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2   Textural, fluid inclusion and in-situ oxygen isotope studies of quartz:

3   constraints on vein formation, disequilibrium fractionation and gold

4   precipitation at the Bilihe gold deposit, Inner Mongolia, China

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6   **Xueyuan Qiao [1], Wenbo Li [1*], Lejun Zhang [2], Fanghua Zhang [1], Xuefeng Zhu [3],**

7   **Xiaoping Xia [4]**

8   *1, Key Laboratory of Orogenic Belt and Crustal Evolution, School of Earth and Space*

9   *Sciences, Peking University, Beijing 100871, China*

10   *2, Centre for Ore Deposit and Earth Sciences (CODES) University of Tasmania, Private*

11   *Bag 79, Hobart 7001, Australia*

12   *3, School of Mining and Coal, Inner Mongolia University of Science and Technology,*

13   *Baotou 014010, China*

14   *4, State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry,*

15   *Chinese Academy of Sciences, Wushan, Guangzhou 510640, China*

16   ** Corresponding author. Tel: +86 10 62760820. E-mail address: liwenbo@pku.edu.cn*

17   *(W. Li)*

18

19   Abstract

20   Bilihe is a porphyry gold deposit located in the northern margin of the North China

21   Craton (NCC), Inner Mongolia, China. Different stages of quartz are well developed at

22   this deposit. To document the history of quartz deposition, the fluid evolution and gold

23   precipitation events of the deposit, detailed oxygen isotope signatures of quartz from

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24   Bilihe were studied using high-resolution secondary ion mass spectroscopy (SIMS),

25   integrated with scanning electron microscope-cathodoluminescence (SEM-CL) and

26   fluid inclusion microthermometry. The SEM-CL features show that the hydrothermal

27   veins at Bilihe have a complex growth history, with multiple generations of quartz

28   developed in each set of veins. Fluid inclusions in different quartz stages yield variable

29   homogenization temperatures, ranging from 178 °C to above 600 °C. These quartz

30   stages exhibit variable $\delta^{18}O$ values of 3.5–15.4‰, corresponding to $\delta^{18}O_{fluid}$ ranging

31   from -8.7‰ to 12.0‰. There are two abnormal peaks of $\delta^{18}O_{quartz}$ and $\delta^{18}O_{fluid}$ values

32   occurring in a sub-generation of A type veins and auriferous banded quartz veins,

33   suggesting that the vein quartz may have experienced sporadic disequilibrium oxygen

34   fractionation with water when crystallizing, thus resulting in local ^{18}O-enrichment. The

35   overall $\delta^{18}O_{fluid}$ values, which show a gradual decrease from early to late stages, suggest

36   a progressive decrease in the proportion of magmatic hydrothermal fluids. The

37   relationship between quartz textures and gold occurrence shows that gold precipitated

38   twice at Bilihe. The first precipitation in the UST quartz may have resulted from rapid

39   cooling and indicates that addition of meteoric water was not necessary for gold

40   precipitation, whereas the progressive incursion of meteoric water probably had a

41   significant effect on the second gold precipitation.

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45

46   **Introduction**

47   Porphyry ore deposits are an important source of copper, molybdenum and gold

48   (Sillitoe, 2010). The magmatic-hydrothermal evolution of porphyry ore-forming

49   systems has been extensively studied using bulk sample isotopic analysis. Quartz veins

50   are a characteristic feature of porphyry deposits (Sillitoe, 2010; Richards, 2011) and

51   quartz can be valuable indicators of fluid origin, as their oxygen isotopic composition

52   is derived from the parental fluid, with the fluid-quartz fractionation factor controlled

53   by temperature at isotopic equilibrium conditions (Matsuhisa et al., 1979). Oxygen

54   isotopes, combined with hydrogen isotopes, have been widely used to constrain the

55   source and evolution of ore-forming fluids (Taylor, 1974). An important factor for

56   oxygen isotope calculations is the requirement that isotopic equilibrium fractionation

57   was achieved between quartz and the aqueous fluid. However, very complex zoning in

58   porphyry-related quartz is commonly observed in cathodoluminescence (CL) images

59   (Rusk et al., 2008) and extreme $\delta^{18}O_{quartz}$ heterogeneity is commonly observed in

60   individual quartz grains (Allan and Yardley, 2007; Tanner et al., 2013). These suggest

61   that isotopic fractionation during quartz growth may not have been achieved under

62   equilibrium, which would greatly affect the calculation of $\delta^{18}O_{fluid}$. In most studies, the

63   variations of oxygen isotope compositions or isotopic dynamic disequilibrium

64   fractionation during quartz growth are difficult to identify and always overlooked,

65   especially when using the bulk sample isotopic analysis. Consequently, the final

66   calculated $\delta^{18}O_{fluid}$ may be not representative.

67   The texture of quartz is also a useful monitor of fluid characteristics (e.g.,

68   composition and temperature) in hydrothermal processes (Rusk and Reed, 2002).

3

69   Crystal size, zones, generations and fluid inclusion properties are valuable indicators of

70   growth history. Variations in CL intensity are generally considered to be in response to

71   structural defects or differences in chemical composition (Allan and Yardley, 2007;

72   Rusk and Reek, 2002). Variations of $\delta^{18}O_{quartz}$ and calculated $\delta^{18}O_{fluid}$ in different CL

73   zones of quartz veins may reflect spatial and temporal changes in fluid composition and

74   growth rate (Tanner et al., 2013; Fekete et al., 2016; Rottier et al., 2018).

75   Bilihe deposit is located in Inner Mongolia, China, and is the first reported gold

76   deposit in which mineralization occurs in both unidirectional solidification texture

77   (UST) and hydrothermal quartz veins. Based on the temporal and spatial relationships

78   between the orebody and porphyry intrusions, the alteration types and zones, and the

79   ore characteristics, this deposit is classified as a porphyry gold deposit (Ge et al., 2009;

80   Qing et al., 2010; Zhu et al., 2018; Huang et al., 2020). In this paper, we analyze the O-

81   isotope compositions of quartz formed at different stages of the deposit using secondary

82   ion mass spectrometry (SIMS), combined with cathodoluminescence and fluid

83   inclusion studies, to explore the oxygen isotope distribution in each quartz sub-

84   generation, and to constrain the quartz growth history and investigate the precipitation

85   mechanism of gold.

86

Geological Background

88   The Central Asian Orogenic Belt (CAOB) is one of the largest accretionary

89   orogenic collages on Earth (Windley et al., 2007), restricted by the southern Tarim

90   Craton and North China Craton (NCC) and the northern Siberian Craton (Fig. 1). The

4

91   CAOB contains multiphase accretionary complexes, including micro-continents,

92   accretionary wedges, island arcs, forearc basins, backarc basins and ophiolitic belts.

