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

26 Impure calcite marbles from the Precambrian metamorphic basement of the Wuhe 27 Complex, southeastern margin of the North China Craton, provide an exceptional opportunity to understand the depositional processes during the Late Archean and the 28 29 subsequent Palaeoproterozoic metamorphic evolution of one of the oldest cratons in the world. The studied marbles are characterized by the assemblage calcite + 30 31 clinopyroxene + plagioclase + K-feldspar + quartz + rutile  $\pm$  biotite  $\pm$  white mica. Based on petrography and geochemistry, the marbles can be broadly divided into two 32 33 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, 34 35 all marbles exhibit remarkably uniform REE patterns with moderate LREE/HREE 36 fractionation, suggesting a close genetic relationship.

Cathodoluminescence imaging, trace elements and mineral inclusions reveal that 37 most zircons from two dated samples display distinct core-rim structures. Zircon cores 38 39 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 40 maximum age of deposition of the protolith. Zircon rims overgrew during 41 granulite-facies metamorphism, as evidenced by calcite + clinopyroxene + rutile + 42 plagioclase + quartz inclusions, by Ti-in-zircon temperatures in the range 660-743 °C 43 and by the low Th/U (mostly < 0.1) and Lu/Hf (< 0.001) ratios. Zircon rims from two 44 45 samples yield ages of  $1839 \pm 7$  Ma and  $1848 \pm 23$  Ma, respectively, suggesting a Palaeoproterozoic age for the granulite-facies metamorphic event. These ages are 46 consistent with those found in other Precambrian basement rocks and lower-crustal 47 xenoliths in the region, and are critical for the understanding of the tectonic history of 48 the Wuhe Complex. 49

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.

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

## 61 **1. Introduction**

62 Marbles have been widely used to characterize metamorphic P-T evolution and 63 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 64 formation and age of metamorphism because of the lack of appropriate 65 geochronometers and/or the failure of datable minerals to grow during diagenesis or 66 metamorphism. Although detrital zircons are ubiquitous in continental clastic 67 sediments, they are rare in marbles. Under certain circumstances, however, marbles 68 69 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 70 71 the formation of the marble protoliths. Because U and Pb are less mobile in zircon 72 than in carbonate rocks, U-Pb dating on zircon can provide reliable geochronological constrains on the deposition timing of impure carbonate rocks. Furthermore, zircon 73 74 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 75 U-Pb dating of metamorphic events as defined and characterized by inclusions of 76 metamorphic minerals in zircon. 77

78 The North China Craton (NCC) is one of the oldest cratons in the world and there 79 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., 80 81 1992; Zheng et al., 2004; Wu et al., 2008), basement rocks have U-Pb zircon ages 82 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., 83 84 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 85 a stage of major crustal growth of the NCC (Liu et al., 2009a, 2013). In addition, the 86 87 basement rocks show a large range of Nd and Hf model ages with a peak at ~2.7 Ga, 88 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 89 90 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 91 episode in the NCC, and that the  $\sim 2.5$  Ga age reflects a high-grade metamorphic event. 92 However, very few geochronological studies have focused on the Precambrian of the 93

94 southeastern margin of the NCC.

95 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; 96 97 Liu et al., 2009b; Wan et al., 2010; Yang et al., 2012; Wang et al., 2013) (Fig. 1), and 98 mainly includes the Huoqiu Complex and the Wuhe Complex. The Huoqiu Complex consists mainly of biotite-plagioclase gneiss, quartzite, mica schist, marble, banded 99 100 iron formation and amphibolite, and the meta-sedimentary rocks contain abundant  $\sim$ 3.0 and  $\sim$ 2.7 Ga detrital zircons with metamorphic overgrowths at  $\sim$ 1.85 Ga (Wan et 101 102 al., 2010). The Wuhe Complex consists of Precambrian metamorphic mafic and felsic 103 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 104 the Wuhe Complex are still observable in the field, and the Mesozoic granitoids have 105 been extensively investigated (Xu et al., 2005; Wang et al. 2009; Yang et al., 2010; 106 Liu et al., 2012; Li et al., 2014). 107

108 The main rock types in the Wuhe Complex are garnet-granulite, garnet-amphibolite, mica schist, quartzite, meta-sandstone, marble and various 109 gneisses; this rock association is similar to that of the Houqiu Complex, west of 110 111 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 112 113 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 114 regional geological map of the Bureau of Geology and Mineral Resources of Anhui 115 116 Province (1979). Tu (1994) obtained zircon U-Pb ages of  $2408 \pm 13 - 2455 \pm 10$  Ma by conventional isotope dilution multigrain or single zircon analysis for 117 biotite-plagioclase gneisses, and considered these ages as representative of the 118 protolith age. Recently, several precise U-Pb geochronological data were reported for 119 120 the Wuhe Complex. Xu et al. (2006b) reported LA-ICP-MS zircon U-Pb ages from a garnet-plagioclase pyroxenite and interpreted the obtained  $1833 \pm 8$  Ma age to 121 represent the timing of formation of the Wuhe Complex; they further proposed that 122 123 the Wuhe Complex experienced metamorphism shortly after its formation. Guo and Li (2009) reported a metamorphic age of  $1870 \pm 10$  Ma for the granulite-facies stage 124 125 from a garnet-amphibolite by zircon SHRIMP dating. Liu et al. (2009b) and Wang et al. (2013) yielded 1839  $\pm$  31 Ma and 1876  $\pm$  18 Ma ages through SHRIMP zircon 126

