1 Revision 2

2 Two discrete gold mineralization events recorded by hydrothermal xenotime and

3 monazite, Xiaoqinling gold district, central China

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ABSTRACT

We present in situ LA-ICP-MS U-Pb dating of xenotime and monazite in assemblages with native 26 27 gold and Au (Ag) tellurides from the Xiaoqinling lode gold district in central China. Composite xenotime and monazite grains formed through coupled dissolution-reprecipitation reactions reveal 28 two discrete gold mineralization events. The first gold mineralization event, recorded by monazite 29 30 $(158.6 \pm 3.3 \text{ Ma}, \text{Tera-Wasserburg lower intercept age})$ and xenotime cores $(157.11 \pm 0.83 \text{ Ma}, \text{Tera-Wasserburg lower intercept age})$ weighted mean ²⁰⁶Pb/²³⁸U age), is characterized by the mineral assemblage of lingbaoite (AgTe₃)-31 sylvanite ([Au,Ag]₂Te₄)-stützite (Ag₅-xTe₃)/native tellurium-sylvanite-stützite. The second gold 32 mineralization event, recorded in the rims of xenotime (135.46 ± 0.93 Ma, weighted mean 206 Pb/ 238 U 33 34 age), is characterized by the mineral assemblage of native gold-calaverite (AuTe₂)-petzite 35 (AuAg₃Te₂)-tellurobismuthite (Bi₂Te₃). Our study implies that the large-scale Jurassic mineralization event in eastern China, related to flat subduction of the paleo-Pacific plate beneath the eastern China 36 37 continent, also caused widespread gold mineralization in the Qinling-Dabie Orogen, in addition to production of its world-class porphyry Mo deposits. The fact that only a few Jurassic gold 38 mineralization ages have been reported before, may be due to the lack of suitable geochronometers to 39 record the earlier Jurassic hydrothermal processes, which have been overprinted by the better-40 recognized Early Cretaceous gold mineralization event. This study also presents a rare example of 41 42 xenotime compositional alterations and resetting of U-Pb ages induced by low to moderate salinity 43 carbono-aqueous fluids at low temperatures. The textural relationships between gold minerals in contact with such composite xenotime crystals demonstrate that they could have precipitated before, 44 coeval with, or after the dated domains. Since low to moderate salinity carbono-aqueous fluids are 45

46	commonly involved in the formation of lode gold deposits, it's crucial to examine xenotime textures
47	and recognize potential alteration textures before carrying out isotopic dating of xenotime collected
48	from these deposits. Without prior compositional and textural characterization, attempts to date such
49	composite crystals could yield mixed dates and meaningless ages.

50 Keywords: Xenotime, monazite, gold deposit, LA-ICP-MS U-Pb dating, Xiaoqinling, central China

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INTRODUCTION

52 The formation of lode gold deposits commonly involves multiple hydrothermal stages or events 53 (e.g., Arne et al. 2001; Essarraj et al. 2001; Bateman and Hagemann, 2004; Meffre et al. 2016; 54 Fougerouse et al. 2017). The episodic nature of hydrothermal systems may be identified by well-55 developed superimposed textures, such as breccias, ribbons, and a cross-cutting network of veinlets 56 (e.g., Dowling and Morrison, 1989; Goldfarb et al. 2005; Voisey et al. 2020; Jian et al. 2021). However, it is challenging to determine whether vein systems result from the gradual cooling of a 57 single hydrothermal fluid or multiple hydrothermal events that occur millions of years apart. It is 58 59 especially difficult to accurately determine the timing of each individual hydrothermal event and the 60 timing of gold deposition. The difficulties mainly arise from the scarcity of suitable dating 61 minerals/mineral domains directly related to gold precipitation that remain closed to isotope re-62 equilibration during subsequent hydrothermal events.

Monazite and xenotime are robust geochronometers that have low rates of Pb diffusion and low
susceptibility to Pb loss at high temperatures, with Pb closure temperatures of 890°C for xenotime
and 940°C for monazite (for a 10 µm grain with a cooling rate of 10°C/Ma: Cherniak et al. 2004;
Cherniak, 2006). However, the two minerals undergo coupled dissolution–reprecipitation reactions at

67	temperatures <400°C (Townsend et al. 2000; Rasmussen and Muhling, 2007; Budzyń et al. 2015a,b),
68	leading to crystals that may have multiple, but discrete, age domains from which precise dates for
69	multiple hydrothermal events may be obtained (e.g., Fielding et al. 2017; Budzyń et al. 2018).
70	Although many lode gold deposits contain trace amounts of hydrothermal monazite or xenotime, the
71	size of most hydrothermal xenotime grains is typically ${<}10~\mu\text{m},$ and combined with its low
72	abundance make it difficult to find suitable crystals from which complex, multi-stage hydrothermal
73	histories may be reconstructed (e.g., McNaughton and Rasmussen, 2018).
74	This study presents detailed in situ LA-ICP-MS U-Pb dating of xenotime and monazite in
75	assemblages with native gold and Au (Ag) tellurides from the Xiaoqinling lode gold district, central
76	China. Composite xenotime and monazite crystals formed through coupled dissolution-
77	reprecipitation reactions reveal two discrete gold mineralization events, with an early Cretaceous
78	gold mineralization event preceded by a previously overlooked middle Jurassic gold mineralization
79	event.

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GEOLOGICAL SETTING

Marginal parts of the North China Craton host hundreds of lode gold deposits of mainly Early Cretaceous age (Mao et al. 2005; Li et al. 2012a; Deng et al. 2016), with a total gold resource exceeding 3,600 tonnes Au (Li et al. 2012a; Deng et al. 2016). The Xiaoqinling gold district in the southern margin of the North China Craton represents the second-largest gold production area in China, with a proven gold reserve of more than 630 tonnes (Jian et al. 2015, 2022a).

