**Fluid and metal sources of the Wenquan porphyry molybdenum deposit, Western
Qinling, NW China**

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Abstract The Wenquan porphyry molybdenum deposit, Western Qinling, NW China, with a resource of 247 million tonnes at 0.048% Mo, formed during Triassic collision between South China and North China blocks. Ore fluids at Wenquan vary widely in composition from single-phase, low-salinity aqueous to low-salinity vapor, and hypersaline inclusions. Fluid inclusion assemblages in a quartz-molybdenite vein contain >60 vol. % vapor, are equant to negative-crystal shaped, and form clusters or distinct inclusion trails. They yield homogenization temperatures of 285~295 °C, with an estimated trapping temperature of 425 °C, suggesting a paleodepth of about 5 km calculated at a pressure correction of 100~150 MPa. Hydrothermal K-feldspar from early stockwork veins related to potassic alteration have calculated $\delta^{18}\text{O}_{\text{fluid}}$ values of -1.9 ‰ to +1.9 ‰. Hydrothermal sericite from an overprinting phyllic alteration associated with late quartz-pyrite veins has calculated $\delta\text{D}_{\text{fluid}}$ values between -68 and -60 ‰, and $\delta^{18}\text{O}_{\text{fluid}}$ values from -3.7 to +1.4 ‰. These isotopic data suggest that both early- and late-stage fluids are dominated by magmatic fluids, with influx of meteoric water during the late stage. Exsolution of volatiles from magma in a late-stage open system, results in more variable δD values than an earlier closed-system.

Molybdenite and pyrite have $\delta^{34}\text{S}$ values ranging from 1.1 ‰ to 6.6 ‰, indicating that sulfur at Wenquan had a magmatic source. A linear relationship between $\delta^{34}\text{S}$ values of sulfides separated from early potassic alteration and late phyllic alteration could reflect incorporation of isotopically heavy evaporate sulfate into source magmas from underlying Devonian sedimentary rocks during late alteration. The $\delta^{56}\text{Fe}$ whole-rock values of altered porphyries range from 0.08 ‰ to 0.26 ‰, similar to $\delta^{56}\text{Fe}$ values of 0.15 ‰ to 0.32 ‰ for pyrite from quartz veins related to both the potassic and phyllic alteration assemblages. The $\delta^{56}\text{Fe}$ values of pyrite are positively correlated to, but in general slightly lighter than, those of altered porphyries, indicating similar metal sources. Moreover, both altered porphyries and the pyrite are progressively enriched in heavy Fe isotopes from biotite, through potassic to late phyllic alteration, consistent with isotopic evolution from an early lithostatic load to a late hydrostatic load.

The Triassic intrusive rocks and fluids responsible for mineralization were derived from a deeply-sourced hybrid mantle-crustal magma crystallizing at a paleodepth of 5 km under lithostatic load. External Late Triassic meteoric or Devonian formational fluids became a part of the hydrothermal system during the post-fracturing final stage of ore formation under a hydrostatic regime. The formation of the Wenquan magmatic-hydrothermal systems spans the ductile-brittle transition based on a normal thermal gradient as constrained by the temperature range of 550~300 °C. The early, high-temperature potassic alteration developed under a ductile regime,

49 whereas the later, low-temperature phyllic alteration correlates to a brittle environment, where
50 hydraulic rock fracturing enhances permeability and fluid circulation. Most sulfur and metals were
51 precipitated from vapor-rich fluids resulting from cooling and expansion of a single-phase fluid
52 exsolved from a hybrid magma.

53

54 **Key words:** microthermometry; H-O-S-Fe isotopes; fluid and metal sources; Wenquan porphyry
55 deposit; Western Qinling

1. Introduction

The Central China Orogenic Belt, consisting of the Kunlun, Qilian, Qinling and Dabie Mountains from west to east, is located in central Eastern Asia, and formed during ocean basin closures and subsequent collision between the North China Block and Tarim Block to the north, and South China Block and Tibet to the south (Fig. 1A, Meng and Zhang, 2000; Deng et al., 2013; Pirajno and Zhou, 2015). The Qinling Orogenic Belt, linking the Kunlun and Qilian Mountains in the west and the Dabie Mountain to the east, is separated into the Western Qinling and Eastern Qinling segments (shown as blue dash line in Fig. 1B; Zhang et al., 2007; Liu et al., 2010; Tang et al., 2015), on the basis of regional geology and lithospheric features defined by geophysical studies. Several studies have reviewed the evolution of the Qinling Orogen that culminated with collision between the North China and South China Blocks (Chen and Santosh, 2014; Dong and Santosh, 2016). Eastern Qinling is well endowed with porphyry Mo deposits, with a proven and inferred resource exceeding 6 million tonnes (Mt) Mo metal (Mao et al., 2008; Li et al., 2013). In contrast, porphyry systems in Western Qinling have been poorly documented, although they were first recognized as early as the 1970s (GSBGME, 1979; Xiang et al., 1985) and now comprise dozens of porphyry and associated skarn deposits (Fig. 1B; Qiu et al., 2016; Qiu and Deng, 2016 and references therein). These include the Jiangligou W-Mo, Xiekeng, Nianmuer Cu-As-Au, Amangshaji Cu, Longdegang Cu-As, Zaozigou Au, Dewulu Cu, Nanban Cu, Laodou Au-Cu, Riduoma Fe, Xiahejiangang Fe, Shanglanggang Fe, Wenquan Mo, and Taiyangshan Cu deposits. Ore genesis studies using modern methodologies on select deposits, as well as reconstructions of the regional structural and tectonic setting for the porphyry magmatism, are critically needed to increase targeting strategies for exploration in Western Qinling.

Besides the world-famous Late Mesozoic (Late Jurassic–Early Cretaceous) porphyry Mo systems located in the Eastern Qinling, Early Mesozoic (mainly Triassic) Mo deposits throughout the Qinling Orogen have been discovered and recognized (Li and Pirajno, 2017). Wenquan, the only large Triassic porphyry Mo deposit in the Western Qinling, however displays different characteristics on ore fluids compared to those coeval porphyry Mo deposit to the Eastern Qinling (Ren, 2009; He, 2012; Chen et al., 2017). The Wenquan Mo deposit is easily accessible and has well-developed alteration zonation, distinct mineralization styles, and clear mineral assemblages, making it amenable to a comprehensive ore genesis study. The Wenquan deposit comprises 247 Mt ore in the measured and indicated categories, and 0.12 Mt Mo metal at a grade of 0.048 % Mo (He, 2012). Previous robust Re–Os dating on molybdenite from quartz-molybdenite veins, and

numerous geochronological and geochemical studies on the associated granitoids, combined with geological investigations, have provided a basic framework for the geological environment and outlined possible genetic relationships at Wenquan (e.g., Han, 2009; Zhu et al., 2011). However, there remains no consensus on a holistic genetic model for ore formation at Wenquan. The key to understanding the uncertainties in ore genesis lies in the defining the nature of the ore fluids and metal sources for the deposit.

Four types of fluid inclusions have been recognized in the Wenquan deposit based on detailed petrography (Han, 2009; Ren, 2009; He, 2012; Wang et al., 2012): single-phase aqueous inclusions, vapor-rich fluid inclusions, hypersaline liquid inclusions, and low-salinity aqueous inclusions. However, no specific geological information has been provided to illustrate which of the multi-generations of quartz in a complex paragenetic sequence was chosen for fluid inclusion analyses in the past research. Moreover, most microthermometric data recorded from these previous studies were not collected following the procedure of defining Fluid Inclusion Assemblages (that carefully discriminated groups of petrographically associated fluid inclusions trapped at the same time and conditions as proposed by Goldstein and Reynolds, 1994), which is essential for identifying post-entrapment modification of fluid inclusions from necking down, stretching, or leakage and refilling (Bodnar, 2003). Measurements of ice-melting temperature ($T_{m,ice}$), halite dissolution temperature ($T_{s,halite}$), and homogenization temperatures of fluid phases in these fluid inclusions ($T_{h,total}$) thus inevitably provide little accurate information about ore fluid characteristics at the pressure and temperature of entrapment of the fluids.