127 dating of a garnet-amphibolite and a garnet-granulite, respectively, and interpreted 128 these ages as representative of the timing of the high-pressure (HP) granulite-facies 129 metamorphism, in combination with zircon trace-element, mineral inclusion and 130 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 136 elements and mineral inclusions study and thermodynamic modeling, was conducted 137 for the first time on zircons of two samples of impure marble from the Wuhe Complex. 138 Our aim is to provide new insights on the age and tectonic setting of the Precambrian 139 140 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 141 depositional age of the marble's protolith, as well as on the minimum (or retrograde) 142 age of the granulite-facies metamorphic event. This study also provides evidence 143 supporting the use of refractory zircons as provenance indicators, and provides insight 144 145 into the petrogenesis and element mobility of the marbles.

146

### 147 **2. Geological setting**

148 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 149 metamorphic terrains or lower crustal xenoliths (Liu et al., 1992; Song et al., 1996; 150 Zheng et al., 2004; Wu et al., 2008; Zhang et al., 2012). The NCC is bounded by 151 faults and younger orogenic belts (Fig. 1): the early Palaeozoic Qilianshan orogen and 152 the late Palaeozoic Tianshan-Inner Mongolia-Daxinganling orogen bound the NCC to 153 the west and to the north, respectively, whereas to the south the Mesozoic 154 Qinling-Dabie-Sulu high- to ultrahigh-pressure belt separates the NCC from the 155 Yangtze Craton. The NCC underwent a series of tectonothermal events in the late 156 157 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., 158 2005; Wan et al., 2006, 2011, 2014; Hou et al., 2006, 2008; Tang et al., 2007; Guo and 159

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 169 consists predominantly of the Huoqiu Complex (Wan et al., 2010) and the Wuhe 170 Complex (Xu et al., 2006b; Liu et al., 2009b; Wang et al., 2013). The deformed 171 172 Neoproterozoic to late Paleozoic cover and the late Archean to Paleoproterozoic metamorphic basement are intruded by small Mesozoic intrusions (Fig. 1b), 173 composed mainly of granite and dioritic porphyry. The Precambrian metamorphic 174 basement in the study area is mainly located around Bengbu (Xu et al., 2006b; Liu et 175 176 al., 2009b; Wan et al., 2010; Wang et al., 2013) (Fig. 1a); in contrast, the Precambrian 177 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., 178 179 2006a; Liu et al., 2009b, 2013; Wang et al., 2012).

The Wuhe Complex comprises a variety of lithologies, among which the most 180 181 studied are meta-basic rocks. Previous studies documented that meta-basic rocks in the region have experienced HP granulite- and amphibolite-facies metamorphic events 182 183 (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 184 conventional thermobarometry applied to mineral assemblages observed in 185 garnet-amphibolite (Liu et al., 2009b). Metamorphic peak has been inferred at  $1839 \pm$ 186 31 Ma on the basis of zircon geochronology on the same lithology (Liu et al., 2009b). 187 This study focuses on impure calcite marbles enclosing these meta-basic rocks; the 188 189 samples were collected at Fengyang near Bengbu (Figs. 1 and 2).

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#### 191 **3. Petrography of samples**

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Five marble samples from the Precambrian basement of the Wuhe Complex were

193 selected for this study. All the samples are impure calcite marbles with similar paragenesis but different mineral modes. Beside calcite, they contain variable 194 amounts of silicates and accessory minerals, in particular clinopyroxene, plagioclase, 195 K-feldspar, quartz, hornblende, white mica, biotite, epidote, titanite, magnetite 196 197 (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 198 199 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), 200 201 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).