86 Mesozoic tectonomagmatic evolution of the Qinling-Dabie orogen

87 The Xiaoqinling district is located at the southern margin of the North China craton and belongs to the Qinling-Dabie orogen (Fig. 1). The WNW-trending Qinling-Dabie orogen delineates the 88 boundary between the North China craton and the Yangtze craton. This orogenic belt resulted from 89 multistage collisional events between the North China craton and the Yangtze craton; the final 90 91 collision between the two cratons occurred in the Triassic (Dong and Santosh, 2016). During the Late 92 Triassic, the Qinling-Dabie orogen evolved into a post-collisional extensional domain, which is 93 indicated by the emplacement of post-collisional intrusions, including alkaline intrusions (Wang et al. 2007; Li et al. 2012a; Cao et al. 2015), carbonatites (Xu et al. 2010; Du et al. 2020; Zheng et al. 94 2020; Tang et al. 2021), and rapakivi-textured granitoids (Wang et al. 2011). 95 Since the Jurassic, eastern China, including the eastern part of the Qinling-Dabie orogen, became a 96 97 part of the circum-Pacific tectonic regime, with the subduction of the Izanagi plate (or paleo-Pacific 98 plate) beneath the Eurasian continental margin (Mao et al. 2021a). The subduction began with a steep 99 angle but changed to a flat angle in the Middle-Late Jurassic (Wu et al. 2019; Mao et al. 2021a). 100 Since the Early Cretaceous, eastern China evolved into an extensional setting (Mao et al. 2021a) due to lithospheric thinning driven by the rollback of the paleo-Pacific plate (Wu et al. 2019; Ma et al. 101 2021). The flat subduction and subsequent rollback of the paleo-Pacific plate gave rise to widespread 102 magmatism and ore formation, making the Late Mesozoic the most important magmatic and 103

104 metallogenic period in eastern China.

105 Geology of the Xiaoqinling gold district

106 The strata exposed in the Xiaoqinling gold district are dominated by Archean amphibolite-facies

107 metamorphic rocks of the Taihua Group (Fig. 1), which consists of biotite plagiogneiss, amphibolite 108 gneiss, amphibolite, quartzite, and marble (Cai and Su, 1985). These rocks probably formed in the Neoarchean and have been subjected to amphibolite-facies metamorphism in the Paleoproterozoic 109 110 (Zhou et al. 1998; Ni et al. 2003; Li et al. 2007). The Archean rocks were intruded by Paleoproterozoic pegmatite/granite (Li et al. 1996; Li et al. 2007), Proterozoic and Mesozoic granitic 111 intrusions (Wang et al. 2010; Hu et al. 2012; Li et al. 2012), and Paleoproterozoic and Early 112 Cretaceous mafic dikes (Wang et al. 2008; Bi et al. 2011). Jurassic magmatism, although widespread 113 114 in eastern China, has rarely been reported in the Xiaoqinling gold district. The Huashan granite 115 complex has a zircon age of 146 ± 2 Ma (Mao et al. 2010). Several Jurassic porphyritic stocks, 116 however, have been reported from the Xiong'ershan gold district, about 100 km east of the Xiaoqinling district, and in a similar geologic setting (e.g., Niutougou, Miaoling, and Qiyugou gold 117 deposits: Wang et al. 2012; Li et al. 2014; Wang et al. 2020). However, these Jurassic porphyries do 118 not appear to be directly related to gold mineralization since they all postdate gold mineralization 119 120 (Wang et al. 2020). At the Qiyugou Au deposit, for instance, the quartz porphyries were emplaced at 158.6 ± 1.1 to 157.3 ± 1.1 Ma (LA-ICP-MS zircon U–Pb age), while gold mineralization occurred at 121 122 132.9 ± 1.5 Ma (molybdenite Re-Os age of gold ore samples) and is genetically related to the 130.9 \pm 1.9 Ma hornblende monzogranite (LA-ICP-MS zircon U–Pb age). 123 Early Cretaceous plutons are widely exposed across the gold district. These are, from east to west, 124 125 the Niangniangshan biotite monzogranite (142 ± 3 to 129 ± 2 Ma: Wang et al. 2010; Li et al. 2012b), the Wenyu biotite monzogranite (141 \pm 2 to 136 \pm 3 Ma: Wang et al. 2010; Li et al. 2012b), and the 126 outer phase of the Huashan granite complex $(132 \pm 1 \text{ Ma: Hu et al. } 2012)$. 127

128 The nearly E-W–striking Taiyao and Xiaohe faults define the northern and southern boundaries of

129 the Xiaoqinling gold district. The two normal faults developed during the Cenozoic extension, 130 resulting in the exposure of the basement rocks (Li et al. 2020). The more than 1,200 gold-bearing quartz veins concentrate along the axes of several EW-striking steep folds and are controlled by 131 small- to medium-size EW-striking faults. The S16 gold-bearing quartz vein, from which the studied 132 ore samples were collocated, is about 30 km southwest of Lingbao city, Henan province, central 133 China. The S16 gold-bearing quartz vein, from which the studied ore samples were collocated, is a 134 newly discovered concealed vein with an average gold grade of ~ 6 g/t. It is 0.1 to 2.5 m wide and 135 extends about 1.5 km in a roughly east-west direction, dipping to the south (Fig. 1). The S16 gold-136 bearing quartz vein is about 30 km southwest of Lingbao city, Henan province, central China, and 137 138 belongs to the south ore belt of the Xiaoqinling gold district. The south ore belt hosts most of the 139 gold-bearing quartz veins, which concentrate along the Laoyacha anticline (Fig. 1).

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SAMPLE MATERIAL AND METHODS

141 Sample selection

The studied ore samples were collected underground from the S16 gold-bearing quartz vein. The ore samples for geochronological study consist mainly of quartz and pyrite (Fig. 2). Other minerals present in small or trace amounts include xenotime, monazite, scheelite, celestine, gold, native tellurium, muscovite, as well as a variety of sulfides (e.g., chalcopyrite, bornite, sphalerite, and galena) and tellurides (e.g., sylvanite, petzite, calaverite, stützite, hessite, altaite, rucklidgeite, and tellurobismuthite).

