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**Mineralogical, Fluid Inclusion and Multiple Isotope (H-O-S-Pb) Constraints  
on the Genesis of the Sandaowanzi Epithermal Au-Ag-Te Deposit, NE China**

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## Abstract

The Sandaowanzi gold deposit in the Great Hinggan Range Metallogenic Belt, NE China, is unusual for the fact that the mineralization takes the form of Au- and Ag-bearing tellurides. This mineralization, which constitutes a resource of 28 t Au, is hosted in NW-trending, syntaxial, layered quartz veins and tension gashes within almost synchronous trachyandesites and andesitic breccias that overlie the Sandaowanzi monzogranite. Alteration halos are developed around the quartz veins and tension gashes. They consist of an inner silicic zone, two intermediate zones containing quartz-illite and quartz-adularia, and an outer zone containing a quartz-calcite-kaolinite-chlorite assemblage.

Fluid inclusion microthermometric data reveal that the Sandaowanzi ores precipitated from moderate-temperature (210° to 280°C), low pressure (70 to 130 bars) and low to moderate salinity (mostly <6.0 wt.% NaCl equiv.) hydrothermal fluids. Temperature and pressure are interpreted to have decreased with the evolution of the system. The  $\delta^{34}\text{S}_{\text{H}_2\text{S}}$  (-2.2 to -0.2‰) values indicate that the sulfur is of magmatic origin and suggest that it was leached by the ore fluid from the host volcanic rocks. A magmatic origin is also interpreted for the metals, based on Pb isotope data (i.e., a  $^{206}\text{Pb}/^{204}\text{Pb}$  value of 18.2366 to 18.3146, a  $^{207}\text{Pb}/^{204}\text{Pb}$  value of 15.5404 to 15.5624 and a  $^{208}\text{Pb}/^{204}\text{Pb}$  value of 38.0901 to 38.2293). In contrast, the  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  (-13.6 to -7.6‰) and  $\delta\text{D}_{\text{H}_2\text{O}}$  (-127 to -96‰) values indicate that the hydrothermal fluids are dominantly meteoric. Physicochemical modeling shows that sulfidation of the host rocks (decrease of  $\alpha_{\text{HS}^-}$ ) and condensation of the  $\text{H}_2\text{Te}$  vapor (increase of  $\alpha_{\text{HTe}^-}$ ) were the dominant controls on the precipitation of the Au- and Ag-telluride ores. The generation of a  $\text{H}_2\text{Te}$  vapor is mostly derived from a magma degassing, and the close genetic relationship between the gold-telluride ore formation and the coeval alkaline magmatism is helpful to understand gold-telluride ore genesis in comparable conditions.

**Key words:** Gold-telluride deposit; Fluid inclusion; Isotope geochemistry; Sandaowanzi; NE China

## Introduction

In most epithermal gold deposits, telluride minerals are minor or absent; only a few deposits are dominated by telluride minerals, e.g., Cripple Creek (Kelley et al. 1998), Emperor (Pals and Spry 2003), Golden Sunlight (Spry et al. 1997), Acupan (Cooke and McPhail 2001), Săcărîmb (Ciobanu et al. 2008), Panormos Bay (Tombros et al. 2010), Kochbulak (Kovalenker et al. 1997), Porgera (Richards and Kerrich 1993) and Gies (Zhang and Spry 1994). Telluride-dominant epithermal

48 Au-Ag deposits are relatively rare in China, although several deposits, including Sandaowanzi  
49 (Tran et al. 2008), Guilaizhuang (Hu et al. 2006), and Dashuigou (Mao et al. 1995), fit this  
50 description. The Sandaowanzi deposit has a total reserve of  $\geq 28$  tonnes Au and an average grade of  
51 15 g/t. Mining began at Sandaowanzi in 2006, and  $\geq 20$  tonnes of gold have been recovered to date.  
52 The deposit has attracted broad attention for two reasons: (1) it is the first example of a gold deposit  
53 in NE China, in which  $>95\%$  of the gold is present as coarse-grained tellurides (Tran et al. 2008);  
54 and (2) it contains bonanza Au- and Ag-telluride ores, with grades of Au, Ag, and Te up to 35,000,  
55 25,000 and 30,000 g/t, respectively.

56 The Sandaowanzi deposit is located in the northeastern segment of the Great Hinggan Range  
57 Metallogenic Belt, northeastern China (Fig. 1a), which hosts Fe $\pm$ Sn skarns, Cu $\pm$ Mo porphyry and  
58 epithermal Au $\pm$ Ag deposits (Zhai et al. 2014, 2017a), all of which are related to a 140-110 Ma  
59 magmatic event (Mao et al. 2003, 2011; Wu et al. 2011; Zhai et al. 2017b, Fig. 1b). Although  
60 previous studies of the deposit, mostly published in Chinese, have addressed its geology (Wu ZY et  
61 al. 2005; Liu and Lu 2006; Tran et al. 2008; Lu et al. 2009a), mineralogy (Lu et al. 2009b; Han et al.  
62 2011; Xu et al. 2011, 2012; Zhai et al. 2013; Zhai and Liu 2014; Liu et al. 2017), geochronology  
63 and tectonic setting (Chen and Sun 2011; Liu et al. 2011; Zhai et al. 2015; Gao et al. 2017; Wang et  
64 al. 2017), geophysics (Kong et al. 2006), stable isotope geochemistry (S, H, O) (Lu et al. 2005; Liu  
65 et al. 2013) and fluid inclusions (Zhao et al. 2010; Yu et al. 2012; Chen et al. 2012), issues related  
66 to fluid source, physicochemical conditions, and precipitation mechanisms remain unresolved and  
67 greatly debated. For example, Lu et al. (2005) considered that meteoric water was the dominant  
68 component of the hydrothermal fluid, whereas Liu and Lu (2006) concluded that the fluid system  
69 was dominantly magmatic. Zhao et al. (2010) argued that the ore fluid was a mixture of magmatic  
70 and meteoric fluids. Most recently, Zhai et al. (2015) have proposed that a significant proportion of  
71 mantle-derived fluid was added to the ore fluid and contributed to formation of the gold ore.

72 In this contribution, previously published data are briefly summarized, and new results of  
73 mineralogical, stable (O, H, and S) and Pb isotope and fluid inclusion analyses are presented. This  
74 integrated fluid inclusion and isotope geochemical study is based on a suite of representative  
75 samples from the different mineralization stages, ore types and depths in the hydrothermal system.  
76 These new data, in combination with physicochemical modeling, provide new insights into the

77 origin of the ore fluids and metals, and the mechanisms of Au-Ag telluride deposition. They should,  
78 therefore, also help guide genetic interpretation of the genesis of other large epithermal Au-Ag-Te  
79 deposits in comparable geological settings elsewhere.