205

# 206 *3.1. Type 1 marble*

The silicate-rich Type 1 marble (samples 12FY1-1 and 12FY1-2) consists mainly 207 of calcite, quartz, clinopyroxene and minor biotite, plagioclase and K-feldspar (Fig. 208 3a-c); hornblende and epidote are secondary phases. Titanite, rutile, apatite, opaque 209 minerals (magnetite, replaced by limonite), and barite occur as accessory minerals 210 (Figs 3a-d & 4a,b). Plagioclase locally occurs as inclusion in clinopyroxene (Fig. 3c 211 212 & 4a) and it is preserved in the overgrowth rim domains of zircon; it locally shows a 213 discontinuous rim of K-feldspar (Fig. 4a). K-feldspar is mostly microcline; it locally contains few vermicular quartz inclusions (Fig. 3b), this microstructure being 214 compatible with partial melting (Zhou et al., 2004). Hornblende partially replaces 215 clinopyroxene at its rim (Fig. 3d). White mica is lacking in the matrix, but it has been 216 observed as inclusion in the zircon metamorphic rims, thus suggesting that it was a 217 stable phase during the prograde metamorphic evolution of this marble type. 218

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## 220 *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  $\pm$  biotite (type 1)  $\pm$  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  $\pm$  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 235 access must have been very limited thus explaining the lack of complete retrograde 236 reactions and the preservation of small-scale compositional gradients in feldspar. 237 Furthermore, early K-feldspar porphyroblasts are often rimmed by late Ba-rich 238 fine-grained K-feldspar together with quartz and plagioclase (Fig. 4c,e) or replaced by 239 Ba-rich K-feldspar (Fig. 4d; Table 1). These microstructures are compatible with late 240 241 K-feldspar being formed from a melt (Vernon and Collins, 1988; Holness and Sawyer, 2008; Sawyer, 2010; Holness et al., 2011). 242

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## 244 **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 ( $2\sigma$ ). A spot size of about 30µm was used. Common Pb corrections were made using measured <sup>204</sup>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.

263 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. 264 The Geolas Pro laser-ablation system was used for the laser ablation experiments. The 265 Laser wavelength is 193 nm and ablation spot size is 32 µm. The laser frequency and 266 267 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 268 et al. (2004). Element concentrations of zircons were calculated using Pepita software 269 with the zircon SiO<sub>2</sub> contents as internal standard and the NIST610 as external 270 271 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 272 REE varied from 0.02 to 0.09 ppm. The analytical data are listed in Table 3 and 273 chondrite-normalized REE patterns are presented in Fig. 7. 274

Mineral inclusions in zircon were identified by a Nicolet FT Raman 960-ESP 275 276 spectrometer with a 532 nm Ar laser excitation at CAS Key Laboratory of Crust-Mantle Materials and Environments at University of Science and Technology 277 278 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 279 280 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 281 282 were analyzed with a JEOL JXA-8800R EMPA at the Institute of Mineral Resources, Chinese Academy of Geological Sciences (CAGS) in Beijing (operating conditions: 283 284 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  $\pm 1$  to  $\pm 5\%$  for major elements and  $\pm 5\%$  to  $\pm 10\%$  for trace elements. Whole-rock analytical data are given in Table 4.

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## 291 **5. Results**

#### 292 5.1. CL images, trace elements and mineral inclusions in zircon

On the basis of CL images, mineral inclusions and trace elements, core-rim 293 domains with sharp boundaries have been clearly recognized in zircons from the dated 294 samples 12FY1-1 (Type 1) and 12FY4 (Type 2) (Figs. 5–9). Most of the cores exhibit 295 296 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; 297 298 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, 299 300 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 301 302 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 (<303 0.2, mostly < 0.1) Th/U ratios, respectively. Generally, metamorphic zircons have 304 Th/U ratio < 0.1-0.2, whereas igneous zircons have high Th/U ratio (> 0.2) (e.g. 305 Rubatto et al., 1999; Hoskin and Schaltegger, 2003). Hence, the rim domains of the 306 307 zircons are interpreted as metamorphic overgrowths on detrital igneous cores. This interpretation is supported by the clinopyroxene, plagioclase, white mica, rutile and 308 309 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, 310 311 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).

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#### 319 5.2. *P*-*T*-*X*(*CO*<sub>2</sub>) metamorphic evolution

The P-T-X(CO<sub>2</sub>) evolution of the studied marbles has been qualitatively constrained by calculating two isobaric T-X(CO<sub>2</sub>) pseudosections, using the bulk compositions of samples 12FY1-1 (Type 1) and 12FY3 (Type 2) (Table 4), because of their highest SiO<sub>2</sub> 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<sub>2</sub>) evolution of the studied marbles is beyond the aim of this work.

Isochemical diagrams in the NKCFMAST-HC 331 phase (Na2O-K2O-CaO-FeO-MgO-Al2O3-SiO2-TiO2-H2O-CO2) system were calculated 332 333 using Perple X (version 6.7.1, Connolly 1990, 2009) and the thermodynamic dataset and equation of state for H<sub>2</sub>O–CO<sub>2</sub> fluid of Holland and Powell (1998, revised 2004). 334 The following solid solution models were used: dolomite (Holland and Powell, 1998), 335 garnet (Holland and Powell, 1998), amphibole (Wei and Powell, 2003; White et al., 336 2003), biotite (Tajcmanova et al., 2009), white mica (Coggon & Holland, 2002; 337 Auzanneau et al., 2010), clinopyroxene (Holland and Powell, 1996), plagioclase 338 (Newton et al., 1980) and scapolite (Kuhn, 2004), in addition to the binary H<sub>2</sub>O-CO<sub>2</sub> 339 fluid. Calcite, quartz, microcline, zoisite, rutile and titanite were considered as pure 340 341 end-members.