Stable isotope geochemistry is typically applied to furnish invaluable information concerning the genesis and physiochemical aspects of ore-forming hydrothermal solutions, as well as to constrain the origin and evolution of some ore-forming components (Calagari, 2003; Goldfarb and Groves, 2015). Some workers reported hydrogen and oxygen isotopic compositions ($\delta D = -96 \sim -68 \text{ ‰}$; $\delta^{18}O_{fluid} = -0.9 \sim +0.6 \text{ ‰}$) from inclusion fluids extracted from quartz grains separated from quartz-molybdenite veins at Wenquan deposit, and proposed that the ore fluids were a mixture of magmatic and meteoric waters (Han, 2009; Ren, 2009; He, 2012). Fluid inclusions in quartz, a ubiquitous gangue mineral of hydrothermal deposits, have long been extensively used to define fluid sources. Scanning electron microscope and cathodoluminescence (CL) techniques, however, have confirmed that early-formed quartz grains are readily overprinted by later hydrothermal events, and these techniques define different generations not observed under an optical microscope (Rusk et al., 2006, 2008; Qiu et al., 2015). This observation indicates that the quartz

120 that has been overprinted could host fluid inclusions correlated to multiple hydrothermal events.
121 The isotopic data collected from such quartz and trapped fluid inclusions therefore cannot be used
122 to interpret the formation of the ore deposit.

123 Han (2009) and He (2012) measured sulfur isotopes on molybdenite ($\delta^{34}\text{S} = +4.69 \sim +6.61 \text{ ‰}$)
124 separated from quartz-molybdenite veins, and proposed that sulfur was sourced from the lower
125 crust and upper mantle. Wang (2011) and Zhu et al. (2011) reported sulfur isotopic values of pyrite
126 ($\delta^{34}\text{S} = +5.02 \sim +5.58 \text{ ‰}$) and molybdenite ($\delta^{34}\text{S} = +5.46 \sim +5.66 \text{ ‰}$) from quartz-sulfide veins, and
127 suggest that magmatic-hydrothermal fluids associated with granitoids were the major sulfur
128 source at Wenquan. They suggested that mineralization resulted from internal fractional
129 crystallization of fluids within the Triassic magmatic system. However, the lack of detailed
130 paragenetic information on these sulfides hinders interpretation. Pyrite occurs as a ubiquitous
131 mineral in different quartz-sulfide veins at Wenquan (Zhu et al., 2011; Qiu et al., 2015), so only
132 pyrite that can be clearly ascribed to a specific stage can provide meaningful genetic information.

133 The principal aim of this study is to elucidate the source and evolution of fluids and metals for
134 porphyry mineralization in order to provide a comprehensive ore genesis model for the Wenquan
135 mineral system. Previous research at Wenquan has provided a geologic framework for geodynamic
136 setting, the duration of magmatic-hydrothermal processes, and the nature of alteration zonation
137 and mineralization styles. This previous work has been enhanced here through drill core logging
138 and new fieldwork. We present carefully constrained fluid-inclusion microthermometric data for
139 least-overprinted quartz samples following careful petrography using the Goldstein and Reynolds
140 (1994) approach, in concert with SEM and CL imaging. Furthermore, stable isotope geochemistry is
141 presented for minerals of different well-defined mineralization and alteration generations.

142

143 **2. Geological background**

144 **2.1. Regional geology**

145 The Triassic Western Qinling Orogenic Belt is an important geological boundary that separates
146 the North and South China Blocks. This belt is tectonically bounded by the North China Block and
147 Qilian Mountain Terrane to the north of the Shangdan suture zone (Fig. 1B), and
148 A'nimaqing-Mianlue suture zone (Fig. 1B; Deng et al., 2014b; Dong et al., 2016; Wang CM et al.,
149 2016), which defines the eastern branch of Paleotethys Ocean, to the south (Bian et al., 2004;
150 Wang et al., 2014; Deng et al., 2014a). The Paleozoic Shangdan suture zone reflects closure of the
151 Shangdan Ocean and multistage amalgamation of the South China Block-South Qinling Block to the

152 North China Block during the Paleozoic (Meng and Zhang, 2000; Yang et al., 2015b; Tang et al.,
153 2016). This suture zone comprises discontinuously exposed mélangé, mainly Paleozoic ophiolitic
154 assemblages, and subduction-related volcanic and sedimentary rocks, all intensely deformed
155 during Paleozoic thrusting, Late Triassic sinistral ductile-shearing, and Cretaceous brittle faulting
156 (Ratschbacher et al., 2003; Li et al., 2014; Liu et al., 2015). The Triassic A'nimaqing-Mianlue suture
157 zone represents the closure of a northern branch of the eastern Paleotethyan Ocean which
158 separated the South Qinling Block from the South China Block (Chen and Santosh, 2014). The
159 suture zone is characterised by intensively dismembered ophiolite and arc-related volcanic rocks,
160 high-pressure/temperature metamorphic rocks, and continental-margin sedimentary rocks of
161 Paleozoic to Middle Triassic age. These were later affected by south-directed overthrusting during
162 the Late Jurassic to Cretaceous (Dong and Santosh, 2016).

163 The Triassic Western Qinling Orogenic Belt underwent a multistage amalgamation process
164 between the South and North China Blocks, from the Proterozoic up to late Mesozoic (Dong et al.,
165 2016). The widely-exposed Devonian to Middle Triassic sedimentary rocks record deformation
166 related to this subduction and collision history, whereas the Precambrian basement rocks are
167 rarely exposed (Luo et al., 2012). Mesozoic magmatism is widespread in Western Qinling, with
168 hundreds of Triassic granitic plutons intruded throughout the belt between the Paleozoic Shangdan
169 and Triassic A'nimaqing-Mianlue suture zones (Li et al., 2013; Wang et al., 2013; Deng and Wang,
170 2016). Subsequent uplift and exhumation led to the widespread exposure of Triassic granitoids in
171 the belt (Chen and Santosh, 2014), with closely-related porphyry-skarn metallogenic systems (Qiu
172 et al., 2015; Qiu and Deng, 2016 and references therein).

173

174 **2.2. Geology of the Wenquan deposit**

175 The Wenquan porphyry Mo deposit is hosted by the Wenquan batholith (E105°04'~ E105°08',
176 N34°35'~ N34°38'), which is irregular in shape, and covers an area of about 250 km² (Fig. 1B). The
177 Wenquan batholith consists of five units: biotite granite, biotite monzogranite porphyry,
178 porphyritic monzogranite, monzogranite porphyry, and porphyritic syenogranite (Fig. 1C; Han,
179 2009). The composite batholith intruded a suite of gently-dipping strata, represented by the
180 Paleoproterozoic to Mesoproterozoic Qinling Group to the northeast, consisting predominantly of
181 schist and gneiss, and the Devonian Dacotan Group, primarily composed of clastic and carbonate
182 rocks to the southwest (Qiu et al., 2014). Three NW-trending mafic dikes named Lannigou (~8km),
183 Yangjiashan-Shijishan (~8km) and Heigou (~4km) intrude the batholith to the northeast (Han,

2009). Abundant mafic enclaves are hosted mainly by biotite monzogranite porphyry, porphyritic monzogranite, and monzogranite porphyry (Fig. 1C; Cao et al., 2011; Qiu et al., 2014). These mafic enclaves show consistent directional alignment as well as mineral assemblages and geochemical composition to that of mafic dikes (Han, 2009; Zhu et al., 2011).

The host granite porphyries of the Wenquan complex batholith are an intermediate to felsic, and high-K calc-alkaline to shoshonitic suite of peraluminous to metaluminous granites with I-type affinity (Zhu et al., 2011). They have relatively higher MgO contents and $Mg^\#$ compared to normal crustal-derived felsic magmas, but lower Nb/Ta ratios compared to the mafic enclaves (Cao et al., 2011; Zhu et al., 2011). These hybrid magmas resulted from magma mixing during their Late Triassic emplacement at roughly the transition from a collisional setting, between the South Qinling and South China Blocks, to a post-collision setting (Zhu et al., 2011; Chen and Santosh, 2014). At the Wenquan deposit, biotite granite porphyry and monzogranite porphyry are the two prominent phases associated with Mo mineralization (Fig. 2).

