1 Revision 1

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3	Upper temperature limits of orogenic gold deposit formation:
4	constraints from TiO ₂ polymorphs in the Dongyuan Au deposit,
5	Jiangnan Orogen, China
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15	ABSTRACT
16	Gold (Au) deposits have formed in orogenic belts throughout Earth's history. However, the upper
17	temperature limits of orogenic Au vein formation are difficult to constrain because measurements made
18	on fluid inclusions focus on intermediate to late-stage minerals (e.g., quartz and calcite), or are based
19	on $P-T$ estimates for the metamorphic mineral assemblages of the host rocks. We conducted a study of
20	TiO ₂ polymorphs that are ones of the earliest minerals that grew in Au-bearing veins of the Dongyuan
21	deposit, Jiangnan orogenic Au belt, South China. Based on Raman analyses, we identified TiO2
22	polymorphs of anatase (with Raman peaks at 396, 515, and 638 cm ⁻¹) and rutile (with Raman peaks at
23	235, 447, and 613 cm ⁻¹) and anatase-rutile intergrowths. Transmission electron microscope (TEM)
24	identified the [111] zone axis of anatase, [110] zone axis of rutile, and [111] and [111] zone axes of
25	rutile-anatase intergrowths. The TiO ₂ polymorphs in the Dongyuan Au veins constrain a temperature

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32	INTRODUCTION
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30	Keywords: Temperature, Rutile, Anatase, Raman, TEM, Orogenic gold deposit
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28	crustal levels (e.g., high-grade metamorphic rocks in the middle to lower crust).
27	fluids for this orogenic Au deposit emplaced in the shallow crust originated from deeper and hotter
26	range for early mineral precipitation in the veins of 450-550°C. The results show that ore-forming

33 The upper temperature limits of ore deposit formation are a key factor for improving our 34 understanding of mineral deposits, as they may reflect the ore source(s) and control mineral species 35 stability and precipitation sequences. Although deeply sourced fluids contributed to mineralization in 36 many orogenic Au deposits, the deposits were much more commonly found in the shallow crust 37 (Groves et al. 1998; Goldfarb et al. 2001, 2005; Mao et al. 2002; Wang et al. 2014). Orogenic Au 38 deposits are also commonly defined as mesothermal deposits, but the upper temperature limits for early 39 mineral precipitation in Au ore veins are difficult to constrain because: (1) fluid inclusion 40 microthermometry of minerals such as quartz and calcite only constrains the temperature of 41 intermediate to late stages of mineral formation, which may be lower than the initial temperature of Au 42 vein formation; and (2) temperature estimates based on the metamorphic mineral assemblages of the 43 host rocks may not represent the temperature of initial vein propagation.

44 Orogenic Au deposits hosted by low-medium-grade metamorphic rocks (i.e., schists and slates) 45 generally contain TiO₂ phases (Goldfarb et al. 2005). Although the geochemistry and geochronology of 46 rutile in Au deposits have been studied (Wong et al. 1991; Meinhold 2010), characterization of the 47 other genetically related TiO₂ polymorphs is rarer. Furthermore, the mechanisms that TiO₂ polymorphs 48 exist in orogenic Au deposits are unclear, and the implications for the occurrence of different 49 polymorphs are not particularly well understood. Anatase and rutile are two common TiO₂ polymorphs, 50 with morphologies and stabilities that are controlled by temperature and time (Navrotsky and Kleppa 51 1967; Hanaor and Sorrell 2011) and the thermodynamic properties of TiO_2 polymorphs have been 52 systematically investigated (Navrotsky and Kleppa 1967; Jamieson and Olinger 1969; Chen et al. 1995; 53 Gennari and Pasquevich 1998). Based on extrapolation of these experimental data, it is proposed that 54 TiO_2 polymorphs may provide important insights for constraining upper temperature limits in orogenic 55 Au deposits.

56 The Jiangnan orogen is an ENE-trending Neoproterozoic orogenic belt located along the 57 southeastern margin of the Yangtze Block in China, which hosts numerous orogenic Au deposits, such 58 as the Wan'gu, Huangjindong, and Dongyuan. The Au orebodies of the recently discovered Dongyuan 59 deposit are hosted by Neoproterozoic slates, structurally controlled by E-W-trending ductile shear 60 zones, and consist of quartz-dominant veinlets or veins and sulfide (mainly arsenopyrite) veinlets or 61 veins. The quartz veinlets or veins also contain some sulfides, chlorite, and carbonate minerals 62 (ankerite, manganocalcite, and calcite), along with minor albite, scheelite, TiO₂ minerals, and monazite. 63 The Au is mainly hosted in arsenopyrite. Through observation of the mineral assemblages, combining 64 electron-probe micro-analysis (EPMA), Raman spectroscopy, and TEM analyses, demonstrates that 65 anatase, anatase–rutile intergrowths, and rutile are present. The TiO₂ polymorphs, which precipitated 66 during the early stage of the Au mineralization, are used to infer the upper temperature limits of Au 67 vein formation in this orogenic Au deposit.

