016).

6.2. Petrogenesis and element mobility of impure marbles

In detrital zircon analysis, the interpreted provenance of the zircon is commonly used to reconstruct the geological history of sedimentary basins and their surrounding source regions (Fedo et al., 2003). Zircon chemistry has been considered a potential provenance indicator because it is sufficiently variable in different source rocks to enable their identification (Amelin, 1998; Wilde et al., 2001; Fedo et al., 2003).

In this study, the igneous zircon cores showing late Archaean ages preserved in the impure marbles could be interpreted as deriving from either terrigenous detritus or volcaniclastic rocks that were deposited synchronously with the marble's protolith (i.e. limestone). The investigated igneous zircon cores mostly show prismatic and pyramidal faces and oscillatory growth zoning (Figs. 5a,f,j and 6c,e) while only a few exhibit poorly-rounded grains (Fig. 5d,i), indicating that they did not experience abrasion by long-distance mechanical transportation. Except for two older inherited grains, these zircon cores have similar ages and trace-element characters (Fig. 7). Therefore, we suggest that the zircon cores were derived from volcaniclastic deposits with a single igneous source, rather than from terrigenous detritus. A terrigenous origin is also ruled out by the lack of complex age-patterns and pitted surfaces and micro-fractures related to long distance mechanical abrasion (Fedo et al., 2003). The Ti-in-zircon thermometric results show that the investigated igneous zircon cores crystallized at high-T (up to 906 °C) conditions (Table 3), thus supporting the possibility that the igneous zircon cores might be formed in an arc system related to the late Archean (*c*. 2.5 Ga) oceanic subduction as previously proposed by Liu et al.

(2013).

This interpretation is also supported by the positive Eu anomalies observed for some of the analyzed marbles (Fig. 11), because the positive Eu anomalies in ancient marine sediments might be attributed to coeval magmatism and high-temperature (>250 °C) hydrothermal activity during the deposition of the marble's protolith (Michard and Albarède, 1986; Mitra et al., 1994; Mills and Elderfield, 1995; Bau and Dulski, 1996; Craddock et al., 2010). Such a hydrothermal activity has been described so far in mid-ocean ridge settings (e.g., Michard and Albarede, 1986; Campbell et al., 1988; Mitra et al., 1994; Bau and Dulski, 1999; Douville et al., 1999) and back-arc basins (Fouquet et al., 1993; Douville et al., 1999; Craddock and Bach, 2010; and references therein). On the other hand, the breakdown of K-feldspar during melting and minor silicate minerals may provide an alternative explanation for the positive Eu anomalies, low LREE and HREE.

In the two dated samples the igneous zircon cores with Th/U ratios of 0.2–0.8 (Table 2) possibly crystallized in a felsic melt, because zircons with Th/U > 1 and < 1 crystallize in mafic and felsic melts, respectively (Amelin, 1998). This hypothesis is further supported by the quartz and plagioclase inclusions (Figs. 5 and 6) preserved within igneous zircon cores (Wilde et al., 2001), and by the survival of the zircon cores themselves (Figs. 5 and 6), that was probably related to their originally large size (e.g. >120 μm radius; Watson, 1996), which is consistent with zircons crystallized in a felsic melt related to a coeval back-arc magma activity.

Owing to the northward oceanic subduction and the consequent arc magma activity reported in the region in the late Archean (*c*. 2.5 Ga), we therefore suggest that the growth of zircon cores was related to a high-*T* hydrothermal activity coeval with the deposition of carbonate sediments in a deep-sea back-arc setting. Therefore, the impure marble's protolith likely formed in a back-arc basin within a convergent plate margin. This hypothesis is also supported by the occurrence of the late Archean (*c*. 2.5 Ga) subduction-related magma activity in the region (Liu et al., 2013).

Further insights into the petrogenesis and element mobility of the studied marbles are provided by their REE abundances and patterns. It is commonly observed that the relative REE abundance in ancient marine limestones is not significantly modified by extensive diagenetic alteration (Banner et al., 1988). Elements with high charge density, especially the high field strength elements (HSFE; Nb, Ta, Zr and Hf) but also