Uranium–lead ages on zircons separated from these ore-hosting granites are reported as 223 ± 3 Ma and 225 ± 3 Ma (Cao et al., 2011), 218 ± 2.4 Ma and 221 ± 1.3 Ma (Xiong et al., 2016), and 217.2 ± 2.0 Ma and 216.2 ± 1.7 Ma (Wang, 2011; Zhu et al., 2011), respectively. The mafic enclaves hosted in the porphyries yield zircon U–Pb ages of 217 ± 2.0 Ma and 218 ± 2.5 Ma (Xiong et al., 2016), respectively. Zircons from host porphyries have negative $\epsilon_{Hf}(t)$ values of -3.6 to -0.1, with two-stage Hf model ages (T_{DM2}) of 1056 to 1234 Ma, and positive $\epsilon_{Hf}(t)$ values ranging from +0.1 to +3.0, with single-stage Hf model ages (T_{DM1}) of 739 to 868 Ma (Wang, 2011; Xiong et al., 2016). This indicates that the host porphyries are most likely formed by partial melting of Mesoproterozoic lower continental crust. Zircons in the mafic enclaves have negative $\epsilon_{Hf}(t)$ values ranging from -10.1 to -0.1 and T_{DM2} of 1052 to 1565 Ma, and have positive $\epsilon_{Hf}(t)$ values of +0.5 to +10.8 and corresponding T_{DM1} of 441 to 856 Ma (Zhu et al., 2011; Xiong et al., 2016), suggesting an origin by partial melting of Neoproterozoic subcontinental lithosphere mantle.

Alteration zones at Wenquan are well developed outward from a potassic, to a phyllic, and then to propylitic silicate+sulfide+oxide assemblage (Fig. 2A; Han, 2009). Porphyry-style Mo mineralization at Wenquan consists predominantly of stockworks, veinlets, and disseminated sulfides (Fig. 3). The NS-trending orebodies comprise planar to irregular veins that dip 30° to 75° northeast (Fig. 2B, Han, 2009). The disseminated Mo mineralization is generally developed within the biotite granite porphyry and monzogranite porphyry bodies, which contain widespread mafic enclaves. Previous Re–Os dating on molybdenite separated from quartz-molybdenite veins yielded

216 model ages of 214.4 ± 7.1 Ma (Song et al., 2008; Zhu et al., 2009) and 219 ± 5.2 Ma (Xiong et al.,
217 2016). The molybdenite from quartz-molybdenite veins has Re contents of 20 to 33 $\mu\text{g/g}$,
218 suggesting mantle involvement for the magma and metal source (Song et al., 2008; Zhu et al.,
219 2009).

220

221 **3. Samples and analytical methods**

222 **3.1. Optical and QEMSCAN microscopy**

223 All 53 samples collected from the Wenquan deposit were preliminarily surveyed by
224 transmitted and reflected microscopy, and then seven selected samples were analysed using
225 automated scanning electron microscopy (QEMSCAN) at the Colorado School of Mines to more
226 comprehensively determine mineral assemblages. The samples were loaded into the QEMSCAN
227 instrument and analyses were initiated using the control program (iDiscover, FEI). Four energy
228 dispersive X-ray (EDX) spectrometers acquired spectra from each particle with a beam stepping
229 interval (i.e., spacing between acquisition points) of 20 μm , an accelerating voltage of 25 keV, and
230 a beam current of 5 nA. Interactions between the beam and the sample were modeled through
231 Monte Carlo simulation. The EDX spectra were compared with known spectra allowing an
232 assignment to be made of a composition at each acquisition point. The assignment makes no
233 distinction between mineral species and amorphous grains of similar composition. Results were
234 output by the QEMSCAN software as a spreadsheet giving the area percent of each composition in
235 the pre-existing spectra. This procedure allows a compositional map of each sample to be
236 generated. Composition assignments were grouped appropriately.

237 **3.2. Fluid inclusion petrography**

238 Reconnaissance fluid-inclusion petrography was conducted on quartz veins from all
239 paragenetic stages recognized by observing intersection and overprinting relationships between
240 different veins (veinlets), intrusive contacts, and alteration types (halos) and temporal-spatial
241 relationship of gangue and ore minerals by using microscope and QEMSCAN. Subsequently, optical
242 microscopy and detailed fluid inclusion petrography were performed on selected quartz vein
243 samples with an Olympus BX51 microscope using a series of doubly polished, 60 μm -thick sections
244 at the U.S. Geological Survey in Denver. Microthermometric data on selected fluid inclusions were
245 collected using a Fluid Inc.-adapted U.S. Geological Survey gas-flow heating and freezing stage that
246 was calibrated using synthetic fluid inclusions. Freezing temperatures were accurate to $\pm 0.1^\circ\text{C}$. The
247 accuracy of heating measurements ranged from approximately $\pm 2^\circ\text{C}$ at 200°C to approximately

248 $\pm 10^\circ\text{C}$ at temperatures above 600°C . Imaging of representative fluid inclusions was conducted
249 using an Optronics Microfire A/R camera at the Colorado School of Mines.

250 **3.3. Hydrogen and oxygen isotopes**

251 Oxygen and hydrogen isotope analyses were conducted on ore-related sericite separates from
252 quartz-pyrite-sericite phyllic assemblage veins. Additional oxygen isotope analyses were performed
253 on K-feldspar separates from the potassic halos surrounding
254 quartz-chalcopyrite-pyrite-molybdenite veins and quartz-molybdenite-chalcopyrite veins truncated
255 by late quartz-pyrite-sericite veins. Pure sericite aggregates and K-feldspar flakes were obtained by
256 crushing, washing and drying, and then hand-picking under a binocular microscope. The isotopes
257 were measured in the Isotope Laboratory at the U.S. Geological Survey in Denver. Oxygen was
258 extracted from 15-20 mg silicate minerals by reaction with BrF_5 and then reacted with carbon to
259 give CO_2 (Clayton and Mayeda, 1963), whereas hydrogen was liberated as water by the fusion of
260 the samples and then reacted with zinc to give H_2 (Coleman et al., 1982). The resultant CO_2 was
261 analysed for oxygen isotopes using a Finnigan MAT-252 mass spectrometer, whereas the hydrogen
262 isotopes were obtained using a MAT 253. The precisions for O and H isotopes were ± 0.1 and ± 2
263 per mil (1σ), respectively. The $^{18}\text{O}/^{16}\text{O}$ and D/H ratios are reported in normal δ -notation relative to
264 V-SMOW standard. Hydrogen isotopic compositions of ore fluids ($\delta\text{D}_{\text{fluid}}$) in equilibrium with the
265 hydrothermal sericite were calculated using the sericite-water equilibrium function of Marumo et
266 al. (1980): $\delta\text{D}_{\text{fluid}} = \delta\text{D}_{\text{mineral}} + 22.1 \times 10^6 \text{T}^{-2} - 19.1$. Oxygen isotopic compositions of ore fluids ($\delta^{18}\text{O}_{\text{fluid}}$)
267 were calculated using the K-feldspar-water equations ($\delta^{18}\text{O}_{\text{fluid}} = \delta^{18}\text{O}_{\text{mineral}} - 2.91 \times 10^6 \text{T}^{-2} + 3.41$), and
268 muscovite-water fractionation factors ($\delta^{18}\text{O}_{\text{fluid}} = \delta^{18}\text{O}_{\text{mineral}} - 2.38 \times 10^6 \text{T}^{-2} - 3.89$) of Zheng (1993).

269 **3.4. Sulfur isotopes**

270 Sulfur isotope measurements were collected for sulfide minerals separated from
271 quartz-sulfide veins in the Isotope Laboratory at the U.S. Geological Survey in Denver. Mineral
272 separations using standard methods of concentration were performed by conventional preparation
273 techniques including crushing, heavy liquids, and magnetic separation. Prior to subsequent
274 preparation for isotopic analyses, the purity of all concentrates was checked by examination under
275 a binocular microscope to ensure they were not oxidized, and contaminant-free, and thus
276 essentially monomineralic. Purities were 95 % to, more commonly, 99 % or better. Aliquots of
277 pyrite and molybdenite were combined with V_2O_5 and combusted in an elemental analyzer. Sulfur
278 isotope ratios were determined by an on-line method using an elemental analyzer coupled to a
279 Micromass Optima mass spectrometer (Giesemann et al., 1994). Analytical results are generally

280 reproducible within ± 0.2 per mil (2σ). Isotope data are reported in conventional δ notation relative
281 to the Canyon Diablo Troilite (CDT) standard. The measured and calculated oxygen and hydrogen
282 isotopic compositions are listed in Table 1. Sulfur isotope data in this study and previous literature
283 are summarized in Table 2.

284 **3.5. Iron isotopes**

285 Iron isotopic analyses were conducted on pyrite separates (B01, C01, C02, D01 and E01) and
286 altered monzogranite porphyry samples (B02, C03, D02, E02 and E03) that are cut by
287 quartz-sulfide veins (Fig. 3). Sample W31 is altered with hydrothermal biotite and crosscut by a
288 quartz-chalcopyrite-pyrite vein (Fig. 3B). Sample W32 is potassically altered and crosscut by a
289 quartz-chalcopyrite-pyrite-molybdenite vein (Fig. 3C). Sample W33 represents potassically altered
290 rock crosscut by a quartz-molybdenite-pyrite vein (Fig. 3D), whereas Sample W34 is characterized
291 by sericitic selvages along a quartz-pyrite-sericite vein within an area of potassic alteration (Fig. 3E).
292 The Fe isotopic compositions of granitoid samples and pyrite separates from the Wenquan deposit
293 are presented in Table 3.