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REGIONAL GEOLOGICAL SETTING

The Jiangnan Orogen is located along the southeastern margin of the Yangtze Block, South China, and is an approximately1500-km-long NE-trending fold belt that extends from southern Anhui Province, through northern Jiangxi and northeastern Guizhou provinces, to northern Guangxi Province (Yin et al. 2013). The orogen was formed by the amalgamation of the Yangtze and Cathaysia blocks during the early Neoproterozoic (Fig. 1a), which was followed by rifting along the Qin–Hang (Qinzhou Bay to Hangzhou Bay) belt during the late Neoproterozoic (Shu et al. 2008).

76 Neoproterozoic strata, mainly slates intercalated with bentonites that have been dated at 822 Ma 77 (Yin et al. 2013), are dominant in the north Jiangnan Orogen, and units include the Shuangqiaoshan 78 Group in the northwestern Jiangxi and northern Hunan provinces. The Au deposits in the north 79 Jiangnan Orogen, including the Dongyuan, Jinshan, Wangu, and Huangjingdong deposits, are hosted 80 mainly in Neoproterozoic strata (Sun et al. 2018). The Neoproterozoic strata are unconformably 81 overlain by Silurian to Lower Triassic neritic clastic and carbonate rocks, and Middle Triassic to Lower 82 Jurassic paralic clastic rocks (Mao et al. 2017). A series of Middle to Late Jurassic-Cretaceous, 83 NE-trending, continental sedimentary basins have developed on the Middle Triassic to Lower Jurassic 84 strata.

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The northern Jiangnan Orogen contains Neoproterozoic and Late Jurassic to Early Cretaceous

86 granitic rocks. The Neoproterozoic (820 Ma) Jiuling granite intrusions, which form the largest 87 composite granitoid complex in South China, include biotite-rich cordierite-bearing granodiorite and 88 minor two-mica leucogranite (Zhao et al. 2013). The Late Jurassic to Early Cretaceous granitic plutons 89 are widely distributed, and possibly related to subduction of the paleo-Pacific plate beneath the 90 Eurasian continent (Mao et al. 2013). These granitic rocks consist of biotite granite, granodiorite, and 91 granite porphyry, occur as small stocks and intruded both the Neoproterozoic granodiorite batholith and 92 sedimentary strata. The Late Jurassic to Early Cretaceous biotite granite and granodiorite in the region 93 are associated with large-scale W mineralization events of South China (Mao et al. 2017; Wu et al. 94 2018, 2019a,b).

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GEOLOGY OF THE DONGYUAN GOLD DEPOSIT

97 The Dongyuan Au deposit is located ~20 km west of Xiushui County center, northwestern Jiangxi 98 Province, and is situated within the northwestern part of the Jiangnan Orogen. The Au deposit is 99 located between two NE-trending regional faults that record NW-directed thrusting. 100 East–West-trending ductile shear zones that host the deposit are characterized by rock elongation. The 101 Au deposit is hosted by basement rocks of the Neoproterozoic Shuangqiaoshan Group (Fig. 1b). The 102 Group consists of slate, blastopsammite, and phyllite, which are metamorphosed flysch rocks, 103 intercalated with volcaniclastic rocks. This lithological assemblage reflects a continental marginal 104 setting of littoral-zone shelf-to-slope depositional sequences. Weak regional metamorphism and strong 105 structural deformation have affected the strata (Huo et al. 2018). The Liyangdou granodiorite and 106 Donggang granitic rocks crop out extensively in the area, and are located about two kilometers north 107 and five kilometers south of the deposit, respectively.

108 The Au orebodies occur as veins that are several hundred meters long and several meters wide. The 109 veins were emplaced along the E–W-trending ductile shear zones that dip steeply towards the north. 110 The orebodies are nearly parallel to the bedding planes of the Neoproterozoic strata. The orebodies 111 with sulfide veinlets show (sub)-horizontal zoning, central veins and outer or 112 quartz-chlorite-sulfide-calcite veinlets or veins (Fig. 2).