Th and REE, are thought not to be easily transported by the fluid phase (e.g., Tatsumi et al., 1986; Keppler, 1996; Elliott et al., 1997; Kessel et al., 2005; Hermann and Rubatto, 2009). Therefore these elements (and/or related pairs) can be used as petrogenetic tracers of the marble protoliths (Plank and Langmuir, 1998; Boulvais et al., 2000; Tang et al., 2006; Liu et al., 2013). The studied marbles show similar constant values for "fluid-immobile" element ratios such as Nb/Ta, Zr/Hf, Er/Nd and Y/Ho (Table 4), thus suggesting a submarine hydrothermal sedimentary origin, because Nb–Ta, Zr–Hf and Y–Ho are considered analog element pairs, and their ratios are fairly constant in marine sediments (Nb/Ta ~14 and Zr/Hf ~35) (Plank & Langmuir, 1998) and high-T hydrothermal sediments/fluids (Y/Ho 26–34 and Zr/Hf 26–46) (Bau, 1996; Bau and Dulski, 1996; Bolhar and Van Kranendonk, 2007; and references therein). High major-element and REE abundances in the Type 1 are unlikely to be related to the influx of seawater from which the chemical sediment precipitated, but they are typical of clastic detritus instead (Boulvais et al., 2000). In other words, high or low major-element and REE abundances in marbles chiefly arise from the variable modal amount of silicates and accessory phases. The similar REE patterns and related element ratios are in good agreement with both similar precursor and metamorphic ages, indicative of a common formation and metamorphic process. In this regard, the positive Eu anomalies are largely derived from syn-depositional or closely coeval hydrothermal activity (Michard and Albarède, 1986; Bau and Dulski, 1996; Lewis et al., 1997) in the back-arc deep-sea basin at 2.53–2.48 Ga, whereas the negative Eu anomalies might be the result of dissolution of Eu-enriched minerals (feldspar) or of a progressive metasomatic overprint during hydrothermal alteration or post-sedimentation processes as suggested by Fulignati et al. (1999) and Boulvais et al. (2000). It could be argued that variable Eu anomalies may reflect fluctuations of the mixing ratios of high-T and low-T hydrothermal fluids as proposed by Bau and Dulski (1996). However, in that case, Eu anomalies should be either positive (strong high-T component) or absent (strong low-T hydrothermal component). This explanation is therefore not applicable to the investigated marbles, because they were collected from the same locality at Fengyang (Fig. 1b) and share a common formation and evolution history as mentioned above. Most of the samples show exceptionally high Ba and Sr contents, up to 1062 ppm and 1276 ppm, respectively (Table 4), and significant Ba and Sr enrichment in a spider diagram (Fig. 14), indicative of the occurrence of barite-and plagioclase-bearing assemblages (Figs. 3 and 4) as the possible result of the aforementioned syn-depositional felsic hydrothermal activity at 2.53−2.48 Ga and partial melting at the Palaeoproterozoic.

In addition, the HP granulite-facies metamorphism, and the subsequent LP granulite and amphibolite-facies retrogression might have modified to some extent the element and isotope zircon composition. On the one hand, these processes could have significantly re-equilibrated the Ti contents in both zircon cores and rims, resulting in a large spread of Ti concentrations which define a wide range of temperatures as stated before. Some zircon cores also underwent a pervasive recrystallization, as suggested by the young ages (e.g., 1853 ± 8 Ma and 1857 ± 12 Ma for analytical spots 12FY1-1-5.2 and 12FY4-9.1) statistically indistinguishable from the age of granulite-facies metamorphic rims. However, these zircon cores still preserve the elemental signatures of the protolith, characterized by high REE and P contents and high Lu/Hf ratios (> 0.001) (Tables 2 and 3; Figs. 7 and 12) and are commonly called recrystallized zircons (Hoskin and Black, 2000; Corfu et al., 2003).

In conclusion, the formation and evolution of the impure marbles was a multistage process involving a syn-depositional high-*T* hydrothermal alteration event of a calcareous sediment in a back-arc basin during late Archean, and a granulite-facies peak and early-retrograde metamorphic event during Palaeoproterozoic. Furthermore, the results presented in this paper combined with those previously published, indicate that the different lithologies from the Wuhe Complex experienced a common metamorphic evolution after 1.95 Ga, albeit with different protolith environments.

7. Conclusions

The integrated studies on zircon geochronology, petrology and geochemistry of impure marbles from the Precambrian metamorphic basement of the Wuhe Complex, provide new insights on the depositional processes and subsequent HP-HT metamorphic evolution that affected the southeastern margin of the NCC during the Late Archean and Paleo-Proterozoic. More in detail, the following conclusions can be drawn:

(1) The protolith of the impure marbles is a limestone rich in detrital silicates of igneous origin with a single source that was deposited in the late Archean (2.48−2.53

Ga) in a back-arc basin setting within an active continental margin and was affected by synchronous high-*T* hydrothermalism.