## 80 **Geological framework**

### 81 *Geology of the Great Hinggan Range*

82 The Great Hinggan Range (GHR) was the product of closure of the Mongol-Okhotsk Ocean (160  
83 Ma), which separated the North China Craton from the Siberian Craton (Fan et al. 2003; Wang et al.  
84 2006; Fig 1a). This coincided with subduction of the oceanic Pacific and Izanagi plates beneath the  
85 continental Eurasian Plate (Wang et al. 2006; Wilde 2015); the GHR evolved through collision,  
86 which was followed by lithospheric thinning that was probably related to extensional detachment of  
87 core complexes (Pirajno 2013). These geotectonic processes resulted in formation of a Late Jurassic  
88 to Early Cretaceous, WNW-trending, intracontinental rift zone (Liu et al. 2011).

89 A distinctive feature of the GHR Metallogenic Belt was the development of a Permian  
90 metamorphic core complex (Niu et al. 2006), facilitated by intracontinental rifting, which was  
91 intruded by numerous A- and I-type granitoids during three discrete episodes of plutonism (Wu et al.  
92 2002). A Late Permian (~270 to 250 Ma) episode was characterized by the emplacement of early  
93 calc-alkaline, I-type plutons (diorites, tonalites and granodiorites and late A-type syenites). This  
94 was followed by Triassic to Jurassic (~220 to 150 Ma) intrusion of highly fractionated, I- and  
95 A-type granodiorites, monzogranites, syenogranites and granites, including the Sandaowanzi  
96 monzogranite. The latest episode was characterized by the emplacement of Cretaceous (~130 to 120  
97 Ma) I-type granodiorites, monzogranites, syenites and A-type granites (Wu FY et al. 2005).  
98 Compilations of available geochronological data for the igneous belt in NE China have  
99 demonstrated that the granitic rocks mainly formed in the Jurassic (~180 to 150 Ma) or Early  
100 Cretaceous (~130 to 120 Ma) (Wu FY et al. 2005). Widespread intrusion of Early Cretaceous  
101 granites coincided with regional delamination and lithospheric thinning (Wang et al. 2006; Zhang et  
102 al. 2008).

103 In the northeastern part of the GHR, the intrusions were contemporaneous with the formation of  
104 two major types of hydrothermal ore deposits, porphyry Cu±Mo deposits such as Duobaoshan and

105 Tongshan, and epithermal Au-Ag±Te deposits such as Sandaowanzi and Beidagou (Fig. 1b). There is  
106 no genetic relationship between the porphyry and epithermal deposits, as the porphyry systems  
107 formed much earlier (Paleozoic) than the epithermal deposits (Mesozoic), which have been  
108 interpreted to be related to oblique subduction and regional extension (Goldfarb et al. 2014).

#### 109 *Geology of the Sandaowanzi deposit*

110 Volcanic rocks are widespread in the Sandaowanzi ore district (Fig. 1c), where they overlie the  
111 Sandaowanzi pluton. They are divided into two units, a lower Longjiang Formation, and an upper  
112 Guanghua Formation (Lu et al. 2005; Wang et al. 2006, Fig. 1c). The Longjiang Formation, which  
113 covers 80% of the ore district, is composed of basaltic trachyandesites overlain by continental flood  
114 basalts (Lu et al. 2009a). The former includes varieties of basalt, trachyte and andesite, with  
115 intercalations of andesitic breccias, rhyolite and tuff (Fan et al. 2003; Lu et al. 2005). Compositions  
116 of the latter vary from alkaline in the north to subalkaline in the south (Liu et al. 2011). Based on  
117 results of U-Pb age determinations for zircon in the trachyandesite, the Longjiang Formation was  
118 emplaced between  $122 \pm 1$  and  $124 \pm 1$  Ma (Cheng et al. 2017; Gao et al. 2017). The Guanghua  
119 Formation, which occurs mainly in the northeastern part of the deposit (Fig. 1c), is composed of  
120 rhyolite, perlite, tuff breccias, and tuffs (Fan et al. 2003; Lu et al. 2005). Zircon U-Pb ages for the  
121 rhyolite range from  $125 \pm 2$  to  $122 \pm 1$  Ma (Liu et al. 2011; Gao et al. 2017). The Sandaowanzi  
122 pluton, which is located in the southeastern part of the ore district (Fig. 1c), is a monzogranite with  
123 a zircon U-Pb age of  $182 \pm 1$  Ma (Zhai et al. 2015). Numerous N-trending, mafic, syenitic, dioritic  
124 to granitic sills and dikes intrude the main granitoid body, the Longjiang volcanic rocks, and in rare  
125 cases also the mineralized veins (Fig. 2). These dikes have widths up to several meters, and ages of  
126 between  $118 \pm 1$  and  $115 \pm 1$  Ma (Liu et al. 2011; Zhao et al. 2013). A large volume of Quaternary  
127 gravels, which host placer gold orebodies, occur in river valleys to the west of the quartz vein  
128 orebodies (Fig. 2). These placers are interpreted to be weathering products of the Sandaowanzi  
129 veins (Zhai et al. 2013).

130 The distribution of the regional and local volcanic rocks is controlled mainly by  
131 NE-NNE-oriented fault-bounded basins (Liu et al. 2013), whereas the Sandaowanzi Au- and

132 telluride-bearing quartz veins represent the filling of NW-oriented faults (Lu et al. 2005). These  
133 faults typically strike of 120-300 m, and have a width of 1-10 m.

#### 134 *The Sandaowanzi vein system*

135 The Sandaowanzi quartz vein system and associated Au-Ag-Te ores are hosted mainly in  
136 trachyandesites and andesitic breccias, and to a lesser extent, in andesites and trachytes of the  
137 Longjiang Formation (Figs. 1c and 2). Seven major high-grade quartz veins and thirteen minor,  
138 subparallel, steeply dipping, quartz veins and extensive stockworks were identified during  
139 geochemical surveys (Liu and Lu 2006). These veins extend vertically for as much as 700 m, and  
140 their maximum widths vary from ~3 to ~15 m and average ~6 m (Figs. 2 and 3).

