Textural, fluid inclusion and in-situ oxygen isotope studies of quartz: constraints on vein formation, disequilibrium fractionation and gold precipitation at the Bilihe gold deposit, Inner Mongolia, China

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Abstract

Bilihe is a porphyry gold deposit located in the northern margin of the North China Craton (NCC), Inner Mongolia, China. Different stages of quartz are well developed at this deposit. To document the history of quartz deposition, the fluid evolution and gold precipitation events of the deposit, detailed oxygen isotope signatures of quartz from...
Bilihe were studied using high-resolution secondary ion mass spectroscopy (SIMS), integrated with scanning electron microscope-cathodoluminescence (SEM-CL) and fluid inclusion microthermometry. The SEM-CL features show that the hydrothermal veins at Bilihe have a complex growth history, with multiple generations of quartz developed in each set of veins. Fluid inclusions in different quartz stages yield variable homogenization temperatures, ranging from 178 °C to above 600 °C. These quartz stages exhibit variable δ¹⁸O values of 3.5–15.4‰, corresponding to δ¹⁸Ofluid ranging from -8.7‰ to 12.0‰. There are two abnormal peaks of δ¹⁸Oquartz and δ¹⁸Ofluid values occurring in a sub-generation of A type veins and auriferous banded quartz veins, suggesting that the vein quartz may have experienced sporadic disequilibrium oxygen fractionation with water when crystallizing, thus resulting in local ¹⁸O-enrichment. The overall δ¹⁸Ofluid values, which show a gradual decrease from early to late stages, suggest a progressive decrease in the proportion of magmatic hydrothermal fluids. The relationship between quartz textures and gold occurrence shows that gold precipitated twice at Bilihe. The first precipitation in the UST quartz may have resulted from rapid cooling and indicates that addition of meteoric water was not necessary for gold precipitation, whereas the progressive incursion of meteoric water probably had a significant effect on the second gold precipitation.

Key words: porphyry gold deposit, quartz, cathodoluminescence, in situ oxygen isotopes, magmatic-hydrothermal evolution, disequilibrium fractionation

Introduction
Porphyry ore deposits are an important source of copper, molybdenum and gold (Sillitoe, 2010). The magmatic-hydrothermal evolution of porphyry ore-forming systems has been extensively studied using bulk sample isotopic analysis. Quartz veins are a characteristic feature of porphyry deposits (Sillitoe, 2010; Richards, 2011) and quartz can be valuable indicators of fluid origin, as their oxygen isotopic composition is derived from the parental fluid, with the fluid-quartz fractionation factor controlled by temperature at isotopic equilibrium conditions (Matsuhisa et al., 1979). Oxygen isotopes, combined with hydrogen isotopes, have been widely used to constrain the source and evolution of ore-forming fluids (Taylor, 1974). An important factor for oxygen isotope calculations is the requirement that isotopic equilibrium fractionation was achieved between quartz and the aqueous fluid. However, very complex zoning in porphyry-related quartz is commonly observed in cathodoluminescence (CL) images (Rusk et al., 2008) and extreme $\delta^{18}O_{\text{quartz}}$ heterogeneity is commonly observed in individual quartz grains (Allan and Yardley, 2007; Tanner et al., 2013). These suggest that isotopic fractionation during quartz growth may not have been achieved under equilibrium, which would greatly affect the calculation of $\delta^{18}O_{\text{fluid}}$. In most studies, the variations of oxygen isotope compositions or isotopic dynamic disequilibrium fractionation during quartz growth are difficult to identify and always overlooked, especially when using the bulk sample isotopic analysis. Consequently, the final calculated $\delta^{18}O_{\text{fluid}}$ may be not representative.

The texture of quartz is also a useful monitor of fluid characteristics (e.g., composition and temperature) in hydrothermal processes (Rusk and Reed, 2002).
Crystal size, zones, generations and fluid inclusion properties are valuable indicators of growth history. Variations in CL intensity are generally considered to be in response to structural defects or differences in chemical composition (Allan and Yardley, 2007; Rusk and Reek, 2002). Variations of $\delta^{18}$O$_{\text{quartz}}$ and calculated $\delta^{18}$O$_{\text{fluid}}$ in different CL zones of quartz veins may reflect spatial and temporal changes in fluid composition and growth rate (Tanner et al., 2013; Fekete et al., 2016; Rottier et al., 2018).

Bilihe deposit is located in Inner Mongolia, China, and is the first reported gold deposit in which mineralization occurs in both unidirectional solidification texture (UST) and hydrothermal quartz veins. Based on the temporal and spatial relationships between the orebody and porphyry intrusions, the alteration types and zones, and the ore characteristics, this deposit is classified as a porphyry gold deposit (Ge et al., 2009; Qing et al., 2010; Zhu et al., 2018; Huang et al., 2020). In this paper, we analyze the O-isotope compositions of quartz formed at different stages of the deposit using secondary ion mass spectrometry (SIMS), combined with cathodoluminescence and fluid inclusion studies, to explore the oxygen isotope distribution in each quartz sub-generation, and to constrain the quartz growth history and investigate the precipitation mechanism of gold.

Geological Background

The Central Asian Orogenic Belt (CAOB) is one of the largest accretionary orogenic collages on Earth (Windley et al., 2007), restricted by the southern Tarim Craton and North China Craton (NCC) and the northern Siberian Craton (Fig. 1). The
CAOB contains multiphase accretionary complexes, including micro-continents, accretionary wedges, island arcs, forearc basins, backarc basins and ophiolitic belts. The Bilihe gold deposit is hosted in the early Paleozoic Bainaimiao arc, which forms part of the southern accretionary zone between the Solonker suture and northern NCC (Fig. 1b).

The igneous rocks in the Bainaimiao arc are dominated by calc-alkaline rhyolite, andesite, basalt, and a magmatic complex consisting of granite, granodiorite, diorite, and gabbro. To date, several Au-mineralized zones (e.g., Belts I and II, III and Veins 22–26) have been identified in the Bilihe area (Fig. 1c, d). The ore Belt I contained about three tons of gold, and has been mined out. The Ore Belt II (Fig. 1d), containing most of the gold at Bilihe, is about 1 km from the ore Belt I and contains over 25 tons of gold. The ore Belt II is spatially and temporally associated with a buried tongue-shaped high-K calc-alkaline granodiorite porphyry (Supplementary Fig. 1; Ge et al., 2009; Zhu et al., 2018). Zircon U–Pb SIMS dating of the granodiorite porphyry (269 ± 2 Ma; Zhu et al., 2018) and a Re–Os isochron age of post-ore molybdenite (268 ± 1 Ma; Zhu et al., 2018) restricts the age of the gold mineralization to ca. 269 Ma.

This deposit is identified as the first large-sized high-grade porphyry gold deposit on the northern NCC (Ge et al., 2009; Zhu et al., 2018; Huang et al., 2020). Sulfides are rare (less than 1 wt. %) in the ore, predominantly chalcopyrite, pyrite, bornite, molybdenite and galena, based on metallurgical analysis results (Ge et al., 2009). The mainly alteration types include early potassic alteration and late superposed sericite-quartz and chlorite-sericite-illite alterations, but a large-scale potassic alteration only
can be found at depth (>150m; Ge et al., 2009; Zhu et al., 2018). The distribution of the alteration zones in the Belt II is shown in Supplementary Fig. 1.