148 Analytical methods

149 Xenotime and monazite in polished thick sections were first examined in reflected light and then by electron probe microanalysis (EPMA) and scanning electron microscopy (SEM). SEM 150 151 investigation was carried out at the Institute of Geology, Chinese Academy of Geological Sciences, using a FEI NOVA nanoSEM equipped with an Oxford X-Max 50 detector. EPMA wavelength-152 153 dispersive X-ray spectrometry (WDS) analysis was carried out at the Institute of Mineral Resources, 154 Chinese Academy of Geological Sciences, using a JXA-iHP200F electron microprobe. Details on 155 EPMA settings for WDS analysis are available in Table A1. EPMA X-ray mapping was carried out at the State Key Laboratory of Plateau Ecology and Agriculture, Qinghai University, China, using a 156 JXA-8230 electron microprobe. 157 LA-ICP-MS U-Th-Pb isotope analysis of xenotime and monazite, as well as LA-ICP-MS trace 158 159 element analysis of xenotime, were carried out at the State Key Laboratory of Lithospheric 160 Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences. Analytical procedure for U-Th-Pb isotope analysis follows Wu et al. (2020). Analytical details are available in Tables A2, 161 A3. LA-ICP-MS trace element analysis of monazite was carried out at the Yanduzhongshi 162

- 163 Geological Analysis Laboratories Ltd., Beijing, using a New Wave NWR 193 laser ablation system
- 164 coupled to an Analytikjena M90 quadrupole ICP-MS. Analytical details are available in Table A4.
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RESULTS

166 Vein mineralogy and paragenesis

167 At least three hydrothermal stages, including two gold-mineralization stages, are recognized in the

168 studied ore samples (Figs. 2, 3, 4). The first hydrothermal stage (I) is characterized by the precipitation of milky white quartz, which makes up more than 90% of the vein volume. The second 169 stage (II) is characterized by the growth of pyrite, scheelite, xenotime, monazite, and celestine on 170 171 fracture planes in quartz (Fig. 2). Pyrite contains composite mineral inclusions (<1-50 µm in 172 diameter) consisting mainly of lingbaoite (a recently named mineral with the chemical formula of AgTe₃, Jian et al. 2020), sylvanite [(Au,Ag)₂Te₄], stützite [Ag_{5-x}Te₃], native tellurium, and 173 chalcopyrite, with minor bornite, galena, and altaite (Figs. 3A-G). These inclusions outline the 174 primary growth zones in pyrite and generally display a negative crystal shape. They were interpreted 175 176 as primary melt inclusions, which were trapped as polymetallic melt droplets during the growth of the host pyrite (Jian et al. 2021, 2022b). The third stage (III) is the main gold deposition stage. This 177 stage is characterized by native gold and tellurides (petzite [AuAg₃Te₂], calaverite [AuTe₂], 178 tellurobismuthite [Bi₂Te₃], altaite [PbTe], and rucklidgeite [PbBi₂Te₄]) as inclusions or fracture 179 fillings in early minerals (e.g., quartz, pyrite, and scheelite, Figs. 2–4). The stage III gold-bearing 180 mineral assemblages (e.g., native gold-calaverite-petzite-tellurobismuthite) commonly coexist with 181 low to moderate salinity H₂O-CO₂ fluid inclusions along healed fractures in guartz (Figs. 3I–K). The 182 183 total homogenization temperatures of these fluid inclusions have been investigated from many goldquartz veins in the Xiaoqinling gold district and cluster at 200 to 400°C (Fan et al. 2003; Li et al. 184 2012b; Xiong et al. 2013). The cross-cutting relation between stage II and stage III gold-bearing 185 minerals is illustrated in Figures 3A-B, in which stage II tellurides occur as inclusions in pyrite 186 187 while stage III gold and tellurobismuthite occur along quartz grain boundaries.

188 Characterization of xenotime and monazite

189 Xenotime and monazite crystals occur as inclusions in pyrite and scheelite, or along quartz fractures (Figs. 2D, 4). Individual xenotime and monazite crystals are typically 10-80 µm in 190 diameter (Figs. 4-6), but large crystals (up to 350 µm in diameter, Figs. 4H, I) have also been 191 observed. The two minerals most commonly occur in contact with each other, and monazite has also 192 193 been observed as inclusions in xenotime. Cathodoluminescence (CL) imaging of xenotime reveals 194 that xenotime crystals have a dark, pristine core surrounded by bright altered domains, which developed near grain rims or healed microfractures (Figs. 4I, 5). There is a sharp reaction front 195 between altered and pristine xenotime domains (Figs. 4D-I, 5). The xenotime cores display distinct 196 oscillatory zoning truncated at the boundary with the altered domains (Fig. 5). There is an epistatic 197 relationship between altered and pristine xenotime domains. For example, examination of the 198 199 xenotime crystals using polarized light shows that altered and pristine xenotime domains in each 200 grain are optically continuous (Figs. 4D, F, H). Altered xenotime also preserves the external dimension of pristine xenotime. These textural features suggest that the altered xenotime domains in 201 202 our sample set formed through coupled dissolution-reprecipitation reactions (e.g., Putnis, 2002, 2009). Native gold and stage III tellurides have been observed as inclusions in the altered domains of 203 204 xenotime, or occur in contact with the altered domains (Figs. 4D–I).

Xenotime cores and rims show distinct major and trace element features (Tables A5, 6, Fig. A2).
EPMA analysis shows cores contain higher and more consistent Y concentrations (0.91–0.92 apfu, atoms per formula unit on the basis of 4 oxygens) whereas Y concentrations in the altered rims vary
from 0.81 to 0.92 apfu. LA-ICP-MS trace element analysis reveals xenotime cores contain 1.4–4.1
wt% LREE (La to Eu), 9.0–13.0 wt% HREE (Gd to Lu,), 1000–2600 ppm Si, 730–4600 ppm Ca, 10

12–19 ppm Rb, 5–19 ppm Sr, 29–220 ppm Zr, 240–620 ppm Pb, 1000–5800 ppm Th, and 1900–
5900 ppm U, while xenotime rims have higher concentrations of HREE (12.4–19.5 wt%), Si (0.1–2.1
wt%), and Rb (25–37 ppm), and lower concentrations of LREE (0.7–1.2 wt%), Zr (10–106 ppm), Pb
(84–256 ppm), Th (500–1900 ppm), and U (800–2400 ppm). In the chondrite-normalized REE
pattern (Fig. 7), neither the cores nor rims have an Eu anomaly. This differs from igneous xenotime,
which is commonly characterized by a pronounced negative Eu anomaly (e.g., Rasmussen, 2005;
Aleinikoff et al. 2015).