(2) The impure marbles together with the associated rocks such as garnet-amphibolite and garnet-granulite experienced 1.83−1.88 Ga granulite-facies metamorphism in the lower crust, and possibly a nearly coeval partial melting.

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Figure captions

Figure 1 (a). Geological sketch map of the Qinling–Dabie–Sulu collision zone and adjacent portions of the North China Craton (modified after Xu *et al.*, 2006a). (b). Geological sketch map of the Bengbu area. The inset shows the major tectonic division of China. YZ: Yangtze Craton; SC: South China Orogen. Also shown are the tectonic subdivisions of the North China Craton (Zhao *et al.*, 2005), where WB, TNCO and EB denote the Western Block, Trans-North China Orogen and Eastern Block, respectively.

Figure 2 Field occurrence of garnet amphibolite lens within marble (a) and impure marble with thin black layering (b) in the Wuhe complex of the Precambrian metamorphic basement at Fengyang.

Figure 3 Photomicrographs of impure marbles from the Wuhe complex at Fengyang in southeastern margin of the North China Craton. (a) Clinopyroxene + calcite + titanite + K-feldspar + quartz assemblage (sample 12FY1-1), plane-polarized light (PPL); (b) same view of (a) with microcline underlined by “tartan” twinning, cross-polarized light (CPL); (c) Plagioclase inclusion in clinopyroxene and calcite inclusion in hornblende (sample 12FY1-1), PPL; (d) Clinopyroxene partially replaced by hornblende at its rim (sample 12FY1-2), PPL; (e) Calcite and white mica porphyroclasts (sample 12FY2), PPL; (f) Tourmaline + calcite + titanite + hornblende assemblage and calcite porphyroblasts surrounded by fine-grained secondary calcite (sample 12FY3-1), PPL; (g) Clinopyroxene + calcite + titanite assemblage and calcite porphyroblasts surrounded by fine-grained aggregates of secondary calcite with evidence of deformation (sample 12FY3-1), PPL; (h) Foliation defined by oriented calcite and white mica porphyroclasts (sample 12FY4), PPL.

Figure 4 Back scattered electron (BSE) images showing characteristic mineral textures. (a) Plagioclase with quartz inclusions surrounded by a thin rim of K-feldspar in clinopyroxene, sample 12FY1-1; (b) K-feldspar + limonite + barite + epidote + Plagioclase + calcite assemblage, sample 12FY1-1; (c) K-feldspar porphyroblast with Ba-rich Kfs and Qz rim, sample 12FY2; (d) K-feldspar porphyroblast with replacement of Ba-rich Kfs, Qz and Mus, sample 12FY2; (e) K-feldspar porphyroblast with replacement of Ba-rich Kfs, Pl and Qz, sample 12FY3-1; (f)

Plagioclase porphyroblast with replacement of Kfs and Ep, sample 12FY3-1.

Figure 5 Cathodoluminescene (CL) images (a, b, d, f, h, j and l) and plane-polarized light (PL) images (c, e, g, i and k) of zircons from sample 12FY1-1. Zircons (b) and (c), (d) and (e), (f) and (g), (h) and (i), and (j) and (k) are the same grain, respectively. The open circles are spot analysis with available $^{206}Pb/^{238}U$ ages.

Figure 6 Cathodoluminescene (CL) images (a, c–f and h) and plane-polarized light (PL) images (b, g and i) of zircons from sample 12FY1-1. Zircons (a) and (b), (f) and (g), and (h) and (i) are the same grain, respectively. The open circles are spot analysis with available $^{206}Pb/^{238}U$ ages.

Figure 7 Chondrite-normalized REE patterns of zircons from samples 12FY1-1 (a) and 12FY4 (b). Black and red solid circles denote metamorphic overgrowth rim and igneous core domains of zircon, respectively; red open circles denote recrystallized zircons. Chondrite values are after Sun & McDonough (1989).

Figure 8 Representative Raman spectra of mineral inclusions in zircon from sample 12FY1-1. (a) Calcite; (b) white mica; (c) plagioclase; (d) clinopyroxene and calcite; (e) quartz; (f) rutile. These spectra also contain host zircon peaks at 201, 224–227, 354–358, 438–439, 972–975 and 1010 cm^{-1}.

Figure 9 Representative Raman spectra of mineral inclusions in zircon from sample 12FY4. (a) Calcite; (b) plagioclase and quartz; (c) clinopyroxene; (d) biotite and clinopyroxene; (e) white mica and graphite; (f) rutile and graphite. These spectra also contain host zircon peaks at 201–204, 223–227, 353–359, 437–441, 972–976 and 1000–1010 cm^{-1}.