93   The Bilihe gold deposit is hosted in the early Paleozoic Bainaimiao arc, which forms

94   part of the southern accretionary zone between the Solonker suture and northern NCC

95   (Fig. 1b).

96   The igneous rocks in the Bainaimiao arc are dominated by calc-alkaline rhyolite,

97   andesite, basalt, and a magmatic complex consisting of granite, granodiorite, diorite,

98   and gabbro. To date, several Au-mineralized zones (e.g., Belts I and II, III and Veins

99   22–26) have been identified in the Bilihe area (Fig. 1c, d). The ore Belt I contained

100   about three tons of gold, and has been mined out. The Ore Belt II (Fig. 1d), containing

101   most of the gold at Bilihe, is about 1 km from the ore Belt I and contains over 25 tons

102   of gold. The ore Belt II is spatially and temporally associated with a buried tongue-

103   shaped high-K calc-alkaline granodiorite porphyry (Supplementary Fig. 1; Ge et al.,

104   2009; Zhu et al., 2018). Zircon U–Pb SIMS dating of the granodiorite porphyry (269 ±

105   2 Ma; Zhu et al., 2018) and a Re–Os isochron age of post-ore molybdenite (268 ± 1 Ma;

106   Zhu et al., 2018) restricts the age of the gold mineralization to ca. 269 Ma.

107   This deposit is identified as the first large-sized high-grade porphyry gold deposit

108   on the northern NCC (Ge et al., 2009; Zhu et al., 2018; Huang et al., 2020). Sulfides

109   are rare (less than 1 wt. %) in the ore, predominantly chalcopyrite, pyrite, bornite,

110   molybdenite and galena, based on metallurgical analysis results (Ge et al., 2009). The

111   mainly alteration types include early potassic alteration and late superposed sericite-

112   quartz and chlorite-sericite-illite alterations, but a large-scale potassic alteration only

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113   can be found at depth (>150m; Ge et al., 2009; Zhu et al., 2018).The distribution of the

114   alteration zones in the Belt II is shown in Supplementary Fig. 1.

115   In the intermediate-upper part of the granodiorite porphyry, dendritic quartz (Fig.

116   2a) and unidirectional solidification texture (UST) quartz (Fig. 2b, c) are well

117   developed. There are also many quartz–magnetite ± K-feldspar veins (A veins;

118   Gustafson and Hunt, 1975) in this area, cutting the UST quartz and producing a K-

119   feldspar alteration halo (Fig. 2b-d). In addition, abundant banded quartz veinlets

120   (banded veins) are distributed in the intrusions and surrounding rocks, locally

121   overprinting the dendritic quartz and UST quartz (Fig. 2e). This type of vein occurs in

122   rectilinear networks and is filled by granular quartz with central sutures, and contains

123   chalcopyrite and pyrite. In the upper part of the orebody and overlying tuff, quartz–

124   pyrite–carbonate-tourmaline veins (late veins) are well developed (Fig. 2f).

125   The Au mainly occurs as native gold grains in the UST quartz and banded veins,

126   and less than 20% of Au is hosted in the surrounding altered rocks (Ge et al., 2009).

127   The gold-bearing USTs (~ 8 tonnes reserves) are mainly located in the central zone of

128   Belt II (Supplementary Fig. 1), with an average grade of ~15.0 g/t, and the auriferous

129   banded quartz veinlets (over 20 tonnes reserves) are mainly distributed in the

130   granodiorite porphyry and wall rocks, with an average grade of ~2.7 g/t. The banded

131   veins gold zone is around the UST gold zone. Only minor gold grains were observed in

132   the A veins, and the late veins are barren.

133

134   **Analytical Methods**

135 **Scanning Electron Microscope Cathodoluminescence (SEM-CL)**

136   SEM-CL images of quartz veins were obtained at the School of Physics, Peking

137 University, using a FEI Quanta 200FEG with a Gatan mini-CL detector with a

138 wavelength range between 185 and 850 nm. Images were obtained under conditions of

139 10 kv accelerating voltage, 3.5 μm spot size, 10 mm working distance, and 1024 x 884

140 pixels resolution. To avoid re-polishing after imaging, the samples were photographed

141 under low vacuum mode, without being coated with carbon.

142

143 **Microthermometry of fluid inclusions**

144   Closely associated groups of fluid inclusions with similar shapes and identical

145 phases were studied. Microthermometry measurement was performed on a Linkam

146 THMSG600 heating–freezing stage equipped with a transmitted light microscope at the

147 Guangzhou Institute of Geochemistry, Chinese Academy of Science. The

148 heating/freezing rate was set as 0.2 to 5°C/min, and was reduced at 0.1°C/min when

149 close to phase transformation. The stage was calibrated using synthetic fluid inclusions.

150 The uncertainty of temperature measurements is ±0.1°C in the range of −100°C to 25°C,

151 ±1.0°C between +25°C and +400°C, and ±2°C above +400°C. Salinities of fluid

152 inclusions (wt % NaCl equiv) were calculated using the equations of Bodnar (1994)

153 and Bodnar and Vityk (1994) for the H_2O-NaCl system. Pressures were calculated from

154 the equations of Driesner and Heinrich (2007).

155

156 **Secondary Ion Mass Spectrometer (SIMS)**

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157   In situ oxygen isotope measurements were carried out on a CAMECA IMS-1280

158   SIMS at the Guangzhou Institute of Geochemistry, Chinese Academy of Science. The

159   Cs+ primary beam was accelerated at 10 kV, with an intensity of ~2 nA. The spot size

160   was ~10 μm. Detailed description for operating and analytical conditions can be found

161   in Li et al. (2018). NBS-28 quartz, with $\delta^{18}O$ value of 9.5 ‰, was used to calculate the

162   instrumental mass fractionation (IMF) factor by a "standard-sample-standard"

163   bracketing external standardization method. Measured $^{18}O/^{16}O$ ratios were normalized

164   to the V-SMOW ($^{18}O/^{16}O = 0.0020052$), and then were corrected using the IMF factor.

165   The observed internal uncertainty of individual analyses was typically around 0.3‰.

166   Qinghu quartz, with a mean $\delta^{18}O$ values of 8.6 ± 0.3 ‰ (2SD, n = 41, Li et al., 2018),

167   was used to monitor the long-term drift. The quartz-water oxygen isotope fractionation

168   equations in Matsuhisa et al. (1979) were used to calculate the corresponding $\delta^{18}O_{fluid}$

169   values.

170

Results

Quartz occurrences and ore mineralogy

173   The analyzed samples were collected from the ore Belt II and are representative

174   of magmatic and hydrothermal stages (Fig. 2), including: (1) quartz phenocrysts from

175   the granodiorite porphyry; (2) dendritic quartz grains from the highly fractionated

176   granodiorite porphyry (Fig. 2a); (3) gold-bearing UST quartz (Fig. 2b, c); (4) A veins

177   cutting the UST quartz (Fig. 2b−d); (5) gold-bearing banded veins (Fig. 2e), and (6)

178   late quartz–pyrite–carbonate-tourmaline veins (Fig. 2f). An overview of the quartz

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179   generations is given in Table 1.

