High resolution SIMS U-Th-Pb geochronology of small size (< 5 μm) monazite; Constraints on the timing of Qiuling sediment-hosted gold deposit, South Qinling Orogen, central China

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Abstract

Accurately determining the timing of hydrothermal mineralization for the sediment-hosted disseminated gold (SHDG) deposits is difficult because of a lack of both suitable chronometers and in-situ techniques with the required spatial resolution and precision. The lack of precise age determinations on gold deposits has hindered understanding of their genesis and relation to the geodynamic setting. The Qinling orogen is one of the most important gold regions in China and contains numerous SHDG deposits. The Qiuling-Jinlongshan deposit is a typical SHDG deposit located in the eastern of the South Qinling Orogen (SQO), with 109 t Au at an average grade of 6.17 g/t. Devonian and Carboniferous metasedimentary rocks host structurally controlled gold mineralization, which is associated with silica-carbonate alteration. Pyrite, arsenopyrite, and arsenian pyrite are major gold carriers and gold also occurs as native gold grains and invisible gold in the sulfides. In this study, the well-defined hydrothermal overgrowth rims (~ 2 μm) of single monazite grains-associated with disseminated auriferous arsenian pyrite and arsenopyrite in low-grade metasedimentary rocks yield U-Pb age of 239 ± 13 Ma (2σ) by high spatial resolution secondary ion mass spectrometry (SIMS). The hydrothermal monazites are cogenetic to the primary gold mineralization where they are closely associated with gold-bearing sulfides. This new age implies that the early to middle Triassic mineralization event in the eastern SQO was related to the Triassic tectonic transition from compression to transpression in the Qinling Orogen after the closure of the Mianlue Ocean. This study highlights 2-μm high spatial resolution SIMS monazite U-Th-Pb dating method as a powerful tool for determining the timing of SHDG deposit worldwide elsewhere. It is crucial to examine monazite textures and its link to hydrothermal alteration before carrying out the isotopic dating of monazite.

Keywords: Monazite overgrowth U-Th-Pb dating, SIMS, sediment-hosted gold deposits.
Radiometric dating of mineral deposits has critical importance in better understanding ore genesis and associated geological processes, which aids to develop genetic models for successful mineral exploration. However, precise and accurate age constraints on the timing of metal mineralization have long been a big challenge, largely due to the lack of suitable mineral phases that can be unequivocally linked to metal deposition and that have remained closed to isotope diffusion since the time of formation. Sediment-hosted disseminated gold (SHDG) deposits are a significant current source of world gold production (Sillitoe, 2020), mostly including orogenic and Carlin-type gold deposits, typically formed under low-to-mEDIATE temperature, and are featured by very fine-grained alteration assemblages (Hofstra et al. 1999; Muntean et al. 2011). Continuous efforts to precisely date SHDG gold deposits have been made by using various radioactive isotopes methods such as $^{39}\text{Ar}/^{40}\text{Ar}$ dating of K-bearing silicate minerals (Arehart et al. 1993), Re-Os dating of gold-bearing sulfides minerals (Kerr and Selby, 2012), Rb-Sr dating of galkhaite and illite (Tretbar et al. 2000; Wang et al. 2023), Sm-Nd or U-Pb dating of calcite (Su et al. 2009; Jin et al. 2021), and U-Pb isotopes of U-Th-bearing accessory phases (Vielreicher et al. 2003; Pi et al. 2017; Gao et al. 2024). Notably, recent advances in \textit{in-situ} analytical techniques have promoted age dating of sediment-hosted gold mineralization using U-Th-bearing accessory minerals, because such minerals (e.g., monazite, rutile, xenotime, zircon, apatite) typically have blocking temperatures for U-Pb isotopes significantly higher than the temperature of gold deposition. However, problems remain because (1) in many cases those minerals are too fine relative to the spatial resolution of \textit{in-situ} analysis (e.g., 16 microns for laser ablation) and (2) the minerals may contain multiple generations with some of them have no relation to gold mineralization (e.g., inheritance from the wall rocks). Moreover, many chronometers either are scarce
in these SHDG deposits or are susceptible to isotopic resetting during subsequent metamorphism and
deformation events, which makes the reliable ages of many SHDG deposits worldwide still limited.
The lack of agreement on the age and tectonic setting for the deposits remains a topic of debate (Cline