141 Three different mineralized zones referred to as I, II and III, with lengths of ~500, ~200 and  
142 400 m and widths of X, Y and Z m, respectively, have been discovered (Liu and Lu 2006). They  
143 contain 15 steeply dipping (55-75°) Au-Ag-Te orebodies, most of which consist of single (multiply  
144 filled, veins and veinlets) quartz veins (Fig. 3). Several of the orebodies, however, comprise  
145 low-grade disseminations hosted by intensely silicified andesitic breccias and trachyandesites (Fig.  
146 3). A few oxidized trachyandesite-hosted mineralized veins were observed in outcrops in which the  
147 trachyandesite was altered and brecciated (Fig. 4a and b).

148 This study focused mainly on the number I orebody (Fig. 3), because it is the only one currently  
149 being mined underground. This Au-bearing quartz vein varies in width from ~0.8 to ~14.3 m,  
150 extends up to 300 m down dip (58-77° NW), and strikes to the NNW (Fig. 3). The mineralization is  
151 in the form of micro-stockworks of almost pure coarse-grained telluride hosted by vein quartz.  
152 Macroscopically, the Au- and Ag-tellurides occur as massive veinlets or disseminated aggregates  
153 intergrown with chalcopyrite within colloform layers. Two ore shoots were distinguished. The first  
154 is located between the +270 and +210 m mining-levels, and has grades ranging from ~77 to 543 g/t  
155 Au (averaging ~215 g/t), whereas the second occurs between the +170 and +130 m mining-levels  
156 and has unusually high contents of Au (~31 to 35,000 g/t; average grade 791 g/t) and maximum Ag  
157 and Te grades of 25,000 and 30,000 g/t, respectively. These ore shoots were first identified at the  
158 +170 m mining-level but the highest grades are located at the +130 m mining-level where a veinlet  
159 ~50 cm wide consisting almost entirely of Au- and Ag-tellurides was identified. The high grade

160 ores, with Au grades up to 324 g/t (average of 17 g/t), occur almost exclusively between the + 300  
161 and + 90 m mining-levels (Lu et al. 2009b), and are commonly surrounded by the disseminated ores  
162 in the +320 to +50 m mining-levels. The disseminated ore has a variable Au grade (~0.4 to ~85 g/t  
163 with an average of ~9 g/t). From the +50 to +10 m mining-levels, low-grade disseminated ores  
164 (averaging ~1.1 g/t) are dominant. The disseminated ores contain chalcopyrite and minor sphalerite,  
165 pyrite, tetrahedrite and galena intergrown with Au- and Ag-tellurides.,

166 Crustification is common in the quartz veins, particularly in the veins comprising them that are  
167 wider than 5 cm. Four types of vein material (Type A to D; Fig. 4c-f) have been distinguished based  
168 on mineralogy, grain size and texture. The general sequence of vein crustification, from the margins  
169 of the vein to the center, is: (i) fine-grained milky quartz  $\pm$  illite, with colloform banding, comb,  
170 cockade and open space filling by clear quartz (>90 vol.%) and abundant angular fragments of  
171 altered and pyritic trachyandesite (Type A) (Fig. 4c-f); (ii) fine- to medium-grained grey  
172 quartz-illite with minor colloform and vug textures (>70 vol.%) and abundant poorly-sorted  
173 variably-sized fragments of milky quartz and rare altered trachyandesite (>10 vol.%) (Fig. 4e),  
174 containing substantial sulfide and minor telluride mineralization (Fig. 4c-e) (Type B); (iii)  
175 medium-grained clear quartz  $\pm$  fine-grained adularia, with crack-seal textures (>50 vol.%) and  
176 abundant aggregates, masses or isolated crystals of telluride (Type C) (Fig. 4c-e); and (iv)  
177 coarse-grained white quartz (<70 vol.%) and calcite (<30 vol.%)  $\pm$  chlorite or calcite veinlets  
178 containing native gold (Type D) (Fig. 4d, f). Isolated veinlets of Types B, C and D commonly  
179 accompany the major crustiform veins. The milky, grey and white quartz veins are locally cut by  
180 clear quartz vein, mostly reflecting multiple episodes of quartz vein formation (Fig. 4f).

### 181 *Hydrothermal alteration*

182 The major gold-bearing quartz veins are hosted by intensely pyritized and silicified andesitic  
183 breccias and trachyandesites. Locally the pyritized trachyandesites have been incorporated in the  
184 quartz veins as isolated fragments or breccias (Fig. 4f). In addition, the quartz veins are  
185 accompanied by well-developed alteration halos comprising an inner silicic zone, two intermediate  
186 zones containing quartz-illite-sericite and quartz-adularia, and an outer zone of  
187 quartz-calcite-kaolinite-chlorite, all of which are accompanied by abundant pyrite. These minerals

188 replaced orthoclase, albite, anorthite, biotite, muscovite, hornblende, and tremolite. The alteration is  
189 distributed asymmetrically around the veins and locally is discontinuous, but is generally thickest  
190 adjacent to the widest veins. Furthermore, the different alteration assemblages may be overlapped  
191 and thus superimposed, although commonly, the youngest alteration is characterized by illite and  
192 grey quartz. Silicic alteration is observed near milky quartz veins. Micro-stockworks of  
193 silica-veinlets filled with crypto- to micro-crystalline milky quartz and chalcedony cut the host  
194 andesitic breccias and trachyandesites. Based on the alteration mineral assemblage, the deposit is  
195 classified as an adularia-sericite type epithermal deposit (Heald et al. 1987).

### 196 **Sampling and analytical methods**

197 Approximately 80 samples were collected from the different mining levels (+170 to +50 m). The  
198 samples include crustified quartz veins of the Number I ore body from Type A to D vein material,  
199 pyrite samples from alteration zones, and whole-rock samples from the host trachyandesites,  
200 basaltic dikes, and the Sandaowanzi monzogranite. Polished and doubly-polished thin sections were  
201 examined with reflected and transmitted light microscopes. Primary ore textures were identified  
202 using a Hitachi Scanning Electron Microscope equipped with an Oxford IE350 energy-dispersive  
203 detector at the China University of Geosciences, Beijing (CUGB). Mineral compositions were  
204 determined with a JEOL 8230 Superprobe, equipped with wavelength- and energy-dispersive and  
205 back-scattered detectors at the Chinese Academy of Geological Sciences (CAGS), Beijing. The  
206 operating conditions were a 15 kV acceleration voltage, a 20 nA beam current and a 20 s counting  
207 time for all elements. Natural and synthetic mineral standards of chalcopyrite, pyrite, sphalerite,  
208 galena, CoNiAs, SnO<sub>2</sub>, MnTi and native Ag, Sb, Au, Se, Te, and Cd were used for calibration. ZAF  
209 corrections were made with proprietary JEOL software. The analytical results (sulfides, sulfosalts  
210 and tellurides) are presented in Table 1.