180   The quartz phenocrysts (QM1; Fig. 3a−b) are weakly CL-zoned with a gray color

181   and are overgrown by a thin CL-bright rim. As shown in Figure 3a−b, the CL-bright

182   quartz is widely distributed in the matrix. The brightness of the phenocryst rim is similar

183   to that of the adjacent dendritic quartz (Fig. 3c), and to the hydrothermal quartz in USTs.

184   Dendritic quartz (QM2) intergrown with K-feldspar is developed at the top of the

185   granodiorite porphyry and does not have a preferred orientation. CL images show that

186   the quartz core has a mosaic texture with no zoning, whereas the quartz rim is gray with

187   weakly developed zoning (Fig. 3c−d). Melt inclusions are abundant in QM2 with a

188   diameter of 1~20 μm (Fig. 3e). This kind of melt inclusion, containing glass and

189   translucent crystals, are referred to as crystallized silicate melt inclusions (SMI). Vapor

190   phase is not obvious in these melt inclusions. Minor chalcopyrite and native gold grains

191   occur in cracks of QM2 (Fig. 3f).

192   The quartz (QU) with unidirectional solidification textures (UST) also formed near

193   the top of the porphyry, characterized by large quartz grains all growing from the same

194   side. The CL images show that the UST quartz grains contain both bright QU1 cores

195   and dark QU2 surroundings (Yang et al., 2015; Fig. 4a−c). Gold grains mostly occur as

196   trails in QU (Yang et al., 2015; Fig. 4a, d). The size of gold grains is typically about 5

197   μm, surrounded by many small ones < 2 μm (Fig. 4e). Primary SMI, melt-fluid

198   inclusion (MFI) and fluid inclusions (FIs) can be found in QU, varying from 5 to 15

199   μm in diameter (Fig. 4f−j). The MFI contains liquid, vapor and glass phases (Fig. 4f).

200   Vapor-rich inclusions, containing over 95 vol% of vapor, dominate the FIs in QU (Fig.

201   4i). Minor hypersaline fluid inclusions containing halite, hematite, and some

202   unidentified minerals, were observed locally (Fig. 4j). The vapor-rich inclusions can be

203   observed coexisting with the MFI locally (Fig. 4i), whereas the hypersaline fluid

204   inclusions always exist alone.

205   The quartz in A veins (QA) grew from both sides of the vein wall to the center,

206   and has three sub-generations (Fig. 5a−d). QA1 has distinct CL zoning and is

207   overgrown by QA2 with lower brightness, and lacking zoning (Fig. 5c). Extremely

208   bright quartz (QA3) overprints the QA2 near the center of the vein; it has a width of

209   ~100 μm (Fig. 5d). Some magnetite deposited in QA1 and QA2 (Fig. 5e) and a few

210   fissure gold grains were found, which are assumed as coeval with banded veins.

211   Chalcopyrite grains can be seen locally in QA2 (Fig. 5f). Quartz zones containing

212   abundant magnetite are always CL-dark (Fig. 5a, b). Fluid inclusions have not been

213   found in QA1. FIs in QA2 and QA3 are mainly vapor-rich (Fig. 5g-i), containing over

214   70 vol% of vapor.

215   In the gold-bearing banded veins, the quartz (QB) consists of four sub-generations,

216   growing from the rim to the center of the vein (Fig. 6a−f). It can be seen from the CL

217   images that: (1) QB1 is located on the side of a banded vein and is weakly zoned, with

218   gray-CL and a diameter of ~100–300 μm (Fig. 6b, c); (2) QB2 is yellowish under

219   transmitted light (Fig. 6a), and its CL zones are distinct and bright, showing a growth

220   continuity with QB1 (Fig. 6b, c); (3) QB3 grows on the rim of QB2 or appears as

221   individual grains with diameters of less than 50 μm (Fig. 6d, e). QB3, containing

222   variable amounts of fine-grained magnetite, is very "dirty" under the transmitted light

223   (Fig. 6a). (4) QB4 envelopes QB3 to form a rim, or fills the central part of the banded

224   veins as aggregates (Fig. 6e, f). Abundant native gold (Fig. 6g) and minor metal sulfides

225   (pyrite and chalcopyrite) are observed in QB1 and QB2. The magnetite grains in QB3

226   are generally less than 5 μm in size (Fig. 6h). Vapor-rich inclusions and liquid-rich

227   inclusions are developed in QB1 and QB2 (Fig. 6i, j), occurring as primary fluid

228   inclusion assemblages. Fluid inclusions in QB3 are similar to those in QB1 and QB2,

229   and some liquid-rich FIs contain a magnetite crystal are observed in QB3 (Fig. 6k). In

230   contrast to QB1-QB3, liquid-rich FIs are well developed in QB4, typically with 10-20

231   vol% of vapor (Fig. 6l−m).

232   The late veins, consisting of quartz, pyrite, tourmaline and carbonate (calcite +

233   dolomite), are the last mineralization stage. The quartz (QC) has a bright and CL-zoned

234   core (QC1) and a "dirty-CL" rim (QC2) (Fig. 7a, b). Pyrite is abundant in this stage,

235   growing on the edge of late veins or intergrown with the dolomite (Fig. 7c). Many

236   aqueous liquid-rich inclusions occur in primary assemblages along the growth zones in

237   QC1 and QC2 (Fig. 7d). They are usually irregularly shaped and up to 15 μm in size,

238   with a ~10 vol% vapor.

239

240   **Fluid Inclusions**

241   Most of the FIs analyzed in this study had a diameter of 8–12 μm. To investigate

242   the characteristics of ore-forming fluids, only primary fluid inclusions assemblages

243   were studied, based on the CL textures of their host quartz. Microthermometric results

244   are summarized in Fig. 8 and Table 2. The full data set is given in Supplementary Table

11

245   A.

246   In UST quartz, the brine and vapor-rich inclusions were trapped at temperatures

247   above 600°C, which is consistent with the crystallization temperature of granodiorite

248   porphyry estimated by the Ti-in-Zircon thermometer (~750-850 °C; Yang et al., 2016).

249   Jiang (2011) ever reported the homogenization temperatures of the SMI are above

250   900°C. Carbon dioxide in the vapors of vapor-rich inclusions was identified by laser

251   Raman spectroscopy, but there is no visible liquid CO_2 at room temperature, and no

252   clathrate dissociation was observed in this study, thus CO_2 only occurs as a minor

253   component ($\leq$ 2 mol%; Azbej et al. 2007). The ice-melting temperatures of vapor-rich

254   FIs, containing over 95 vol% of vapor, could not be determined due to difficulties in

255   observing the phase transformation. The dissolution temperatures of halite in a limited

256   number of brine inclusions are between 342 and 401°C (n=5), suggesting a salinity of

257   41.7–47.6 wt.% NaCl equiv.