In the intermediate-upper part of the granodiorite porphyry, dendritic quartz (Fig. 2a) and unidirectional solidification texture (UST) quartz (Fig. 2b, c) are well developed. There are also many quartz–magnetite ± K-feldspar veins (A veins; Gustafson and Hunt, 1975) in this area, cutting the UST quartz and producing a K-feldspar alteration halo (Fig. 2b-d). In addition, abundant banded quartz veinlets (banded veins) are distributed in the intrusions and surrounding rocks, locally overprinting the dendritic quartz and UST quartz (Fig. 2e). This type of vein occurs in rectilinear networks and is filled by granular quartz with central sutures, and contains chalcopyrite and pyrite. In the upper part of the orebody and overlying tuff, quartz–pyrite–carbonate-tourmaline veins (late veins) are well developed (Fig. 2f).

The Au mainly occurs as native gold grains in the UST quartz and banded veins, and less than 20% of Au is hosted in the surrounding altered rocks (Ge et al., 2009). The gold-bearing USTs (~ 8 tonnes reserves) are mainly located in the central zone of Belt II (Supplementary Fig. 1), with an average grade of ~15.0 g/t, and the auriferous banded quartz veinlets (over 20 tonnes reserves) are mainly distributed in the granodiorite porphyry and wall rocks, with an average grade of ~2.7 g/t. The banded veins gold zone is around the UST gold zone. Only minor gold grains were observed in the A veins, and the late veins are barren.

**Analytical Methods**
Scanning Electron Microscope Cathodoluminescence (SEM-CL)

SEM-CL images of quartz veins were obtained at the School of Physics, Peking University, using a FEI Quanta 200FEG with a Gatan mini-CL detector with a wavelength range between 185 and 850 nm. Images were obtained under conditions of 10 kv accelerating voltage, 3.5 μm spot size, 10 mm working distance, and 1024 x 884 pixels resolution. To avoid re-polishing after imaging, the samples were photographed under low vacuum mode, without being coated with carbon.

Microthermometry of fluid inclusions

Closely associated groups of fluid inclusions with similar shapes and identical phases were studied. Microthermometry measurement was performed on a Linkam THMSG600 heating–freezing stage equipped with a transmitted light microscope at the Guangzhou Institute of Geochemistry, Chinese Academy of Science. The heating/freezing rate was set as 0.2 to 5°C/min, and was reduced at 0.1°C/min when close to phase transformation. The stage was calibrated using synthetic fluid inclusions. The uncertainty of temperature measurements is ±0.1°C in the range of −100°C to 25°C, ±1.0°C between +25°C and +400°C, and ±2°C above +400°C. Salinities of fluid inclusions (wt % NaCl equiv) were calculated using the equations of Bodnar (1994) and Bodnar and Vityk (1994) for the H2O-NaCl system. Pressures were calculated from the equations of Driesner and Heinrich (2007).

Secondary Ion Mass Spectrometer (SIMS)
In situ oxygen isotope measurements were carried out on a CAMECA IMS-1280 SIMS at the Guangzhou Institute of Geochemistry, Chinese Academy of Science. The Cs+ primary beam was accelerated at 10 kV, with an intensity of ~2 nA. The spot size was ~10 μm. Detailed description for operating and analytical conditions can be found in Li et al. (2018). NBS-28 quartz, with δ\(^{18}\)O value of 9.5 ‰, was used to calculate the instrumental mass fractionation (IMF) factor by a “standard-sample-standard” bracketing external standardization method. Measured \(^{18}\)O/\(^{16}\)O ratios were normalized to the V-SMOW (\(^{18}\)O/\(^{16}\)O = 0.0020052), and then were corrected using the IMF factor. The observed internal uncertainty of individual analyses was typically around 0.3‰. Qinghu quartz, with a mean δ\(^{18}\)O values of 8.6 ± 0.3 ‰ (2SD, n = 41, Li et al., 2018), was used to monitor the long-term drift. The quartz-water oxygen isotope fractionation equations in Matsuhisa et al. (1979) were used to calculate the corresponding δ\(^{18}\)O\(_{\text{fluid}}\) values.

Results

Quartz occurrences and ore mineralogy

The analyzed samples were collected from the ore Belt II and are representative of magmatic and hydrothermal stages (Fig. 2), including: (1) quartz phenocrysts from the granodiorite porphyry; (2) dendritic quartz grains from the highly fractionated granodiorite porphyry (Fig. 2a); (3) gold-bearing UST quartz (Fig. 2b, c); (4) A veins cutting the UST quartz (Fig. 2b–d); (5) gold-bearing banded veins (Fig. 2e), and (6) late quartz–pyrite–carbonate-tourmaline veins (Fig. 2f). An overview of the quartz
generations is given in Table 1.

The quartz phenocrysts (QM1; Fig. 3a−b) are weakly CL-zoned with a gray color and are overgrown by a thin CL-bright rim. As shown in Figure 3a−b, the CL-bright quartz is widely distributed in the matrix. The brightness of the phenocryst rim is similar to that of the adjacent dendritic quartz (Fig. 3c), and to the hydrothermal quartz in USTs.

Dendritic quartz (QM2) intergrown with K-feldspar is developed at the top of the granodiorite porphyry and does not have a preferred orientation. CL images show that the quartz core has a mosaic texture with no zoning, whereas the quartz rim is gray with weakly developed zoning (Fig. 3c−d). Melt inclusions are abundant in QM2 with a diameter of 1~20 μm (Fig. 3e). This kind of melt inclusion, containing glass and translucent crystals, are referred to as crystallized silicate melt inclusions (SMI). Vapor phase is not obvious in these melt inclusions. Minor chalcopyrite and native gold grains occur in cracks of QM2 (Fig. 3f).

The quartz (QU) with unidirectional solidification textures (UST) also formed near the top of the porphyry, characterized by large quartz grains all growing from the same side. The CL images show that the UST quartz grains contain both bright QU1 cores and dark QU2 surroundings (Yang et al., 2015; Fig. 4a−c). Gold grains mostly occur as trails in QU (Yang et al., 2015; Fig. 4a, d). The size of gold grains is typically about 5 μm, surrounded by many small ones < 2 μm (Fig. 4e). Primary SMI, melt-fluid inclusion (MFI) and fluid inclusions (FIs) can be found in QU, varying from 5 to 15 μm in diameter (Fig. 4f−j). The MFI contains liquid, vapor and glass phases (Fig. 4f).

Vapor-rich inclusions, containing over 95 vol% of vapor, dominate the FIs in QU (Fig.
4i). Minor hypersaline fluid inclusions containing halite, hematite, and some unidentified minerals, were observed locally (Fig. 4i). The vapor-rich inclusions can be observed coexisting with the MFI locally (Fig. 4i), whereas the hypersaline fluid inclusions always exist alone.