Monazite [(Ce, La, Nd, Th)PO$_4$] commonly contains high U and/or Th, but negligible common Pb
and its U-Th-Pb system have closure temperatures greater than 700°C (Parrish, 1990; Williams et al.
2007), which could be highly resistant to weathering and post-ore modifications (Chiaradia et al. 2013).
Thus, it has been well-known that monazite is highly suited for isotopic dating (Seydoux-Guillaume et
al. 2002; Cherniak et al. 2004). In recent years, the use of hydrothermal monazite for dating gold ore
deposits increased markedly, because of the availability of in-situ analytical techniques [e.g., secondary
ion mass spectrometry (SIMS), sensitive high-resolution ion microprobe (SHRIMP), NanoSIMS,
electron probe microanalysis (EPMA), and laser ablation inductively coupled plasma mass
spectrometry (LA-ICP-MS)]. The in-situ dating of hydrothermal monazite intergrown with ore
minerals has successfully constrained the ages of gold deposits worldwide, such as several large
orogenic gold deposits in Australia (Brown et al. 2002; McNaughton et al. 2005; Rasmussen et al. 2006;
Vielreicher et al. 2010; Fielding et al. 2017), gold deposits of Quadrilátero Ferrífero district in Brazil
(Lobato et al. 2007), giant Sukhoi Log SHDG in Russia (Meffre et al. 2008; Yudovskaya et al. 2011),
the Hutti gold deposit in southern India (Sarma et al. 2008; Sarma et al. 2011), the gold reefs in the
Witwatersrand basin in South Africa (Rasmussen et al. 2007), orogenic gold deposits in Jiaodong gold
province eastern China (Deng et al. 2020) and Qinling gold province central China (Yang et al. 2006;
Li et al. 2011; Zhao et al. 2019; Qiu et al. 2020; Liu et al. 2021; He, 2022; Zhao et al. 2022; Jian et al.
2024), and many others (Zhou et al. 2019; Yu et al. 2020; Gao et al. 2021; Zhang et al. 2021; Li et al.
However, the application of U-Pb geochronology of monazite in SHDG deposits is still hampered by the low temperature alteration assemblages, small grain size, low abundance, and sporadic occurrence, the abundance of mineral inclusions, typically low U and Th contents, common compositional zoning and presence of multi-aged domains (Rasmussen et al. 2001; Rasmussen et al. 2023).

More than 100 SHDG deposits (>2000 t of proven gold reserves) in the South Qinling Orogen (SQO), are hosted in Cambrian to early Triassic marine sedimentary rocks with variable degrees of metamorphism and constitute the second-largest gold province in China (Mao et al. 2002; Chen et al. 2004; Goldfarb et al. 2005; Goldfarb et al. 2014; Liu et al. 2015; Wu et al. 2019). The ages of these gold deposits have been determined by many studies for decades in an attempt to relate the ore-forming episode to the geotectonic evolution of the SQO. Previous geochronologic studies yielded reliable isotopic dates on these gold deposits ranging from 250 to 110 Ma (Table A1), mainly consisting of zircon U-Pb dated igneous rocks crosscutting gold lodes, ore-related mica (sericite/muscovite, biotite, fuchsite) $^{40}\text{Ar}/^{39}\text{Ar}$, calcite Sm-Nd, sphalerite/pyrite Rb-Sr, and hydrothermal accessory minerals (zircon, monazite, titanite) U-Pb. In several major gold deposits (e.g., Zaozigou, Zhaishang, Ma’anqiao, Qiuling-Jinlongshan), different methods yielded contrasting age results for the same deposits (Zhao et al. 2001; Lu et al. 2006; Zhu et al. 2010; Hua, 2012; Liu et al. 2016; Sui et al. 2018; Qiu et al. 2020; He et al. 2023). Therefore, the timing of gold precipitation in SQO is not well constrained, which hinders our understanding of the exact temporal-spatial gold metallogenic events and genesis of the gold deposit.

The Qiuling-Jinlongshan gold deposit is a large-tonnage and representative SHDG deposit in the eastern SQO with a gold reserve of 109 t at an average grade of 6.17 g/t (Liu, 2006). Our recent study
on the Qiuling SHDG deposit found that high grade of 3.63 g/t ores contain disseminated monazite grains. Detailed mineralogical and textural studies have shown that these monazite grains are closely related to auriferous arsenian pyrite and arsenopyrite. These findings make the Qiuling deposit an ideal object for dating the gold mineralization by monazite U-Th-Pb geochronology in SHDG deposits. In this contribution, we show that high spatial resolution (2-µm scale) SIMS U-Th-Pb dating of hydrothermal monazite-(Ce) from Qiuling gold deposit in the SQO can provide timing constraints on representative SHDG mineralization. We present detailed textural and temporal relationships of monazite with gold mineralization, geochemical, and geochronological analyses on the timing of gold mineralization and its potential relationship to tectonic events in the region. Together with previous work, our results confirm that early-middle Triassic gold mineralization in the eastern SQO is more widespread than previous studies.

**Geological setting**

The Qinling orogen is tectonically situated between the North China Craton and South China Block (Fig. 1a; Dong et al. 2011). Traditionally, the Qinling orogen was divided into the North Qinling and South Qinling Orogen (Fig. 1b), which are separated by the Paleozoic Shangdan suture (Ratschbacher et al. 2003; Dong et al. 2011). The North Qinling Orogen consists of an early Paleozoic arc that was accreted to the North China Craton at ca. 450 Ma along the Shangdan suture (Meng and Zhang, 2000). This area hosts minor gold mineralization (Mao et al. 2002). The South Qinling Orogen is further subdivided into the northern domain and southern domain along the Zhen’an–Fengxian Fault (Zeng et al. 2012). The northern part of SQO is characterized by a highly deformed basinal flysch sequence (Xue et al. 1996). The southern part of the SQO is covered by Paleozoic strata in the east and...
characterized by the easternmost exposure of Triassic turbiditic deposits in the west that are partly calcareous and form part of the immense Songpan–Ganzi Basin (Fig. 1b; Mao et al. 2002). The Paleozoic and Triassic sedimentary rocks were intensely deformed during the Qinling orogeny, and along with this, numerous regional northwestern striking folds and thrust faults were also produced (Li et al. 2020). These faults are the first control on the distribution of the gold deposits in the SQO (Mao et al. 2002; Chen and Santosh, 2014), and most of which are hosted in Devonian rocks composed of carbonate, siliciclastic and argillaceous rocks with a total thickness of ca. 3000–8000 m that were deposited in several extensional fault-bounded basins (Liu and Yang, 1990).