294 Iron isotopic analyses were conducted in the Isotope Geochemistry Laboratory at the China
295 University of Geosciences, Beijing (CUGB). The analytical procedures were previously reported by
296 He et al. (2015). Bulk samples were carefully cleaned ultrasonically in purified Elga H₂O (18.2 M Ω)
297 before crushing and milling into minus-200 mesh powders. Approximately 30 mg of whole-rock
298 powder was dissolved with a concentrated in a HF-HNO₃-HClO₄ mixture, whereas pyrite separates
299 were dissolved using a concentrated HF-HNO₃-HCl mixture at 130°C. Sample solutions were then
300 evaporated to dryness after complete dissolution, and refluxed with aqua regia (HCl:HNO₃=3:1)
301 and excess HNO₃ aqua regia (HCl:HNO₃=2:1) successively at 130°C. The solutions were
302 subsequently evaporated to dryness at 100 °C. Finally, residues were dissolved in 6 N HCl for
303 chromatographic purification. Iron was separated from matrix elements and potential isobars with
304 AG1X-8 resin (200-400 mesh) in a HCl medium. Isotopic ratios were analysed by the
305 sample-standard bracketing method using a Thermo-Finnigan Neptune Plus MC-ICPMS on high
306 resolution modes. The measurement sequence was repeated four times to get better
307 reproducibility and accuracy, and the data are reported in the traditional δ values relative to
308 IRMM-014 ($\delta^i\text{Fe} = [({}^i\text{Fe}/{}^{54}\text{Fe})_{\text{sample}} / ({}^i\text{Fe}/{}^{54}\text{Fe})_{\text{IRMM-014}} - 1] \times 1000$, where i can be 56 or 57). Internal
309 errors are reported as 2se, 95% confidence interval after Dauphas et al. (2004) and He et al. (2015).
310 The long-term external reproducibility and accuracy on $\delta^{56}\text{Fe}$ are estimated to be better than $\pm$
311 0.05 ‰ (2SD) (He et al., 2015). Geostandard GSP-2 (granodiorite) and BCR-2 (basalt) were

312 processed during the course of this study.

313

314 **4. Analytical Results**

315 **4.1. Mineral assemblage**

316 The Wenquan deposit display stockworks veins (Fig. 3A, B, D) typically defined by two or three
317 preferred vein orientations with conjugate or orthogonal relationships, and occur together with
318 sheeted vein arrays (Fig. 3C, D). The scheme of quartz-sulfide vein classification at Wenquan, with
319 distinctive silicate + copper-iron sulfide + oxide assemblages, was determined by previous work
320 and new careful paragenetic study of drill core and hand samples (Fig. 3F). The earliest dark-quartz
321 veinlets with minor copper sulfides (Fig. 3A) are irregular, discontinuous, and segmented. The
322 quartz-chalcopyrite-pyrite veins (Fig. 3B), comprising mineral assemblages of quartz, K-feldspar,
323 biotite, with minor magnetite and pyrite, are generally associated with biotite alteration. The
324 quartz-chalcopyrite-pyrite-molybdenite veins (Fig. 3C), composed of quartz, K-feldspar, biotite,
325 magnetite and chalcopyrite, with minor pyrite, molybdenite and bornite, are spatially related to
326 potassic alteration in which plagioclase was altered to potassium feldspar. The quartz-molybdenite
327 veins (Fig. 3D), characterised by continuous, planar veins with parallel walls, contain
328 coarse-grained quartz and molybdenite, with minor pyrite and chalcopyrite, which normally occur
329 in cracks or along the margins of molybdenite. Molybdenite grains are predominantly along the
330 contacts between the quartz veins and host granite. The quartz-pyrite-sericite veins (Fig. 3E)
331 represent the final mineralization event at Wenquan. They invariably cut and overprint earlier
332 quartz-sulfide veins, and are also cut by fractures filled with kaolinite and clays. These phyllic veins,
333 with low copper and molybdenum grades, occur as a radial array of continuous, systematically
334 oriented veins (Han, 2009). These late-stage veins comprise abundant euhedral quartz and pyrite,
335 with lesser chalcopyrite, chlorite and sphalerite, and are surrounded by sericitic selvages.

336 Micropetrography and QEMSCAN analyses indicate that ore minerals are dominated by
337 molybdenite, pyrite, and chalcopyrite, with minor bornite, tetrahedrite, and sphalerite (Fig. 4).
338 Gangue minerals include quartz, calcite, K-feldspar, plagioclase, biotite, sericite, chlorite, epidote,
339 and apatite (Fig. 4). The best developed zones of mineralization are closely associated with
340 potassic- and phyllic-altered porphyries (Fig. 3). The molybdenite aggregates occur normally along
341 the margin of the granites and quartz-stockwork veins (Figs. 3D, 4A, C), and sparsely disseminated
342 in the K-feldspar alteration zone (Fig. 4A, B, C, F). Pyrite, a major constituent of the stockworks, is
343 mainly developed in the center of the veins (Fig. 4C, D, F), and is disseminated in the altered

344 granitoids (Fig. 4C). Chalcopyrite, with subordinate pyrite along its margins, and bornite occur as
345 disseminated and late fracture-fillings within the quartz veins (Fig. 4B, E) and intrusions (Fig. 4C).
346 Accessory phases are Ti-bearing minerals chiefly occurring along margins of vein in alteration halo
347 side. They probably formed as a result of hydrothermal alteration of host porphyries. Gangue
348 minerals including chlorite and muscovite/kaolinite are locally present in secondary alteration
349 processes occur pervasively in the vein selectively, alteration halo and wallrock.

350 **4.2. Fluid inclusion petrography, fluid composition, and temperature/pressure estimates**

351 Dozens of fluid inclusion assemblages, including those dominated by hypersaline inclusions,
352 liquid-rich inclusions, and gas-rich inclusions were observed to be randomly occurring in numerous
353 quartz veins. Only one isolated quartz grain in a quartz-molybdenite vein (W33: Figs 3D, 4C, 5A)
354 has been recognized to exactly represent the Mo mineralization based on extensive petrographic
355 study, and thus was used for detailed microthermometric investigation. Sample W33 is a
356 potassically-altered porphyry, which is crosscut by a planar 2-cm-wide quartz-molybdenite vein
357 (Figs 3D, 4A, C). Minor pyrite and chalcopyrite are disseminated in altered porphyry (Fig. 4A, C) and
358 along the cracks or margins of molybdenite aggregates within the quartz vein (Fig. 4B, C, D, F).
359 Pyrite is also rarely present at the margins of chalcopyrite grains (Fig. 4C, E). Three fluid inclusion
360 assemblages (FIAs-1, FIAs-2 and FIAs-3) among numerous fluid inclusions in the isolated quartz
361 within molybdenite aggregates of sample W33 (Fig. 4A, C) were sophisticatedly chosen for
362 microthermometry. These three fluid-inclusion assemblages (Fig. 5D, E, F) provide information on
363 the fluid that deposited the coeval molybdenite (Fig. 5A, B, C). Moreover, the FIAs-2 and two
364 molybdenite flakes show a close spatial relationship (Fig. 5C, D). The microthermometric data from
365 these three FIAs undoubtedly provide the most robust PTX information for molybdenite-depositing
366 fluid at Wenquan.

367 The isolated quartz (Fig. 4A, C) contains variable numbers of fluid inclusions (Fig. 5A). Three
368 vapor-rich fluid inclusions (Fig. 5C, D, E) within the isolated quartz were selected for
369 microthermometric measurements based on detailed fluid inclusion petrography. The 5-10 μm
370 vapor-rich inclusions are equant to negative-crystal shaped, indicating a relatively high entrapment
371 temperature (cf. Bodnar, 2003), and form clusters or distinct inclusion trails. The FIAs-1 (Fig. 5E)
372 yield homogenization temperatures of 285~290 $^{\circ}\text{C}$ ($n=3$). The FIAs-2 (Fig. 5D) closely associated
373 with two molybdenite flakes have homogenization temperatures of 285~290 $^{\circ}\text{C}$ ($n=4$). The FIAs-3
374 (Fig. 5F) have homogenization temperatures of 290~295 $^{\circ}\text{C}$ ($n=4$). The ice-melting temperatures of
375 the fluid inclusions in all FIAs are between -4.0 and -3.2 $^{\circ}\text{C}$, and the presence of clathrate indicates

376 contamination by a non-aqueous phase, likely CO_2 . Therefore the ice melting data only give a
377 maximum salinity, which is <6.5 equiv.wt.% NaCl.