The quartz in A veins (QA) grew from both sides of the vein wall to the center, and has three sub-generations (Fig. 5a–d). QA1 has distinct CL zoning and is overgrown by QA2 with lower brightness, and lacking zoning (Fig. 5c). Extremely bright quartz (QA3) overprints the QA2 near the center of the vein; it has a width of ~100 μm (Fig. 5d). Some magnetite deposited in QA1 and QA2 (Fig. 5e) and a few fissure gold grains were found, which are assumed as coeval with banded veins. Chalcopyrite grains can be seen locally in QA2 (Fig. 5f). Quartz zones containing abundant magnetite are always CL-dark (Fig. 5a, b). Fluid inclusions have not been found in QA1. FIs in QA2 and QA3 are mainly vapor-rich (Fig. 5g-i), containing over 70 vol% of vapor.

In the gold-bearing banded veins, the quartz (QB) consists of four sub-generations, growing from the rim to the center of the vein (Fig. 6a–f). It can be seen from the CL images that: (1) QB1 is located on the side of a banded vein and is weakly zoned, with gray-CL and a diameter of ~100–300 μm (Fig. 6b, c); (2) QB2 is yellowish under transmitted light (Fig. 6a), and its CL zones are distinct and bright, showing a growth continuity with QB1 (Fig. 6b, c); (3) QB3 grows on the rim of QB2 or appears as individual grains with diameters of less than 50 μm (Fig. 6d, e). QB3, containing variable amounts of fine-grained magnetite, is very "dirty" under the transmitted light.
(Fig. 6a). (4) QB4 envelopes QB3 to form a rim, or fills the central part of the banded veins as aggregates (Fig. 6e, f). Abundant native gold (Fig. 6g) and minor metal sulfides (pyrite and chalcopyrite) are observed in QB1 and QB2. The magnetite grains in QB3 are generally less than 5 μm in size (Fig. 6h). Vapor-rich inclusions and liquid-rich inclusions are developed in QB1 and QB2 (Fig. 6i, j), occurring as primary fluid inclusion assemblages. Fluid inclusions in QB3 are similar to those in QB1 and QB2, and some liquid-rich FIs contain a magnetite crystal are observed in QB3 (Fig. 6k). In contrast to QB1-QB3, liquid-rich FIs are well developed in QB4, typically with 10-20 vol% of vapor (Fig. 6l–m).

The late veins, consisting of quartz, pyrite, tourmaline and carbonate (calcite + dolomite), are the last mineralization stage. The quartz (QC) has a bright and CL-zoned core (QC1) and a “dirty-CL” rim (QC2) (Fig. 7a, b). Pyrite is abundant in this stage, growing on the edge of late veins or intergrown with the dolomite (Fig. 7c). Many aqueous liquid-rich inclusions occur in primary assemblages along the growth zones in QC1 and QC2 (Fig. 7d). They are usually irregularly shaped and up to 15 μm in size, with a ~10 vol% vapor.

Fluid Inclusions

Most of the FIs analyzed in this study had a diameter of 8–12 μm. To investigate the characteristics of ore-forming fluids, only primary fluid inclusions assemblages were studied, based on the CL textures of their host quartz. Microthermometric results are summarized in Fig. 8 and Table 2. The full data set is given in Supplementary Table.
In UST quartz, the brine and vapor-rich inclusions were trapped at temperatures above 600°C, which is consistent with the crystallization temperature of granodiorite porphyry estimated by the Ti-in-Zircon thermometer (~750-850 °C; Yang et al., 2016). Jiang (2011) ever reported the homogenization temperatures of the SMI are above 900°C. Carbon dioxide in the vapors of vapor-rich inclusions was identified by laser Raman spectroscopy, but there is no visible liquid CO$_2$ at room temperature, and no clathrate dissociation was observed in this study, thus CO$_2$ only occurs as a minor component (≤ 2 mol%; Azbej et al. 2007). The ice-melting temperatures of vapor-rich FIs, containing over 95 vol% of vapor, could not be determined due to difficulties in observing the phase transformation. The dissolution temperatures of halite in a limited number of brine inclusions are between 342 and 401°C (n=5), suggesting a salinity of 41.7–47.6 wt.% NaCl equiv.

Vapor-rich inclusions in A veins are also CO$_2$-bearing and did not show double freezing and clathrate dissociation during microthermometry. At room and lower temperatures, no liquid CO$_2$ was observed. These FIs in QA2 and QA3 have homogenization temperatures in range 464–552°C, with the average value of 502 °C (n = 22). Their ice-melting temperatures are between −17.6°C and −9.2°C, corresponding to 13.1–20.7 wt.% NaCl equiv.

Fluid inclusions in different quartz sub-generations of banded veins were recorded separately, as the sub-generations can be distinguished clearly under the microscope (Fig. 6a). QB1 and QB2 have a good growth continuity (Fig. 6b, c) and their
homogenization temperatures are bracketed together. In QB1+QB2, QB3 and QB4, the FIs (vapor-rich + liquid-rich) have homogenization temperatures of 368–421°C, 361–401°C and 298–334°C, with salinities of 7.9–14.9 wt.% NaCl equiv, 7.3–19.8 wt.% NaCl equiv and 6.6–17.3 wt.% NaCl equiv, respectively (Table 2). All vapor-rich FIs homogenized into the vapor phase, as opposed to the liquid-rich ones. Minor CO₂ (≤2 mol%) also occurs in FIs in QB1–QB3; but no CO₂ was detected in FIs in QB4.

Unlike the other veins, only aqueous liquid-rich inclusions are developed in late veins. Microthermometry shows ice-melting temperatures between -4.2°C and -0.6°C, corresponding to 1.1–6.7 wt.% NaCl equiv. They finally homogenized into the liquid phase with homogenization temperatures between 177°C and 218°C (mean = 191°C).

**Oxygen isotopes**

SIMS analyses (N = 152) of δ¹⁸O for quartz are shown in Fig. 9 and Table 3, and the complete dataset can be found in Supplementary Table B, including the used quartz reference materials. Quartz phenocryst and dendritic quartz in granodiorite porphyry yield constant δ¹⁸O values of 9.4–10.4‰ and 9.6–10.1‰, respectively. UST quartz yields δ¹⁸O values ranging from 9.5‰ to 10.5‰. No distinct variations were found between quartz zones with different CL densities. In A veins, quartz of different sub-generations exhibits variable δ¹⁸O values. QA1 has δ¹⁸O values of 9.2–9.7‰, which are similar to QA2 (δ¹⁸O = 9.3–9.8‰). However, QA3 is obviously enriched in ¹⁸O, yielding δ¹⁸O values between 10.4‰ and 14.3‰, with a mean value of 12.2‰ (n = 10). In banded veins, δ¹⁸O ranges of QB1, QB2, QB3 and QB4 are 9.2–
10.5‰, 9.6–10.5‰, 11.2‰–15.4‰ and 8.9‰–10.4‰, respectively. For the late veins, QC has a notable isotopic difference between cores (6.4‰ to 7.9‰) and rims (3.5‰ to 6.7‰), with the cores more enriched in $^{18}$O than the corresponding rims (Fig. 7a, b). Except for QA3 and QB3, individual quartz generations have a relatively homogeneous $\delta^{18}$O values, regardless of the CL zoning (Fig. 9).