113 The sulfide veinlets or veins, are millimeter to centimeter in thickness, display parallel swarms 114 and were commonly emplaced along or cut the foliation of the Neoproterozoic rocks. The veinlets 115 consist mainly of arsenopyrite, pyrite, pyrrhotite, quartz, and calcite. Arsenopyrite is either

disseminated or massive in the veinlets or veins, and occurs as euhedral needle-like and columnar crystals, with grain sizes of 50 μ m to 2 mm (Fig. 3a). Arsenopyrite is the dominant Au host and accounts for >80 vol.% of the veins, which also contain minor gangue calcite and quartz. The euhedral arsenopyrite is sometimes enveloped by pyrrhotite and pyrite (Fig. 3b,c). Pyrite also grew along the edges of pyrrhotite (Fig. 3d). Therefore, the minerals within the sulfide veinlets or veins crystallized in the following sequence: arsenopyrite \rightarrow pyrrhotite \rightarrow pyrite \rightarrow quartz \rightarrow calcite. In addition, some arsenopyrite is disseminated in the host rocks along the edges of the veinlets or veins.

123 The quartz-chlorite-sulfide-calcite veinlets or veins are several millimeters to centimeters wide, 124 and were emplaced along or cut the foliation of the Neoproterozoic rocks. The veinlets or veins 125 mainly comprise quartz, arsenopyrite, chlorite, pyrite, pyrrhotite, and carbonate minerals, with minor 126 sphalerite, chalcopyrite, TiO₂ minerals, monazite, albite, and scheelite. Two grain shapes of TiO₂ 127 minerals are observed: needle-like and platy TiO₂ minerals. The needle-like TiO₂ minerals are swarms, 128 are enveloped by quartz grains, and are several microns wide and several hundred microns long (Fig. 129 3e). In addition, some larger euhedral platy TiO_2 minerals are enveloped by albite and calcite (Fig. 3f), 130 or disseminated within the veins. Euhedral monazite is rare in the guartz-chlorite-sulfide-calcite 131 veins, and together with platy TiO_2 minerals grew along edges of the veins (Fig. 3g). The arsenopyrite 132 is disseminated in the veins and is present as euhedral needle-like and columnar crystals. The grain 133 size of arsenopyrite varies from 50 µm to 2 mm. Pyrite grew along the edges of arsenopyrite, with 134 some coexisting sphalerite and chalcopyrite (Fig. 3h). The pyrite displays various textures, including: 135 (1) fine- to coarse-grained disseminated pyrite, (2) massive, irregular aggregates of pyrite, and (3) 136 pyrite veinlets. Chlorite is both disseminated within the veins and occurs in larger abundances along 137 the vein edges. Ankerite grew along quartz-grain-boundary interstices, followed by growth of manganocalcite, and disseminated some arsenopyrite grains (Fig. 3i). Based on these observations the 138 139 sequence of mineral growth in these veinlets and veins was: TiO₂ minerals/monazite \rightarrow albite \rightarrow 140 Au-bearing arsenopyrite \rightarrow pyrrhotite \rightarrow pyrite \rightarrow sphalerite \rightarrow chalcopyrite \rightarrow chlorite \rightarrow quartz \rightarrow 141 carbonate minerals (calcite, ankerite, and manganocalcite), but with some degree of overlap.

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SAMPLES AND ANALYTICAL METHODS

Eighty-seven rock samples of the Dongyuan Au deposit were collected for analysis from the No.
504 drill core (supported by the Project of Jiangxi Provincial Fund). The samples were selected from

vertical continuous core that intersects quartz-chlorite-sulfide-calcite veins and sulfide veinlets and
veins. The samples were prepared into polished thin-sections for optical examination, electron-probe
micro-analysis (EPMA), *in situ* laser Raman spectroscopy, and transmission electron microscope (TEM)
analyses. All analyses were undertaken at the Institute of Mineral Resources, Chinese Academy of
Geological Sciences, Beijing, China.

151 Minerals were identified in polished thin-sections by optical microscopy before being analyzed by 152 EPMA using a JEOL JXA-8230 Superprobe instrument. The analyses of the TiO₂ minerals were 153 performed under condition of a 1 µm beam diameter, a 15 keV accelerating potential, and a beam 154 current of 20 nA. The following natural and synthetic standards, spectral lines, and analyzing crystals 155 were used: hematite (FeKa, LIF), rutile (TiKa, LIF), and V_2O_5 (VKa, LIFH). Before analyzing the samples, the V and Ti within standard samples were analyzed in order to deduct the relevant 156 157 information of the both spectral line systems. After the correction of the overlapping peaks was done by 158 the internal program acquired in the EPMA, the outputs of the quantitative analysis results are the true 159 concentrations of V. All data were reduced using a ZAF correction procedure. The detection limits of V 160 and Fe are 175 ppm and 190 ppm, respectively.