378 When pressure corrected to 100~150 MPa (4~6 km paleodepth under lithostatic load), which
379 is consistent with the calculated paleodepth of the host porphyries at approximately 5 km (He,
380 2012). Hydrothermal activity occurred at the same depth of porphyry host emplacement, and the
381 formation temperature is calculated to be $\sim 425^\circ\text{C}$ by using the calculation proposed by Potter
382 (1977).

383 4.3. Hydrogen and oxygen isotope data

384 The temperature used for calculation of the isotopic composition of the hydrothermal
385 K-feldspar from the potassic alteration (Fig. 3C) is the above 425°C estimation. The equilibrium
386 temperatures of hydrothermal K-feldspar (550°C : Rusk et al., 2008) and sericite (300°C : Han, 2009;
387 Ren, 2009; He, 2012) separates, from a potassic halo surrounding a quartz-molybdenite-pyrite vein
388 (Fig. 3D) and quartz-pyrite-sericite vein (Fig. 3E), were estimated by using the trapping
389 temperature of primary fluid inclusions in quartz coexisting with these different alteration minerals.
390 The measured and calculated oxygen and hydrogen isotopic compositions are listed in Table 1. The
391 analysed hydrothermal K-feldspars have $\delta^{18}\text{O}_{\text{mineral}}$ values of $+0.6\text{‰}$ to $+2.8\text{‰}$, and corresponding
392 calculated $\delta^{18}\text{O}_{\text{fluid}}$ values of -1.9‰ to $+1.9\text{‰}$. The analysed hydrothermal sericite separates yield
393 δD values from -105 to -98‰ , which correspond to calculated $\delta\text{D}_{\text{fluid}}$ values from -68 to -60‰ . Two
394 hydrothermal sericite separates have $\delta^{18}\text{O}_{\text{mineral}}$ values of -1.4‰ and $+3.6\text{‰}$, with calculated
395 $\delta^{18}\text{O}_{\text{fluid}}$ values of -3.7 and $+1.4\text{‰}$. In the $\delta^{18}\text{O}_{\text{fluid}}$ vs. $\delta\text{D}_{\text{fluid}}$ plot (Fig. 6), all samples of early
396 silicates plot in or proximal to the magmatic water field, with later-stage silicates plotting nearer to
397 the meteoric water line (Fig. 6).

398 4.4. Sulfur isotope data

399 Sulfur isotope data obtained for nine sulfide minerals from different paragenesis or alteration
400 zones in this study and data from literature are summarized and shown in Figure 7. One pyrite
401 separate from a quartz-chalcopyrite-pyrite vein crosscutting biotite-altered porphyry yields the
402 lowest $\delta^{34}\text{S}$ value of $+1.1\text{‰}$. Two pyrite separates from quartz-chalcopyrite-pyrite-molybdenite
403 veins which crosscut potassically-altered porphyries have $\delta^{34}\text{S}$ values of $+2.3\text{‰}$ to $+3.1\text{‰}$. Two
404 pyrite separates from quartz-molybdenite-pyrite veins crosscutting potassically-altered porphyries
405 exhibit $\delta^{34}\text{S}$ values of $+1.6\text{‰}$ to $+3.5\text{‰}$. Four pyrite separates from the latest quartz-pyrite veins,
406 with sericitic selvages, that crosscut potassically altered porphyries have $\delta^{34}\text{S}$ values from $+5.0\text{‰}$
407 to $+5.6\text{‰}$. Molybdenites from quartz-chalcopyrite-pyrite-molybdenite veins related to potassic

alteration have $\delta^{34}\text{S}$ values from +5.0 ‰ to +5.7 ‰. The quartz-molybdenite veins with minor pyrite and chalcopyrite related to potassic alteration yield $\delta^{34}\text{S}$ values for molybdenite of +4.7 ‰ to +6.6 ‰.

4.5. Iron isotope data

All samples including geostandards (GSP-2 and BCR-2) analysed in this study define a mass fractionation line in three-isotope space. The correlation between $\delta^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$ is $\delta^{57}\text{Fe} = 1.6248 * \delta^{56}\text{Fe} + 0.002$, and $R^2 = 0.9371$ (Fig. 8), indicating no analytical artefacts from unresolved isobaric interferences on Fe isotopes. Considering $\delta^{57}\text{Fe}$ is a minor isotope, accurate $^{57}\text{Fe}/^{54}\text{Fe}$ ratio analyses need relative large ion beams and accordingly more concentrated introducing sample solutions. The Isotope Geochemistry Laboratory at CUGB, which performed the analyses in this study, thus optimizes the conditions for $\delta^{56}\text{Fe}$, and therefore data on the $\delta^{56}\text{Fe}$ scale is discussed in the manuscript, although theoretically $\delta^{57}\text{Fe} = 1.475 * \delta^{56}\text{Fe}$.

All analysed bulk samples have $\delta^{56}\text{Fe}$ values in a range of 0.08‰ to 0.26‰, with an average of 0.22‰ (Fig. 9), falling within the range of igneous rocks (e.g., Beard et al., 2003; Heimann et al., 2008). The biotite-altered sample (B02) exhibits a $\delta^{56}\text{Fe}$ value of 0.17‰, whereas the potassically altered samples (C03 and D02) yield $\delta^{56}\text{Fe}$ values of 0.19‰ and 0.21‰. Sample W34 exhibits a $\delta^{56}\text{Fe}$ value for potassically altered bulk rock (E03) of 0.08‰, and highest $\delta^{56}\text{Fe}$ value is for the phyllically altered bulk rock (E02) of 0.26‰.

Five pyrite separates analysed from Wenquan yield $\delta^{56}\text{Fe}$ values in a range of 0.15‰ to 0.32‰ (Fig. 9), consistent with the range of igneous rocks (e.g., Beard et al., 2003; Heimann et al., 2008). The $\delta^{56}\text{Fe}$ value of pyrite (B01) separated from the quartz-chalcopyrite-pyrite vein is 0.15‰, and the pyrites (C01 and C02) separated from the quartz-chalcopyrite-pyrite-molybdenite vein yield $\delta^{56}\text{Fe}$ values of 0.17‰. The $\delta^{56}\text{Fe}$ value of pyrite (D01) separated from the quartz-molybdenite-pyrite vein is 0.21 ‰, whereas the pyrite (E01) separated from the quartz-pyrite-sericite vein exhibits the highest $\delta^{56}\text{Fe}$ value of 0.32‰.

5. Discussion

5.1. Genetic relationship between Mo mineralization and Wenquan composite batholith

Previous geologic studies have established an intimate relationship between high-temperature hydrothermal mineral assemblages, abundant stockwork veining, and Triassic porphyries at Wenquan, demonstrating a close connection of mineralization in space and time to magma emplacement (Han, 2009; Zhu et al., 2009, 2011; Wang, 2011; He, 2012; Qiu et al., 2014,

2015; Xiong et al., 2016). The Mo mineralization at Wenquan is spatially related to the composite granitic pluton (Fig. 3). The main ore minerals (molybdenite, pyrite, and chalcopyrite) occurs disseminated in the porphyritic phases of the pluton (Figs 4, 5), and are also ubiquitous in the quartz stockworks, and as infills in joints and cracks in the stockwork veins and their host porphyries (Fig. 5). These mineralization styles are consistent with those of typical porphyry deposits worldwide (Seedorff et al., 2005). Moreover, the granitoids of Wenquan composite display high degree of crystallization (Han, 2009; Wang, 2011), resulting in that more Mo will be concentrated into the aqueous fluid phase because of its favorable partitioning coefficient.

Previous geochronological data also support a genetic relationship between Mo mineralization and Triassic granite magmatism. Previous robust U–Pb data on zircons from ore-hosting porphyries and hosted mafic enclaves yield emplacement ages of ca. 225 to 217 Ma (Cao et al., 2011; Zhu et al., 2011; Xiong et al., 2016). They are identical or slightly older, within analytical error, than robust Re–Os isochron ages on molybdenite of ca. 219 to 214 Ma (Song et al., 2008; Xiong et al., 2016). This close spatial and temporal connection between metal precipitation and magma crystallization suggests that the Late Triassic hybrid magma was responsible for generating the Mo mineralization (Cao et al., 2011; Xiong et al., 2016).