The Qiuling-Jinlongshan gold deposit is situated in the northern part of the Zhen’an Basin of the SQO (Fig. 2a), which is an EW-trending rift basin formed during the opening of the Mianlue Ocean at the Early to Middle Devonian (Hu et al. 2002; Dong and Santosh, 2016; Cheng et al. 2019). Previous studies have elaborated on the ore deposit geology, structural characteristics, fluid inclusions, and H-O-S-Pb isotopes of the Qiuling-Jinlongshan SHDG deposits (Zhang et al. 2000; Zhao and Feng, 2002; Zhao et al. 2005; Zhang et al. 2006; Chen et al. 2015; Li et al. 2020; Ma et al. 2020). The main host horizon for the gold deposit is a turbiditic sequence of fine-grained sandstone, siltstone-silty shale, calcareous siltstone, and limestone of the Upper Devonian Nanyangshan Formation (D3n) that contains about 90% of the Au reserve (Fig. 2b). Siltstone, intercalated with silty shale, is the important ore-bearing host. Another horizon, representing about 10% of the Au ore, is in the Carboniferous Yuanjiagou Formation (C1y) and consists of chert, banded limestone that is intercalated with silty shale, silty sandstone, argillaceous limestone, and calcareous shale (Fig. 2b). There are no exposures of igneous rocks in the mine area. Hydrothermal alteration types associated with Au occurrences in the Qiuling-Jinlongshan gold deposit area include silicification and calcite as replacements and veinlets.
with lesser veinlets of pyrite, arsenopyrite, barite, and kaolinite, although no systematic zonation has
been documented. Gold ores are closely related to silicate and pyrite. Gold ore characteristically is
massive, banded, brecciated, and present in veinlets and disseminations (Fig. 3a), but also developed in
mesoscopic fracture networks. Stages of ore genesis most likely began with replacement or
precipitation of 0.5– to 2–mm-thick, or less, pyrite and arsenopyrite along bedding (S0) layers (Fig. 3b),
which also contain sporadic As-rich, zoned pyrite (Fig. 4). Invisible gold in disseminated in very
fine-grained arsenian pyrite and arsenopyrite, low-temperature alteration assemblages, and has a
geochemical association of Au-As-Hg-Sb-(Tl) (Chen et al. 2015). Gold mineralization is dominated by
dissemination of fine-grained auriferous pyrite and arsenopyrite in carbonaceous shales and siltstones,
with minor amounts of veinlets composed of coarse-grained pyrite, arsenopyrite, and quartz.

Samples and analytical methods

Sample preparation

The monazite-bearing ore sample (QL105, Fig. 3a), from the No. 304 ore body comprising
high-grade banded As-pyrite and arsenopyrite gold ores, containing 3.63 g/t Au, has been studied in
detail. This sample is representative ore in the Qiuling gold deposit, consisting of quartz, mica, calcite,
ankerite, pyrite, arsenopyrite, and calcite with minor monazite. The sample was prepared as a polished
thin section and was examined under optical microscopy to characterize the mineralogy and textures of
monazite. After petrographic examination, the sample was investigated using scanning electron
microscopy (SEM) to characterize the morphological and textural features of monazite grains (Figs.
3b-c). Then, the thin section was cut out with a diamond wire saw and mounted in 25-mm-diameter
epoxy discs together with pieces of monazite standards for SIMS U-Th-Pb dating (Figs. 3d and e). The
discs were polished to produce a smooth, flat sample surface with relief of less than a few μm, which is critical for high-accuracy, high-precision isotope ratio analysis by SIMS and compositional analysis by EPMA.

Textural and compositional analysis

SEM investigation was carried out at the Institute of Geology, Chinese Academy of Geological Sciences, using an FEI NOVA nanoSEM equipped with an Oxford X-Max 50 detector. The sample was coated with a 250 Å carbon film and then imaged using SEM with secondary electron imaging (SEI) and back-scattered electron (BSE) modes. The EDAX GENESIS energy-dispersive spectroscopy (EDS) was performed using an accelerating voltage of 15 kV and a working distance of 15 mm.

The mineral/phase distribution map and the mineral proportions (vol.%) were determined for the thin section (whole domains) of the QL105 sample using a TESCAN integrated mineral analyser (TIMA) at Nanjing Hongchuang Geological Exploration Technology Service Company, Limited, China. The TIMA comprises a Mira-3 scanning electron microscope equipped with four EDS (EDAX Element 30). The measurements were performed at an acceleration voltage of 25 kV, a probe current of 9 nA, a working distance of 15 mm, a pixel spacing of 3 μm, and a dot spacing of 9 μm; the scanning time was 6 h. The current and BSE signal intensity was calibrated on a platinum Faraday cup using the automated procedure. The EDS performance was checked using a manganese standard. The samples were scanned using the TIMA liberation analysis module.