258   Vapor-rich inclusions in A veins are also CO_2-bearing and did not show double

259   freezing and clathrate dissociation during microthermometry. At room and lower

260   temperatures, no liquid CO_2 was observed. These FIs in QA2 and QA3 have

261   homogenization temperatures in range 464–552°C, with the average value of 502 °C (n

262   = 22). Their ice-melting temperatures are between –17.6°C and –9.2°C, corresponding

263   to 13.1–20.7 wt.% NaCl equiv.

264   Fluid inclusions in different quartz sub-generations of banded veins were recorded

265   separately, as the sub-generations can be distinguished clearly under the microscope

266   (Fig. 6a). QB1 and QB2 have a good growth continuity (Fig. 6b, c) and their

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267   homogenization temperatures are bracketed together. In QB1+QB2, QB3 and QB4, the

268   FIs (vapor-rich + liquid-rich) have homogenization temperatures of 368–421°C, 361–

269   401°C and 298–334°C, with salinities of 7.9–14.9 wt.% NaCl equiv, 7.3–19.8 wt.%

270   NaCl equiv and 6.6–17.3 wt.% NaCl equiv, respectively (Table 2). All vapor-rich FIs

271   homogenized into the vapor phase, as opposed to the liquid-rich ones. Minor CO_2 (≤ 2

272   mol%) also occurs in FIs in QB1–QB3; but no CO_2 was detected in FIs in QB4.

273   Unlike the other veins, only aqueous liquid-rich inclusions are developed in late

274   veins. Microthermometry shows ice-melting temperatures between -4.2°C and -0.6°C,

275   corresponding to 1.1–6.7 wt.% NaCl equiv. They finally homogenized into the liquid

276   phase with homogenization temperatures between 177°C and 218°C (mean = 191°C).

277

278   **Oxygen isotopes**

279   SIMS analyses (N = 152) of $\delta^{18}O$ for quartz are shown in Fig. 9 and Table 3, and

280   the complete dataset can be found in Supplementary Table B, including the used quartz

281   reference materials. Quartz phenocryst and dendritic quartz in granodiorite porphyry

282   yield constant $\delta^{18}O$ values of 9.4–10.4‰ and 9.6–10.1‰, respectively.

283   UST quartz yields $\delta^{18}O$ values ranging from 9.5‰ to 10.5‰. No distinct variations

284   were found between quartz zones with different CL densities. In A veins, quartz of

285   different sub-generations exhibits variable $\delta^{18}O$ values. QA1 has $\delta^{18}O$ values of 9.2–

286   9.7‰, which are similar to QA2 ($\delta^{18}O$ = 9.3–9.8‰). However, QA3 is obviously

287   enriched in ^{18}O, yielding $\delta^{18}O$ values between 10.4‰ and 14.3‰, with a mean value of

288   12.2‰ (n = 10). In banded veins, $\delta^{18}O$ ranges of QB1, QB2, QB3 and QB4 are 9.2–

13

289   10.5‰, 9.6–10.5‰, 11.2‰–15.4‰ and 8.9‰–10.4‰, respectively. For the late veins,

290   QC has a notable isotopic difference between cores (6.4‰ to 7.9‰) and rims (3.5‰ to

291   6.7‰), with the cores more enriched in ^{18}O than the corresponding rims (Fig. 7a, b).

292   Except for QA3 and QB3, individual quartz generations have a relatively homogeneous

293    $\delta^{18}O$ values, regardless of the CL zoning (Fig. 9).

294

Discussion

Formation history of quartz

297   Dendritic and UST quartz (Fig. 2b, c) are well developed in the mineralized

298   granodiorite porphyry. The dendritic quartz, containing abundant SMI, is generally

299   considered to be the product of highly fractionated magma (Swanson and Fenn, 1986;

300   Yang et al., 2015). Primary Au grains are abundant in the UST quartz (QU) and are

301   regularly distributed. UST quartz is interpreted to have formed during the magmatic-

302   hydrothermal transitional stage, where exsolved fluid gathered at the top of the

303   porphyry intrusion (Erdenebayar et al., 2014; Hong et al., 2019). The gold can be

304   observed coexisting with both FI and MI locally (Fig. 4g−h), when precipitating from

305   the magmatic hydrothermal fluid (e.g., Koděra et al., 2014). Yang et al. (2015) ever

306   proposed that the gold directly precipitated from the magma due to the SMIs are

307   abundant in UST, whereas Huang et al. (2020) observed that tiny vapor-rich inclusions

308   is more closely related to the gold trails and the SMIs were trapped at the melt-fluid

309   interface accompanied by rare gold precipitation. Therefore, the Bilihe Au deposit,

310   which shows typical characteristics of porphyry deposits, is inferred to be a porphyry

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311   type deposit, but in contrast to other porphyry gold deposits, it experienced a high

312   temperature gold precipitation event during the UST quartz stage.

313   The occurrence of crystallized SMI is not common in porphyry Au deposits. Their

314   formation requires high temperatures but relatively low pressure to promote the

315   exsolution of volatiles (Harris et al., 2003; Rottier et al., 2016). The UST and dendritic

316   quartz at Bilihe have experienced heterogeneous entrapment of melt and vapor phases,

317   thus making the melt inclusions in them difficult to homogenize (Harris et al., 2003;

318   Rottier et al., 2016) even at high temperatures (> 950°C) as measured by Jiang (2011).

319   The crystallization temperature of granodiorite porphyry was estimated at ~750-850 °C

320   using the Ti-in-Zircon thermometer (Yang et al., 2016), suggesting that the UST quartz

321   was deposited at similar or lower temperatures.

322   SEM-CL images demonstrate that the hydrothermal quartz veins at Bilihe are

323   composed of multiple sub-generations of quartz and yield complex textures of

324   fracturing, dissolution, recrystallization and overgrowth, indicating complicated

325   changes in the physicochemical conditions of the ore-forming fluid (Rusk and Reed,

326   2002; Rusk et al., 2008). Some textures can be used to monitor specific episodes of

327   mineralization at Bilihe. Based on the textures of quartz and associated mineral

328   assemblages, it is apparent that gold precipitated twice at Bilihe deposit, once in the

329   UST quartz stage and again in the banded veins stage. Both gold mineralization events

330   were accompanied by minor sulfide precipitation. Due to the banded veins zone is

331   around the UST zone and the two stages gold yields a similar fineness (~980; Qing,

332   2010), it is inferred that the gold in banded veins was remobilized from the UST stage

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333   (Yang et al., 2015; Koděra et al., 2018).