211 Prior to microthermometric analyses, the internal zoning of quartz was examined using a  
212 cathodoluminescence (CL) spectrometer (Garton Mono CL3+) attached to a Quanta 200F ESEM at  
213 Peking University. The operating conditions were a 15 kV acceleration voltage and a 120 nA beam  
214 current, coupled to a 45-s scanning time. Microthermometric measurements of fluid inclusions were  
215 performed on a LINKAM MDSG600 heating-freezing stage mounted on a ZEISS microscope in the



216 School of Earth Sciences and Resources, CUGB. Most analyzed quartz crystals were directly in  
217 contact with sulfides, tellurides and native gold. The temperature range for the stage varied from  
218 -196 to +600 °C. The LINKAM stage was calibrated at -56.6 °C, +0.0 °C, and +374.1 °C with  
219 synthetic fluid inclusions. Measurements were accurate to within  $\pm 0.1$  °C below zero Celsius,  
220 whereas at higher temperature the error ranged up to  $\pm 1$  °C. Freezing-heating rates were between  
221 0.2 and 5 °C/min. When approaching a phase transition, however, the rate was dropped to  
222 0.1-0.5 °C/min. The microthermometric data were reduced using FLINCOR software (Brown 1989)  
223 and are summarized in Table 2.

224 Fluid inclusion laser Raman spectroscopic analysis was carried out in the Beijing Research  
225 Institute of Uranium Geology, Beijing, China, using a Renishaw RM-2000 Raman microscope. This  
226 instrument records peaks in the range of 100-4000  $\text{cm}^{-1}$  full-band with a resolution of 1-2  $\text{cm}^{-1}$ ; the  
227 laser beam spot size was about 1  $\mu\text{m}$ . The inclusions were analyzed for the common gases,  
228 monoatomic and polyatomic ions and molecules. Analyses of the gas composition of the bulk  
229 included fluid were carried out at CAGS using a crusher attached to a gas chromatograph following  
230 the method described by Salvi and Williams-Jones (1997). The composition of the liquid was  
231 analyzed using the crush-leach method and a Shimadzu HIC-SP Super ion chromatograph. These  
232 analyses were restricted to samples dominated by a single generation of fluid inclusions. Reference  
233 materials for gaseous analysis were synthetic fluid inclusions and liquids selected from the national  
234 standard materials study center. The results of the bulk analyses are presented in Table 3.

235 Stable isotope analyses were conducted on milky, grey, clear and white quartz vein material  
236 (Types A to D), sulfides (chalcopyrite and pyrite) and host trachyandesites and monzogranites. All  
237 minerals selected were handpicked and checked under a binocular microscope to ensure a purity  
238 of >98%. Isotopic compositions of oxygen and hydrogen (quartz) and sulfur (sulfides) were  
239 analyzed using a MAT-253 stable isotope ratio mass spectrometer (CAGS). Oxygen was extracted  
240 for analysis using the  $\text{BrF}_5$  technique (Clayton and Mayeda 1963) and hydrogen from  $\text{H}_2\text{O}$  released  
241 from fluid inclusions (Coleman et al. 1982). Sulfur was released as  $\text{SO}_2$  (Fritz et al. 1974). The  
242 isotopic ratios are reported in standard  $\delta$  notation (‰) relative to SMOW for oxygen and hydrogen,  
243 and CDT for sulfur. The analytical precision was better than  $\pm 0.2$  ‰ for  $\delta^{18}\text{O}$ ,  $\pm 2$  ‰ for  $\delta\text{D}$ , and  $\pm$

244 0.2 ‰ for  $\delta^{34}\text{S}$ . Results of the sulfur isotope analyses are given in Table 4, and of the D and O  
245 isotope analyses in Table 5.

246 Pyrite in altered trachyandesites, and whole-rock samples of the Sandaowanzi monzogranites  
247 and host trachyandesites were analyzed for their lead isotope composition. The analyses were  
248 carried out at CAGS using an England Nu Plasma, high-resolution, multi-collector  
249 inductively-coupled plasma mass spectrometer (MC-ICP-MS) and a standard from the National  
250 Bureau of Standards (NBS981). Long-term repeated measurements of the Pb isotopic ratios of  
251 standard NBS981 yielded  $^{206}\text{Pb}/^{204}\text{Pb} = 16.9397 \pm 0.0111$ ,  $^{207}\text{Pb}/^{204}\text{Pb} = 15.4974 \pm 0.0089$ , and  
252  $^{208}\text{Pb}/^{204}\text{Pb} = 36.7147 \pm 0.0262$  (all errors are reported at  $\pm 2\sigma$ ). The lead isotope data are given in  
253 Table 6.

## 254 **Results**

### 255 *Mineralogy*

256 More than 35 sulfide, sulfosalt, telluride and gangue minerals have been identified at  
257 Sandaowanzi. The ore and alteration minerals have been classified into four paragenetic stages  
258 based on their textural relationships, the nature of the quartz and partly the accompanying alteration  
259 minerals (Zhai and Liu 2014). Stage I mainly contains milky quartz, Stage II is composed of grey  
260 quartz and illite, Stage III comprises clear quartz with an alteration assemblage of quartz and  
261 adularia, and Stage IV consists of white quartz, calcite and kaolinite with chlorite. These stages  
262 correspond to the Type A to Type D vein materials referred to earlier.

263 Stage I is dominated by intergrowths of milky quartz, pyrite and rare pyrrhotite (reported by Wu  
264 ZY et al. 2005; Liu and Lu 2006). In the milky quartz veins, pyrite is typically euhedral, and was  
265 replaced or cemented by other sulfides (mainly chalcopyrite) and/or tellurides in Stages II and III.  
266 Stage II is dominated by massive aggregates of sulfides, sulfosalts, minor tellurides and native gold,  
267 and is developed mainly in the disseminated ores. Chalcopyrite is very common and aggregates of  
268 sphalerite and galena are also observed. Sulfides (i.e., chalcopyrite) and sulfosalts (i.e., tennantite)  
269 commonly coexist with minor tellurides, i.e., petzite ( $\text{Ag}_3\text{AuTe}_2$ ), calaverite ( $\text{AuTe}_2$ ), altaite ( $\text{PbTe}$ )  
270 and hessite ( $\text{Ag}_2\text{Te}$ ) in this stage (Fig. 5a).