While xenotime crystals may show well-formed crystal faces, monazite occurs as subhedral-217 218 anhedral grains, which form larger aggregates with irregular outlines (Fig. 6). Occasionally, elongate 219 monazite grains grow as radial, flower-shaped assemblages (Figs. 6, A3). Monazite shows a faint 220 core-rim texture under high-contrast SEM-BSE imaging (Fig. 6). The core has a heterogeneous 221 texture with chaotic, patchy zoning, and contains a dense population of mineral inclusions ($\leq 10 \mu m$, mainly iron oxides) and smaller fluid inclusions. The rim is relatively homogenous and inclusion-222 223 free, with faint patchy zoning. Like xenotime, the monazite rim may preserve the external dimension 224 of pristine monazite (e.g., the top right monazite grain in Fig. 6), suggesting the altered rim formed 225 through coupled dissolution-reprecipitation reactions. The heterogeneous core represents a mixture 226 of pristine and secondary monazite.

EPMA WDS analysis (Table A5) and X-ray mapping reveal that monazite rims contain 0.01–0.08

228 apfu Si, 0.007–0.014 apfu Th, 0.23–0.26 apfu La, 0.41–0.45 apfu Ce, 0.09–0.12 apfu Pr, and 0.12–

229 0.15 apfu Nd, while the partially altered cores have lower concentrations of Si (0.01–0.06 apfu), Th

230 (0.005–0.007 apfu), and La (0.21–0.23 apfu), and higher concentrations of Nd (0.15–0.16 apfu).

231 Other elements show little systematic variation between the core and rim. LA-ICP-MS trace element

232	data of monazite are available in Table A7. LA-ICP-MS analysis (a spot size of 10 μm) does not have
233	the spatial resolution to resolve the altered monazite rim and the partially altered monazite core.
234	Monazite shows an LREE-enriched smooth pattern in the chondrite-normalized REE diagram,
235	without a distinct Eu anomaly (Fig. 7).

236 U-Th-Pb isotope data

237 One hundred and thirteen U-Th-Pb isotopic analyses were carried out on ten xenotime crystals. The locations of analyses, along with the analytical numbers and apparent 206 Pb/ 238 U ages, are 238 239 presented in Figure 5. U-Th-Pb isotope data are listed in Tables A8 and presented graphically in Figure 9. Among them, 33 analyses are not considered geologically significant and are excluded 240 from the age analysis. The omitted analyses include 20 analyses with discordance values (1 -241 206 Pb/ 238 U/ 207 Pb/ 235 U) × 100) >5% or <-5% and 13 analyses obtained from the incompletely altered 242 243 domains of xenotime. Explanations for the discordance and incompletely altered domains are presented in the "Discussion" section. 244

After exclusion of the omitted analyses, the 46 analyses of pristine xenotime cores yield ²⁰⁶Pb/²³⁸U 245 dates from 164.4 ± 6.1 to 153.2 ± 5.6 Ma, 207 Pb/ 235 U dates from 160.6 ± 6.9 to 152.2 ± 6.0 Ma, and 246 208 Pb/ 232 Th dates from 168.2 ± 11 to 139.1 ± 7.6 Ma. These data define a weighted mean 206 Pb/ 238 U 247 age of 157.11 \pm 0.83 Ma (MSWD = 0.71), a weighted mean 207 Pb/ 235 U age of 155.93 \pm 0.93 Ma 248 249 (MSWD = 0.60), and a Tera-Wasserburg lower intercept age of 156.49 ± 0.94 Ma (MSWD = 0.55). The three ages overlap with each other within the margin of error. The remaining 41 analyses of 250 xenotime rims yield 206 Pb/ 238 U dates from 142.4 ± 5.8 to 128.5 ± 5.1 Ma, 207 Pb/ 235 U dates from 146.9 251 \pm 9.4 to 129.4 \pm 7.2 Ma, and $^{208}\text{Pb}/^{232}\text{Th}$ dates from 150.0 \pm 21 to 121.5 \pm 9.1 Ma. These data define 252 12

253	a weighted mean ${}^{206}\text{Pb}/{}^{238}\text{U}$ age of 135.46 ± 0.93 Ma (MSWD = 1.07), a weighted mean ${}^{207}\text{Pb}/{}^{235}\text{U}$
254	age of 135.2 \pm 1.4 Ma (MSWD = 1.05), a Tera-Wasserburg lower intercept age of 135.5 \pm 1.1 Ma
255	(MSWD = 1.05), and a Concordia age of 135.33 ± 0.91 Ma (MSWD = 0.41). The four ages overlap
256	with each other within the margin of error.
257	Thirty eight U. The Dhigotopic analyzes were collected on 11 monorite errotals. The locations of
201	Thirty-eight 0-Th-Fo isotopic analyses were conected on TT monazite crystais. The locations of
258	analyses and analytical numbers, along with the apparent ²⁰⁶ Pb/ ²³⁸ U ages, ²⁰⁷ Pb/ ²³⁵ U ages, and
259	²⁰⁸ Pb/ ²³² Th ages, are shown in Figure 6. Results are listed in Table A9 and presented graphically in
260	Tera-Wasserburg Concordia diagram in Figure 8. Monazite shows large variations in ²⁰⁷ Pb/ ²³⁵ U
261	$(3730 \pm 36 \text{ to } 208 \pm 8 \text{ Ma})$, $^{206}\text{Pb}/^{238}\text{U}$ (1897 ± 61 to 161 ± 6 Ma), and $^{208}\text{Pb}/^{232}\text{Th}$ dates (463 ± 15 to
262	141 \pm 5 Ma). The U–Pb ages are highly discordant, with discordance values ranging from 23 to 79.
263	Nevertheless, the U-Pb isotope dataset forms a linear array in the Tera-Wasserburg Concordia
264	diagram, yielding an upper intercept age of >4.5 Ga and a lower intercept age of 158.6 ± 3.3 Ma
265	(MSWD = 3.7), which overlaps with the ages of xenotime cores within the margin of analytical error.