334   Considering that the erosion depth does not exceed 2 km after the deposit forming

335   based on the Ti-in-quartz thermobarometer (as low as 0.5 kbar; Huang et al., 2020), the

336   maximum lithostatic pressure for the formation of the porphyry-type mineralization at

337   Bilihe can be estimated at 600 bars, which is consistent with the minimum entrapment

338   pressure calculated using fluid inclusions in A veins (Fig. 8). As shown in Table 2, the

339   estimated pressures of hypersaline fluid inclusions (n = 5) in UST are ~1300 bars,

340   suggesting that they were trapped under a relatively high-pressure condition. Due to the

341   hypersaline fluid inclusions are very few and always exist alone, we thought this high-

342   pressure phenomenon is only a local character, which may result from the fluid

343   gathering at the top of the porphyry intrusion (e.g., Shu et al., 2013). The exsolved

344   magmatic fluid ascended, forming A veins, but precipitating little or no sulfides and

345   gold as it cooled to ~500°C. Minimum pressure estimates of 431–678 bars for vapor-

346   rich FIs at 464–552°C indicate a ~2 km paleodepth under lithostatic conditions (Fig. 8).

347   As the temperature decreased to ~390°C, some gold and minor amounts of metal

348   sulfides (pyrite and chalcopyrite) deposited with QB1 and QB2 quartz in banded

349   veinlets. Variable pressure estimates of 76–307 bars for FIs in QB at 298–421°C suggest

350   that the banded veins were formed in the transition from lithostatic to hydrostatic

351   pressure conditions (Fig. 8; e.g., Redmond et al., 2004).

352

353   **Equilibrium oxygen fractionation**

354   When using $\delta^{18}O_{quartz}$ to calculate $\delta^{18}O_{fluid}$, the deposition temperature of quartz is

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355   needed. For most fluid inclusions at Bilihe, homogenization temperatures are the

356   minimum trapping temperature estimates. However, due to the true ore-forming

357   pressures are sufficiently low (< 600 bars) as mentioned above, the homogenization

358   temperatures are expected to be within 50 °C of the trapping temperatures (Allan and

359   Yardley, 2007; Li et al., 2016). Therefore, the $\delta^{18}O_{fluid}$ calculated using homogenization

360   temperatures in this study can be used to trace the $\delta^{18}O$ fluctuation of the ore-forming

361   fluids (e.g., Allan and Yardley, 2007; Fekete et al., 2016; Li et al., 2019). The $\delta^{18}O$

362   values of fluids forming QU, QA, QB1+QB2, QB3, QB4 and QC are calculated using

363   750°C, 502°C, 394°C, 375°C, 317°C and 191°C, respectively.

364   In addition to knowing the deposition temperature, another important condition

365   for a correct calculation of $\delta^{18}O_{fluid}$ is that the quartz crystallized under isotopic

366   equilibrium conditions (Matsuhisa et al., 1979; Allan and Yardley, 2007; Tanner et al.,

367   2013). The equilibrium would be achieved if the duration of quartz deposition was

368   longer than the time required for isotope exchange between quartz and the hydrothermal

369   fluid (Cole et al., 1992). The different quartz generations at Bilihe have variable grain

370   sizes, ranging from dozens of microns to several centimeters. Previous studies show

371   that in porphyry deposits individual quartz grains exceeding hundreds of microns in

372   diameter potentially precipitated over hundreds of years (Mercer et al., 2015; Cernuschi

373   et al., 2018), which is long enough for water and quartz to reach the isotopic equilibrium

374   (<20 yr; Cole et al., 1992; Li et al., 2018). It can be inferred from previous experimental

375   studies that relatively high fluid temperatures are beneficial for rapid growth of quartz

376   (Pollington et al., 2016 and references therein), which may result in locally

17

377   inhomogeneous isotopic ratios within one grain (e.g., Tanner et al., 2013). However,

378   most of the quartz grains at Bilihe, whether they crystallized at either high or low

379   temperatures, show constant isotope compositions, with a narrow range of $\delta^{18}O$ values

380   (Fig. 9). Therefore, most of the vein quartz at Bilihe can be considered to have formed

381   under oxygen isotope equilibrium conditions (Li et al., 2018).

382

383   **Disequilibrium oxygen fractionation**

384   As shown in Fig. 9, $\delta^{18}O_{quartz}$ and the corresponding $\delta^{18}O_{fluid}$ values exhibits great

385   fluctuations from QU to QC. Usually, the $\delta^{18}O_{quartz}$ and $\delta^{18}O_{fluid}$ values would decrease

386   gradually with the incursion of isotopically light meteoric water in porphyry deposits

387   (e.g., Fekete et al., 2016). However, two peaks of $\delta^{18}O_{quartz}$ and $\delta^{18}O_{fluid}$ occur in QA3

388   and QB3 at Bilihe, suggesting the quartz has experienced an unusual growth at these

389   two sub-stages.

390   In some studies, the sudden enrichment of heavy oxygen in quartz is explained as

391   the quartz deposition under equilibrium conditions but at lower temperatures, leading

392   to a high fractionation factor between quartz and water (Matsuhisa et al., 1979; Fekete

393   et al., 2016). The homogenization temperatures of FIs in QA3 and QB3 show that the

394   quartz precipitated at relatively high temperatures. Therefore, the low temperature

395   isotopic fractionation can be excluded.

396   Disequilibrium O-isotope fractionation between quartz and water, which is

397   typically ignored in studies of the evolution of fluids, is a possible reason for the

398   observed fluctuations of $\delta^{18}O$ in QA3 and QB3 stages. Disequilibrium isotopic

399   fractionation is common during hydrothermal mineral growth (Tanner et al., 2013) and

400   results in changes in the isotopic composition of minerals. Compared with the

401   equilibrium isotopic fractionation, the heavy oxygen would be more likely to partition

402   into silicate minerals and quartz under non-equilibrium conditions (e.g., Huang et al.,

403   2006; Clayton and Mayeda, 2009), and thus would result in their abnormal high $\delta^{18}O$

404   values. Disequilibrium O-isotopic fractionation between fluid and quartz can be caused

405   by three mechanisms: (1) the influence of sector zoning texture of quartz (Onasch and

406   Vennemann, 1995; Jourdan et al., 2009). However, the mechanism is still under debate

407   (Tanner et al., 2013). (2) The fast growth rate of quartz, which can be indicated by the

408   increase of the trace element concentrations (Ihinger and Zink, 2000) and small crystal

409   size (Huang et al., 2006; Gabitov, 2013). (3) The maturation of colloidal or amorphous

410   silica, accompanied by the cryptocrystalline textures, would create high O-isotopic

411   signature (Tanner et al., 2013). At Bilihe, no sector zoning and cryptocrystalline

412   textures were observed in QA3 and QB3. In contrast, the fast growth rate may be

413   responsible for the disequilibrium isotopic fractionation in QA3 and QB3, suggested by

414   their small crystal size (< 100 μm).