Laser Raman spectroscopic analysis of TiO_2 polymorphs was acquired with a Renishaw inVia reflex-type confocal Raman system, using 514 nm laser excitation and a spectral resolution of $\sim 2 \text{ cm}^{-1}$. A 20 mW laser light was focused on TiO_2 minerals in the doubly polished thin-sections with a 1 μ m laser beam spot diameter. The calibration of the spectrometer was performed by a standard silicon wafer. Relative to the 520 cm⁻¹ band of silicon, the deviation was $\sim 1 \text{ cm}^{-1}$ throughout the experiments. Raman spectroscopy identified rutile, anatase–rutile intergrowths, and anatase grains, which were then prepared for TEM foils (Fig. 4a-c).

168 Three TEM foils of the TiO₂ minerals were prepared by focused ion beam scanning electron 169 microscopy (FIB/SEM) at the Beijing Research Institute of Uranium Geology, Beijing, China. The 170 method is described in detail by Wirth (2004). A Ga⁺ ion beam was operated at 30 kV for the lift-out, and a low voltage (5 kV) was used for a final polishing. The TEM foils made are $\sim 6 \mu m \log_2 3 \sim 4 \mu m$ 171 172 wide, and 60~100 nm thick (Fig. 4d-e). The foils were analyzed by TEM using a JEOL JEM-2100 173 instrument operated at 200kV, equipped with an energy dispersive spectroscopy (EDS) system (OXFORD instruments model INCA Energy TEM100). The microstructures of the TiO₂ minerals were 174 175 observed in selected area electron diffraction (SAED) and high-resolution images. Computer-simulated

electron diffraction patterns for various zone axes of anatase, anatase–rutile intergrowths, and rutilewere obtained using computer software (Digital Micrograph).

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RESULTS

179 Raman spectroscopy

180 Raman analyses of the TiO₂ minerals from the Dongyuan Au veins identified three populations: 181 anatase, anatase-rutile intergrowths, and rutile. Needle-like anatase grains are euhedral, are 182 disseminated in quartz, are several microns wide and several hundred microns long, and have Raman 183 peaks at 396, 515, and 638 cm⁻¹. Needle-like rutile disseminated in the same microdomain in the quartz has a similar grain sizes and Raman peaks at 235, 447, and 613 cm⁻¹. Anatase–rutile intergrowths also 184 185 disseminated in the same microdomain in the quartz have similar grain sizes, with Raman peaks of both 186 anatase and rutile (Fig. 5). In addition, platy TiO_2 minerals disseminated in albite and quartz have the main Raman peaks of anatase. The strong or weak peaks near 613 and 638 cm⁻¹ (in blue lines of Fig. 5) 187 reflect the rutile/anatase ratio detected by beam spot diameter of Raman laser. The weak peak near 447 188 cm⁻¹, as compared with the peak at 396 cm⁻¹ for anatase (in green lines of Fig. 5), reflects the onset of 189 190 anatase-rutile transformation (Ma et al. 1998).

191 Transmission electron microscopy

TEM was used to examine the crystallinity and morphology of the TiO_2 polymorphs. The anatase and rutile single crystals are usually several microns in size (Fig. 6a-c). SAED patterns for anatase, rutile, and rutile–anatase intergrowths are shown in Fig. 6d-f. The electron diffraction patterns indicate that foil-1 and foil-3 are anatase and rutile, respectively, and foil-2 contains intergrowths of rutile and anatase. Figure 6d-f shows the SAED patterns of $[1\overline{11}]$ zone axis of anatase, $[1\overline{10}]$ zone axis of rutile, and $[1\overline{11}]$ and $[11\overline{1}]$ zone axes of anatase–rutile intergrowths, respectively. TEM images show the crystal lattice planes in Fig. 6g-i. The transition zone of anatase–rutile intergrowths is shown in Fig. 6i.

199 Major and minor element data

Needle-like anatase in quartz has TiO_2 concentrations of 96.78–98.81 wt.%, with relatively high V₂O₃ and FeO concentrations (0.97–1.08 and 0.05–0.40 wt.%, respectively) (Table 1). Needle-like rutile disseminated in the same microdomain in quartz has TiO_2 concentrations of 94.57–98.46 wt.%, with relatively high V₂O₃ and FeO concentrations (1.02–1.14 and 0.24–0.63 wt.%, respectively) (Table 1). Needle-like anatase–rutile intergrowths disseminated in the same microdomain in quartz have TiO_2 concentrations of 96.46–97.75 wt.%, also with relatively high V₂O₃ and FeO concentrations (0.92–1.02 and 0.08–0.89 wt.%, respectively) (Table 1).