342 The T-X(CO<sub>2</sub>) pseudosection for Type 1 marbles is dominated by tri- and four-variant fields, with few five-variant fields. The most relevant features of the 343 344 pseudosection are (Fig. 10): (i) calcite-bearing, dolomite-absent, mineral assemblages are limited to relatively high-T (> 700 °C), except for low X(CO<sub>2</sub>) values; (ii) quartz 345 is completely consumed at T > 800 °C; (iii) the clinopyroxene + K-feldspar 346 assemblage is only stable in dolomite-absent fields, i.e. at T > 700 °C for  $X(CO_2) >$ 347 0.2; (iv) plagioclase is stable in the whole  $T-X(CO_2)$  region of interest; (v) biotite 348 mainly occurs in a narrow stability field at 700-800 °C, together with calcite, quartz 349 and clinopyroxene, whereas white mica is stable at T < 750 °C; (vi) garnet occurs at 350 351 relatively high-T, only for low X(CO<sub>2</sub>) 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, 352 depending on X(CO<sub>2</sub>), whereas titanite appears at higher T. The observed mineral 353 354 assemblage in Type 1 marbles (Cal + Cpx + Pl + Kfs + Qz + Bt) is modeled by a narrow four-variant field at 775–820 °C and  $0.4 < X(CO_2) < 0.8$ . 355

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<sub>2</sub>) 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<sub>2</sub>) < 0.42, limited toward high-T by the disappearance of white mica.

The observed mineral assemblages in both marble types thus define 365 granulite-facies high-T conditions of 730-800°C (at 15 kbar), and relatively high 366 X(CO<sub>2</sub>) values of the coexisting fluid. These peak P-T conditions are in agreement 367 with those estimated for the associated garnet-amphibolite using conventional 368 thermobarometry (670-850 °C, 10-12 kbar; Liu et al., 2009b). The occurrence of Rt 369 (and Wm for Type 1 marbles) included in zircon rims suggest that these zircon 370 domains grew at T slightly lower than peak-T conditions (because these phases are not 371 stable at peak-T conditions); on the other hand, the Cpx included in the same domains 372 373 point to  $T > 700^{\circ}$ C. Microstructural evidence thus constrains the growth of zircon rims at 700–750°C, for P = 15 kbar. However, neither micro-structural evidence nor 374 375 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 376 377 fact, any prograde T-X(CO<sub>2</sub>) internally buffered path crossing the Cpx-in and Dol-out 378 curves (Figs. 10 and 11) may explain the mineral inclusions preserved in the 379 overgrowth rims of zircon, as well as any retrograde path in the opposite direction.

380 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 381 independently estimated Ti-in-zircon temperatures obtained from the zircon rims (i.e. 382 660-743 °C; see the following section 5.3; Figs. 10b and 11b), thus confirming that 383 15 kbar is a reliable estimate for peak P conditions. Conversely, pseudosections 384 modelled at lower pressures (i.e. 10 kbar; Supplementary Figs. 1 and 2) for the same 385 386 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 387 388 at T < 630-640°C, and this is not compatible with the occurrence of white mica 389 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, 390

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).

- 395
- 396 5.3. Ti-in-zircon temperatures

397 Ti-in-zircon temperatures were calculated following the revised calibration of 398 Ferry and Watson (2007) at  $\alpha_{TiO2} = 0.6$  and 1, respectively. Quartz is present in all the studied samples; the activity of SiO<sub>2</sub> thus was considered as 1. The activity of TiO<sub>2</sub> 399 for zircons coexisting with rutile inclusions was set to be 1 whereas for the others it 400 was considered as 0.6 as suggested by Watson and Harrison (2005). The Ti contents in 401 zircons and the corresponding calculated temperatures are listed in Table 3 (using 402 403 minimum temperature estimations at  $\alpha_{TiO2} = 1$  for discussion in the text). Core and rim domains in the analyzed zircons have Ti contents of 4.67-43.5 ppm and 3.69-9.73 404 ppm respectively (Table 3), yielding Ti-in-zircon temperatures of 679–906 °C (detrital 405 igneous cores) and 660-743 °C (metamorphic rims), respectively. 406

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 414 been estimated by Ti contents in zircons from the garnet-amphibolite coexisting with 415 416 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 417 suggest a T of 700-750 °C for the growth of metamorphic zircon rims. These 418 temperatures are lower than those estimated for the peak assemblages based on the 419 T-X(CO<sub>2</sub>) pseudosections (i.e. 730-820°C) as well as the temperatures of 670–850 °C 420 estimated for the HP granulite-facies metamorphism on the basis of 421 garnet-clinopyroxene pairs and Zr-in-rutile thermometers for the garnet-amphibolite 422 coexisting with marbles (Liu et al., 2009b). Both microstructural 423 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).