271 Stage III is dominated by abundant tellurides ( $\geq 95$  vol.%), which replaced Stage II sulfides  
272 and/or tellurides (Figs. 4c-f and 5b-i). Subhedral altaite is commonly associated with petzite, hessite,  
273 sylvanite  $[(\text{Au},\text{Ag})_2\text{Te}_4]$  and krennerite  $[(\text{Au},\text{Ag})\text{Te}_2]$  (Fig. 5b, d, h). Assemblages of hessite-petzite,  
274 hessite-stützite ( $\text{Ag}_{5-x}\text{Te}_3$ ), and hessite-empressite ( $\text{AgTe}$ )-petzite (Fig. 5c-i) are very common.  
275 Gold-bearing telluride assemblages, containing krennerite, sylvanite, calaverite, and traces of native  
276 gold (Fig. 5e-h) are also present in this stage. Sulfides (i.e., chalcopyrite and sphalerite) and  
277 sulfosalts (i.e., tetrahedrite) ( $\leq 5$  vol.%) are present in minor amounts (Fig. 5c-f, h). Stage III ended  
278 with precipitation of Cu-Zn and Pb-Zn-Cu alloys (Zhai and Liu 2014), which occur as isolated  
279 grains in a clear quartz matrix. Finally, Stage IV is dominated by native gold, hematite and goethite.  
280 Native gold appears as isolated grains in quartz or as veinlets crosscutting Stage III petzite and  
281 hessite (Fig. 5d, e).

#### 282 *Fluid inclusions*

283 Fluid inclusions are common in quartz and were classified as primary, pseudo-secondary or  
284 secondary with the assistance of cathodoluminescence. Scanning electron microscope and  
285 cathodoluminescence images show that a high proportion of the quartz crystals experienced  
286 oscillatory zoning (Fig. 6a). The early quartz displaying oscillatory zoning was commonly  
287 overprinted by later quartz that also displays oscillatory zoning (Fig. 6b-d). In places, however, the  
288 later quartz filled fractures in the early quartz displaying oscillatory zoning and is relatively  
289 homogeneous (Fig. 6e, f). This study reports microthermometric data for ten samples covering  
290 mineralization Stages I to IV. Primary inclusions were identified mainly on the basis of their  
291 occurrence along growth zones (Fig. 7a, b) and only such inclusions with no signs of necking were  
292 used in the microthermometric study. Each cluster or set of inclusions along a growth zone was  
293 considered to represent a separate fluid inclusion assemblage (FIA), which was carefully  
294 documented and measured. The primary inclusions are typically 5-15  $\mu\text{m}$  in diameter and are either  
295 spherical, elliptical or irregular in shape (Fig. 7a-g). They are found in quartz from each of the four  
296 mineralization stages. Numerous secondary inclusions and a small population of pseudosecondary  
297 inclusions were also observed.

298 At room temperature, three types of fluid inclusions were recognized: (i) L-V inclusions, which  
299 consist of aqueous liquid + vapor with a dominant liquid phase ( $V/L+V = 10-20$  vol.%, Fig. 7a-d, g);  
300 (ii) V-L inclusions consisting of aqueous liquid + vapor with a dominant vapor phase ( $V/L+V =$   
301  $60-80$  vol.%); and (iii) L-V-S inclusions consisting of aqueous liquid + vapor + solid (Fig. 7e, f).  
302 The solids in inclusions almost invariably show inconsistent volume ratios with the other phases,  
303 indicating that they are accidentally trapped solids. Significantly, liquid-rich (L-V) and vapor-rich  
304 (V-L) inclusions are observed coexisting in single growth zones in quartz from each of the  
305 mineralization stages, providing petrographic evidence that the fluid boiled during each of these  
306 stages (Fig. 7c, d). No  $\text{CO}_2$ -rich fluid inclusions or inclusions that developed clathrates on cooling  
307 were observed.

308 Liquid-vapor homogenization temperatures were determined for 364 fluid inclusions, including  
309 60 FIAs for both homogenization and final ice melting temperatures (Fig. 9, Table 2). Fluid  
310 inclusion assemblages of L-V and V-L types in stage I, II, III and IV veins have mean liquid-vapor  
311 homogenization temperatures of 330 °C, 280 °C, 240 °C and 200 °C, respectively (Fig. 8). The final  
312 ice melting temperature ( $T_m$ ) for the different FIAs ranged from -11.6 to -0.3 °C (Table 5),  
313 corresponding to a salinity range from 0.5 to 15.6 wt.% NaCl equiv. (salinity was estimated from  
314 the equations of Brown and Lamb 1989). Most of the FIAs from the different mineralized stages are  
315 characterized by a salinity lower than 6.0 wt.% NaCl equiv. (Fig. 9). The exceptions are those from  
316 Stage III, some of which report relatively high values (as high as 15.6 wt.% NaCl equiv.). Fluid  
317 inclusion assemblages of the four mineralized stages have a median salinity of 1.5, 2.2, 4.7 and 2.2  
318 wt.% NaCl equiv., respectively (Table 2; Fig. 8). In summary, the homogenization temperature  
319 decreased from an excess of 300 °C during Stage 1 to less than 200 °C during Stage IV (Fig. 9). The  
320 salinity, in contrast, increased from values during Stage I that were  $< 4$  wt% NaCl equiv. to values  
321 during Stage III that locally reached nearly 16 wt% NaCl equiv. and then decreased to values during  
322 Stage IV that were similar to or slightly less than those of Stage 1 (Fig. 9).

323 Gas chromatographic analyses of the bulk inclusion fluid indicate that  $\text{CO}_2$  was the principal  
324 incondensable gas and was accompanied by trace proportions of  $\text{CH}_4$  (Table 3). Ion  
325 chromatographic analyses indicate that  $\text{Ca}^{2+}$  was the dominant cation except in Stage IV for which  
326  $\text{K}^+$  was the dominant cation. Significantly  $\text{K}^+$  was the next most cation for all other stages and for

327 all stages Na<sup>+</sup> only ranked third (Table 3). Sulfate was the dominant anion followed by Cl<sup>-</sup> and F<sup>-</sup>.  
328 The dominant cation is Ca<sup>+2</sup> and the dominant anion is SO<sub>4</sub><sup>-2</sup> (Table 3).