EPMA wavelength-dispersive X-ray spectrometry (WDS) analysis and elemental mapping were applied to reveal the internal texture and chemistry variation of the monazite grains. All analyses were performed using a JEOL JXA-iSP100 EPMA at the Nanjing Hongchuang Geological Exploration
Technology Service Company. An accelerating voltage of 15 kV was used for monazite. The spot beam
diameter was 1~2 μm. Higher current gave the optimal count rate for trace elements and excitation of
less intense analytical lines such as REE. The EPMA was calibrated by natural and synthetic standards
(Table A2). Details on EPMA settings for WDS analysis are available in Table A2. The content of the
elements in the mineral formula is expressed in atoms per formula unit (apfu). The formula of monazite
was normalized on 4 oxygen atoms. The probe current of 500 nA was for elemental mapping. The step
size for elemental mapping was 0.5 μm, and the dwell time was set to 200 ms for each step/pixel.

SIMS U-Th-Pb dating of monazite

In-situ monazite SIMS U-Th-Pb dating was conducted using a Cameca IMS1280HR ion
microprobe at the Institute of Geology and Geophysics, Chinese Academy of Sciences in Beijing. The
instrument description and operating protocol applied to monazite have been detailed by Li et al.
(2013). A primary beam of O- was focused to a size of < 3 μm on the monazite surface with an
intensity of ca. 0.2 nA. Monazite RW-1 (207Pb/235U age=904.15 ± 0.26 Ma [2σ], Th=11.8 ± 1.0 wt%
[2σ], and Th/ U=42.5 ± 3.0 [2σ]; Ling et al. 2017) was interspersed with unknowns as the standard to
calibrate U and Th concentrations and U-Th-Pb isotope ratios. To choose the exact location of different
Th concentrations from the single monazite grain, the image of 232Th/16O2 signals was set up (Fig. 3f). A
repeatability of 1.5% (1σ RSD) was derived from the long-term 206Pb/238U measurement of the
monazite standard. As a measure of the accuracy of SIMS U-Th-Pb monazite analyses calibrated
against RW-1 standard, in-house monazite M6 was employed as a secondary standard. A concordia age
of 484.7 ± 14 Ma (2σ RSD) is obtained for monazite M6 (Table A4), which agrees with the
recommended value, within errors (unpublished). For monazite SIMS analysis, the 204Pb-based
The common Pb correction is inappropriate because of large analytical uncertainty owing to low $^{204}$Pb concentrations and the probability of isobaric interferences derived from $^{232}$Th$^{144}$Nd$^{16}$O$^{2+}$ (Ireland et al. 1999; Li et al. 2013). Therefore, a $^{207}$Pb-based correction (Williams, 1997; Li et al. 2013) was done to subtract common Pb (initial Pb) using the terrestrial Pb isotope composition for the corresponding ages (Stacey and Kramers, 1975). Age calculations and plots were performed with the ISOPLOT add-in (Ludwig, 2012).

**Results**

**Monazite occurrence**

The sample QL105 is composed of quartz (66 vol.%), mica (26 vol.%), ankerite (3.2 vol.%), arsenopyrite (1.7 vol.%), pyrite (1.5 vol.%), biotite (0.7 vol.%), and calcite (0.7 vol.%). Monazite is heterogeneously distributed in this sample (red marked spots in Fig. 3d). Monazite is small in size (3 to 30 μm) and euhedral to subhedral in shape (Figs. 3c and 4). Although monazite grains appear to be rather homogeneous optically, they frequently show strong zonation in BSE imaging (Fig. 5). The zoning pattern revealed by SEM is concentric zonation. Monazite I occur particularly abundant in metamorphosed fine-grained sandstone and interbedded siltstones from the Nanyangshan Formation (Fig. 4a). The monazite grains occur as isolated, clustered, and beaded crystals in ankerite and quartz (Fig. 4), are commonly elongate and parallel with the slaty cleavage (Fig. 4a). Most cores appear to be compositionally homogeneous in BSE images (Fig. 4). The cores are clearly visible in high-contrast BSE images, and typically form more than 50% of the entire crystal, delineated by a bright rim zone (typically < 3 μm) of monazite, which in places, contains minute specks of a Th-rich silicate mineral (Fig. 4b). Within a single sample, monazite cores range in shape from broadly oval to highly irregular.
with scalloped and embayed outlines (Fig. 5). The core-rim boundary of some of the more complete
and unaltered cores is irregular with serrated outlines in places (Fig. 5).

Monazite II with ‘intergrowth-like’ zonation coexists with arsenopyrite in strongly altered and
mineralized belts of the Nanyangshan Formations (Fig. 3b). The grain is small euhedral and skeletal
crystals and their intergrowths incorporated into auriferous sulfides (Fig. 4c), as inclusions in pyrite
(Figs. 4d-g), and some form rims on sulfides (Figs. 4h, i and 6b).