Within the porphyritic intrusions, estimated formation depth of which is 5 km, the early veinlets (Fig. 3A, B) are irregular, discontinuous, and segmented. In contrast, the later quartz-chalcopyrite-pyrite-molybdenite veins (Fig. 3C) and quartz-molybdenite veins (Fig. 3D) tend to be more continuous and planar, some with internal symmetry. This evolution in vein structures is broadly consistent with a transition from >550°C early-stage vein formation in a ductile crystal mush to formation in a coherent, solidified brittle granite during potassic alteration. By the time quartz-pyrite-sericite veins (Fig. 3E) form, where euhedral grain textures and open-space fill textures are most common in the phyllic alteration zones, the magmatic-hydrothermal system evolved to lower temperatures (~300°C) and brittle fractures predominated. The late quartz-pyrite-sericite veins, generally with low Mo and Cu grades, have coarse-grained quartz and pyrite, but no chalcopyrite and molybdenite. They appear to mark the end of magmatic-hydrothermal system, and probably just complicate the original ore shells by locally redistributing metals to form complex zones of overprinting hydrogen-ion metasomatism.

5.2. Possible fluid sources and evolution: constraints from fluid inclusion and H-O isotope data

Fluid inclusion types in porphyry deposits are well described with respect to pressure and

472 thus paleodepth of emplacement (Bodnar, 2003). Fluids that formed the Wenquan porphyry Mo
473 deposit vary widely in composition, from single-phase and low-salinity aqueous inclusions (this
474 study; Han, 2009; Ren, 2009; He, 2012), through low-salinity vapor inclusions (this study; Han,
475 2009; Ren, 2009) to dilute liquid to high-salinity brine inclusions (at room temperature; Ren, 2009;
476 He, 2012). The early veins at Wenquan are intimately related to potassic-silicate, including biotite
477 and/or K-feldspar, alteration (Fig. 3B, C, D). Fluid inclusion petrography indicates that quartz grains
478 of these veins generally contain a diagnostic primary fluid-inclusion population of coexisting
479 hypersaline brines and low density vapor, for which micro analytical research is critical to
480 understand fluid phase behavior in terms of metallogenesis. At the early potassic-silicate alteration
481 stage, a single-phase fluid unmixes into a hypersaline liquid and a vapor through condensation at a
482 temperature exceeding 550 °C. Hydraulic fracturing under lithostatic conditions causes transient
483 permeability, which could be manifested as permeability waves (Landtwing et al., 2010; Weis et al.,
484 2012; Deng et al., 2015; Wang YH et al., 2016), producing irregular, discontinuous, and segmented
485 veins.

486 Although copper orebodies are not currently mined at Wenquan, the Cu-Fe sulfides occurred
487 in the early quartz-chalcopyrite veins indicating that extreme metal partitioning occurs in
488 magmatic fluids (Qiu et al., 2015). Such magmatic fluids subsequently underwent immiscibility
489 with the low-salinity and vapor-rich component being significantly metal-enriched compared to
490 coexisting hypersaline liquids (Ren, 2009; He, 2012), the same case for ore formation to typical
491 porphyry deposits worldwide (Redmond et al., 2004; Pudack et al., 2009; Weis et al., 2012; Liu et
492 al., 2012). The estimated ore formation temperature of quartz-chalcopyrite veins related to biotite
493 alteration is about 550 °C identical to typical porphyry deposits, and that of quartz-molybdenite
494 veins related to potassic alteration is 425 °C based on calculation in this study. These veins have
495 low-salinity (< 6.5 eq. wt. % NaCl), vapor-rich fluid inclusions and locally hypersaline liquid
496 inclusions with an extremely high salinity. As described above, pressure constraints from these
497 inclusions typically indicate shallow conditions (less than 5 km), consistent not only with field
498 observations for subvolcanic emplacement and brittle-stockwork vein systems, but also the
499 observed immiscibility (Muntean and Einaudi, 2001). This pressure includes lithostatic and
500 hydrostatic components because the formation of the Wenquan magmatic-hydrothermal systems
501 spans the ductile-brittle transition (550~300 °C), where crustal rocks are both resistant to
502 fracturing and fluid circulation under ductile conditions or fracture readily and exhibit enhanced
503 fluid circulation under brittle ones.

504 Hydrogen and oxygen isotopic signatures show that K-feldspar and sericite from potassic and
505 phyllic assemblages in this study, together with quartz from ore-bearing veins from literatures, plot
506 between the magmatic water field and the meteoric water line (Fig. 6). This suggests that both the
507 early- and late-stage fluids are dominated by magmatic fluids, and hydrothermal system was
508 subjected to an influx of meteoric water in the late mineralization event. Because the
509 homogenization temperatures of fluid inclusion assemblages used for calculation of the fluid
510 isotope values generally represent the minimum trapping temperature of the ore-forming fluids,
511 presented $\delta^{18}\text{O}_{\text{fluid}}$ values could be erroneously low. Our refined H-O isotopic compositions suggest
512 that ore fluid compositions varied through time. Early potassic alteration is characterized by fluid
513 compositions similar to magmatic water ($\delta^{18}\text{O}_{\text{fluid}}$ from 5 to 9 ‰, and δD from -20 to -80 ‰:
514 Giggenbach, 1992; Taylor, 1992; John et al., 2010), as observed in some typical porphyry deposits
515 around the world, such as from the early alteration phases at El Salvador (Watanabe and
516 Hedenquist, 2001), Bingham (Bowman et al., 1987), and OyuTolgoi (Khashgerel et al., 2008). In
517 contrast, later stage sericite from phyllic alteration is characterized by $\delta^{18}\text{O}_{\text{fluid}}$ values that are
518 nearer to the meteoric water line or lower $\delta^{18}\text{O}_{\text{fluid}}$ isotopic values (Fig. 6), consistent with those at
519 Bingham (Bowman et al., 1987) and OyuTolgoi (Khashgerel et al., 2008), reflecting the input of
520 meteoric water during phyllic alteration under a hydrostatic load.

521 The δD fluid values related to different ore and alteration stages within the Wenquan system
522 also vary over a large range. This may indicate that the δD values are controlled by magma
523 degassing, in addition to mixing of early magmatic and later meteoric waters, similar to what is
524 observed at the Bingham (Bowman et al., 1987) and OyuTolgoi (Khashgerel et al., 2008) porphyry
525 deposits. This is because the later open-system degassing, where exsolved volatiles separate from
526 magma, generally results in more variable δD values than an earlier closed-system, where exsolved
527 volatiles and magma co-exist.

528 In summary, based on a detailed study of the paragenesis of alteration and mineralization,
529 and fluid inclusion and H-O data at Wenquan, it is proposed that both the Triassic intrusive rocks
530 and fluids responsible for mineralization were derived from a deeper magma chamber with a
531 paleodepth of 5 km under a lithostatic load (Fig. 10A). However, external fluids were likely involved
532 during the late stage of ore formation spanning the ductile-brittle transition under a hydrostatic
533 load (Fig. 10B).

534

535 **5.3. Sulfur and iron isotope implications for metal sources**

536 The average $\delta^{34}\text{S}$ values of sulfide minerals are considered to represent the $\delta^{34}\text{S}$ composition
 537 of hydrothermal fluids because $\delta^{34}\text{S}_{\text{sulfide}} \approx \delta^{34}\text{S}_{\text{H}_2\text{S}} \approx \delta^{34}\text{S}_{\text{fluid}}$ in hydrothermal systems, where H_2S is
 538 the dominant sulfur species in the fluids or the fluid redox state is below the $\text{SO}_2/\text{H}_2\text{S}$ boundary
 539 (Kelly and Rye, 1979; Rollinson, 1993). As discussed above, quartz stockwork veins at Wenquan
 540 have pyrite and molybdenite as the main sulfides, and lack oxide phases and sulfate minerals,
 541 suggesting that H_2S was the dominant sulfur species, and that the average $\delta^{34}\text{S}$ values of pyrite and
 542 molybdenite do represent the $\delta^{34}\text{S}$ composition of the hydrothermal fluids. Sulfur isotopic
 543 signatures of all analysed molybdenite and pyrite separates yield $\delta^{34}\text{S}$ values ranging from 1.1 ‰ to
 544 6.6 ‰ (Fig. 7A), with an average of 4.5 ‰. These relatively homogeneous $\delta^{34}\text{S}$ values of the
 545 Wenquan deposit are consistent with those of the fluids in equilibrium with porphyry magmas
 546 ($\delta^{34}\text{S}=0.0$ ‰: Ohmoto, 1972), suggesting a magmatic origin for sulfur and metal sources. The
 547 $\delta^{13}\text{C}_{\text{PDB}}$ values (-8.3 ‰ to -7.9 ‰: Wang et al., 2012) of calcite separated from post-mineralization
 548 calcite-quartz veins are consistent with those of typical magmatic sources (-8 ‰ to -4 ‰: Ohmoto,
 549 1972; Pirajno, 2016), indicating the carbon at Wenquan had a dominant magmatic source.