**Discussion**

**Formation history of quartz**

Dendritic and UST quartz (Fig. 2b, c) are well developed in the mineralized granodiorite porphyry. The dendritic quartz, containing abundant SMI, is generally considered to be the product of highly fractionated magma (Swanson and Fenn, 1986; Yang et al., 2015). Primary Au grains are abundant in the UST quartz (QU) and are regularly distributed. UST quartz is interpreted to have formed during the magmatic-hydrothermal transitional stage, where exsolved fluid gathered at the top of the porphyry intrusion (Erdenebayar et al., 2014; Hong et al., 2019). The gold can be observed coexisting with both FI and MI locally (Fig. 4g–h), when precipitating from the magmatic hydrothermal fluid (e.g., Kodéra et al., 2014). Yang et al. (2015) ever proposed that the gold directly precipitated from the magma due to the SMIs are abundant in UST, whereas Huang et al. (2020) observed that tiny vapor-rich inclusions is more closely related to the gold trails and the SMIs were trapped at the melt-fluid interface accompanied by rare gold precipitation. Therefore, the Bilihe Au deposit, which shows typical characteristics of porphyry deposits, is inferred to be a porphyry
type deposit, but in contrast to other porphyry gold deposits, it experienced a high
temperature gold precipitation event during the UST quartz stage.

The occurrence of crystallized SMI is not common in porphyry Au deposits. Their
formation requires high temperatures but relatively low pressure to promote the
exsolution of volatiles (Harris et al., 2003; Rottier et al., 2016). The UST and dendritic
quartz at Bilihe have experienced heterogeneous entrapment of melt and vapor phases,
thus making the melt inclusions in them difficult to homogenize (Harris et al., 2003;
Rottier et al., 2016) even at high temperatures (> 950°C) as measured by Jiang (2011).
The crystallization temperature of granodiorite porphyry was estimated at ~750-850 °C
using the Ti-in-Zircon thermometer (Yang et al., 2016), suggesting that the UST quartz
was deposited at similar or lower temperatures.

SEM-CL images demonstrate that the hydrothermal quartz veins at Bilihe are
composed of multiple sub-generations of quartz and yield complex textures of
fracturing, dissolution, recrystallization and overgrowth, indicating complicated
changes in the physicochemical conditions of the ore-forming fluid (Rusk and Reed,
2002; Rusk et al., 2008). Some textures can be used to monitor specific episodes of
mineralization at Bilihe. Based on the textures of quartz and associated mineral
assemblages, it is apparent that gold precipitated twice at Bilihe deposit, once in the
UST quartz stage and again in the banded veins stage. Both gold mineralization events
were accompanied by minor sulfide precipitation. Due to the banded veins zone is
around the UST zone and the two stages gold yields a similar fineness (~980; Qing,
2010), it is inferred that the gold in banded veins was remobilized from the UST stage.
(Yang et al., 2015; Koděra et al., 2018).

Considering that the erosion depth does not exceed 2 km after the deposit forming based on the Ti-in-quartz thermobarometer (as low as 0.5 kbar; Huang et al., 2020), the maximum lithostatic pressure for the formation of the porphyry-type mineralization at Bilihe can be estimated at 600 bars, which is consistent with the minimum entrapment pressure calculated using fluid inclusions in A veins (Fig. 8). As shown in Table 2, the estimated pressures of hypersaline fluid inclusions \((n = 5)\) in UST are \(\sim 1300\) bars, suggesting that they were trapped under a relatively high-pressure condition. Due to the hypersaline fluid inclusions are very few and always exist alone, we thought this high-pressure phenomenon is only a local character, which may result from the fluid gathering at the top of the porphyry intrusion (e.g., Shu et al., 2013). The exsolved magmatic fluid ascended, forming A veins, but precipitating little or no sulfides and gold as it cooled to \(\sim 500^\circ\text{C}\). Minimum pressure estimates of 431–678 bars for vapor-rich FIs at 464–552°C indicate a \(\sim 2\) km paleodepth under lithostatic conditions (Fig. 8). As the temperature decreased to \(\sim 390^\circ\text{C}\), some gold and minor amounts of metal sulfides (pyrite and chalcopyrite) deposited with QB1 and QB2 quartz in banded veinlets. Variable pressure estimates of 76–307 bars for FIs in QB at 298–421°C suggest that the banded veins were formed in the transition from lithostatic to hydrostatic pressure conditions (Fig. 8; e.g., Redmond et al., 2004).

**Equilibrium oxygen fractionation**

When using \(\delta^{18}\text{O}_{\text{quartz}}\) to calculate \(\delta^{18}\text{O}_{\text{fluid}}\), the deposition temperature of quartz is
needed. For most fluid inclusions at Bilihe, homogenization temperatures are the minimum trapping temperature estimates. However, due to the true ore-forming pressures are sufficiently low (< 600 bars) as mentioned above, the homogenization temperatures are expected to be within 50 °C of the trapping temperatures (Allan and Yardley, 2007; Li et al., 2016). Therefore, the δ¹⁸O_{fluid} calculated using homogenization temperatures in this study can be used to trace the δ¹⁸O fluctuation of the ore-forming fluids (e.g., Allan and Yardley, 2007; Fekete et al., 2016; Li et al., 2019). The δ¹⁸O values of fluids forming QU, QA, QB1+QB2, QB3, QB4 and QC are calculated using 750°C, 502°C, 394°C, 375°C, 317°C and 191°C, respectively.

In addition to knowing the deposition temperature, another important condition for a correct calculation of δ¹⁸O_{fluid} is that the quartz crystallized under isotopic equilibrium conditions (Matsuhisa et al., 1979; Allan and Yardley, 2007; Tanner et al., 2013). The equilibrium would be achieved if the duration of quartz deposition was longer than the time required for isotope exchange between quartz and the hydrothermal fluid (Cole et al., 1992). The different quartz generations at Bilihe have variable grain sizes, ranging from dozens of microns to several centimeters. Previous studies show that in porphyry deposits individual quartz grains exceeding hundreds of microns in diameter potentially precipitated over hundreds of years (Mercer et al., 2015; Cernuschi et al., 2018), which is long enough for water and quartz to reach the isotopic equilibrium (<20 yr; Cole et al., 1992; Li et al., 2018). It can be inferred from previous experimental studies that relatively high fluid temperatures are beneficial for rapid growth of quartz (Pollington et al., 2016 and references therein), which may result in locally
inhomogeneous isotopic ratios within one grain (e.g., Tanner et al., 2013). However, most of the quartz grains at Bilihe, whether they crystallized at either high or low temperatures, show constant isotope compositions, with a narrow range of $\delta^{18}O$ values (Fig. 9). Therefore, most of the vein quartz at Bilihe can be considered to have formed under oxygen isotope equilibrium conditions (Li et al., 2018).