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DISCUSSION

209 The Factor causing the formation of TiO₂ polymorphs in the Dongyuan Au deposit

Rutile and anatase–rutile intergrowths may be formed by heating of anatase or be directly precipitated from solution. The first process is an example of a thermally controlled thermodynamic transformation (Gennari and Pasquevich 1998; Ovenstone and Yanagisawa 1999), whereas the latter process is controlled by the physicochemical conditions (e.g. temperature and ion concentrations) of the solution (Chen et al. 1995; Li et al. 2007). In addition, the minerals in the natural ores of this study precipitated from fluids, and may subsequently have undergone multi-stage alteration and/or regional metamorphism, which may transform the TiO₂ morphologies after ore formation.

217 There are several lines of evidence that may be used to argue that the veins were not subjected to 218 post-emplacement deformation or chemical alteration. Firstly, the orebodies represent sub-parallel 219 veins and veinlets in slates (Fig. 2), and there is no sign of younger (multi-stage) alteration or 220 deformation superimposed on the veins and host slates, therefore no evidence for the late hydrothermal 221 fluids affecting the TiO_2 morphologies or crystallography. Secondly, irrespective of whether the deposit formed before or after the regional metamorphic event, the low-grade metamorphic slates of the host 222 223 rocks were metamorphosed at temperatures far below the thresholds (~550 °C at 4 kbar) of the 224 anatase-rutile transformation. Based on these two pieces of evidence it is argued that the TiO_2 225 polymorphs in the veins were not caused by regional metamorphism and there is no evidence that they 226 were altered by younger hydrothermal processes.

227 Pure rutile may precipitate from solution under highly acidic conditions (pH = 0-1) at relatively 228 low temperatures of ~220 °C (Chen et al. 1995; Penn and Banfield 1999; Li et al. 2007). However, the 229 veins contain calcite, which implies that the fluids impossibly had low hydrogen ion concentrations 230 (about 0.1-1 mol/L). NaCl, NH₄Cl, and SnCl₄ in solution may accelerate the anatase-rutile 231 transformation (Li et al. 2007). However, these species are not critical factors for the precipitation of 232 pure rutile, and low-salinity fluid inclusions develop in orogenic Au deposits (Lu et al., 2018), 233 including the Dongyuan Au deposit (no halite-bearing fluid inclusions). Gennari and Pasquevich (1998) 234 suggested that anions (e.g., chloride, sulfate, and fluoride) suppress the transition of anatase to rutile, 235 while cations (e.g., alkali and transition metal ions) promote (accelerate) the transformation. For

236 example, at Mn concentrations of >1.5 mol.%, the anatase-rutile transformation accelerates (Arroyo et al. 2002) and, at relatively high Fe^{3+} concentrations, the temperature of the anatase-rutile transition is 237 238 lowered (Gennari and Pasquevich 1998). However, V and Fe concentrations in TiO_2 polymorphs in the 239 Dongyuan Au veins have ranges of 0.92-0.63 wt.% and 0.05-0.89 wt.%, respectively, and the 240 abundances of these elements in anatase, rutile, and anatase-rutile intergrowths are nearly consistent 241 (see above). Therefore, there is no evidence of fluctuations in ion concentrations to cause the formation 242 of TiO₂ polymorphs. Therefore, it is concluded that the formation of the various TiO₂ polymorphs in 243 the Dongyuan Au deposits was not the result of the chemical conditions (e.g., ion concentrations) of the 244 ore-forming fluids systematically changing or varying.

245 Unlike rutile, anatase is thermodynamically unstable, and tends to transform into rutile at all 246 temperatures (Smith et al. 2009). Hence, after anatase precipitation in a fluid, it tends to transform into 247 rutile, depending on time (kinetics). Although it is not possible to constrain the anatase cooling rate, but 248 a group of anatase in the same microdomain in the quartz (Fig. 3e) would undergo similar cooling 249 histories. If the cooling rate was sufficiently slow and could induce the anatase-to-rutile transformation, 250 then pure anatase grains would not exist and the anatase/rutile ratios in TiO₂ minerals analyzed would 251 be nearly constant. However, we do not observe this texture, and must therefore conclude that there 252 was no occurrence of anatase-to-rutile transformation during the cooling.