550 A declining/increasing trend of $\delta^{34}\text{S}$ values is documented from many different metal-bearing
 551 porphyry systems (e.g., Wenquan, Butte, Bingham, Marysdale, Sierrita, Twin Butte, Sungun, Ajo
 552 and El Salvador). When compared to these porphyry deposits, Wenquan deposit has relatively
 553 heavy sulfur, similar to Butte and Bingham (Fig. 7B). Ohmoto and Rye (1979) pointed that $\delta^{34}\text{S}$
 554 values are very sensitive to the oxidation state of fluid, which is largely determined by $\text{H}_2\text{S}/\text{SO}_4^{2-}$,
 555 and temperature. As mentioned above, temperatures of the early potassic alteration stage are
 556 higher than those of the late phyllic alteration stage in the Wenquan magmatic-hydrothermal
 557 system. Therefore, the heavy $\delta^{34}\text{S}$ values for early sulfides could be interpreted to reflect late
 558 incorporation of isotopically heavy evaporate sulfate into the porphyry magma (Field et al., 2005;
 559 Rye, 2005; John et al., 2010; Liu et al., 2011; Zhang et al., 2014; Yang et al., 2016) from underlying
 560 Devonian sedimentary rocks. The Pb isotopes of K-feldspar from porphyries and bulk samples plot
 561 close to orogenic Pb evolution line, and between the upper crust and mantle Pb evolution lines.
 562 This indicates that the granitic magmas were sourced from the middle-lower crust with lesser
 563 involvement of mantle-derived materials. Moreover, the ore-forming materials could be
 564 incorporated into the hydrothermal fluid during differentiation of the Triassic magmatic system
 565 with only a minor contribution of sedimentary country rock (Wang, 2011; Zhu et al., 2011; He,
 566 2012).

567 Anbar et al. (2007) reviewed iron isotopic composition reservoirs, including $\delta^{56}\text{Fe}$ values of

igneous rocks (0.1 ‰), deep sea clays (-0.1 ‰), altered oceanic crust (-1.5 to 1.5 ‰), aerosols (0.1 ‰), and rivers (-1 to 0 ‰), among which the altered oceanic crust yields the most variable $\delta^{56}\text{Fe}$ composition probably due to its complex formation. The $\delta^{56}\text{Fe}$ values of the altered intrusive rocks (0.08 to 0.26 ‰) and pyrite separates (0.15 to 0.32 ‰) from Wenquan are higher and more variable than that of unaltered igneous rocks. This relatively wide range of $\delta^{56}\text{Fe}$ values may be attributed to variable degrees of fluid:rock interaction. The $\delta^{56}\text{Fe}$ values of pyrite separates are positively correlated to those of bulk samples (Fig. 9), indicating their possible relationship on metal sources. Moreover, the $\delta^{56}\text{Fe}$ values for pyrite are generally slightly lower than those of their host granitoid samples, suggesting that iron in pyrite is sourced, or at least partially sourced, from altered porphyries. The $\delta^{56}\text{Fe}$ values of both bulk samples and pyrite grains related to early biotite, potassic, and later phyllic alteration show a declining trend with time, and are enriched in heavy Fe, which indicates $\delta^{56}\text{Fe}$ in the hydrothermal system at Wenquan became lighter as it transitioned from an early lithostatic to late hydrostatic regime.

In conclusion, it is suggested that early potassic-silicate alteration assemblages formed under lithostatic loads, during which increased water-rock interaction and wallrock buffering, at temperatures ranging from 550 to 425°C. This resulted in progressive alteration zonation out from center of Wenquan magmatic-hydrothermal system (Fig. 10A). Transitions to phyllic alteration correlate with a progression from lithostatic to hydrostatic load at 300 °C, possibly due to the ingress of meteoric water. Such a process marks the end of porphyry ore formation. Sulfur and metals in the Wenquan Mo deposit mainly originated from a magmatic-hydrothermal fluid associated with crystallization of granitic magmas. They were possibly incorporated by contamination from the underlying Devonian sedimentary rocks during the late stage (Fig. 10B).

6. Conclusions

Geologic, petrographic, and fluid-chemical-isotopic evidence indicate that the formation of the Wenquan porphyry Mo deposit involves an interplay between magmatic metal sources and hydrothermal fluid systems in spatially, temporally, and genetically related Triassic porphyries. An early, high-temperature hypersaline fluid of magmatic origin resulted in potassic alteration under a lithostatic load, whereas phyllic alteration under a hydrostatic load likely involved some involvement of later, lower-temperature and less-saline non-magmatic meteoric or formation water. The bulk of the metals were precipitated from an expanding vapor-rich fluid, coexisting with a hypersaline fluid, both resulted from cooling and expansion of a single-phase fluid exsolved

600 during magma crystallization during Late Triassic collision between the South China and North
601 China Blocks. The sulfur and metals were incorporated into the porphyries that were derived from
602 a hybrid magma, and they were originated from lower crust and mantle due to deep magma
603 mixing, with possible incorporation from the underlying Devonian sedimentary rocks at a higher
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605

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865 **Figure captions**

866 Fig.1 (A) Tectonic subdivision of China, showing the location of Western Qinling. (B) Generalized
867 geological map of Western Qinling, showing major Triassic porphyry-skarn systems and distribution
868 of their associated granites (modified after Meng and Zhang, 2000; Yang et al., 2015a). (C) Sketch
869 geological map of the Wenquan area, showing the five phases: biotite granite (I), biotite
870 monzogranite porphyry (II), porphyritic monzogranite (III), monzogranite porphyry (IV), and
871 porphyritic syenogranite (V) of the composite Wenquan granite batholiths (Modified after Han,
872 2009; Wang, 2011 and this field investigation).

873
874 Fig. 2 (A) Generalized geological map of the Wenquan porphyry Mo deposit illustrating principal
875 geology and alteration zonings. (B) Profile of diamond drill core section through Line A-B in Figure
876 A.

877
878 Fig. 3 Photographs of quartz stockwork veins at Wenquan. (A) The barren early irregular,
879 discontinuous, and segmented dark-quartz veinlets. (B) The quartz-chalcopyrite-pyrite veins with
880 mineral assemblage of quartz, K-feldspar, biotite, magnetite and minor pyrite, generally associated
881 with biotite alteration. (C) The quartz-chalcopyrite-pyrite-molybdenite veins, consisting of quartz,
882 K-feldspar, biotite, magnetite and chalcopyrite, with minor pyrite, molybdenite and bornite. (D)
883 The quartz-molybdenite vein, with mineral assemblage of quartz and molybdenite, with minor
884 pyrite and chalcopyrite. (E) The quartz-pyrite-sericite vein, filled predominantly with mineral
885 assemblage of quartz, pyrite, sericite, chlorite and lesser sphalerite. (F) The silicate, sulfide and
886 oxide assemblages in hydrothemral quartz vein sequences showing ore and gangue minerals
887 paragenesis and their associated alteration types. The mineral abbreviations below in the text, and
888 also in figures and tables are after Whitney and Evans (2010): Bn=bornite, Bt=biotite,
889 Ccp=chalcopyrite, Chl=chlorite, K-spar=K-feldspar, Mag=magnetite, Moly=molybdenite, Py=pyrite,
890 Qtz=quartz, Ser=sericite, Sph=sphalerite. The black full lines indicate high abundance and the black
891 dash lines represent the minor amounts in the paragenetic sequence box.

892
893 Fig. 4 Scanning thin-section images (A and B), quantitative evaluation of minerals by scanning
894 electron microscopy (QEMSCAN) image (C), and photomicrographs (D, E, F) of quartz-molybdenite
895 veins at Wenquan.