### 329 *Stable isotopes*

#### 330 Sulfur isotopic compositions

331 Sulfur isotope analyses were conducted on pyrite samples from alteration zones and quartz veins,  
332 and chalcopyrite samples from quartz veins (Table 4). The measured  $\delta^{34}\text{S}_{\text{CDT}}$  values of pyrite from  
333 the altered rocks and Stage II mineralization range from -0.5 to +0.9 and -0.9 to +0.6 ‰,  
334 respectively, whereas those of chalcopyrite from Stages II and III are -1.8 and -2.2 ‰, respectively  
335 (Table 4). Temperatures ranging from 267° to 318 °C (average of  $292 \pm 5^\circ\text{C}$ ) for Stage II were  
336 calculated for coexisting pyrite and chalcopyrite in the veins using the equations of Ohmoto and  
337 Lasaga (1982). The calculated values of  $\delta^{34}\text{S}_{\text{H}_2\text{S}}$  for the mineralizing fluid in equilibrium with these  
338 minerals range from -2.2 to -0.2 ‰ assuming the temperatures for each stage predicted by the fluid  
339 inclusion homogenization temperatures (Table 4).

#### 340 Hydrogen and oxygen isotopic compositions

341 The  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values for the Stage I, II, III and IV quartz veins are -2.5 ‰ and -123 ‰, -1.9 to  
342 -0.3 ‰ and -116 to -98 ‰, -3.9 to -0.3 ‰ and -123 to -96 ‰, -3.5 to -2.6 ‰ and -127 to -109 ‰,  
343 respectively (Table 5). Based on their average homogenization temperatures, the calculated  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$   
344 values of the mineralizing fluids are -10.6 ‰ (Stage I), -10.1 to -8.3 ‰ (Stage II), -12.9 to -9.8 ‰  
345 (Stage III) and -13.6 to -7.6 ‰ (Stage IV) (Table 5); the  $\delta\text{D}$  values are -123 ‰ (Stage I), -116 to  
346 -98 ‰ (Stage II), -123 to -96 ‰ (Stage III) and -127 to -109 ‰ (Stage IV) (Table 5). The  
347 whole-rock  $\delta^{18}\text{O}$  isotopic values of the host trachyandesite and the Sandaowanzi monzogranite  
348 range from -4.4 to -1.4 ‰ and +1.5 to +3.1 ‰, respectively (Table 5).

#### 349 Lead isotopes

350 Lead isotope data were obtained for pyrite in trachyandesites and whole-rock samples of  
351 Sandaowanzi monzogranite and host trachyandesite (Table 6). The  $^{206}\text{Pb}/^{204}\text{Pb}$  (18.2093 to 18.8377  
352  $\pm 0.0008$ ),  $^{207}\text{Pb}/^{204}\text{Pb}$  (15.5409 to 15.6255  $\pm 0.0008$ ),  $^{208}\text{Pb}/^{204}\text{Pb}$  (38.0901 to 38.6944  $\pm 0.0020$ ),  
353  $^{208}\text{Pb}/^{206}\text{Pb}$  (2.0541 to 2.0994  $\pm 0.0001$ ) and  $^{207}\text{Pb}/^{206}\text{Pb}$  (0.8274 to 0.8577  $\pm 0.0001$ ) ratios reveal  
354 homogenous compositions. On the  $^{206}\text{Pb}/^{204}\text{Pb}$  versus  $^{207}\text{Pb}/^{204}\text{Pb}$  uraniumogenic and  $^{206}\text{Pb}/^{204}\text{Pb}$  versus

355  $^{208}\text{Pb}/^{204}\text{Pb}$  thorogenic plots, most pyrite and monzogranite samples plot on the global mantle  
356 growth curve (Fig. 11a, b; Zartman and Doe 1981). Two trachyandesite samples appear just above  
357 the global orogen growth plumbotectonic curve (Zartman and Doe 1981); one monzogranite sample  
358 plots between the mantle and orogen curves (Fig. 11a, b).

## 359 Discussion

### 360 *Temperature-pressure conditions*

361 The homogenization temperatures of fluid inclusions trapped in the different stage quartz veins  
362 demonstrate that milky quartz (Stage I) mainly formed at temperatures between 280° and 350°C  
363 (average 330°C), grey quartz (Stage II) from 240° to 320°C (average 280°C), clear quartz (Stage III)  
364 at 210° to 280°C (average 240°C), and white quartz (Stage IV) (post-telluride stage) from 150° to  
365 220°C (average 200°C) (Fig. 8). An independent estimate of temperature is provided by the sulfur  
366 isotope data for pyrite and chalcopyrite in Stage II veins. These data indicate a temperature of 292  
367 °C which is only marginally higher than the average homogenization temperature for fluid  
368 inclusions in these veins. This suggests that any pressure correction for the latter data would be  
369 relatively minor. The temperatures (from 200° to 330°C) reported above are slightly higher than  
370 those for most epithermal gold and silver deposits (they are mostly from 150° to 300°C, Simmons et  
371 al. 2005 and references therein), although similar temperatures have been reported for some  
372 epithermal precious and base metal deposits (Bodnar et al. 2014).

373 As shown earlier, L-V inclusions coexisted with V-L inclusions in growth zones of quartz  
374 representing each of the mineralization stages, indicating that the fluid boiled throughout the  
375 mineralizing event. In order to constrain the pressure of ore deposition during different mineralizing  
376 stages, we calculated this pressure using the 'HOKIE FLINCS\_H2O-NACL' spreadsheet of  
377 Steele-MacInnis et al. (2012) for a boiling fluid system. The results of these calculations show that  
378 pressure was highest during formation of Stage I veins, ranging from 150 to 200 bars. Assuming  
379 hydrostatic conditions (suggested by the nature of the veins) these pressures are equivalent to  
380 paleodepths of 1.5 to 2.0 km. These pressures and the corresponding depths are slightly higher and  
381 deeper, respectively, than those for most epithermal deposits (typically <150 bars and <1.5 km,  
382 Simmons et al. 2005). In contrast, the pressures for Stages II and III range from 80 to 160 bars and

383 from 70 to 130 bars, respectively. These results predict that the depths were 0.8 to 1.6 km and 0.7 to  
384 1.3 km for Stage II and III veins, respectively. The late stage gold-quartz-calcite veins formed  
385 temperatures between 150° and 220°C and pressures corresponding to predicted depths of 0.2 to 0.8  
386 km assuming hydrostatic conditions. As the paleodepth would have been constant for all  
387 mineralizing stages, it seems likely that the pressure was somewhat greater than hydrostatic during  
388 the early stages and approached hydrostatic during Stage IV, suggesting that the vein system was  
389 probably emplaced at a depth significantly less than 1 km.

390 In summary, based on fluid inclusion microthermometry, gold-telluride mineralization at  
391 Sandaowanzi was deposited at a temperature range of 280° to 210°C under near hydrostatic  
392 conditions at a depth of < 1 km; the native gold was deposited later at a temperature of 220° to  
393 150°C.