429

## 430 *5.4. Zircon U-Pb ages*

Twenty-six U-Pb spot analyses were made on 21 zircon grains from sample 431 432 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 433 igneous cores (10 spots) and metamorphic rim domains (11 spots) define a discordia 434 line with an upper intercept age of  $2498 \pm 86$  Ma and a lower intercept age of  $1780 \pm$ 435 66 Ma, corresponding to the Neoarchean crystallization ages of detrital zircons and 436 late Paleoproterozoic metamorphism, respectively (Fig. 12a). The upper intercept age 437 of  $2498 \pm 86$  Ma is in good agreement with one near-concordant igneous core age of 438  $2489 \pm 13$  Ma within error. Eight metamorphic rim domains of zircon record 439 <sup>206</sup>Pb/<sup>238</sup>U concordant ages ranging from 1807 to 1878 Ma with a weighted mean age 440 of  $1835 \pm 6$  Ma, consistent with the upper intercept age of  $1839 \pm 7$  Ma defined by 11 441 spot analyses of rim domains within error. In addition, one inherited igneous zircon 442 with a Th/U ratio of 0.34 defines a  $^{206}$ Pb/ $^{238}$ U concordant age of 2680 ± 13 Ma. 443

Twenty-eight U-Pb spot analyses were made on 15 zircon grains from sample 444 445 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 446 447 line with an upper intercept age of  $2407 \pm 64$  Ma and a lower intercept age of  $1683 \pm$ 448 67 Ma, corresponding to the Neoarchean crystallization and the late Paleoproterozoic 449 metamorphism, respectively (Fig. 12b). One near-concordant igneous core age is 2533  $\pm$  11 Ma. Three metamorphic rim domains of zircon record <sup>206</sup>Pb/<sup>238</sup>U concordant ages 450 ranging from 1843 to 1864 Ma with a weighted mean age of  $1850 \pm 28$  Ma, consistent 451 with the upper intercept age of  $1848 \pm 23$  Ma defined by 12 spot analyses of rim 452 domains within error. 453

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  ${}^{206}\text{Pb}/{}^{238}\text{U}$  concordant ages within analytical uncertainty, i.e.  $1835 \pm 6$  Ma (sample 12FY1-1, Type 1) and  $1850 \pm 28$  Ma (sample 12FY4, Type 2), respectively. In addition, detrital igneous cores of zircon preserved in the samples record  $2489 \pm 13$ Ma and  $2533 \pm 11$  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).

464

## 465 5.5. Whole-rock major and trace elements

466 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). 467 To facilitate the identification and understanding of geochemical trends, the samples 468 are divided into two groups based on SiO<sub>2</sub> contents and rare earth element (REE) 469 470 concentrations. This subdivision is consistent with the aforementioned petrographic classification based on the silicate assemblages. The first group (Type 1, samples 471 12FY1-1 and 12FY1-2) has high SiO<sub>2</sub> (37.22-45.17 wt%), Na<sub>2</sub>O (2.26-2.59 wt%) 472 and Al<sub>2</sub>O<sub>3</sub> (7.66–9.40 wt%) contents, and is rich in REE ( $\Sigma$ REE = 55.05~80.14 ppm) 473 with a marked negative Eu anomaly (Eu/Eu\*= 0.59-0.63). By contrast, the second 474 475 group (Type 2, samples 12FY2, 12FY3-1 and 12FY4) has low SiO<sub>2</sub> (4.63–12.63 wt%), Na<sub>2</sub>O (0.06-0.44 wt%) and Al<sub>2</sub>O<sub>3</sub> (0.86-1.82 wt%) contents, and it is relatively poor 476 477 in REE ( $\Sigma REE = 8.56 - 18.77$  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 478 479 (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 0.38-0.87 480 481 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, 482 483 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 484 REE patterns with moderate LREE/HREE fractionation (La<sub>N</sub>/Yb<sub>N</sub>= 7.19-9.96 and 485 9.64-13.79) (Fig. 13). In addition, the samples have high Ba and Sr contents of 486 172.6-1062 ppm and 306.4-1276 ppm, respectively (Table 4) and mostly display 487 primitive-mantle normalized negative Nb- Ta and Ti anomalies (Fig. 14). 488

489

### 490 **6. Discussion**

491 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).

498 Under certain circumstances, however, the age of the youngest detrital zircon in a population can approach the age of deposition (Nelson, 2001). Furthermore, the 499 500 youngest U-Pb ages of zircon grains in a population of detrital zircons have been used 501 to constrain maximum depositional ages of stratigraphic units (Rainbird et al., 2001; 502 Brown and Gehrels, 2007; Dickinson and Gehrels, 2009). This approach is especially valuable for Precambrian strata lacking biostratigraphic age control (Jones et al., 2009) 503 and for metamorphosed Phanerozoic strata lacking preserved fossils (Barbeau Jr et al., 504 2005). Therefore, U-Pb geochronology applied on detrital zircons may be a powerful 505 method for constraining the depositional ages of carbonate rocks (Fedo et al., 2003; 506 Tang et al., 2006). However, difficulties are often encountered in obtaining reasonable 507 508 isochrones because the U-Pb isotopic system of carbonate rocks is prone to be 509 disturbed by diagenesis or alteration.