**Disequilibrium oxygen fractionation**

As shown in Fig. 9, $\delta^{18}O_{\text{quartz}}$ and the corresponding $\delta^{18}O_{\text{fluid}}$ values exhibits great fluctuations from QU to QC. Usually, the $\delta^{18}O_{\text{quartz}}$ and $\delta^{18}O_{\text{fluid}}$ values would decrease gradually with the incursion of isotopically light meteoric water in porphyry deposits (e.g., Fekete et al., 2016). However, two peaks of $\delta^{18}O_{\text{quartz}}$ and $\delta^{18}O_{\text{fluid}}$ occur in QA3 and QB3 at Bilihe, suggesting the quartz has experienced an unusual growth at these two sub-stages.

In some studies, the sudden enrichment of heavy oxygen in quartz is explained as the quartz deposition under equilibrium conditions but at lower temperatures, leading to a high fractionation factor between quartz and water (Matsuhisa et al., 1979; Fekete et al., 2016). The homogenization temperatures of FIs in QA3 and QB3 show that the quartz precipitated at relatively high temperatures. Therefore, the low temperature isotopic fractionation can be excluded.

Disequilibrium O-isotope fractionation between quartz and water, which is typically ignored in studies of the evolution of fluids, is a possible reason for the observed fluctuations of $\delta^{18}O$ in QA3 and QB3 stages. Disequilibrium isotopic
Fractionation is common during hydrothermal mineral growth (Tanner et al., 2013) and results in changes in the isotopic composition of minerals. Compared with the equilibrium isotopic fractionation, the heavy oxygen would be more likely to partition into silicate minerals and quartz under non-equilibrium conditions (e.g., Huang et al., 2006; Clayton and Mayeda, 2009), and thus would result in their abnormal high $\delta^{18}O$ values. Disequilibrium O-isotopic fractionation between fluid and quartz can be caused by three mechanisms: (1) the influence of sector zoning texture of quartz (Onasch and Vennemann, 1995; Jourdan et al., 2009). However, the mechanism is still under debate (Tanner et al., 2013). (2) The fast growth rate of quartz, which can be indicated by the increase of the trace element concentrations (Ihinger and Zink, 2000) and small crystal size (Huang et al., 2006; Gabitov, 2013). (3) The maturation of colloidal or amorphous silica, accompanied by the cryptocrystalline textures, would create high O-isotopic signature (Tanner et al., 2013). At Bilihe, no sector zoning and cryptocrystalline textures were observed in QA3 and QB3. In contrast, the fast growth rate may be responsible for the disequilibrium isotopic fractionation in QA3 and QB3, suggested by their small crystal size (< 100 μm).

A discontinuous input of magmatic-hydrothermal fluid would also intermittently make the fluids enriched in heavy oxygen (Li et al., 2018). The corresponding $\delta^{18}O_{fluid}$ values of QA3 and QB3 are very close to the isotopic signature of the magmatic quartz (Table 3) and may record other two separate magmatic-hydrothermal events. However, the $\delta^{18}O$ values of QA3 and QB3 are very variable and much higher than vein quartz in most porphyry deposits, which generally yield constant $\delta^{18}O$ values of less than 10‰.
(Taylor, 1974; Fekete et al 2016; Rottier et al., 2016, 2018; Li et al., 2018; Cernushi et al., 2018). Besides, the volumes of QA3 and QB3 are too small and only occur as a minor part of A and banded veins respectively, with no separated veins formed by them. Considering these factors, disequilibrium O-isotope fractionation is a preferred explanation for the enrichment of $^{18}$O in QA3 and QB3.

**Incursion of meteoric water and gold precipitation**

After excluding the anomalously $^{18}$O-enriched quartz that probably formed during disequilibrium fractionation, the $\delta^{18}$O$_{quartz}$ and $\delta^{18}$O$_{fluid}$ values still show significant variations (Fig. 9). The calculated $\delta^{18}$O$_{fluid}$ in equilibrium with QU could be interpreted as the oxygen isotopic signature of the initial magmatic-hydrothermal fluid (Harris et al., 2004; Hong et al., 2019). For A, banded and late veins, $\delta^{18}$O$_{fluid}$ values are lower than those of the initial magmatic water. The trend of $\delta^{18}$O$_{fluid}$ values suggests that meteoric water was progressively mixed with a magmatic-hydrothermal fluid during ore deposition.

As noted above, gold precipitated during two stages at Bilihe, once in the UST quartz and the other in the banded vein quartz. For porphyry deposits, it is generally agreed that the ore-forming fluid was initially derived from magma, and meteoric water added in later stages. However, it is still controversial when the meteoric water became involved in the ore-forming system, and whether it had a direct influence on the precipitation of sulfides. Some studies suggest that meteoric water participates in mineralization in the early stage, and even had an important role in mineralization.
(Taylor, 1974; Wilkinson, 2013; Fekete et al., 2016), whereas others conclude that it invaded the system in later stages and only affected peripheral and post-mineralization alteration (Sillitoe, 2010; Richards, 2011). The abundant Au precipitated in the UST quartz at Bilihe suggests that the incursion of meteoric water is not essential for gold deposition. Instead, quenching of the melt and magmatic-hydrothermal fluid may have strongly influenced the Au deposition (Yang et al., 2015). This is supported by the well-developed dendritic quartz in the mineralized granodiorite porphyry, which indicate rapid cooling or supercooling (Swanson and Fenn, 1986) that could dramatically decrease the solubility of Au in fluid (Pokrovski et al., 2014). Besides, the phase separation, indicated by condensation of a hypersaline liquid from the dominant low-salinity vapor phase, can result in enrichment of vapor in Au and S. This process is typical for most porphyry environments, whereas at Bilihe, the hypersaline fluid inclusions are rare and no one was observed coexisting with vapor-rich inclusions. Therefore, the influence of phase separation on gold precipitation in UST is probably limited.

For A veins, although the oxygen isotopes fall within the range of magmatic water defined by Taylor (1974), they are still slightly lower than those of the UST quartz, indicating that a small volume of ground water might have been involved. Fluid-rock reactions, involving the formation of abundant hydrous silicates (e.g., chlorite and muscovite), would also reduce the $\delta^{18}O_{fluid}$ (Cole and Ripley, 1999). However, at temperatures of $> 500^\circ$C, the O-isotope fractionation between water and these silicates is very low ($< 0.5\%o$) and can be ignored (Cole and Ripley, 1999). In the QB1 stage,
gold precipitated at the temperature of ~390°C. Such a low temperature can be attained by fluid-rock reaction, the addition of another cooler fluid and simple cooling on fluid ascent (Sillitoe, 2010; Fekete et al., 2016). As shown in Fig. 8, minimum pressure estimates of 76–307 bars for FIs in banded veins suggest a transition from lithostatic to hydrostatic environment at a paleodepth of 0.8–1.2 km, which provided conditions for meteoric water to progressively invade the hydrothermal system (Redmond et al., 2004).