266

DISCUSSION

267 Remarks on monazite and xenotime ages

Although many monazite and xenotime dates are concordant or near concordant, the two minerals may be affected by low-temperature hydrothermal alteration and yield discordant ages (e.g., Rasmussen et al. 2011; Seydoux-Guillaume et al. 2012; Didier et al. 2013; Budzyń et al. 2018, 2021, 2022; Budzyń and Sláma, 2019). Factors causing age discordance during hydrothermal alteration include incomplete replacement of mineral domains (Grand'Homme et al. 2016; 2018) and

incorporation of initial Pb in secondary monazite and xenotime (e.g., Seydoux-Guillaume et al. 2012;
Didier et al. 2013; Budzyń et al. 2022). For instance, altered monazite domains with apparently
homogeneous composition at a microscale may correspond to nanomixtures of primary and
secondary monazite, yielding discordant ages (Grand'Homme et al. 2016; 2018). During
hydrothermal alteration of monazite, initial Pb could accumulate in the monazite lattice along the
microcracks (e.g., Budzyń et al. 2022) or be incorporated as nanosized Pb-rich inclusions (Seydoux-

279 Guillaume et al. 2003; Fougerouse et al. 2018).

Twenty analyses of xenotime yield highly discordant dates with >5% or <-5% discordance, 280 281 suggesting the incorporation of common Pb. Among them, thirteen analyses were obtained from the 282 rims, two from the cores, and three from the incompletely altered domains. Eleven analyses 283 with >5% discordance were placed on micro-fracture or porous places (e.g., analytical points 1 and 7 in section V16-101A, see the top left xenotime grain in Figs. 5, A1). Common Pb could present as 284 nano-scale Pb-bearing minerals, such as altaite (Pb as an essential element) or tellurobismuthite (Pb 285 as a minor component), along monazite microcracks and grain boundaries. Two minerals are 286 commonly observed to occur in contact with xenotime and monazite (Fig. 4C). Accordingly, we 287 288 propose the source of common Pb can be attributed to micro-cracks or porous spaces, which are more developed in xenotime rims. Quartz is another source of common Pb. Eight analyses designed 289 to analyze the thin xenotime rims are contaminated by the quartz matrix; it is visible from the laser 290 ablation pits that quartz was ablated (e.g., analytical points 19-21 in section V16-103A, see the 291 central right xenotime grain in Figs. 5, A1). Common Pb could be present within quartz-hosted fluid 292 inclusions or along the grain boundaries between quartz and xenotime. Thirteen analyses obtained 293 294 from the incompletely altered domains (i.e., mixture of pristine and secondary xenotime) of xenotime

are also excluded from the age analysis. In Figure 5 (section V16-103A, the large grain in the top right) and Figure A2 (xenotime in the third row), for instance, the incompletely altered domain in the upper part of a xenotime grain partially preserves the oscillatory zoning of the pristine xenotime core. Ages and U-Th concentrations of this domain fall between the pristine core and the completely altered rim on the left.

Monazite shows highly discordant U–Pb ages (discordance values ranging from 23 to 79) and large variations in 207 Pb/ 235 U (3730–208 Ma), 206 Pb/ 238 U (1897–161 Ma), and 208 Pb/ 232 Th ages (463– 141 Ma). Nevertheless, the U-Pb isotope dataset forms a linear array in the Tera-Wasserburg Concordia diagram, with an upper intercept age of >4.5 Ga and a lower intercept age of 158.6 ± 3.3 Ma (MSWD = 3.7), suggesting the discordance is caused by the incorporation of common Pb (e.g., Schoene, 2004), which affected the more sensitive 207 Pb/ 235 U ratio (e.g., Budzyń et al. 2022).

The source of common Pb may be attributed to the extensive micro-cracks and grain boundaries, 306 which are not easily recognized under the optical microscope but become apparent under high-307 contrast SEM-BSE imaging. Analytical spots placed within individual monazite grains without 308 visible micro-cracks (e.g., analytical spots 15-21 in section V16-103a, Fig. 6) show younger 309 ²⁰⁷Pb/²³⁵U and ²⁰⁶Pb/²³⁸U ages than those placed in monazite aggregates with grain boundaries and 310 311 micro-cracks (e.g., analytical spots 1-14 in section V16-103a, Fig. 6). Common Pb could accumulate 312 in the monazite lattice along the microcracks (e.g., Budzyń et al. 2022). Similar to xenotime, common Pb could also present as nano-scale Pb-bearing minerals, such as altaite or 313 tellurobismuthite, along monazite microcracks and grain boundaries. The abundant mineral 314 inclusions in monazite are less likely to the sources for common Pb, because X-ray mapping shows 315 316 that the inclusions contain lower Pb concentrations than the surrounding monazite (Fig. A3).

Due to the limited width (i.e., $<10 \ \mu m$) of the altered rim (i.e., secondary monazite) and the 317 chaotic patchy zoning of the partially altered core (i.e., mixture of pristine and secondary monazite), 318 the laser spot size (i.e., 10 µm) does not have the spatial resolution to resolve pristine and secondary 319 320 monazite. Nevertheless, despite the mixture sampling of pristine and secondary monazite, monazite U–Pb data form a linear array and yield a lower intercept age of 158.6 ± 3.3 Ma (MSWD = 3.7). One 321 possible explanation is that the alteration of monazite occurred shortly after the precipitation of 322 pristine monazite, less than the error of the lower intercept age. Accordingly, these altered (or 323 partially altered) monazite domains with high common Pb could yield geologically reasonable lower 324 intercept ages, which overlap with the ages of pristine monazite within the margin of error. Similar 325 326 results have been reported from the Sri Lanka monazite (Seydoux-Guillaume et al. 2012) and the 327 Montasset monazite, France (Didier et al. 2013).