253 In the absence of evidence for the scenarios described above, it is proposed that formation of the 254 TiO_2 polymorphs in the Dongyuan Au deposit was primarily controlled by the physical conditions of 255 the ore-forming fluids. The phase transformation from anatase to rutile is not susceptible to the effects 256 of pressure in the crustal domain (Hanaor and Sorrell 2011). Therefore, the changes of pressure ranges, 257 corresponding to the small vertical extension of the deposit and the microdomain containing TiO_2 258 minerals, are too small and could not produce the TiO₂ polymorphs. The crystalline phase of an 259 individual TiO₂ morphology is thermodynamically stable only when its free energy is at a minimum for 260 a given temperature and pressure. Rutile has been identified as the stable phase along with 261 comparatively unstable anatase (Gouma and Mills 2001). The unstable and stable phases are separated 262 by energy barriers, and an unstable phase will change to the stable phase with a free energy minimum 263 when the energy barrier(s) are overcome (Anderson, 2005). Anatase forms easily due to its 264 less-constrained molecular construction and lower surface free energy (Hanaor and Sorrell, 2011). 265 However, based on thermodynamics (Gennari and Pasquevich 1998; Anderson 2005; Zhang 2008),

rutile will be stable if the initial temperature is high enough. In addition, if anatase forms first at low temperatures, then it is not easily transformed to rutile by increasing the temperature (Miao et al. 2004). Therefore, swarms of needle-like TiO_2 polymorphs in microdomains demonstrate that a fluid temperature range around the temperatures of anatase to rutile phase transformation would lead to the occurrence of intergrown TiO_2 polymorphs in the Dongyuan deposit. In other words, the rutile, anatase, and rutile–anatase intergrowth formation temperatures are slightly higher than, lower than, and approximate to the temperatures of anatase to rutile transformation, respectively.

273 Upper temperature limits of formation of the Dongyuan Au deposit

274 Equilibrium between TiO_2 polymorphs does not exist and, as such, there is no specific temperature 275 for the anatase-rutile transformation (Hanaor and Sorrell 2011). Previous studies have reported 276 temperatures for the anatase-to-rutile phase transformation that vary from 400°C to 1100°C, depending 277 on the experimental conditions and methods, such as particle size, crystal size, surface area, and purity 278 (Gennari and Pasquevich 1998; Ovenstone and Yanagisawa 1999). It is generally recognized that the 279 phase transformation from pure anatase to rutile starts at 600 °C under latm (Yoganarasimhan and Rao 280 1962; Hanaor and Sorrell 2011). In addition, experiments have verified that TiO₂ mineral precipitation 281 from H₂O solutions at the transition from anatase to rutile occurs at temperatures of >597°C (Matthews, 282 1976). Therefore, combining experimental data for the anatase to rutile transformation and the 283 occurrence of TiO₂ polymorphs (as early stage minerals) in the Dongyuan deposit controlled by 284 temperature (see above), we can tentatively constrain the upper temperature limits of the Au vein 285 formation.

286 The Dongyuan deposit formed from metamorphic fluids, is hosted by slates, and has an ore assemblage of Au-As-Te, corresponding to an emplacement depth of 6-12 km (Groves et al. 1998) and 287 288 static pressure of 2.4 ± 0.6 Kbar (based on a pressure gradient of 0.27 Kbar/km⁻¹, Hu et al. 2003). In a 289 P-T phase diagram (Hanaor and Sorrell 2011), this pressure range corresponds to anatase-rutile 290 transformation temperatures of ~550 °C. Vanadium doping in TiO₂ minerals promotes the 291 transformation from anatase to rutile (Khatun et al., 2017). The V₂O₃ concentrations in TiO₂ minerals 292 from the Dongyuan Au veins are ~ 1 wt.%, which might lower the transformation temperatures slightly (Khatun et al., 2017). The formation of oxygen vacancies in the presence of Fe³⁺ also lowers the 293 294 anatase-rutile transformation temperature (Gennari and Pasquevich 1998). Therefore, the V and Fe 295 doping in TiO₂ minerals might depress the phase boundary between anatase and rutile to lower

temperatures (Fig. 7). Although the magnitude of the change cannot be precisely assessed, the transformation temperature may be as much as 100 °C lower than that of pure anatase (Gennari and Pasquevich 1998). Therefore, while the occurrences of TiO_2 polymorphs in the Dongyuan Au veins may represent a maximum temperature of ~550°C, the temperature may have been as low as 450°C (caused by the doping), representing the temperature window of Au vein formation.