Estimating the δ^{18}O of −12‰ for the late Paleozoic meteoric paleowater in Inner Mongolia (Li et al., 2003), ~15 vol.% of meteoric water may have participated in the gold precipitation in banded veins (Fig. 9). In the quartz-carbonate stage, meteoric water (~60–80 vol.%) dominated the ore-forming process. The decrease of δ^{18}O_{quartz} from core to rim of QC may result from the modification of late meteoric fluids. The mixing processes between magmatic hydrothermal and meteoric can also be documented by the salinity variations of ore-forming fluids. For example, the initial salinity of the magmatic hydrothermal fluid can be approximated by the salinity of the fluid inclusions in A veins (17.1 ± 2.0 wt.% NaCl equiv.). After mixing with 80 vol.% meteoric water, the salinity of ore-forming fluids would be ~3.4 wt.% NaCl equiv., which is very close to the salinity of the fluid inclusions in late veins (4.3 ± 1.6 wt.% NaCl equiv.).

Generally, fluid boiling is an important trigger for gold precipitation in porphyry ore-forming systems (Ni et al., 2015), whereas at Bilihe, the influence of fluid boiling on metals precipitation is not clear, due to the absence of high-salinity inclusions in gold-bearing quartz in banded veins and coexisting aqueous liquid-rich and vapor-rich
Fluid inclusions are only found locally in QB2. Mixing with cooler meteoric water may have played an important role in the second gold mineralizing stage in banded veins. Fluid mixing can be an effective mechanism causing metal deposition in different types of deposits (Olivo and Williams-Jones, 2002). During the mixing process, cooling, neutralization, and dilution of the hydrothermal fluids can result in destabilization of Au-bearing hydrogen sulfide or chloride complexes (Pokrovski et al., 2014). About 15 vol.% of meteoric water (Fig. 9) was involved to precipitate most of the gold at ~390°C, similar to previous studies on porphyry Cu/Mo deposits (Rottier et al., 2016; Li et al., 2019).

**Implications**

By study of quartz CL textures, fluid inclusion microthermometry and in situ O-isotope analysis, we have shown that the ore-forming fluids at Bilihe had a complex evolution, resulting in multiple generations of quartz, diverse quartz growth characteristics and oxygen isotopic compositions. The two peaks of δ\(^{18}\)O\(_{\text{quartz}}\), occurring in QA3 and QB3, suggest that the vein quartz may have experienced sporadic disequilibrium oxygen fractionation during deposition, resulting in local \(^{18}\)O-enrichment. Disequilibrium oxygen fractionation is largely unreported, but may be a common phenomenon in porphyry deposits, which may affect the calculation of δ\(^{18}\)O\(_{\text{fluid}}\) when using bulk quartz isotopic data. The overall δ\(^{18}\)O\(_{\text{fluid}}\) values, with a gradual decrease from early to late stages, suggest a progressive decrease in the proportion of magmatic hydrothermal fluids. Two gold mineralization events have been
recorded in quartz from Bilihe. The first, native gold in high temperature UST quartz (>600 °C), resulting from rapid cooling, suggests that the addition of meteoric water may be unnecessary for the formation of porphyry gold deposits. However, the dominant second gold deposition stage in banded quartz veinlets (~390 °C) indicates that most of the gold was deposited from fluids of mixed magmatic and meteoric water.

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**Figure captions**
Fig. 1. (a) Simplified map of part of China and Mongolia showing the study area (after Xiao et al., 2009). (b) Regional geological map of central Inner Mongolia showing the distribution of magmatic rocks and tectonic belts (modified after Xiao et al., 2009). (c-d) Geological map of the Bilihe gold deposit (modified after Yang et al., 2015).

Fig. 2. Quartz formed at different stages. (a) Dendritic quartz in K-feldspar-altered granodiorite porphyry. (b-c) Gold-bearing UST quartz cut by A veins in granodiorite porphyry, with illite alteration. (d) A vein with potassic alteration halo. (e) Auriferous banded veins with phyllic alteration and cutting the dendritic quartz. (f) Quartz-carbonate-tourmaline vein (late vein) in granodiorite porphyry. Abbreviations: Tur = Tourmaline, Cbn = Carbonate, UST = Unidirectional solidification texture.

Fig. 3. Photomicrographs and CL images of quartz phenocrysts and dendritic quartz. (a-b) CL textures of euhedral quartz phenocrysts in the granodiorite porphyry showing CL-gray core, overgrown by CL-bright quartz. Locations (white spots) and results of SIMS oxygen isotope analyses are also shown. (c-d) CL images of dendritic quartz showing its growth habit, with location (blue dots) and results of SIMS oxygen isotope analyses. (e) SMI groups in the quartz rim. (f) Anhedral chalcopyrite and native gold in cracks of dendritic quartz. Abbreviations: SMI = silicate melt inclusion, Ccp = Chalcopyrite.

Fig. 4. Textures and mineral assemblages of UST quartz. (a-c) CL images showing the
growth habit of quartz and Au distribution, with location (blue dots) and results of oxygen isotope analyses. The UST quartz grains contain both bright QU1 cores and dark QU2 surroundings. (d) Reflected light image of Au grains in one trail. The big Au grains are surrounded by dozens of smaller ones, < 2 μm. (e) Group of gold grains under transmitted light. (f) Crystallized silicate melt inclusions in QU1. Also shown is a melt-fluid inclusion. (g) Native gold coexisting with the SMI in QU1. (h) Native gold coexisting with fluid inclusions. (i) Primary vapor-rich fluid inclusions coexisting with the SMI. (j) A representative hypersaline fluid inclusion containing different daughter minerals. Abbreviations: SMI = Silicate melt inclusion, V = Vapor, L = Liquid, Hal = Halite, Hem = Hematite, Syl = Sylvite.

Fig. 5. Quartz CL, mineral inclusions and fluid inclusions of A veins. (a-d) CL images of a quartz vein showing different quartz generations. Blue dots and red numbers refer to the positions and results of SIMS analyses, respectively. (e) Fine-grained magnetite in quartz zones of QA2. (f) Chalcopyrite grains in QA2. (g) Vapor-rich fluid inclusions in QA2. (h-i) Vapor-rich fluid inclusion in QA3. Abbreviations: Mag = Magnetite, Ccp = Chalcopyrite.

Fig. 6. Quartz sub-generations, mineral inclusions and fluid inclusions of auriferous banded veins. (a-b) Photomicrographs of banded veins under transmitted light and corresponding CL mapping. Blue dots and red numbers refer to the positions and results of SIMS O-isotope analyses, respectively. (c-f) CL images showing the sub-generations
and textures of quartz. (g) Gold group in QB1. The inset is the corresponding reflected light image. (h) Fine grained magnetite in QB3. (i-j) Fluid inclusions in QB1 and QB2. Coexisting vapor-rich and liquid-rich fluid inclusions occur locally. (k) Coexisting vapor-rich and liquid-rich fluid inclusions in QB3. Also shown is a fluid inclusion containing a magnetite crystal. (l-m) Fluid inclusions in QB4. Abbreviations: Mag = Magnetite.

**Fig. 7.** Quartz occurrences, minerals and fluid inclusions in late veins. (a-b) CL images show that a CL-bright quartz is overgrown by a CL-dark rim, with location (blue spots) and results of oxygen isotope analyses. (c) Pyrite and tourmaline intergrown with carbonate (dolomite + minor calcite). (d) Fluid inclusions in the QC. Abbreviations: Tur = Tourmaline, Py = Pyrite, Cbn = Carbonate.