510 Most of the zircons in the studied samples consist of a late-Archean core 511 surrounded by a Palaeoproterozoic metamorphic rim (Figs. 5 and 6). The zircons in 512 both dated samples define a discordia (Fig. 12):

513 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  $2489 \pm 13$ 514 Ma and  $2533 \pm 11$  Ma ages obtained from concordant igneous zircon cores from 515 the two samples. The two concordant ages have been obtained from the magmatic 516 zircons that were not significantly subjected to Pb loss. In view of rare  $\sim 2.7$  Ga 517 inherited zircons (only two grains) in the dated samples, this is a good evidence 518 that the zircons were predominantly derived from a single igneous source with or 519 without rare contribution of terrigenous materials during deposition of the 520 marble's protolith. The calcite, quartz and plagioclase inclusions within the 521 igneous core domains of zircon and the tectonic setting mentioned above, both 522 suggest that the 2.53-2.48 Ga igneous zircon grains should come from the 523 adjacent arc (see below in detail), and are considered to represent the maximum 524

age of deposition of the marble's protolith.

The two lower-intercept ages are similar to the ages of  $1835 \pm 6$  Ma and  $1850 \pm$ 526 28 Ma obtained from concordant metamorphic overgrowth rims of zircons from 527 the two samples. In addition, granulite-facies mineral inclusions such as 528 clinopyroxene, rutile, quartz and plagioclase (Figs. 5h, i and 6b, g, i) were found 529 530 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 531 532 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 533 Platt, 2003; Liu et al., 2006, 2011b). Therefore, the ages of  $1835 \pm 6$  Ma and 1850534  $\pm$  28 Ma should record the age of granulite-facies metamorphism. These results 535 are very similar to the previously reported granulite-facies ages of  $1839 \pm 31$  Ma 536 from the garnet-amphibolite lenses associated to the marbles (Liu et al., 2009b); 537 however, they are younger than the  $1876 \pm 18$  Ma age from garnet-granulite in a 538 nearby locality (Wang et al., 2013) and the 1.88-1.95 Ga age of peak 539 metamorphism (Liu et al., 2016). This suggests that the 1.83–1.85 Ga ages should 540 be interpreted as early-retrograde ages, and that zircon rims grew soon after the 541 542 peak of metamorphism, still under granulite-facies conditions. This conclusion is also supported by mineral assemblages and compositions observed in zircon 543 544 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., 545 2016). In these metabasic rocks, low-Na clinopyroxene (Na<sub>2</sub>O < 0.7 wt%), 546 547 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 548 549 plagioclase are occasionally discovered to be present in the 1.88-1.95 Ga metamorphic zircon domains. Based on thin-section observations and EMP 550 551 analysis, the clinopyroxene inclusions in garnet contain high Na<sub>2</sub>O contents (mostly 1.25–1.6 wt%), and generally coexist with rutile and quartz in the garnet 552 553 amphibolite and garnet granulite, suggesting HP granulite metamorphism (Liu et al., 2009, 2013). 554

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 558 U-Pb dating and Hf-isotope investigations of the lower-crustal xenoliths from the 559 same region (Liu et al., 2013).

In summary, the zircon geochronological data combined with the petrological 560 investigations in this study support a scenario in which the Wuhe Complex formed in 561 562 the late Archean, consistent with data already obtained from the Precambrian granulite 563 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 564 experienced peak HP granulite-facies and early-retrograde metamorphism at 1.8-1.9 565 Ga, corresponding to the Paleoproterozoic collisional orogenic event along the 566 Jiao-Liao-Ji belt (Liu et al., 2016). 567

568

### 569 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 575 576 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. 577 limestone). The investigated igneous zircon cores mostly show prismatic and 578 pyramidal faces and oscillatory growth zoning (Figs. 5a,f,j and 6c,e) while only a few 579 exhibit poorly-rounded grains (Fig. 5d,i), indicating that they did not experience 580 abrasion by long-distance mechanical transportation. Except for two older inherited 581 grains, these zircon cores have similar ages and trace-element characters (Fig. 7). 582 Therefore, we suggest that the zircon cores were derived from volcaniclastic deposits 583 with a single igneous source, rather than from terrigenous detritus. A terrigenous 584 origin is also ruled out by the lack of complex age-patterns and pitted surfaces and 585 586 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 587 crystallized at high-T (up to 906 °C) conditions (Table 3), thus supporting the 588 possibility that the igneous zircon cores might be formed in an arc system related to 589 590 the late Archean (c. 2.5 Ga) oceanic subduction as previously proposed by Liu et al.