301 Implication for models for orogenic Au deposits

302 TiO₂ minerals (rutile and anatase) are commonly observed in orogenic Au deposits, but the 303 significance of TiO₂ polymorphs and their distribution and implications for interpreting Au 304 mineralization are not well understood. The identification of the TiO₂ polymorphs in the orogenic Au 305 deposits hosted at shallow crustal levels may be an indicator that the ore-forming fluids had elevated 306 temperatures, relative to the host-rock, and might have risen from much deeper levels. This hypothesis 307 may be tested by investigating orogenic Au deposits in other orogens. Due to the large range of crustal 308 depth (<15 km) of orogenic Au deposit, continuous ore zonation exists. This includes the epizonal 309 Au-Sb, mesozonal Au-As-Te, and hypozonal Au-As sections, with range of formation temperatures 310 speculated to lie between 180 and 700°C (Groves et al. 1998). Fluid inclusion studies of Au veins have 311 yielded temperatures of 150-400°C, such as, orogenic Au deposits within the Archean Yilgarn Craton 312 and Lachlan Orogen of Australia (Mernagh et al. 2007) and the Mayum deposits in Tibet (Jiang et al. 313 2009). Tomkins and Grundy (2009) suggested that orogenic Au deposits are a mesothermal 314 phenomenon and that their formation temperatures do not exceed 600-650°C, due to the difficulty of 315 transmitting hydrothermal fluids through the rocks at higher temperatures. Furthermore, Tomkins (2013) 316 inferred that the upper temperature limits of orogenic Au deposit formation are around 500-550°C. The 317 Dongyuan Au deposit has an ore-forming element assemblage of Au–As–Te, and Groves et al. (1998) 318 suggested that this orebody formed at mesozonal depth (6-12 km) at temperatures of 300-475°C. Our 319 finding that some orogenic Au deposits in the shallow crust must have a deep-seated fluid source with 320 initial temperatures of 450–550°C is broadly consistent with the conclusions of Tomkins and Grundy 321 (2009) and Groves et al. (1998).

Models for the formation of orogenic Au deposits are controversial, and the most plausible model involves formation by metamorphic fluids, although the exact source(s) of the fluids are unclear (Groves and Santosh 2016; Liang et al. 2019). For example, proposed fluid sources include the metamorphic devolatilization of stalled subduction slabs and oceanic sediments (Groves and Santosh

326 2016) and remobilization of Au-rich zones from the upper mantle into the crust (Hronsky et al. 2012). 327 Low-grade metamorphic rocks are common host rocks for orogenic Au deposits (Pitcairn et al. 2006). 328 Gaboury (2013) and Tomkins (2013) proposed that the greenschist-amphibolite transition zone is the 329 source of the ore-forming fluids. TiO₂ mineral compositions may also provide clues to the fluid sources 330 (Scott 2005). For example, rutile in porphyry Cu-Au deposit is enriched in V, Fe, and Nb (Scott 2005), 331 and TiO₂ minerals in porphyry W–Mo deposits (e.g., the Dongyuan W deposit in Anhui Province, Wu 332 et al. 2019b) are enriched in V, Fe, W, Ba, K, and Al (unpublished data). The TiO_2 minerals in the 333 Dongyuan Au deposit have relatively high V₂O₃ and FeO concentrations, Chen et al. (2018) suggested 334 that biotite decomposition in deep granulite-facies rocks releases V and Fe into fluids. Therefore, there 335 are two options for the fluid source of the Dongyuan Au deposit: (1) the fluids were derived from the 336 granulite-facies rocks; and (2) the fluids originated from deeper sources (e.g., stalled subduction slabs 337 or the upper mantle) and subsequently passed through granulite-facies rocks. When the Au-bearing 338 fluids migrated along secondary faults into shallow crust, most mineral precipitation occurred at 339 moderate temperatures. TiO₂ minerals (anatase and rutile) that precipitated during the early stage from 340 the ore-forming fluids carry primary information regarding the fluid source, providing an option to 341 place some constraints on temperatures and chemistries of the fluids that formed orogenic Au deposits.

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IMPLICATIONS

344 TiO₂ minerals are commonly formed during the early stage of the Au mineralization, and may therefore be used to fingerprint and investigate the formation of orogenic Au deposits. Raman 345 346 spectroscopy, EPMA, and TEM analyses show that orogenic Au deposits, such as the Dongyuan 347 deposit, contain TiO₂ polymorphs of anatase, anatase–rutile intergrowths, and rutile, which formed in 348 the early stage of auriferous veins. The TiO_2 polymorphs constrain the upper temperature limits of the 349 Au vein formation to $450-550^{\circ}$ C, based on the thermodynamics of TiO₂ polymorphs. The relatively 350 high V_2O_3 and FeO concentrations in the TiO₂ suggests that biotite decomposition in deep 351 granulite-facies rocks releases V and Fe into ore-forming fluids, which stemmed from or flowed 352 through metamorphic rocks. Furthermore, orogenic Au deposits widely distributed in the 353 low-intermediate-grade metamorphic rocks stem from the deeply sourced thermo fluids (e.g., from 354 granulite-facies rocks of the middle to lower crust).