While monazite and xenotime do occur in contact with each other, monazite ages do not reflect the *ca.* 135 Ma hydrothermal event recorded by xenotime rims formed through coupled dissolutionreprecipitation reactions. One possible explanation is that this hydrothermal event only induced partial dissolution of monazite, but no compositional alteration. This is supported by the fact that monazite contains abundant unhealed micro-cracks with little to no evidence of compositional change along their edges, and shows a more anhedral shape than xenotime.

334 Compositional alteration of monazite and xenotime

One feature of the studied monazite is Th enrichment in the altered monazite rims. This contrasts with many natural monazite samples, which normally form secondary monazite with lower Th concentrations (e.g., Poitrasson et al. 2000; Rasmussen and Muhling, 2007; 2009; Seydoux-

338	Guillaume et al. 2012) via dissolution-reprecipitation reactions at low temperatures (i.e., \leq 400°C).
339	For these natural samples, that decreasing Th content may be attributed to the high Th content in
340	pristine monazite (i.e., >4 wt% ThO ₂) and limited structural incorporation of Th in secondary
341	monazite at lower temperatures. This is because the substitution of huttonite (ThSiO ₄) into monazite
342	lattice is temperature-dependent (Hetherington et al. 2010; Seydoux-Guillaume et al. 2012), with
343	higher structural incorporation of Th at higher temperatures and vice versa. Accordingly, monazite
344	alteration experiments conducted at high temperatures (i.e., ≥600°C) form secondary monazite with
345	high Th contents (Seydoux-Guillaume et al. 2002; Hetherington et al. 2010; Harlov et al. 2011),
346	while low-temperature alteration experiments (i.e., ≤600°C) result in secondary monazite with low
347	Th contents (e.g., Williams et al. 2011; Budzyń et al. 2015a; Grand'Homme et al. 2018).
348	In our case, Th enrichment in the altered monazite is likely due to the relative low Th
349	concentrations (<4.5 wt% ThO ₂ , Tables A5, A7, A9). A low concentration of Th is typical for
350	hydrothermal monazite (Schandl and Gorton, 2004), which normally contains <4 wt% of ThO ₂ (e.g.,
351	Schandl and Gorton, 2004, Catlos et al., 2013; Janots et al. 2012) and is frequently used to date
352	hydrothermal gold deposits (e.g., Rasmussen et al. 2006; Fielding et al. 2017; Zhao et al. 2019; Deng
353	et al. 2020; Liu et al. 2021). However, the mobility of Th during the alteration of hydrothermal
354	monazite has rarely been addressed, partially due to previous studies focused on isotopic dating and a
355	lack of careful examination to recognize potential alteration textures. This study demonstrates that
356	²⁰⁸ Pb/ ²³² Th ages, commonly overlooked in geochronological studies on hydrothermal monazite,
357	should be presented and discussed due to Th enrichment in the altered monazite.
358	In contrast to monazite, the mechanisms of xenotime alteration are less well-known and
359	understood due to its lower abundance in nature. Several works documented fluid-mediated

360 alteration of xenotime in nature. These studies demonstrate that xenotime may break down into secondary phases such as apatite, epidote, and hingganite (Broska et al. 2005; Hetherington and 361 Harlov, 2008; Majka et al, 2011; Ondrejka et al. 2022). Xenotime could also undergo coupled 362 363 dissolution-reprecipitation reactions, resulting in compositional alterations that affected the age record (e.g., Hetherington et al. 2008; Rasmussen et al. 2011; Fielding et al. 2017; Budzyń et al. 364 2018), but the fluids inducing the dissolution-reprecipitation reactions are not well characterized, 365 partially due to the lack of co-existing fluid inclusions. Experimental studies on xenotime alterations 366 focused on alkali-rich aqueous fluid conditions (e.g., Hetherington et al. 2010; Harlov and Wirth, 367 2012; Budzyń et al. 2015b, 2017; Budzyń and Sláma, 2019). Hetherington et al. (2010) reported 368 369 partial dissolution of xenotime in acid and brine fluids, but no compositional alteration. The recent experimental work of Budzyń and Sláma (2019) confirms that xenotime may be affected by re-370 equilibration induced by alkali-rich aqueous fluid via coupled dissolution-reprecipitation reactions 371 under temperature conditions of 550-650 °C, resulting in U-Pb age disturbance. 372

While it's widely accepted that CO_2 can promote the solubility of REE since CO_3^{2-} forms strong 373 complexes with the REE (e.g., Wood, 1990; Williams-Jones et al. 2000; Hetherington et al. 2010; 374 375 Zhou et al. 2016), the role of CO_2 in xenotime alterations has been rarely addressed. This study presents an example of xenotime compositional alteration and resetting of U-Pb ages caused by 376 coupled dissolution-reprecipitation reactions, which are induced by low to moderate salinity 377 carbono-aqueous fluids at low temperatures (i.e., <400°C). Since these fluids are commonly involved 378 in the formation of lode gold deposits (e.g., Groves et al. 1998; Goldfarb et al. 2005), it's crucial to 379 examine xenotime textures and recognize potential alteration textures before carrying out isotopic 380 381 dating of xenotime collected from these deposits.

382 Two discrete gold mineralization events

383 The ca. 135 Ma hydrothermal event (Fig. 10), recorded by the altered rim of xenotime with a weighted mean ${}^{206}\text{Pb}/{}^{238}\text{U}$ age of 135.46 \pm 0.93 Ma, is responsible for the deposition of native gold 384 385 and stage III tellurides (i.e., petzite, calaverite, altaite, tellurobismuthite) because these minerals occur in contact with or as inclusions in xenotime rims (Figs. 4C-I). While abundant Early 386 387 Cretaceous ages (144-120 Ma, Fig. 10 and Table A10) have been reported from the Xiaoqinling gold 388 district, minerals directly in contact with gold have only been recently dated (i.e., a monazite U-Pb 389 age of 127.5 ± 0.7 and a rutile U-Pb age of 129.7 ± 4.3 Ma: Liu et al. 2021). The paragenetic relationship between dated minerals and gold is unclear in many previous studies. For instance, dated 390 minerals in gold-bearing quartz veins or altered wall rocks do not necessarily result from the same 391 hydrothermal event responsible for gold deposition. This study presents robust textural and 392 393 geochronological evidence to justify a ca. 135 Ma gold mineralization event in the Xiaoqinling gold 394 district.