896

897 Fig. 5 Photomicrographs of fluid inclusions in the Wenquan porphyry Mo deposit.

898

899 Fig. 6 Plot of calculated δD versus δO for K-feldspar, sericite in this study and quartz from
900 literatures at Wenquan (based map modified after Sheppard et al., 1971), with data of typical
901 porphyry deposits for comparison. Sources of data: magmatic water (Taylor, 1992; Giggenbach,
902 1992), silicate minerals of different stages including muscovite, alunite, pyrophyllite, kaolinite and
903 dickite at El Salvador (Watanabe and Hedenquist, 2001) and alunite, pyrophyllite, muscovite and
904 dickite at OyuTolgoi (Khashgerel et al., 2008), and evolving alteration stages including propylitic,
905 potassic, phyllic and argillic alteration at Bingham (Bowman et al., 1987). Samples of dashed line
906 symbol indicate that their hydrogen or oxygen isotopic composition were not measured, but
907 assessed from those of associated minerals.

908

909 Fig. 7 (A) Sulfur isotopic compositions ($\delta^{34}S\%$) of sulfides separated from different
910 silicate+sulfide+oxide assemblages in the Wenquan porphyry Mo deposit. Data from sulfides and
911 sulfates from the Butte deposit (Field et al., 2005) are plotted for comparison. (B) Histograms of
912 $\delta^{34}S$ values at Wenquan, with data from typical porphyry deposits worldwide for comparison.

913

914 Fig. 8 Plot of measured $\delta^{56}Fe$ versus $\delta^{57}Fe$ values of pyrite separates, whole rocks, and
915 geostandards showing that the Fe isotope data analysed in this study plot on a single
916 mass-fractionation line. Error bars are two standard errors from the internal run statistics

917

918 Fig. 9 Iron isotopic compositions ($\delta^{56}Fe\%$) for pyrite separates and bulk samples from the
919 Wenquan Mo deposit.

920

921 Fig. 10 Schematic model for formation of the Wenquan porphyry Mo deposit, illustrating the
922 inferred fluid evolution paths from the deep lithostatic to the shallow hydrostatic environment
923 (Modified after Seedorff et al., 2008; Pudack et al., 2009; John et al., 2010).

924

925 **Headings for tables**

926 Table 1 $\delta^{18}O$ and δD compositions of K-feldspar and sericite separates at Wenquan.

927

928 Table 2 Sulfur isotopic compositions ($\delta^{34}S\%$) of sulfides at Wenquan.

929

930 Table 3 Fe isotopic composition of ore-hosting whole-rock and pyrite separates at Wenquan.

931

Fig.1

Fig.2

Fig.3

F	Alteration	Biotite alteration	Potassic alteration	Propylitic alteration	Phyllic alteration
Hydrothermal veins		Dark quartz veinlet	Quartz-chalcopyrite-pyrite-molybdenite vein		Quartz-pyrite-sericite vein
		Quartz-chalcopyrite-pyrite vein	Quartz-molybdenite vein		
Quartz					
Bornite					
K-feldspar					
Biotite					
Magnetite					
Pyrite					
Chalcopyrite					
Molybdenite					
Sericite					
Chlorite					
Sphalerite					

Fig.4

Fig.5

Fig.6

Fig.7

Fig.8

Fig.9

Fig.10

Table 1 Hydrogen and oxygen isotopic compositions of K-feldspar and sericite separates at Wenquan.

Sample description	Mineral	$\delta^{18}\text{O}_{\text{mineral}}(\text{‰})$	$\delta\text{D}(\text{‰})_{\text{SMOW}}$	T (°C)	$\delta^{18}\text{O}_{\text{fluid}}(\text{‰})$	$\delta\text{D}_{\text{fluid}}(\text{‰})$
Potassic halo along Qtz-Ccp-Py vein	K-feldspar	2.8		550	1.9	-45
Qtz-Py-Ser vein	Sericite		-99	300	-3.4	-51
Qtz-Py-Ser vein	Sericite	3.6	-98	300	0.3	-50
Qtz-Py-Ser vein	Sericite		-105	300	-3.4	-57
Potassic halo along Qtz-Moly-Ccp vein	K-feldspar	0.6		425	-1.9	-45
Qtz-Py-Ser vein	Sericite	-1.4	-103	300	-4.8	-54
Potassic halo along Qtz-Moly-Ccp vein	K-feldspar	1.4		425	-1.2	-45

Table 2 Sulphur isotopic compositions ($\delta^{34}\text{S}\%$) of sulfides at Wenquan.

Sample No.	Silicate+sulfide+oxide assemblage	Mineral	$\delta^{34}\text{S}(\text{‰})$
WQ13S12	Qtz+K-spar+Bt+Mag+Ccp $\pm$ Py	Py	1.1
WQ13S11	Qtz+K-spar+Bt+Mag+Ccp $\pm$ Py $\pm$ Moly $\pm$ Bn	Py	2.3
WQ13S13	Qtz+K-spar+Bt+Mag+Ccp $\pm$ Py $\pm$ Moly $\pm$ Bn	Py	3.1
WQ13S14	Qtz+K-spar+Bt+Mag+Ccp $\pm$ Py $\pm$ Moly $\pm$ Bn	Moly	5.7
WQ13S15	Qtz+K-spar+Bt+Mag+Ccp $\pm$ Py $\pm$ Moly $\pm$ Bn	Moly	5.0
WQ13S21	Qtz+Moly $\pm$ Py $\pm$ Ccp	Py	3.5
WQ13S22	Qtz+Moly $\pm$ Py $\pm$ Ccp	Py	1.6
W-68-1*	Disseminated ore	Moly	5.8
W-24*	Qtz+Moly $\pm$ Py $\pm$ Ccp	Moly	5.6
M-1*	Qtz+Moly $\pm$ Py $\pm$ Ccp	Moly	5.5
W9-1*	Qtz+Moly $\pm$ Py $\pm$ Ccp	Moly	5.7
W18-1*	Qtz+Moly $\pm$ Py $\pm$ Ccp	Moly	5.6
W20-2*	Qtz+Moly $\pm$ Py $\pm$ Ccp	Moly	5.5
W-21*	Qtz+Moly $\pm$ Py $\pm$ Ccp	Moly	5.6
W22-1*	Qtz+Moly $\pm$ Py $\pm$ Ccp	Moly	6.4
W-46-1*	Qtz+Moly $\pm$ Py $\pm$ Ccp	Moly	6.6
W-33-1*	Qtz+Moly $\pm$ Py $\pm$ Ccp	Moly	6.3
W-PD3-1*	Qtz+Moly $\pm$ Py $\pm$ Ccp	Moly	5.1
W-PD7-2*	Qtz+Moly $\pm$ Py $\pm$ Ccp	Moly	4.7
WQ13S31	Qtz+Moly $\pm$ Py $\pm$ Ccp	Moly	5.8
WQ13S32	Qtz+Moly $\pm$ Py $\pm$ Ccp	Moly	5.8
YDZ-2*	Qtz+Moly $\pm$ Py $\pm$ Ccp	Moly	6.3
YX-3*	Qtz+Py+Ser+Chl $\pm$ Sph	Py	5.6
YX-6*	Qtz+Py+Ser+Chl $\pm$ Sph	Py	5.5
W24-1*	Qtz+Py+Ser+Chl $\pm$ Sph	Py	5.0
W20-1*	Qtz+Py+Ser+Chl $\pm$ Sph	Py	5.6

Note: * samples from He (2012), Han (2009) and Zhu et al. (2011).

Table 3 Fe isotopic compositions of host bulk rocks and pyrite separates at Wenquan.

Sample No.	Sample description	Sample analysed	$\delta^{56}\text{Fe}^*$	2se	$\delta^{57}\text{Fe}^*$	2se
B02	Biotite-altered porphyry	Whole rock	0.17	0.03	0.30	0.05
B01	Qtz-Ccp-Py vein	Pyrite separate	0.15	0.03	0.21	0.05
C03	Potassic-altered porphyry	Whole rock	0.19	0.03	0.32	0.05
C01	Qtz-Ccp-Py-Moly vein	Pyrite separate	0.17	0.03	0.25	0.05
C02	Qtz-Ccp-Py-Moly vein	Pyrite separate	0.17	0.03	0.27	0.05
D02	Potassic-altered porphyry	Whole rock	0.21	0.03	0.37	0.05
D01	Qtz-Moly vein	Pyrite separate	0.21	0.03	0.31	0.05
E03	Sericitic alteration overprinting early potassic-altered porphyry	Whole rock	0.08	0.03	0.17	0.05
E02	Sericitic-altered porphyry	Whole rock	0.26	0.03	0.42	0.05
E01	Qtz-Py-Ser vein	Pyrite separate	0.32	0.03	0.55	0.05
GSP-2	Granodiorite	Geostandard	0.15	0.03	0.21	0.05
BCR-2	Basalt	Geostandard	0.09	0.03	0.17	0.05