**Fig. 8.** Pressure-temperature diagram for NaCl-H$_2$O system showing fluid evolution paths for A, banded and late veins in the Bilihe gold deposit (phase diagram after Fournier, 1999). The QU fluids are not included in the diagram due to the estimated pressures of hypersaline fluid inclusions ($n = 5$) in UST are abnormally high and could not represent the true entrapment pressures (see text for details).

**Fig. 9.** $\delta^{18}$O$_{\text{quartz}}$ and $\delta^{18}$O$_{\text{fluid}}$ values for Bilihe deposit sorted by successive quartz generations. The overall $\delta^{18}$O$_{\text{fluid}}$ values show a gradual decrease from early to late stages, and two abnormal peaks of $\delta^{18}$O$_{\text{quartz}}$ and $\delta^{18}$O$_{\text{fluid}}$ values occur in QA3 and QB3.
<table>
<thead>
<tr>
<th>Quartz generation</th>
<th>SEM-CL textures</th>
<th>Luminescence intensity</th>
<th>Minerals and relations</th>
<th>Melt/Fluid inclusions types</th>
</tr>
</thead>
<tbody>
<tr>
<td>QM1 Core</td>
<td>Weakly CL-zoned euhedral quartz crystals;</td>
<td>CL-dark to CL-gray</td>
<td>A small number of HSMI</td>
<td></td>
</tr>
<tr>
<td>QM1 Rim</td>
<td>Thin light overgrowth zone on QM1-Core; widely developed in the matrix</td>
<td>CL-bright</td>
<td></td>
<td></td>
</tr>
<tr>
<td>QM2 Core</td>
<td>Yielding a mosaic texture with no zonings; completely mantled by a rim</td>
<td>CL-bright</td>
<td>HSMI with a diameter of &lt; 5 μm</td>
<td></td>
</tr>
<tr>
<td>QM2 Rim</td>
<td>Overgrowing QM2-Core; non-directional oscillatory zoning</td>
<td>CL-gray</td>
<td>HSMI with a diameter of 1~20 μm</td>
<td></td>
</tr>
<tr>
<td>QU QU1 Core</td>
<td>Unidirectional oscillatory zoning and sector zoning</td>
<td>CL-bright to CL-gray</td>
<td>(1) HSMI and MFI; (2) vapor-rich FI (&gt; 95 vol % vapor), containing CO₂ (no visible liquid CO₂ at room temperature); (3) minor hypersaline liquid FI containing halite, hematite and sylvite</td>
<td></td>
</tr>
<tr>
<td>QU QU1 Rim</td>
<td>Thin rim on QU-Core and developed near the cracks, possibly as replacement of QU-core</td>
<td>CL-gray to CL-dark</td>
<td>HSMI (1~20 μm)</td>
<td></td>
</tr>
<tr>
<td>QA QA1 Core</td>
<td>Distinct oscillatory zoning; overgrown by the lateral QA2</td>
<td>CL-bright to CL-gray</td>
<td>Magnetite, scheelite</td>
<td>Not developed</td>
</tr>
<tr>
<td>QA QA2 Rim</td>
<td>Overgrowing QA1, with no zoning developed</td>
<td>CL-gray, containing one CL-dark zoning</td>
<td>Magnetite, scheelite, chalcopyrite and bornite</td>
<td>(1) mainly vapor-rich (&gt; 60 vol % vapor); (2) liquid-rich FI are rare; -These vapor-rich FIs are CO₂-bearing, but no visible liquid CO₂ at room temperature</td>
</tr>
<tr>
<td>Location</td>
<td>Description</td>
<td>CL Luminescence</td>
<td>Minerals</td>
<td>Fluids</td>
</tr>
<tr>
<td>----------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>-----------------</td>
<td>----------------------------------------------------------------------------------------------------------------</td>
<td>--------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>QA3</td>
<td>Thin bright overgrowth zone on the QA2 near the center of A vein; fractured by late fluids</td>
<td>Brightest luminescence in A vein</td>
<td>Magnetite</td>
<td>Vapor-rich (&gt; 60 vol % vapor) - CO$_2$ bearing, but no visible liquid CO$_2$ at room temperature</td>
</tr>
<tr>
<td>QB1</td>
<td>Growing in the side of B vein; weakly CL-zoned grains</td>
<td>CL-gray</td>
<td>Primary gold, chalcopyrite, pyrite, scheelite</td>
<td>Vapor-rich (&gt; 60 vol % vapor) and liquid-rich; - CO$_2$ bearing, but no visible liquid CO$_2$ at room temperature</td>
</tr>
<tr>
<td>QB2</td>
<td>Growth continuity with QB1; distinct oscillatory zoning; dissolution textures at the contact with QB4</td>
<td>CL-bright to CL-gray; locally CL-dark</td>
<td>Native gold, chalcopyrite, pyrite, and magnetite zoning</td>
<td>vapor-rich (&gt; 60 vol % vapor) and liquid-rich; - CO$_2$ bearing, but no visible liquid CO$_2$ at room temperature</td>
</tr>
<tr>
<td>QB3</td>
<td>Appearing as a thin dark rim on QB2 or as individual fine grains; dissolution textures at the contact with QB4</td>
<td>CL-dark</td>
<td>Micrometer-sized magnetite</td>
<td>vapor-rich (&gt; 60 vol % vapor) and liquid-rich; - CO$_2$ bearing, but no visible liquid CO$_2$ at room temperature</td>
</tr>
<tr>
<td>QB4</td>
<td>Accretive rim on QB3 or filling the center of B vein as aggregates</td>
<td>CL-gray; Its luminescence intensity is weaker than QB1</td>
<td></td>
<td>Liquid-rich (~20 vol % vapor) and minor vapor-rich</td>
</tr>
<tr>
<td>QC1</td>
<td>CL-zoned euhedral quartz crystals up to several millimeters; dissolution textures at the contact with QC2</td>
<td>CL-bright</td>
<td>Carbonates, pyrite, tourmaline and minor chlorite</td>
<td>Liquid-rich (~10 vol % vapor)</td>
</tr>
<tr>
<td>QC2</td>
<td>Thin overgrowth zone on QC1, which probably is the recrystallization of QC2</td>
<td>CL-&quot;dirty&quot;</td>
<td></td>
<td>Liquid-rich (~10 vol % vapor)</td>
</tr>
</tbody>
</table>
Table 2
Summary of microthermometric data of fluid inclusions from the Bilihe deposit