415   A discontinuous input of magmatic-hydrothermal fluid would also intermittently

416   make the fluids enriched in heavy oxygen (Li et al., 2018). The corresponding $\delta^{18}O_{fluid}$

417   values of QA3 and QB3 are very close to the isotopic signature of the magmatic quartz

418   (Table 3) and may record other two separate magmatic-hydrothermal events. However,

419   the $\delta^{18}O$ values of QA3 and QB3 are very variable and much higher than vein quartz in

420   most porphyry deposits, which generally yield constant $\delta^{18}O$ values of less than 10‰

421   (Taylor, 1974; Fekete et al 2016; Rottier et al., 2016, 2018; Li et al., 2018; Cernushi et

422   al., 2018). Besides, the volumes of QA3 and QB3 are too small and only occur as a

423   minor part of A and banded veins respectively, with no separated veins formed by them.

424   Considering these factors, disequilibrium O-isotope fractionation is a preferred

425   explanation for the enrichment of ^{18}O in QA3 and QB3.

426

427   **Incursion of meteoric water and gold precipitation**

428   After excluding the anomalously ^{18}O-enriched quartz that probably formed during

429   disequilibrium fractionation, the $\delta^{18}O_{quartz}$ and $\delta^{18}O_{fluid}$ values still show significant

430   variations (Fig. 9). The calculated $\delta^{18}O_{fluid}$ in equilibrium with QU could be interpreted

431   as the oxygen isotopic signature of the initial magmatic-hydrothermal fluid (Harris et

432   al., 2004; Hong et al., 2019). For A, banded and late veins, $\delta^{18}O_{fluid}$ values are lower

433   than those of the initial magmatic water. The trend of $\delta^{18}O_{fluid}$ values suggests that

434   meteoric water was progressively mixed with a magmatic-hydrothermal fluid during

435   ore deposition.

436   As noted above, gold precipitated during two stages at Bilihe, once in the UST

437   quartz and the other in the banded vein quartz. For porphyry deposits, it is generally

438   agreed that the ore-forming fluid was initially derived from magma, and meteoric water

439   added in later stages. However, it is still controversial when the meteoric water became

440   involved in the ore-forming system, and whether it had a direct influence on the

441   precipitation of sulfides. Some studies suggest that meteoric water participates in

442   mineralization in the early stage, and even had an important role in mineralization

443   (Taylor, 1974; Wilkinson, 2013; Fekete et al., 2016), whereas others conclude that it

444   invaded the system in later stages and only affected peripheral and post-mineralization

445   alteration (Sillitoe, 2010; Richards, 2011). The abundant Au precipitated in the UST

446   quartz at Bilihe suggests that the incursion of meteoric water is not essential for gold

447   deposition. Instead, quenching of the melt and magmatic-hydrothermal fluid may have

448   strongly influenced the Au deposition (Yang et al., 2015). This is supported by the well-

449   developed dendritic quartz in the mineralized granodiorite porphyry, which indicate

450   rapid cooling or supercooling (Swanson and Fenn, 1986) that could dramatically

451   decrease the solubility of Au in fluid (Pokrovski et al., 2014). Besides, the phase

452   separation, indicated by condensation of a hypersaline liquid from the dominant low-

453   salinity vapor phase, can result in enrichment of vapor in Au and S. This process is

454   typical for most porphyry environments, whereas at Bilihe, the hypersaline fluid

455   inclusions are rare and no one was observed coexisting with vapor-rich inclusions.

456   Therefore, the influence of phase separation on gold precipitation in UST is probably

457   limited.

458   For A veins, although the oxygen isotopes fall within the range of magmatic water

459   defined by Taylor (1974), they are still slightly lower than those of the UST quartz,

460   indicating that a small volume of ground water might have been involved. Fluid-rock

461   reactions, involving the formation of abundant hydrous silicates (e.g., chlorite and

462   muscovite), would also reduce the $\delta^{18}O_{fluid}$ (Cole and Ripley, 1999). However, at

463   temperatures of > 500°C, the O-isotope fractionation between water and these silicates

464   is very low (< 0.5‰) and can be ignored (Cole and Ripley, 1999). In the QB1 stage,

21

465   gold precipitated at the temperature of ~390°C. Such a low temperature can be attained

466   by fluid-rock reaction, the addition of another cooler fluid and simple cooling on fluid

467   ascent (Sillitoe, 2010; Fekete et al., 2016). As shown in Fig. 8, minimum pressure

468   estimates of 76–307 bars for FIs in banded veins suggest a transition from lithostatic to

469   hydrostatic environment at a paleodepth of 0.8–1.2 km, which provided conditions for

470   meteoric water to progressively invade the hydrothermal system (Redmond et al., 2004).

471   Estimating the $\delta^{18}O$ of −12‰ for the late Paleozoic meteoric paleowater in Inner

472   Mongolia (Li et al., 2003), ~15 vol.% of meteoric water may have participated in the

473   gold precipitation in banded veins (Fig. 9). In the quartz-carbonate stage, meteoric

474   water (~60–80 vol.%) dominated the ore-forming process. The decrease of $\delta^{18}O_{quartz}$

475   from core to rim of QC may result from the modification of late meteoric fluids. The

476   mixing processes between magmatic hydrothermal and meteoric can also be

477   documented by the salinity variations of ore-forming fluids. For example, the initial

478   salinity of the magmatic hydrothermal fluid can be approximated by the salinity of the

479   fluid inclusions in A veins (17.1 ± 2.0 wt.% NaCl equiv.). After mixing with 80 vol.%

480   meteoric water, the salinity of ore-forming fluids would be ~3.4 wt.% NaCl equiv.,

481   which is very close to the salinity of the fluid inclusions in late veins (4.3 ± 1.6 wt.%

482   NaCl equiv.).

483   Generally, fluid boiling is an important trigger for gold precipitation in porphyry

484   ore-forming systems (Ni et al., 2015), whereas at Bilihe, the influence of fluid boiling

485   on metals precipitation is not clear, due to the absence of high-salinity inclusions in

486   gold-bearing quartz in banded veins and coexisting aqueous liquid-rich and vapor-rich

22

487   fluid inclusions are only found locally in QB2. Mixing with cooler meteoric water may

488   have played an important role in the second gold mineralizing stage in banded veins.

489   Fluid mixing can be an effective mechanism causing metal deposition in different types

490   of deposits (Olivo and Williams-Jones, 2002). During the mixing process, cooling,

491   neutralization, and dilution of the hydrothermal fluids can result in destabilization of

492   Au-bearing hydrogen sulfide or chloride complexes (Pokrovski et al., 2014). About 15

493   vol.% of meteoric water (Fig. 9) was involved to precipitate most of the gold at ~390°C,

494   similar to previous studies on porphyry Cu/Mo deposits (Rottier er al., 2016; Li et al.,

495   2019).