The *ca*. 157 Ma hydrothermal event, recorded by xenotime cores with a weighted mean 206 Pb/ 238 U 395 age of 157.11 \pm 0.83 Ma and monazite with a Tera-Wasserburg lower intercept age of 158.6 \pm 3.3 396 Ma, is responsible for the earlier gold mineralization (i.e., lingbaoite-sylvanite-stützite/native 397 tellurium-sylvanite-stützite), since xenotime, monazite, and stage II tellurides were all observed as 398 primary inclusions in pyrite (Figs. 3, 4). The stage II tellurides, although they now appear much less 399 400 abundant than stage III tellurides and gold, are merely remnants of the stage II gold mineralization (i.e., gold in the form of sylvanite ($[Au, Ag]_2Te_4$) after having been reworked by the later fluid event. 401 The early-stage gold mineralization could have played an important role in the later gold enrichment 402 process. For instance, recent studies (Jian et al. 2021, 2022b) reveal that stage II tellurides are 403 19

primary melt inclusions trapped as polymetallic droplets that scavenged gold from aqueous fluids 404 with high efficiency. During later hydrothermal events, polymetallic melt inclusions could be 405 released from the host mineral and continue to scavenge gold from fluids, due to fracturing of the 406 407 host mineral or migration of the melt inclusions to the crystal surface. Aside from S16 gold-bearing quartz vein, the characteristic lingbaoite-sylvanite-bearing mineral assemblage, and by analogy, the 408 earlier gold mineralization event has also been observed in other parts of the Xiaoqinling gold 409 district, such as the S60 gold-bearing quartz vein (Jian et al. 2020, 2021, 2022b) and the Jinqu gold 410 deposit (Chang et al. 2020). Our study, therefore, reveals a previously overlooked yet important Late 411 412 Jurassic gold mineralization event in the Xiaoqinling gold district.

413 Late Jurassic ages have been only reported from the Luzhougou gold deposit (two Re-Os molybdenite model ages of 149 ± 8.4 Ma and 154 ± 1.1 Ma: Li et al. 2012a) in the Xiaoqinling gold 414 district. The lack of reported Late Jurassic ages likely results from the scarcity of geochronometers 415 that are able to preserve the Late Jurassic age information after the Early Cretaceous hydrothermal 416 overprint. Most of the Early Cretaceous ages in the Xiaoqinling gold district were obtained from 417 ⁴⁰Ar/³⁹Ar dating of micas, with a few Re-Os molybdenite and U-Pb monazite ages (Fig. 10 and Table 418 A10). The low ⁴⁰Ar/³⁹Ar closure temperatures of micas (e.g., ~300°C for biotite and ~400°C for 419 420 muscovite: Harrison et al. 1985, 2009; Schaen et al. 2021), suggest their isotopic system could be easily reset during later hydrothermal events. For instance, our study reveals that the ca. 135 Ma gold 421 mineralization event is characterized by the mineral assemblage of native gold-calaverite-petzite-422 tellurobismuthite, which coexists with low to moderate salinity H₂O-CO₂ fluid inclusions along 423 healed fractures in quartz (Figs. 3I-K). The total homogenization temperatures of these fluid 424 inclusions cluster at 200 to 400°C, a range that overlaps with the ⁴⁰Ar/³⁹Ar closure temperatures of 425

426 biotite and muscovite.

427	To the east of the Xiaoqinling gold district, abundant Late Jurassic ages have been reported in the
428	adjacent Xiong'ershan region. Examples include the Wuzhangshan monzogranite pluton (SHRIMP
429	zircon U–Pb age of 157 \pm 1 Ma: Mao et al. 2010), granitic porphyries in the Shangfanggou Mo
430	deposit (SHRIMP zircon U–Pb age of 158 ± 3 Ma, Mao et al. 2010), Nannihu Mo deposit (SHRIMP
431	zircon U–Pb age of 157 ± 3 Ma, Mao et al. 2010), Balipo Mo deposit (LA-ICP-MS zircon U–Pb age
432	of 155.9 \pm 2.3 Ma, Jiao et al. 2009), Qiyugou Au deposit (SIMS zircon U-Pb ages of 157.3 \pm 1.1 and
433	158.7 ± 1.2 Ma, Wang et al. 2020), a Mo (Au?) mineralized vein in the Huaixiangwa Au deposit (Re-
434	Os molybdenite mean age of 155.0 ± 2.2 Ma, Gao et al. 2018), and a Au mineralized vein in the
435	Luanling Au deposit (Re-Os molybdenite isochron age of 163 ± 2 Ma, Chao et al. 2019).
436	Accordingly, the large-scale Jurassic magmatism and associated mineralization event in eastern
437	China (e.g., Mao et al. 2021a, b; Goldfarb et al. 2021), in relation to the subduction of the paleo-
438	Pacific plate beneath the eastern China continent (Mao et al. 2021a), might have also caused
439	widespread gold mineralization in the Xiaoqinling gold district.

440

IMPLICATIONS

This study presents an example of xenotime compositional alteration and resetting of U–Pb ages caused by coupled dissolution-reprecipitation reactions, which are induced by low to moderate salinity carbono-aqueous fluids at low temperatures. Gold minerals in contact with such composite xenotime crystals could precipitate before, coeval with, or after the dated domains, depending on the relation between the gold minerals and the dated xenotime domains. Since low to moderate salinity carbono-aqueous fluids are commonly involved in the formation of lode gold deposits, it's crucial to

examine xenotime textures and recognize potential alteration textures before carrying out isotopic dating of xenotime collected from these deposits. Without prior compositional and textural characterization, attempts to date such composite crystals could yield mixed age information and meaningless ages.