394

### 395 ***Fluid Composition and Evolution***

396 The fluid salinity (mostly <6 wt.% NaCl equiv.) is in the upper part of the range for  
397 low-sulfidation epithermal gold deposits (commonly <5 wt.% NaCl equiv., Simmons et al. 2005;  
398 Bodnar et al. 2014). However, this salinity is consistent with that of telluride-rich low-sulfidation  
399 epithermal deposits, which typically have slightly higher salinity (commonly 5-10% NaCl equiv.,  
400 Ahmad et al. 1987; Saunders 1991; Zhang and Spry 1994; Tombros et al. 2008). The elevated  
401 salinity was mostly due mainly to intense boiling of the fluid, which concentrated the dissolved  
402 salts. Indeed, the observed increase in the average salinity from Stages I to III (average in 1.5, 2.2,  
403 4.7 wt.% NaCl equiv., respectively) is consistent with this hypothesis (also see Fig. 9). The return to  
404 low salinity during Stage IV (Fig. 9), which represents the waning coolest stage of the system,  
405 could reflect an incursion of meteoric water, although evidence for this is not apparent in our data .

### 406 ***Source of metallic and hydrothermal components of the ore fluids***

407 The calculated  $\delta^{34}\text{S}_{\text{H}_2\text{S}}$  values of the hydrothermal fluids range from -4.8 to +2.7 ‰ with most of  
408 the data being between -2.5 and +0.5 ‰ (Fig. 10). These  $\delta^{34}\text{S}_{\text{H}_2\text{S}}$  values indicate a magmatic source  
409 for the sulfur and are interpreted to mostly reflect leaching of sulfur from the host volcanic rocks.  
410 The  $^{206}\text{Pb}/^{204}\text{Pb}$  vs.  $^{207}\text{Pb}/^{204}\text{Pb}$  uranogenic and  $^{206}\text{Pb}/^{204}\text{Pb}$  vs.  $^{208}\text{Pb}/^{204}\text{Pb}$  thorogenic data (Fig. 11)

411 reveal that the lead was of mantle or magmatic origin, and it is therefore likely that it also was  
412 inherited from the host volcanic rocks during fluid-rock interaction. These rocks have a mantle  
413 origin and probably formed as a result of regional asthenospheric upwelling in NE China (Fan et al.  
414 2003; Wang et al. 2006).

415 The  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  values (-13.6 to -7.6‰) and  $\delta\text{D}_{\text{H}_2\text{O}}$  values of the ore fluid calculated to have been in  
416 equilibrium with vein quartz are consistent with a dominantly meteoric fluid that underwent modest  
417 interaction with the host rocks (Fig. 12). This interpretation is supported by analyses of the  
418 composition of the fluid, which show that the dominant cation is  $\text{Ca}^{2+}$  rather than  $\text{Na}^+$  and that the  
419 dominant anion is a sulfur species rather than  $\text{Cl}^-$  (Table 3). It also agrees with the findings for other  
420 low sulfidation epithermal deposits including those are dominated by telluride minerals (Shelton et  
421 al. 1990; Zhang and Spry 1994).

422

#### 423 ***Genetic association between alkaline magmatism and Au-Te mineralization***

424 It is significant that the Sandaowanzi gold-telluride veins are hosted by alkaline igneous rocks, as  
425 this metallogenic association has attracted much attention due to a possible connection between the  
426 magmatism and the mineralization (Jensen and Barton 2000; Sillitoe 2002). Indeed, numerous  
427 studies of gold-telluride deposits have suggested that tellurium and gold in these deposits mostly  
428 originated from the spatially and temporally associated alkaline magmas (e.g., Golden Sunlight,  
429 Montana, Porter and Ripley 1985; Cripple Creek, Colorado, Thompson et al. 1985; Emperor, Fiji,  
430 Ahmad et al. 1987; Porgera, Papua New Guinea, Richards 1990; Judith Mountains, Montana, Zhang  
431 and Spry 1994). The economic importance of gold-telluride mineralization results from the fact that  
432 some of these deposits are giants in terms of ore reserves (Ciobanu et al. 2006). A possible  
433 explanation for this association is that it may reflect enrichment of tellurium in the lithospheric  
434 mantle, possibly by sediment recycling (Jensen and Barton 2000). According to this explanation, the  
435 tellurium is transported into the crust by the rift-related alkaline magmas that also originate in this  
436 environment. Cooke and McPhail (2001) suggested that the generation of magmatic gases may also  
437 be critical due to the likely transport of Te in the gas phase. It may therefore also be significant that  
438 the available geochronological data show that the gold-telluride veins and their host alkaline



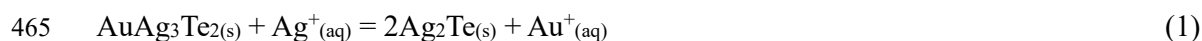
439 volcanic rocks at Sandaowanzi formed synchronously at ~120 Ma (Liu et al. 2011; Zhai et al. 2015;  
440 Wang et al. 2017).

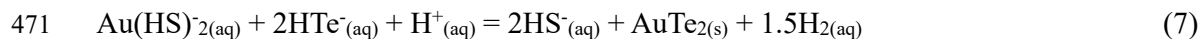
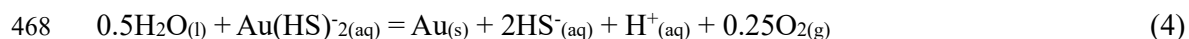
#### 441 *Physicochemical conditions of alteration and ore mineral formation*

442 The physicochemical conditions of alteration and ore mineral deposition, other than temperature  
443 and pressure, were interpreted from phase stability relationships using SUPCRT92 (Johnson et al.  
444 1992) and the recently published extended database (Zimmer et al. 2016). The thermodynamic  
445 properties of the tellurides were compiled from McPhail (1995) and Tombros et al. (2010); all  
446 solids were considered to be ideal solutions.