Monazite chemistry

One hundred and three electron microprobe analytical spots were measured on thirty-seven
monazite crystals. Both generations of monazite are characterized by a heterogeneous internal structure
with markedly varying concentrations of particular REEs and Th (Figs. 5 and 6; Table A3). They are
rich in LREE, with Ce predominant, and are depleted in HREE (contents are below the detection limit
of microprobe). The chemical compositions of monazite make up a continuous series with Ce$_2$O$_3$
contents from 26.99 to 35.20 wt.%. The La$_2$O$_3$ and Nd$_2$O$_3$ contents vary also continuously from 7.86 to
20.65 wt.% and 7.18 to 19.94 wt.%, respectively. The La–Ce, and La–Nd correlation coefficients are
0.21 and –0.74, respectively. Therefore, Ce monazite can be enriched in both La and Nd, whereas Nd
monazite is always depleted in La (Fig. 6a). Their P$_2$O$_5$ contents range from 26.94 wt.% to 30.65 wt.%.
Minor proportions of CaO (0.03 to 1.31 wt.%) and SiO$_2$ (0.01 to 2.44 wt.%) were also detected. The U
and Pb contents are below the detection limit of the microprobe.

X-ray element maps for U, Th, La, Ca, and Y of monazite grains reveal several distinct
compositional differences between the cores and rims (Fig. 5). The cores have higher concentrations of
Th, U, Y, and Ca, and lower concentrations of La, than the rims (Table A3). Monazite II differs from
monazite I in lower ThO$_2$ and lower Y contents. Monazite I is characteristically high in Th content (>1.34 wt.%), and Th/Ce ratio (>0.05), and is typical of high-temperature igneous and metamorphic monazite (Fig. 6b). Monazite II is more enriched in LREE than Monazite I (Fig. 6c). Monazite II is characteristically low in Th content (<1 wt.%) and Th/Ce ratio (<0.04), which is characteristic of hydrothermal monazite (Fig. 6b). Calcium is incorporated into monazite by the brabantite substitution, and there is a strong correlation between Ca and Th in both the cores and the rims of the monazite crystals. It is notable that there is a negative correlation between $(Th + U + Si)$ (apfu) and $(REE + Y + P)$ (apfu) (Fig. 6d), indicating that Th$^{4+}$ is charge-balanced through the coupled substitutions of $Th^{4+} + Ca^{2+} = 2(REE + Y)^{3+}$ and $Th^{4+} + Si^{4+} = P^{5+} + (REE + Y)^{3+}$. Many of the grains contain minute specks (<1 μm) with high Th contents. Qualitative analysis of the Th-rich inclusions by EDS indicates that they also contain Si, suggesting that the mineral may be huttonite or possibly thorite.

Monazite U-Th-Pb ages

In-situ SIMS U-Th-Pb results of monazite are provided in Table A5. Three analyses were made on the core of monazite II. The $^{206}Pb/^{238}U$ dates are 1763 Ma, 738.6 Ma, and 597.5 Ma, respectively. The core of monazite II has high U (1777–11186 ppm) and Th (35880–75594 ppm), resulting in low Th/U ratios (7–23). The remaining 20 analyses of monazite II plot close to the concordant line yielded a lower intercept $^{206}Pb/^{238}U$ age of 245 ± 13 Ma (2σ; MSWD = 0.93; Fig. 7a) on a Tera-Wasserburg plot. After applying the $^{207}Pb$-based correction for common Pb, the weighted mean $^{206}Pb/^{238}U$ age was 239 ± 13 Ma (2σ; MSWD = 0.73; Fig. 7b). The rim of monazite contains highly variable U (18–581 ppm) and Th (2,604–58607 ppm), with Th/U ratios of 18 to 1677. In Fig. 7c, the common-Pb corrected $^{208}Pb/^{232}Th$ age ranged from 216 ± 13 Ma (2σ) to 406 ± 14 Ma (2σ).
Discussion

Formation of the monazite from ore zones

The crystal textures and occurrence of monazite, in combination with mineral geochemistry, can be used to confidently distinguish monazite of different origins (Vielreicher et al. 2003; Rasmussen and Muhling, 2007; Williams et al. 2007; Taylor et al. 2015; Zi et al. 2019). These cores of monazite in the Qiuling gold deposit have a wide range of U-Pb ages that are obviously older than those of the rims of monazite (Fig. 7a), which suggests that the core of monazite was originally introduced into the sedimentary rocks as detritus. The ages of the cores overlap with the ages of detrital zircon grains from the same locality (Dong and Santosh, 2016). We, therefore, propose that the core of monazite is likely detrital in origin. The cores of monazite crystal have a large range of ThO$_2$ (1.52 to 9.68 wt.%) and show concentric zoning with respect to ThO$_2$ (Fig. 6b). This confirms the metamorphic source for the detrital grains.