496

Implications

498   By study of quartz CL textures, fluid inclusion microthermometry and in situ O-

499   isotope analysis, we have shown that the ore-forming fluids at Bilihe had a complex

500   evolution, resulting in multiple generations of quartz, diverse quartz growth

501   characteristics and oxygen isotopic compositions. The two peaks of $\delta^{18}O_{quartz}$, occurring

502   in QA3 and QB3, suggest that the vein quartz may have experienced sporadic

503   disequilibrium oxygen fractionation during deposition, resulting in local ^{18}O-

504   enrichment. Disequilibrium oxygen fractionation is largely unreported, but may be a

505   common phenomenon in porphyry deposits, which may affect the calculation of

506    $\delta^{18}O_{fluid}$ when using bulk quartz isotopic data. The overall $\delta^{18}O_{fluid}$ values, with a

507   gradual decrease from early to late stages, suggest a progressive decrease in the

508   proportion of magmatic hydrothermal fluids. Two gold mineralization events have been

23

509 recorded in quartz from Bilihe. The first, native gold in high temperature UST quartz

510 (>600 °C), resulting from rapid cooling, suggests that the addition of meteoric water

511 may be unnecessary for the formation of porphyry gold deposits. However, the

512 dominant second gold deposition stage in banded quartz veinlets (~390 °C) indicates

513 that most of the gold was deposited from fluids of mixed magmatic and meteoric water.

514

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705

706   **Figure captions**

707   **Fig. 1.** (a) Simplified map of part of China and Mongolia showing the study area (after

708   Xiao et al., 2009). (b) Regional geological map of central Inner Mongolia showing the

709   distribution of magmatic rocks and tectonic belts (modified after Xiao et al., 2009). (c-

710   d) Geological map of the Bilihe gold deposit (modified after Yang et al., 2015).

711

712   **Fig. 2.** Quartz formed at different stages. (a) Dendritic quartz in K-feldspar-altered

713   granodiorite porphyry. (b-c) Gold-bearing UST quartz cut by A veins in granodiorite

714   porphyry, with illite alteration. (d) A vein with potassic alteration halo. (e) Auriferous

715   banded veins with phyllic alteration and cutting the dendritic quartz. (f) Quartz-

716   carbonate-tourmaline vein (late vein) in granodiorite porphyry. Abbreviations: Tur =

717   Tourmaline, Cbn = Carbonate, UST = Unidirectional solidification texture.

718

719   **Fig. 3.** Photomicrographs and CL images of quartz phenocrysts and dendritic quartz.

720   (a-b) CL textures of euhedral quartz phenocrysts in the granodiorite porphyry showing

721   CL-gray core, overgrown by CL-bright quartz. Locations (white spots) and results of

722   SIMS oxygen isotope analyses are also shown. (c-d) CL images of dendritic quartz

723   showing its growth habit, with location (blue dots) and results of SIMS oxygen isotope

724   analyses. (e) SMI groups in the quartz rim. (f) Anhedral chalcopyrite and native gold in

725   cracks of dendritic quartz. Abbreviations: SMI = silicate melt inclusion, Ccp =

726   Chalcopyrite.

727

728   **Fig. 4.** Textures and mineral assemblages of UST quartz. (a-c) CL images showing the

33

729   growth habit of quartz and Au distribution, with location (blue dots) and results of

730   oxygen isotope analyses. The UST quartz grains contain both bright QU1 cores and

731   dark QU2 surroundings. (d) Reflected light image of Au grains in one trail. The big Au

732   grains are surrounded by dozens of smaller ones, < 2 μm. (e) Group of gold grains under

733   transmitted light. (f) Crystallized silicate melt inclusions in QU1. Also shown is a melt-

734   fluid inclusion. (g) Native gold coexisting with the SMI in QU1. (h) Native gold

735   coexisting with fluid inclusions. (i) Primary vapor-rich fluid inclusions coexisting with

736   the SMI. (j) A representative hypersaline fluid inclusion containing different daughter

737   minerals. Abbreviations: SMI = Silicate melt inclusion, V = Vapor, L = Liquid, Hal =

738   Halite, Hem = Hematite, Syl = Sylvite.

739

740   **Fig. 5.** Quartz CL, mineral inclusions and fluid inclusions of A veins. (a-d) CL images

741   of a quartz vein showing different quartz generations. Blue dots and red numbers refer

742   to the positions and results of SIMS analyses, respectively. (e) Fine-grained magnetite

743   in quartz zones of QA2. (f) Chalcopyrite grains in QA2. (g) Vapor-rich fluid inclusions

744   in QA2. (h-i) Vapor-rich fluid inclusion in QA3. Abbreviations: Mag = Magnetite, Ccp

745   = Chalcopyrite.

746

747   **Fig. 6.** Quartz sub-generations, mineral inclusions and fluid inclusions of auriferous

748   banded veins. (a-b) Photomicrographs of banded veins under transmitted light and

749   corresponding CL mapping. Blue dots and red numbers refer to the positions and results

750   of SIMS O-isotope analyses, respectively. (c-f) CL images showing the sub-generations

34

751 and textures of quartz. (g) Gold group in QB1. The inset is the corresponding reflected

752 light image. (h) Fine grained magnetite in QB3. (i-j) Fluid inclusions in QB1 and QB2.

753 Coexisting vapor-rich and liquid-rich fluid inclusions occur locally. (k) Coexisting

754 vapor-rich and liquid-rich fluid inclusions in QB3. Also shown is a fluid inclusion

755 containing a magnetite crystal. (l-m) Fluid inclusions in QB4. Abbreviations: Mag =

756 Magnetite.

757

758 **Fig. 7.** Quartz occurrences, minerals and fluid inclusions in late veins. (a-b) CL images

759 show that a CL-bright quartz is overgrown by a CL-dark rim, with location (blue spots)

760 and results of oxygen isotope analyses. (c) Pyrite and tourmaline intergrown with

761 carbonate (dolomite + minor calcite). (d) Fluid inclusions in the QC. Abbreviations: Tur

762 = Tourmaline, Py = Pyrite, Cbn = Carbonate.

763

764 **Fig. 8.** Pressure-temperature diagram for $NaCl-H_2O$ system showing fluid evolution

765 paths for A, banded and late veins in the Bilihe gold deposit (phase diagram after

766 Fournier, 1999). The QU fluids are not included in the diagram due to the estimated

767 pressures of hypersaline fluid inclusions (n = 5) in UST are abnormally high and could

768 not represent the true entrapment pressures (see text for details).

769

770 **Fig. 9.** $\delta^{18}O_{quartz}$ and $\delta^{18}O_{fluid}$ values for Bilihe deposit sorted by successive quartz

771 generations. The overall $\delta^{18}O_{fluid}$ values show a gradual decrease from early to late

772 stages, and two abnormal peaks of $\delta^{18}O_{quartz}$ and $\delta^{18}O_{fluid}$ values occur in QA3 and QB3.