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480

488 **Figure captions**

490 Figure 1. (a) Geological sketch map of the Jiangnan Orogen, South China (after Yao et al. 2014). (b)

491 Geological map of the Dongyuan Au deposit.

492

493 Figure 2. Geological section-section of the exploration line no. 5 in the Dongyuan Au deposit. (a, b)

- 494 Quartz–chlorite–sulfide–calcite veinlets or veins. (c, d) Sulfide veinlets or veins.
- 495
- 496 Figure 3. Mineral assemblages of the Dongvuan Au veins. (a) Massive and disseminated arsenopyrite. 497 (b) Pyrrhotite grew along edges of arsenopyrite. (c) Pyrite grew along edges of arsenopyrite. (d) Pyrite 498 also grew along the edges of pyrrhotite. (e) Swarms of TiO₂ minerals in the veins, enveloped by quartz. 499 (f) Disseminated and euhedral platy TiO_2 minerals surrounded by albite and calcite. (g) Co-existing 500 TiO_2 minerals and monazite developed along the veinlets. (h) Pyrite precipitated along the edges of 501 arsenopyrite, and some coexisting sphalerite and chalcopyrite. (i) Ankerite growth along the margins of 502 interstices and manganocalcite precipitation in the centers of interstices. (e) and (f) are under 503 transmitting light, (g) and (i) are back-scattered electron images, and the others are under reflecting 504 light. Ab = albite, Apy = arsenopyrite, Ank = Ankerite, Cal = calcite, Ccp = chalcopyrite, Mn-Cal = 505 manganocalcite, Mnz = monazite, Po = pyrrhotite, Py = pyrite, Qz = quartz, Sp = sphalerite.
- 506

507 Figure 4. Secondary electron (SE) images of foils cut from TiO₂ minerals in the Dongyuan Au deposit.

508 (a) Anatase grain. (b) Anatase-rutile intergrowths. (c) Rutile grain. (d) SE image of foil-1 cut from the

anatase grain shown in (a). (e) SE image of foil-2 cut from the anatase–rutile intergrowths shown in (b).

(f) SE image of foil-3 cut from the rutile grain shown in (c). (a–c) are of TiO_2 minerals disseminated in

511 the same quartz microdomain (Fig. 3e). Ant = anatase, Rt = rutile.

512

Figure 5. Raman spectra of TiO_2 minerals in the Dongyuan Au deposit. Raman spectra are of the anatase, anatase–rutile, and rutile grains shown in Fig. 4a–c, respectively.

515

Figure 6. SAED patterns and TEM images of rutile, anatase, and rutile–anatase intergrowths. (a–c)
Low-magnification TEM images of anatase, rutile, and anatase–rutile intergrowths. (d) SAED pattern
of the green-circle area of foil-1. (e) SAED pattern of the green-circled area of foil-3. (f) SAED pattern
of green-circled area of foil-2. (g–i) TEM images of (a–c) foils, respectively. Ant = anatase, Rt = rutile.

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- 521 Figure 7. Phase transitions of TiO₂ with changing temperature and pressure (Hanaor and Sorrell 2011).
- 522 The field outlined in red represents the temperature range of TiO₂ polymorph formation in orogenic Au
- 523 deposits.
- 524

525 Table

 $\label{eq:226} {\ensuremath{\text{Table 1. Electron microprobe analyses of TiO_2 minerals from the Dongyuan deposit}} \\$

Comment	Minerals	${\rm TiO}_2$	V_2O_3	FeO	Total
19R-1	Rutile	97.28	1.14	0.63	99.04
19R-2		98.46	1.03	0.24	99.73
19R-3		94.57	1.06	0.41	96.04
19R-7		97.81	1.02	0.24	99.08
19A-10	anatase	97.68	1.06	0.05	98.78
19A-13		96.78	0.97	0.38	98.13
19A-14		98.67	1.08	0.13	99.88
19A-16		98.81	1.04	0.31	100.16
19A-15		98.74	0.99	0.24	99.97
19A-17		98.79	1.03	0.13	99.96
19A-19		97.47	0.99	0.40	98.85
19RA-2	anatase-rutile	96.46	0.92	0.89	98.26
19RA-5	intergrowths	97.75	1.02	0.08	98.85

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