591 (2013).

This interpretation is also supported by the positive Eu anomalies observed for 592 some of the analyzed marbles (Fig. 11), because the positive Eu anomalies in ancient 593 marine sediments might be attributed to coeval magmatism and high-temperature 594 595 (>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 596 597 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., 598 1988; Mitra et al., 1994; Bau and Dulski, 1999; Douville et al., 1999) and back-arc 599 basins (Fouquet et al., 1993; Douville et al., 1999; Craddock and Bach, 2010; and 600 references therein). On the other hand, the breakdown of K-feldspar during melting 601 and minor silicate minerals may provide an alternative explanation for the positive Eu 602 603 anomalies, low LREE and HREE.

In the two dated samples the igneous zircon cores with Th/U ratios of 0.2-0.8 604 (Table 2) possibly crystallized in a felsic melt, because zircons with Th/U > 1 and < 1605 crystallize in mafic and felsic melts, respectively (Amelin, 1998). This hypothesis is 606 further supported by the quartz and plagioclase inclusions (Figs. 5 and 6) preserved 607 within igneous zircon cores (Wilde et al., 2001), and by the survival of the zircon 608 609 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 610 crystallized in a felsic melt related to a coeval back-arc magma activity. 611

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 624 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 625 Rubatto, 2009). Therefore these elements (and/or related pairs) can be used as 626 petrogenetic tracers of the marble protoliths (Plank and Langmuir, 1998; Boulvais et 627 al., 2000; Tang et al., 2006; Liu et al., 2013). The studied marbles show similar 628 constant values for "fluid-immobile" element ratios such as Nb/Ta, Zr/Hf, Er/Nd and 629 Y/Ho (Table 4), thus suggesting a submarine hydrothermal sedimentary origin, 630 because Nb-Ta, Zr-Hf and Y-Ho are considered analog element pairs, and their ratios 631 are fairly constant in marine sediments (Nb/Ta ~14 and Zr/Hf ~35) (Plank & 632 Langmuir, 1998) and high-T hydrothermal sediments/fluids (Y/Ho 26-34 and Zr/Hf 633 26-46) (Bau, 1996; Bau and Dulski, 1996; Bolhar and Van Kranendonk, 2007; and 634 references therein). High major-element and REE abundances in the Type 1 are 635 unlikely to be related to the influx of seawater from which the chemical sediment 636 precipitated, but they are typical of clastic detritus instead (Boulvais et al., 2000). In 637 638 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 639 640 patterns and related element ratios are in good agreement with both similar precursor and metamorphic ages, indicative of a common formation and metamorphic process. 641 In this regard, the positive Eu anomalies are largely derived from syn-depositional or 642 643 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 644 negative Eu anomalies might be the result of dissolution of Eu-enriched minerals 645 (feldspar) or of a progressive metasomatic overprint during hydrothermal alteration or 646 post-sedimentation processes as suggested by Fulignati et al. (1999) and Boulvais et al. 647 (2000). It could be argued that variable Eu anomalies may reflect fluctuations of the 648 mixing ratios of high-T and low-T hydrothermal fluids as proposed by Bau and Dulski 649 (1996). However, in that case, Eu anomalies should be either positive (strong high-T650 component) or absent (strong low-T hydrothermal component). This explanation is 651 therefore not applicable to the investigated marbles, because they were collected from 652 the same locality at Fengyang (Fig. 1b) and share a common formation and evolution 653 history as mentioned above. Most of the samples show exceptionally high Ba and Sr 654 contents, up to 1062 ppm and 1276 ppm, respectively (Table 4), and significant Ba 655 and Sr enrichment in a spider diagram (Fig. 14), indicative of the occurrence of barite-656

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.

660 In addition, the HP granulite-facies metamorphism, and the subsequent LP 661 granulite and amphibolite-facies retrogression might have modified to some extent the 662 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 663 664 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 665 suggested by the young ages (e.g.,  $1853 \pm 8$  Ma and  $1857 \pm 12$  Ma for analytical spots 666 12FY1-1-5.2 and 12FY4-9.1) statistically indistinguishable from the age of 667 granulite-facies metamorphic rims. However, these zircon cores still preserve the 668 669 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 670 671 recrystallized zircons (Hoskin and Black, 2000; Corfu et al., 2003).

In conclusion, the formation and evolution of the impure marbles was a 672 multistage process involving a syn-depositional high-T hydrothermal alteration event 673 of a calcareous sediment in a back-arc basin during late Archean, and a 674 granulite-facies peak and early-retrograde metamorphic event during 675 Palaeoproterozoic. Furthermore, the results presented in this paper combined with 676 those previously published, indicate that the different lithologies from the Wuhe 677 Complex experienced a common metamorphic evolution after 1.95 Ga, albeit with 678 679 different protolith environments.

680

#### 681 **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 affectedby 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.