<table>
<thead>
<tr>
<th>Quartz type</th>
<th>FI type</th>
<th>L %</th>
<th>Final melting temperature of ice (°C)</th>
<th>Dissolution temperature of halite (°C)</th>
<th>Homogenization temperature (°C)</th>
<th>Salinity (wt.% NaCl equiv)</th>
<th>Minimum pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Range (n), Mean (± S.D.)</td>
<td>Range (n), Mean (± S.D.)</td>
<td>Range, Mean (± S.D.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>QU</td>
<td>H</td>
<td></td>
<td>342–401 (5) 369 ± 21</td>
<td>&gt; 600</td>
<td>41.7 to 47.6 44.3 ± 2.2</td>
<td>1240 to 1332 1293 ± 34</td>
<td></td>
</tr>
<tr>
<td>SMI</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&gt; 950 (Jiang., 2011)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>QA2 and QA3</td>
<td>V</td>
<td>15–30</td>
<td>-17.6 to -9.2 (22) -13.4 ± 2.2</td>
<td>464 to 552 502 ± 21</td>
<td>13.1 to 20.7 17.1 ± 2.0</td>
<td>431 to 678 538 ± 64</td>
<td></td>
</tr>
<tr>
<td>QB1 and QB2</td>
<td>V</td>
<td>15–30</td>
<td>-10.9 to -5.1 (24) -7.9 ± 1.8</td>
<td>368 to 421 396 ± 11</td>
<td>8.0 to 14.9 11.5 ± 2.2</td>
<td>188 to 307 252 ± 27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>L</td>
<td>70–80</td>
<td>-9.8 to -5.0 (8) -7.5 ± 1.7</td>
<td>378 to 397 385 ± 7</td>
<td>7.8 to 13.7 11.0 ± 2.0</td>
<td>207 to 253 227 ± 17</td>
<td></td>
</tr>
<tr>
<td>QB3</td>
<td>V</td>
<td>15–30</td>
<td>-9.3 to -4.6 (11) -7.2 ± 1.7</td>
<td>342 to 389 370 ± 16</td>
<td>7.3 to 13.2 10.6 ± 2.1</td>
<td>149 to 235 201 ± 32</td>
<td></td>
</tr>
<tr>
<td></td>
<td>L</td>
<td>70–80</td>
<td>-16.4 to -5.7 (14) -9.9 ± 3.2</td>
<td>366 to 403 379 ± 13</td>
<td>8.8 to 19.8 13.6 ± 3.4</td>
<td>179 to 268 208 ± 29</td>
<td></td>
</tr>
<tr>
<td>QB4</td>
<td>L</td>
<td>70–85</td>
<td>-13.5 to -4.1 (21) -8.8 ± 2.6</td>
<td>298 to 334 317 ± 10</td>
<td>6.6 to 17.3 12.4 ± 3.0</td>
<td>76 to 124 100 ± 14</td>
<td></td>
</tr>
<tr>
<td>QC</td>
<td>L</td>
<td>85–95</td>
<td>-4.2 to -0.6 (30) -2.6 ± 1.0</td>
<td>177 to 218 191 ± 11</td>
<td>1.1 to 6.7 4.3 ± 1.6</td>
<td>9 to 20 13 ± 3</td>
<td></td>
</tr>
</tbody>
</table>

Note: Detailed information for each FI and FIA measured in this study can be found in Supplementary Table A. S.D. means Standard Deviation. Pressures were calculated from the equations of Driesner and Heinrich (2007). H: Hypersaline; V: Vapor-rich; L: Liquid-rich.
Table 3
Oxygen isotopic compositions of quartz from the Bilihe gold deposit.

<table>
<thead>
<tr>
<th>Quartz type</th>
<th>Lithology</th>
<th>Quartz generation</th>
<th>( \delta^{18}O_{quartz} ) (‰) range</th>
<th>N</th>
<th>( \delta^{18}O_{quartz} ) (‰) Mean ± S.D.a</th>
<th>( \delta^{18}O_{H2O} ) (‰) range</th>
<th>( \delta^{18}O_{H2O} ) (‰) Mean ± S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>QM1</td>
<td>Quartz phenocryst in fresh granodiorite porphyry</td>
<td>Core</td>
<td>9.3 to 9.9</td>
<td>5</td>
<td>9.5 ± 0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rim</td>
<td>9.6 to 10.0</td>
<td>4</td>
<td>9.8 ± 0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>QM2</td>
<td>Dendritic quartz grain in granodiorite porphyry with potassic alteration</td>
<td>Core</td>
<td>9.3 to 10.2</td>
<td>9</td>
<td>9.9 ± 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rim</td>
<td>9.4 to 10.4</td>
<td>12</td>
<td>9.9 ± 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>QU</td>
<td>Gold-bearing UST quartz vein in granodiorite porphyry with potassic alteration,</td>
<td>QU1</td>
<td>9.5 to 10.6</td>
<td>16</td>
<td>10.1 ± 0.3</td>
<td>8.7 to 9.8 b</td>
<td>9.3 ± 0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>QU2</td>
<td>9.4 to 10.2</td>
<td>7</td>
<td>9.8 ± 0.3</td>
<td>8.6 to 9.4</td>
<td>9.0 ± 0.3</td>
</tr>
<tr>
<td>QA</td>
<td>Qtz-Mag-Ksp vein cutting the UST quartz veins</td>
<td>QA1</td>
<td>9.2 to 9.7</td>
<td>7</td>
<td>9.5 ± 0.2</td>
<td>6.9 to 7.4</td>
<td>7.2 ± 0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>QA2</td>
<td>9.2 to 10.0</td>
<td>12</td>
<td>9.6 ± 0.2</td>
<td>6.9 to 7.7</td>
<td>7.4 ± 0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>QA3</td>
<td>10.4 to 14.3</td>
<td>10</td>
<td>12.6 ± 1.1</td>
<td>8.1 to 12.0</td>
<td>10.3 ± 1.1</td>
</tr>
<tr>
<td>QB</td>
<td>Auriferous banded quartz veinlets in mineralized granodiorite porphyry</td>
<td>QB1</td>
<td>9.2 to 10.5</td>
<td>12</td>
<td>10.0 ± 0.4</td>
<td>5.0 to 6.3</td>
<td>5.8 ± 0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>QB2</td>
<td>9.7 to 10.5</td>
<td>16</td>
<td>10.0 ± 0.3</td>
<td>5.5 to 6.3</td>
<td>5.8 ± 0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>QB3</td>
<td>11.2 to 15.4</td>
<td>10</td>
<td>13.3 ± 1.4</td>
<td>6.6 to 10.8</td>
<td>8.6 ± 1.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>QB4</td>
<td>8.9 to 10.4</td>
<td>18</td>
<td>9.8 ± 0.4</td>
<td>2.6 to 4.1</td>
<td>3.5 ± 0.4</td>
</tr>
<tr>
<td>QC</td>
<td>Quartz-Carbonate vein in granodiorite porphyry with strong illite-carbonate ± chlorite alteration</td>
<td>QC1</td>
<td>6.2 to 7.9</td>
<td>8</td>
<td>7.2 ± 0.5</td>
<td>-6.0 to -4.3</td>
<td>-5.0 ± 0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>QC2</td>
<td>3.5 to 5.5</td>
<td>6</td>
<td>4.3 ± 0.7</td>
<td>-8.7 to -6.7</td>
<td>-7.9 ± 0.7</td>
</tr>
</tbody>
</table>

Note: a. S.D. means Standard Deviation of \( \delta^{18}O \) (‰) values. b. The \( \delta^{18}O_{H2O} \) for QU is calculated at an estimated temperature of 750 °C. See text for detail.
Fig. 8

Temperature (°C)

Pressure (bars)

Depth (km, hydrostatic)

Vapor + salt

Late vein

Banded vein

Gold precipitation

A vein

QA

QB1 and QB2

QB3

QB4

QC