Table 1

Overview of quartz generations and SEM-CL textures

Quartz generation		SEM-CL textures	Luminescence intensity	Minerals and relations	Melt/Fluid inclusions types
QM1	Core	Weakly CL-zoned euhedral quartz crystals;	CL-dark to CL-gray		A small number of HSMI
	Rim	Thin light overgrowth zone on QM1-Core; widely developed in the matrix	CL-bright		
QM2	Core	Yielding a mosaic texture with no zonings; completely mantled by a rim	CL-bright	Coexisting with K-feldspar; minor chalcopyrite and gold grains occurring in the cracks	HSMI with a diameter of < 5 μm
	Rim	Overgrowing QM2-Core; non-directional oscillatory zoning	CL-gray		HSMI with a diameter of 1~20 μm
QU	QU1	Unidirectional oscillatory zoning and sector zoning	CL-bright to CL-gray	Primary gold grains, chalcopyrite, needle-like apatite and minor pyrite	(1) HSMI and MFI; (2) vapor-rich FI (> 95 vol % vapor), containing CO_2 (no visible liquid CO_2 at room temperature); (3) minor hypersaline liquid FI containing halite, hematite and sylvite
	QU2	Thin rim on QU-Core and developed near the cracks, possibly as replacement of QU-core	CL-gray to CL-dark		HSMI (1~20 μm)
QA	QA1	Distinct oscillatory zoning; overgrown by the lateral QA2	CL-bright to CL-gray	Magnetite, scheelite	Not developed
	QA2	Overgrowing QA1, with no zoning developed	CL-gray, containing one CL-dark zoning	Magnetite, scheelite, chalcopyrite and bornite	(1) mainly vapor-rich (> 60 vol % vapor); (2) liquid-rich FI are rare; -These vapor-rich FIs are CO_2-bearing, but no visible liquid CO_2 at room temperature

	QA3	Thin bright overgrowth zone on the QA2 near the center of A vein; fractured by late fluids	Brightest luminescence in A vein	Magnetite	Vapor-rich (> 60 vol % vapor) -CO_2 bearing, but no visible liquid CO_2 at room temperature
QB	QB1	Growing in the side of B vein; weakly CL-zoned grains	CL-gray	Primary gold, chalcopyrite, pyrite, scheelite	Vapor-rich (> 60 vol % vapor) and liquid-rich; -CO_2 bearing, but no visible liquid CO_2 at room temperature
	QB2	Growth continuity with QB1; distinct oscillatory zoning; dissolution textures at the contact with QB4	CL-bright to CL-gray; locally CL-dark	Native gold, chalcopyrite, pyrite, and magnetite zoning	vapor-rich (> 60 vol % vapor) and liquid-rich; -CO_2 bearing, but no visible liquid CO_2 at room temperature
	QB3	Appearing as a thin dark rim on QB2 or as individual fine grains; dissolution textures at the contact with QB4	CL-dark	Micrometer-sized magnetite	vapor-rich (> 60 vol % vapor) and liquid-rich; -CO_2 bearing, but no visible liquid CO_2 at room temperature
	QB4	Accretive rim on QB3 or filling the center of B vein as aggregates	CL-gray; Its luminescence intensity is weaker than QB1		Liquid-rich (~20 vol % vapor) and minor vapor-rich
QC	QC1	CL-zoned euhedral quartz crystals up to several millimeters; dissolution textures at the contact with QC2	CL-bright	Carbonates, pyrite, tourmaline and minor chlorite	Liquid-rich (~10 vol % vapor)
	QC2	Thin overgrowth zone on QC1, which probably is the recrystallization of QC2	CL-"dirty"		Liquid-rich (~10 vol % vapor)

Table 2
Summary of microthermometric data of fluid inclusions from the Bilihe deposit

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

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.

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

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 ℃. See text for detail.

Figure 1

(a)

MONGOLIA   CHINA

Fig. 1B

CHINA

(b)

112E   114E   116E   118E

Mongolia

Southern Mongolian active continental margin

China

Hegenshan ophiolite-arc-accretion complex

Chagan Obo-Arongqi fault

Baolidao arc-accretion complex   44N

Erenhot fault

East Gobi Fault Zone   44N

Erenhot   Baolidao

Xilinhot fault

Solonker suture zone

Linxi Fault

Ondor Sum subduction-accretion complex

Bilihe (~269 Ma)

Chifeng

Ondor Sum

Fig. 1c

Bainaimiao arc

Xar Moron Fault

Obo copper

Solonker (Solon Obo)

Bate Obo

Bainaimiao

Chifeng-Bayan Obo fault   42N

42N

Hadamiao (~270 Ma)

Bayan Obo

Jining

Fengning-Longhua Fault

Pangquan-Gubeikou-Chicheng-Shangui Fault

Longhua

Hohhot

108E   110E   112E   114E   116E   118E

South Mongolia:
- Paleozoic continental margin
- Paleozoic arc-accretion complex

North China Block:
- Early Paleozoic Continental margin
- Precambrian craton

- Solonker suture zone
- Permian intrusive rocks

- Ophiolitic blocks
- Gold deposits (deposit age)

(c)

4702

N

Bilihe

Fig. 1d

4692

Hadamiao

0   1   2 Km

(d)

N

4697

Vein 26

Vein 22   Belt I

4696

Belt II

B   A'

A   B'

4695

Supplementary Fig. 1

4694

38462   38463   38464

- Late Carboniferous-Early Permian marine sedimentary rocks
- Early Permian andesitic tuff interbedded with sandstone
- Early Permian rhyolite and rhyolitic tuff
- Middle Permian granodiorite-diorite
- Middle Permian diorite
- Middle Permian granite porphyry
- Basalt, Basalticte andesite
- Late Permian syenogranite
- Late Permian syenogranite porphyry
- Aplite dike
- Breccia
- Quaternary sediments
- Normal fault
- Reverse fault
- Strike-slip fault
- Quartz vein

Fig. 2

Fig. 3

Panel a: scale bar 200 μm

Panel b: scale bar 200 μm. Labeled points: 9.60, 9.97, 9.61, 9.75, 9.47, 9.27, 9.43, 9.92, 9.96

Panel c: rim, core, rim. Labeled points: 9.73, 9.35, 9.74, 9.96, 9.86, 10.07, 9.79, 9.82, 10.12, 9.97, 9.34, 9.67, 9.56, 10.17, 10.05, 10.13, 10.06, 9.63, 10.40, 10.26, 10.18. Scale bar 200 μm

Panel d: rim, core. 4/29/2018 4:59:07 AM | HV 20.0 kV | WD 10.1 mm | Mag 140x | Spot 4.9 | Pressure 0.98 Torr | HFW 0.96 mm | 300.0μm

Panel e: SMI. Scale bar 20 μm

Panel f: Au, Ccp

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9