695

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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.

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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.

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Figure 3 Photomicrographs of impure marbles from the Wuhe complex at Fengyang 1118 1119 in southeastern margin of the North China Craton. (a) Clinopyroxene + calcite + titanite + K-feldspar + quartz assemblage (sample 12FY1-1), plane-polarized light 1120 (PPL); (b) same view of (a) with microcline underlined by "tartan" twinning, 1121 cross-polarized light (CPL); (c) Plagioclase inclusion in clinopyroxene and calcite 1122 1123 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 1124 1125 porphyroclasts (sample 12FY2), PPL; (f) Tourmaline + calcite + titanite + hornblende assemblage and calcite porphyroblasts surrounded by fine-grained secondary calcite 1126 1127 (sample 12FY3-1), PPL; (g) Clinopyroxene + calcite + titanite assemblage and calcite porphyroblasts surrounded by fine-grained aggregates of secondary calcite with 1128 evidence of deformation (sample 12FY3-1), PPL; (h) Foliation defined by oriented 1129 1130 calcite and white mica porphyroclasts (sample 12FY4), PPL.

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**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) 1139 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 <sup>206</sup>Pb/<sup>238</sup>U ages.

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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 <sup>206</sup>Pb/<sup>238</sup>U ages.

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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).

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Figure 8 Representative Raman spectra of mineral inclusions in zircon from sample 1157 12FY1-1. (a) Calcite; (b) white mica; (c) plagioclase; (d) clinopyroxene and calcite; (e) 1158 quartz; (f) rutile. These spectra also contain host zircon peaks at 201, 224–227, 1159 354–358, 438–439, 972–975 and 1010 cm<sup>-1</sup>.

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Figure 9 Representative Raman spectra of mineral inclusions in zircon from sample 1162 12FY4. (a) Calcite; (b) plagioclase and quartz; (c) clinopyroxene; (d) biotite and 1163 clinopyroxene; (e) white mica and graphite; (f) rutile and graphite. These spectra also 1164 contain host zircon peaks at 201–204, 223–227, 353–359, 437–441, 972–976 and 1165  $1000-1010 \text{ cm}^{-1}$ .

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Figure 10 (a) Isobaric T-X(CO<sub>2</sub>) 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<sub>2</sub>) 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<sub>2</sub>) 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).

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Figure 11 (a) Isobaric T-X(CO<sub>2</sub>) pseudosection for Type 2 marbles (bulk composition 1181 12FY3), calculated at P = 15 kbar in the NKCMAST-HC system. White, light-, 1182 1183 medium-, dark- and very dark-grey fields are di-, tri-, guadri-, guini-and esa-variant 1184 fields, respectively. The peak assemblage field is reported in red; mineral phases 1185 observed as inclusions in zircon rims are reported in italic. The two white dashed 1186 arrows are internally buffered T-X(CO<sub>2</sub>) paths compatible with both the observed peak assemblage and the observed mineral inclusions within zircon rims. (b) Stability 1187 fields of quartz, clinopyroxene, rutile, biotite and white mica as predicted by the 1188 T-X(CO<sub>2</sub>) pseudosection reported in (a); the colored dotted lines are the phase-in 1189 1190 boundaries, and the arrows point in the direction of increasing modal amount for each 1191 phase. These mineral phases are observed as inclusions within the metamorphic 1192 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 1193 1194 these mineral phases).

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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.

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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.

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

1207 as Figure 13.

## 1208

1209 **Supplementary Fig. 1** (a) Isobaric T-X(CO<sub>2</sub>) pseudosection for Type 1 marbles (bulk composition 12FY1-2), calculated at P = 10 kbar in the NKCMAST-HC system. 1210 1211 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 1212 1213 italic. (b) Stability fields of quartz, clinopyroxene, rutile and white mica as predicted by the T-X(CO<sub>2</sub>) pseudosection reported in (a); the colored dotted lines are the 1214 phase-in boundaries, and the arrows point in the direction of increasing modal amount 1215 for each phase. These mineral phases are observed as inclusions within the 1216 metamorphic zircon rims; their predicted stability fields are not consistent with the 1217 1218 independently estimated Ti-in-zircon temperatures (i.e. zircon growth occurred 1219 outside the stability field of white mica and rutile).

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**Supplementary Fig. 2** (a) Isobaric T-X(CO<sub>2</sub>) pseudosection for Type 2 marbles (bulk 1221 composition 12FY3), calculated at P = 15 kbar in the NKCMAST-HC system. White, 1222 1223 light-, medium-, dark- and very dark-grey fields as in Fig. 11. The peak assemblage 1224 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 1225 1226 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 1227 1228 modal amount for each phase. These mineral phases are observed as inclusions within 1229 the metamorphic zircon rims; their predicted stability fields are not consistent with the 1230 independently estimated Ti-in-zircon temperatures (i.e. zircon growth occurred 1231 outside the stability field of white mica and rutile).