Figure 10 (a) Isobaric T-X(CO_2) pseudosection for Type 1 marbles (bulk composition 12FY1-2), calculated at P = 15 kbar in the NKCMAST-HC system. White, light-, medium- and dark-grey fields are di-, tri-, quadri- and quini-variant fields, respectively. The peak assemblage field is reported in red; mineral phases observed as inclusions in zircon rims are reported in italic. The two white dashed arrows are internally buffered T-X(CO_2) paths compatible with both the observed peak assemblage and the observed mineral inclusions within zircon rims. (b) Stability fields of quartz, clinopyroxene, rutile and white mica as predicted by the T-X(CO_2) pseudosection reported in (a); the colored dotted lines are the phase-in boundaries, and the arrows point in the direction of increasing modal amount for each phase. These minerals are observed as inclusions within the metamorphic zircon rims; their predicted stability fields are consistent with the independently estimated Ti-in-zircon temperatures (i.e. zircon growth occurred in the presence of these mineral phases).

Figure 11 (a) Isobaric T-X(CO_2) pseudosection for Type 2 marbles (bulk composition 12FY3), calculated at P = 15 kbar in the NKCMAST-HC system. White, light-, medium-, dark- and very dark-grey fields are di-, tri-, quadri-, quini-and esa-variant fields, respectively. The peak assemblage field is reported in red; mineral phases observed as inclusions in zircon rims are reported in italic. The two white dashed arrows are internally buffered T-X(CO_2) paths compatible with both the observed peak assemblage and the observed mineral inclusions within zircon rims. (b) Stability fields of quartz, clinopyroxene, rutile, biotite and white mica as predicted by the T-X(CO_2) pseudosection reported in (a); the colored dotted lines are the phase-in boundaries, and the arrows point in the direction of increasing modal amount for each phase. These mineral phases are observed as inclusions within the metamorphic zircon rims; their predicted stability fields are consistent with the independently estimated Ti-in-zircon temperatures (i.e. zircon growth occurred in the presence of these mineral phases).

Figure 12 Zircon SHRIMP U-Pb dating for impure marbles from Bengbu. (a) Sample 12FY1-1 and (b) Sample 12FY4. Purple, red and black symbols denote U-Pb data from inherited, primary igneous and metamorphic domains of zircon, respectively.

Figure 13 Chondrite-normalized rare earth element patterns for the studied impure marbles. Normalization values are from Sun & McDonough (1989). Red and black symbols denote Type 1 and Type 2 samples, respectively. See the text for detailed explanation.

Figure 14 Primitive-mantle-normalized spider patterns for the studied impure marbles. Normalization values are from Sun & McDonough (1989). The symbols are the same as Figure 13.

Supplementary Fig. 1 (a) Isobaric T-X(CO_2) pseudosection for Type 1 marbles (bulk composition 12FY1-2), calculated at P = 10 kbar in the NKCMAST-HC system. White, light-, medium- and dark-grey fields as in Fig. 10. The peak assemblage field is reported in red; mineral phases observed as inclusions in zircon rims are reported in italic. (b) Stability fields of quartz, clinopyroxene, rutile and white mica as predicted by the T-X(CO_2) pseudosection reported in (a); the colored dotted lines are the phase-in boundaries, and the arrows point in the direction of increasing modal amount for each phase. These mineral phases are observed as inclusions within the metamorphic zircon rims; their predicted stability fields are not consistent with the independently estimated Ti-in-zircon temperatures (i.e. zircon growth occurred outside the stability field of white mica and rutile).

Supplementary Fig. 2 (a) Isobaric T-X(CO_2) pseudosection for Type 2 marbles (bulk composition 12FY3), calculated at P = 15 kbar in the NKCMAST-HC system. White, light-, medium-, dark- and very dark-grey fields as in Fig. 11. The peak assemblage field is reported in red; mineral phases observed as inclusions in zircon rims are reported in italic. (b) Stability fields of quartz, clinopyroxene, rutile, biotite and white mica as predicted by the T-X(CO_2) pseudosection reported in (a)); the colored dotted lines are the phase-in boundaries, and the arrows point in the direction of increasing modal amount for each phase. These mineral phases are observed as inclusions within the metamorphic zircon rims; their predicted stability fields are not consistent with the independently estimated Ti-in-zircon temperatures (i.e. zircon growth occurred outside the stability field of white mica and rutile).