Some monazite crystals occur in contact with auriferous sulfides and are concentrated within small areas (Fig. 4), which is different from the more sparsely and homogeneously distributed magmatic or metamorphic monazite. The rims of monazite crystals have low contents of ThO$_2$ (<1 wt%, Fig. 6b). Indeed, the irregular, scalloped core-rim contact (Fig. 5a) provides strong textural evidence for the partial dissolution of former detrital monazite cores by post-depositional fluids, consistent with experimental results (e.g. Teufel and Heinrich, 1997; Seydoux-Guillaume et al. 2002). All these features fit the criteria of hydrothermal monazite as proposed by Schandl and Gorton (2004) and suggest that the rims of monazite grew synchronously with and/or slightly post-dated the texturally associated sulfides. Our study shows that detrital Th-rich monazite is unstable during hydrothermal
fluid activity, and undergoes replacement via dissolution and reprecipitation, forming relatively low-Th monazite overgrowths with trace amounts of ThSiO$_4$ inclusions (Rasmussen and Muhling, 2007). The presence of minute thorium silicate inclusions in the hydrothermal monazite rims suggest that Th released by dissolution of the detrital monazite core was immobile and could not all be accommodated in the hydrothermal monazite rims, which suggests that the dissolution of the cores was closely linked in time to the growth of the hydrothermal rims (Fig. 4b).

The dissolution and replacement were not isochemical: some elements (e.g. LREE) were added while others (e.g. Ca, Th, U, and Y) were removed. The differences in composition between the detrital monazite cores and the hydrothermal monazite rims, probably reflect the chemical environment under which the new monazite formed. The preservation of detrital monazite cores in the composite crystals suggests that the conditions (e.g. temperature, fluid composition, flow rate) required for complete replacement of all of the detrital cores were not sustained over a sufficiently long period of time. X-ray mapping and WDS analysis show that formed metamorphic detrital monazite contains significantly less LREE than the outer part of the rim (Fig. 5). The outer, broader part of the rim contains significantly more LREE, which rises slightly toward the crystal margin, indicating a pattern of LREE enrichment during hydrothermal monazite growth. It’s widely accepted that CO$_2$ can promote the solubility of REE since CO$_3^{2-}$ forms strong complexes with the REE (e.g., Wood, 1990; Williams-Jones et al. 2000; Hetherington et al. 2010). The much lower Th and higher LREE concentrations of hydrothermal monazite indicate that the solubility of Th$^{4+}$ is relatively low compared to that of LREE$^{3+}$ in hydrothermal fluids responsible for monazite precipitation (Deng et al. 2020). This may result from the fact that thorium tends to be immobile in low temperature, aqueous-carbonic metamorphic fluids (Schandl and Gorton, 2004). Primary fluid inclusion studies indicate ore-forming fluid in the Qiuling
deposit has low homogenization temperatures (120–277°C), low salinity (5.7–8.6 wt.% NaCl eqv), and low CO₂ content (0.89–5.41 mol.%; Zhang et al. 2002). This study presents an example of monazite compositional alteration and resetting of U-Pb ages caused by dissolution-reprecipitation reactions, which are induced by low to moderate salinity carbon-aqueous fluids at low temperatures (i.e., < 300°C). Since these fluids are commonly involved in the formation of orogenic gold deposits (e.g., Groves et al. 1998; Goldfarb et al. 2005), the U-Pb ages of these monazite crystals record the timing of gold mineralization.

**Chemical disturbance and Th-Pb age scattering of monazite**

Most chemical variations observed in the Qiuling monazites could be explained by the huttonite (ThSiO₄) and brabantite [CaTh(PO₄)₂] exchanges (Fig. 6d), which have been attributed to hydrothermal alteration processes (Poitrasson et al. 1996, 2000). Intra-grain variations of the Th content in distinct age and chemical domains (Fig. 5) are a good indication of interaction with fluids. In some natural hydrothermal monazites from sericitized samples, Poitrasson et al. (2000) have observed strong removal of Th leading to the overgrowth of Th-poor domains. This variable behavior of Th during fluid-rock interactions may explain its heterogeneous distribution as well as its variable relations with Y in the Qiuling monazites. In most grains, Th decrease correlates with Th-Pb age decrease from core to rim (Fig. 7d). Experiments have shown that Ca-rich fluids can enhance monazite dissolution and result in the recrystallization of grains with strong chemical modifications (Seydoux-Guillaume et al. 2002). The main host horizon for the Qiuling gold deposit is a turbiditic sequence of fine-grained sandstone, siltstone-silty shale, calcareous siltstone, and limestone of the Upper Devonian Nanyangshan Formation. Chen et al. (2015) analyzed sulfur isotopes of ore-stage pyrite associated with monazite in...
the Qiuling gold deposit and demonstrated a relatively narrow range of positive $\delta^{34}\text{S}$ values, ranging from 8.1‰ to 15.2‰, and suggested the ore-forming fluid was derived from metamorphic devolatilization of Paleozoic marine sedimentary rocks. Hence, in the case of the Qiuling gold deposit, it is not surprising that fluid interactions were able to induce a significant scattering of the monazite Th-Pb ages (Fig. 7c).