This study also demonstrates that monazite and xenotime could be affected by low-temperature 451 hydrothermal alteration and yield discordant ages, resulting from incomplete replacement of mineral 452 domains or incorporation of common Pb. Common Pb could accumulate in the monazite and 453 xenotime along microcracks and grain boundaries. These features may be identified under high-454 455 contrast SEM-BSE images but are not always visible in reflected-light photomicrographs or CL 456 images. During the alteration of hydrothermal monazite that typically contains low Th concentrations, Th may be enriched in secondary monazite through coupled dissolution-457 reprecipitation reactions. Accordingly, ²⁰⁸Pb/²³²Th ages, sometimes neglected in geochronological 458 studies on hydrothermal monazite from ore deposits, should be presented and discussed. This study 459 also highlights the potential of utilizing highly discordant U-Pb age data, which can be discarded in 460 geochronology studies but could potentially be used to constrain the age of metasomatic events as 461 462 the lower intercept in the Tera-Wasserburg Concordia diagrams.

463

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- 793

FIGURE CAPTIONS

Fig. 1. Geologic map of the Xiaoqinling gold district and its position in China (compiled from Jian etal. 2015, 2021; Liu et al. 2021).

796

Fig. 2. Typical features of the S16 gold-bearing quartz vein shown by photographs. A. B.
Underground exposure. C. Hand specimen. D. Polished thick section showing the occurrences of
pyrite (euhedral large crystals), tellurides (black cloudy aggregates), and xenotime (very fine-grained
red cloudy aggregates).

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Fig. 3. Two stages of gold mineralization shown by photomicrographs (A-I: plane-polarized 802 reflected light, J: reflected-transmitted light image created through focus stacking, K: reflected-803 804 transmitted light). A-H. Distribution of two stages (II, III) of minerals within and near two pyrite grains. I. Native gold and tellurides (stage III) occur as inclusions along a healed microfracture in 805 806 quartz. J-K. Native gold and telluride (stage III) coexist with low to moderate salinity H₂O-CO₂ fluid inclusions along healed microfractures in quartz. Abbreviations: Alt = altaite, Au = gold, Bn =807 bornite, Clv = calaverite, Ccp = chalcopyrite, Gn = galena, Lb = lingbaoite, Ptz = petzite, Py = 808 809 pyrite, Qz = quartz, Stz = stützite, Syv = sylvanite, Tbi = tellurobismuthite, Te = native tellurium.

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Fig. 4. Occurrence of xenotime and monazite shown by photomicrographs (D, F, H: plane-polarized reflected light), BSE images (A–C, E, G), and CL image (I). A–C. Xenotime and monazite occur as inclusions in pyrite. D–G. Native gold and tellurides (stage III) occur in contact with xenotime. The two xenotime grains were dated by LA-ICP-MS. Their CL images with analyzed spots and ages labeled are shown in Fig.5. G. Xenotime rims are brighter than core zones in BSE images. H–I. Native gold and tellurides (stage III) occur in contact with the rim of a xenotime grain or as inclusions in the altered domains of the xenotime. Note that altered domains of xenotime are brighter

818	in CL image, while the unaltered domains are darker and show oscillatory zoning. Abbreviations: Alt
819	= altaite, Au = gold, Clv = calaverite, Mnz = monazite, Ptz = petzite, Py = pyrite, Qz = quartz, Xtm =
820	xenotime.
821	
822	Fig. 5. Cathodoluminescence images of xenotime grains after LA-ICP-MS analysis. The 10 μm and
823	16 µm laser pits are for U-Th-Pb isotope and trace element analysis, respectively. SEM-BSE images
824	of the 10 xenotime grains before LA-ICP-MS analysis are shown in Figure A1. WDS X-ray maps (Y,
825	U, Th, Pb) of 6 xenotime grains before LA-ICP-MS analysis are shown in Figure A2.
826	
827	Fig. 6. SEM-BSE images of monazite grains after LA-ICP-MS analysis. ²⁰⁶ Pb/ ²³⁸ U, ²⁰⁷ Pb/ ²³⁵ U and
828	²⁰⁸ Pb/ ²³² Th ages of the analyzed spots are indicated.
829	
830	Fig. 7. REE patterns of the xenotime and monazite. The data are normalized to C1 chondrite
831	composition as compiled in Sun and McDonough (1989).
832	
833	Fig. 8. Tera-Wasserburg Concordia diagrams and weighted mean age diagrams for xenotime and
834	monazite.
835	
836	Fig. 9. Two episodes of gold mineralization and growth of monazite and xenotime illustrated by
837	schematic drawing.
838	

839	Fig. 10. Age distribution of gold deposits from the Xiaoqinling gold district. The age data, detailed	in
840	the Appendix (Table A10), were compiled from Xu et al. (1998), Wang et al. (2002), Li et al. (2012)	2a,
841	b), Qiang, 2012, Qiang et al. 2013, Zhao et al. (2019), and Liu et al. (2021).	
842		
843	Appendix	
844	Fig. A1. SEM-BSE images of the 10 xenotime grains before LA-ICP-MS analysis.	
845		
846	Fig. A2. WDS X-ray maps of 6 xenotime grains before LA-ICP-MS analysis.	
847		
848	Fig. A3. Characterizations of the largest monazite grain before LA-ICP-MS analysis shown by B	SE
849	image (A), photomicrographs (B: plane-polarized reflected light; C: plane-polarized reflected light	ght
850	with gamma enhancement), and WDS X-ray maps (D-H).	
851		
852	Table A1. Analytical conditions of EPMA measurements of xenotime and monazite	
853		
854	Table A2. Analytical conditions of LA-ICP-MS U-Th-Pb analysis of xenotime and monazite	
855		
856	Table A3. Analytical conditions of LA-ICP-MS trace element analysis of xenotime	
857		
858	Table A4. Analytical conditions of LA-ICP-MS trace element analysis of monazite	
859		40

860 Table A5. Electron microprobe data of xenotime and monazite

861

- 862 Table A6. LA-ICP-MS trace element data of xenotime
- 863
- 864 Table A7. LA-ICP-MS trace element data of monazite
- 865
- 866 Table A8. LA-ICP-MS U-Th-Pb data of xenotime
- 867
- 868 Table A9. LA-ICP-MS U-Th-Pb data of monazite
- 869
- Table A10. Age data of gold deposits from the Xiaoqinling gold district









Fig. 5







Fig. 7