Timing of hydrothermal gold mineralization in the Qiuling deposit and its implications

Hydrothermal mineralization at the Qiuling SHDG deposit, however, has been difficult to date directly due to a lack of both suitable chronometers and in-situ techniques with the required spatial resolution and precision. The age of the Qiuling deposit has not been well-constrained. Previous hydrothermal calcite Sm-Nd dating results of fine-grain calcite vein in the Qiuling deposit yielded ages of 232.3 ± 4.3 Ma (Hua, 2012). Moreover, the sericite $^{40}\text{Ar}/^{39}\text{Ar}$ dating results of the ore sample yielded ages of 232.7 ± 6.9 Ma (Zhao et al. 2001) and 142.3 ± 0.8 Ma (Liu et al. 2016), respectively. The interpretations of the geological significance of these ages, however, are questionable. For example, the formation of some dated minerals (e.g., sericite and calcite) may not be coeval with gold deposition. One of the $^{40}\text{Ar}/^{39}\text{Ar}$ plateau ages of sericite is much younger than that of the other in the Qiuling deposit. The sericite has low-closure temperatures (Chiaradia et al. 2013), suggesting its isotopic system could be easily reset during later hydrothermal events. In fact, post-ore calcite and/or quartz veins are widely developed in the Qiuling deposit. It is very likely that these post-ore fluids have reset Ar-Ar isotopic systems. Consequently, a more precise dating method of a syn-mineralization mineral is urgently needed to confine the timing of gold mineralization of the Qiuling deposit. It is, therefore, necessary to evaluate the reliability of our age. The paragenesis of the minerals indicates that fine-grain...
Pyrite and arsenopyrite are closely related to native gold and monazite in the disseminated ore (Figs. 379-4d-i). Abundant invisible gold precipitation is observed in this stage, which is indicated by pyrite and arsenopyrite LA-ICP-MS results (Hua et al. 2012; Chen et al. 2015). Monazite grains were also observed to be closely associated with auriferous pyrite and arsenopyrite in the sulfide band (Fig. 3b), and thus coeval with the main gold mineralization. Indeed, visible gold precipitation is also observed in this stage (Fig. 4c). We thus conclude that the hydrothermal monazite growth is coeval with main gold deposition and our monazite U-Pb geochronological result is, therefore, a reliable age to define the Qiuling gold mineralization. The 20 spot analyses of hydrothermal monazite growth from the Qiuling gold deposit yielded a weighted mean $^{207}\text{Pb}\text{-based corrected }^{206}\text{Pb}/^{238}\text{U}$ age of $239 \pm 13$ Ma (2$\sigma$, MSWD = 0.73), indicating that the Qiuling gold mineralization occurred at ~239 Ma.

Our U-Pb ages of hydrothermal monazite in the Qiuling deposit show that there was a significant episode of gold mineralization in the early to middle Triassic in the eastern SQO, which is more widespread than previously thought in the western SQO (Table A1 and Fig. 8; ca. 248-238 Ma in the Xiahe-Hezuo district; Jin et al. 2017; Sui et al. 2018; Yu et al., 2020a; Yu et al., 2020b). The Qiuling gold mineralization can be classified as orogenic gold deposits (discussed above and in Chen et al. 2015). The gold sources of the orogenic gold deposits in the SQO have been proposed mainly from Paleozoic sediments during Triassic orogeny and metamorphism, especially Devonian and Triassic sediments (Zeng et al. 2012; Chen et al. 2015; Ma et al. 2018; Wu et al. 2018; Qiu et al. 2020). Moreover, a relatively extensional regime has been widely accepted as important for the upwelling of deeply sourced fluid and the precipitation of orogenic gold deposits (Chen et al. 2004; Large et al. 2011; Goldfarb and Groves, 2015). Hence, the new geochronology results presented in this study (~239 Ma) support a model in which the ultimate control of the gold mineralization in the Zhen’an basin is the
Triassic tectonic transition in the geodynamic setting from compression to transpression in the Qinling orogen after the closure of the Mianlue Ocean (Mao et al. 2012).

**Implications**

This study demonstrates that monazite could record early hydrothermal events, and not be affected by later hydrothermal alteration. Considering the high closure temperature of monazite, a full reset of the U-Pb system seems unlikely. It is crucial to examine the monazite textures and recognize alteration textures before carrying out isotopic dating of monazite collected from SHDG deposits. During the alteration of hydrothermal monazite that typically contains low Th concentrations and incorporation of common Pb through coupled dissolution-reprecipitation reactions. These features can be identified under high-contrast BSE images but are not always visible in reflected-light photomicrograph images.

Without prior compositional and textural characterization, the hydrothermal growth rim could be easily neglected. Attempts to date the core of monazite crystals could yield mixed age information and meaningless ages. Our study presents an example of monazite compositional alteration and the 2-μm scale hydrothermal monazite growth of U-Th-Pb ages caused by coupled dissolution-reprecipitation reactions, which are induced by low salinity and CO₂ aqueous fluids at low temperatures are commonly involved in the formation of SHDG deposits. This paper contributes to this area of geological science at the junction between geochronology and economic geology. From the methodological point of view, this study illustrates high resolution SIMS U-Th-Pb geochronology of small size (< 5 μm) monazite can be achieved. It has potential applications in dating precious samples or multistage geological events, as well as revealing the detailed growth history of monazite by image U-Th-Pb acquisition. Monazites have long been recognized in many sediment-hosted gold deposits worldwide elsewhere (Table A6),
such as Sukhoi log gold deposit in the Siberian craton (Russia; Meffre et al., 2008; Yakubchuk et al., 2014), gold deposits in the Telfer area of the Paterson Province (Australia; Rowins et al., 1997; Schindler et al., 2016), and gold deposits in the Muruntau area in the Tian Shan orogenic belt (Uzbekistan; Bierlein and Wilde, 2010; Kempe et al. 2015). Thus, the common presence of monazite closely associated with native gold in many SHDG deposits makes 2-µm scale hydrothermal monazite growth a potential robust U-Pb geochronometer for gold mineralization, especially in the SHDG deposit without suitable geochronometers to record the hydrothermal process.

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Compliance with Ethical Standards

The authors declare that they have no conflict of interest. This article does not contain any studies with human or animal subjects.

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Figure captions

Figure 1 (a) Tectonic division of China showing the Qinling Orogen between the Yangtze and North China Cratons. (b) Sketch geologic map of the South Qinling Belt showing the location of major gold deposits relative to regional faults and granitoid intrusions (modified after Chen et al. 2004, the geochronological data is detailed in the Appendix Table A1 and references therein).

Figure 2 (a) Geological map of the Qiuling sediment-hosted gold deposit; (b) Stratigraphic column of the Nanyangshan Formation and Yuanjiagou Formation (modified after Geology of Jinlongshan microscopic disseminated gold deposit in Shaanxi province, 1997).

Figure 3 (a) Photograph showing the disseminations of pyrite (Py) and arsenopyrite (Apy) in the metasedimentary rock; (b) Backscattered electron image showing the main alteration types of the Qiuling gold deposit, microcrystalline quartz, sericite, and sulfides mainly occur in the side of silty limestone (bedding S₀); (c) Backscattered electron image of zoning monazite (Mnz) crystal; (d) Cut thin section including monazite marked by red spots; (e) Photographs showing the monazite samples used for U-Pb dating; (f) The image of $^{232}$Th-$^{16}$O$_2$ signals from SIMS.

Figure 4 Backscattered electron images showing the textures of monazite (Mnz) occurrences. (a) and (b) The detrital monazites occur in the sedimentary rocks; (c) native gold grain occurs associated with arsenopyrite (Apy); (d-g) Hydrothermal monazite grains coexistence with pyrite (Py) and arsenopyrite; (h) and (i) intergrowths of monazite with pyrite and arsenopyrite. The larger version of each image showing zonations of monazite grains.
Figure 5 High-contrast BSE images (a, b), and WDS X-ray maps for two monazite crystals showing element distribution maps for U (c, d), Th (e, f), Ca (g, h), La (i, j), Y (k, l). Note the similarity of distribution patterns for U, Th, Ca, and Y in the detrital cores.

Figure 6 (a) La vs. Nd plot; (b) Discrimination of monazite with different origins including igneous, metamorphic, and hydrothermal monazite, the arrow arrange was referred from Wu et al. 2019; (c) Ternary diagram of LREE, HREE, and (Th + U); (d) Brabantite Ca(Th, U)REE2 vs. huttonite (Th, U)SiREE·P3; exchange in monazite shon in the cationic plot (per formula units for 4 oxygens) of (Th + U + Si) vs. (REE + P + Y).

Figure 7 Dating results of monazite in the Qiuling deposit. (a) Tera-Wasserburg U-Pb plot for areas with different U contents and common Pb compositions in detrital and hydrothermal monazites; (b) The weighted average 207Pb common Pb corrected 206Pb/238U age for hydrothermal monazite (data-point uncertainties are 2σ); (c) Histogram of monazite 206Pb/232Th ages. BSE images of representative monazite grains show measured 207Pb corrected common Pb 206Pb/238U ages (2σ level); (d) Plot of Th concentrations (ppm) vs. 208Pb/232Th ages.

Figure 8 Age distribution of gold deposits from the South Qinling Terrain gold district. The age data, detailed in the Appendix (Table A1), and this study. The tectonic evolution of the region during the Mesozoic is based upon Wang et al. (2011), Dong and Santosh (2016), Qiu et al. (2018), and Wu et al. (2019) and the references therein.
Appendix

Table A1. Age data of gold deposits from the South Qinling Orogen gold district

Table A2. Analytical conditions of EPMA measurements of monazite

Table A3. Electron microprobe data of monazite

Table A4. In-situ SIMS U-Th-Pb dating results of M6 monazite standard by 2-μm beam size dating

Table A5. In-situ SIMS U-Th-Pb dating results of multi-type monazites from the Qiuling SHDG deposit

Table A6. The monazite closely associated with ores in representative sediment-hosted gold deposits worldwide without well-constrained ages.
Figure 1

North China Craton

Western Qinling

South Qinling Belt

Yangtze Craton

Eastern Qinling
Figure 2

a) Geologic map of the study area

b) Lithologic column and petrographic description

Legend:
- Middle Carboniferous           Lower Carboniferous           Upper unit of the Upper Devonian Nanyangshan Formation
- Sishikou Formation             Yuanjiangou Formation           Lengzhou Formation
- Lower unit of the Upper Devonian Nanyangshan Formation
- Anticline                      Syncline
- Crushed zone
- Stratigraphic Boundary
- Ore body and number
- Fault
Figure 3
Northward subduction of the Paleo-Tethys oceanic slab.

Syn-collision between the South China block and amalgamated South Qinling-North Qinling blocks.

Post-collision between the South China block and amalgamated South Qinling-North Qinling blocks.

Oblique subduction of the paleo-Pacific plate beneath the Eurasian continent.