447 Values of pH were calculated from the bulk composition of the fluid inclusions (Table 3), and  
448 from mineral equilibria in the system. Based on the presence of minor illite and the absence of  
449 K-feldspar in Stage I, the pH values for this stage are estimated to have ranged from 3.0 to 3.2 (Fig.  
450 15a). Similarly, the alteration mineral assemblages of quartz-illite-sericite, quartz-adularia, and  
451 quartz-calcite-kaolinite-chlorite in Stages II, III and IV are interpreted to reflect pH values that  
452 ranged from 4.0 to 4.3 (Fig. 15b), 4.5 to 5.1 (Fig. 15c) and 5.9 to 6.0 (Fig. 15d), respectively. The  
453 presence of pyrite, chalcopyrite and minor tellurides (calaverite and altaite) and absence of  
454 pyrrhotite in Stage II (280°C) suggest  $\log fS_2$  values of -12.1 to -9.2 (Fig. 16a). As the temperature  
455 dropped towards 240°C (Stage III), the coexistence of pyrite and chalcopyrite and abundant  
456 telluride formation required  $\log fS_2$  values between -14.1 and -10.6 (Fig. 16b, Table 7). The presence  
457 of hessite and altaite in Stage III at 240 °C indicates that the  $\log fTe_2$  values ranged from -11.6 to  
458 -8.1 (Fig. 16b). The maximum and minimum  $\log fTe_2$  values for Stage II are based on the presence  
459 of calaverite ( $\log fTe_2 \geq -8.5$ ) and altaite, the absence of native tellurium ( $\log fTe_2 \leq -7.0$ ) and  
460 presence of native gold. Likewise,  $\log fTe_2$  values for Stage III are constrained by the widespread  
461 occurrence of calaverite-native Au ( $\log fTe_2 \approx -9.8$ ) and altaite, and the absence of native tellurium  
462 ( $\log fTe_2 \leq -8.1$ ) (Fig. 16a, b).

463 To constrain the various physicochemical parameters and evaluate possible ore deposition  
464 mechanisms (the next discussion section), the following reactions were considered:





472 From the petzite-hessite and calaverite-petzite equilibria in Stage III, the  $\log\alpha\text{Au}^+_{(aq)}/\alpha\text{Ag}^+_{(aq)}$   
 473 values in solution range were estimated to have been from -6.8 to -5.9 (Reactions 1 and 2). Using  
 474 the bulk composition data for the gas phase in fluid inclusions (Table 3), equilibria involving the  
 475 gas phases and the mineral equilibria, the  $\Delta\log f\text{O}_2$  (HM) values were constrained to have been from  
 476 -2.6 to -2.2 (Stage I), -2.1 to -1.0 (Stage II), -0.6 to -0.4 (Stage III) and +1.9 (Stage IV) (Table 7).  
 477 Utilizing the same data, approach and relevant reactions (3 and 4), the  $\log\alpha_{\text{H}_2\text{S}_{(aq)}}$ ,  $\log f_{\text{H}_2\text{S}_{(g)}}$ ,  
 478  $\log\alpha_{\text{H}_2\text{Te}_{(aq)}}$ ,  $\log f_{\text{H}_2\text{Te}_{(g)}}$ ,  $\log f_{\text{H}_2\text{S}_{(g)}/f\text{SO}_2_{(g)}}$  and  $\log\alpha\text{Au}(\text{HS})^-_{2(aq)}$  values were also estimated for Stages  
 479 I to IV (summarized in Table 7). Finally, based on the saturation in the fluid of pyrite, sphalerite,  
 480 chalcopyrite and galena,  $\log\alpha\text{Fe}^{++}_{(aq)}$ ,  $\log\alpha\text{Zn}^{++}_{(aq)}$  and  $\log\alpha\text{Cu}(\text{HS})^-_{2(aq)}$  values were also  
 481 constrained.

#### 482 *Mechanisms of ore deposition*

483 Deposition of calaverite and hessite from the ore fluids was likely controlled by Reactions 6 and  
 484 7 or possibly analogous reactions involving the species  $\text{Au}(\text{HS})^\circ$  and  $\text{Ag}(\text{HS})^\circ$ , given the estimates  
 485 of  $\log f\text{O}_2$  and pH. From these reactions, it is evident that deposition of these minerals depended  
 486 heavily of the values of  $a\text{HS}^-_{(aq)}$  and  $a\text{HTe}^-_{(aq)}$ , although changing pH, and in the case of Reaction 7  
 487  $a/\text{H}_2$  may also have played a role.

488 Given the importance of boiling in the system, it is attractive to propose that boiling was  
 489 responsible for ore formation, as has been proposed for many adularia-sericite or low sulfidation  
 490 epithermal systems (add references). As is evident from Figure 17, however, effective deposition of  
 491 calaverite and hessite requires a regime of decreasing  $a\text{HS}^-_{(aq)}$  and increasing  $a\text{HTe}^-_{(aq)}$  or at the very  
 492 least decreasing  $a\text{HS}^-_{(aq)}$  at constant  $a\text{HTe}^-_{(aq)}$  or increasing  $a\text{HTe}^-_{(aq)}$  at constant  $a\text{HS}^-_{(aq)}$ . Boiling,  
 493 however, decreases the activity of both  $\text{HS}^-$  and  $\text{HTe}^-$  in the liquid by preferentially fractionating  
 494 them into the vapor. Moreover, as shown by McPhail (1995) and Grundler et al. (2013)  $\text{H}_2\text{Te}$

495 partitions particularly strongly into the vapor (perhaps even more strongly than H<sub>2</sub>S). Thus, in the  
496 context of these parameters, boiling will not promote telluride deposition. Another effect of boiling  
497 is to sharply decrease temperature. As shown, in Figure 17, this effect of boiling, instead of  
498 promoting telluride deposition, will actually promote its dissolution. The other effects of boiling,  
499 increasing the pH of the fluid and lowering  $fH_2$ , also do not provide a satisfactory explanation for  
500 the observed deposition of hessite and calaverite, because, whereas decreasing pH promotes  
501 deposition of hessite, this is not true for calaverite and decreasing  $fH_2$  only promotes deposition of  
502 calaverite. Thus, in summary, it is very unlikely that the Sandaowanzi gold-telluride formed as a  
503 result of boiling, despite the extensive evidence for this phenomenon

504 The widespread pyritization of the host rock particularly in the immediate vicinity of the  
505 gold-telluride quartz veins suggest that sulfidation was temporally associated with ore formation.  
506 Sulfidation would have significantly decreased the activity of HS<sup>-</sup><sub>(aq)</sub> in the ore fluids, driving  
507 Reactions 6 and 7 to the right thereby promoting precipitation of hessite and calaverite (this is also  
508 illustrated in Figure 17). We therefore propose that sulfidation played a significant role in Au-Ag  
509 telluride deposition.

510 A more important control on Au-Ag telluride deposition is suggested by the behaviour of Te in  
511 hydrothermal fluids. Whereas tellurium solubility is extremely low in auriferous liquids, e.g., 0.005  
512 to 5 ppb at 300°C (McPhail 1995), it can reach ppm concentrations in vapors at the same  
513 temperature (Grundler et al. 2013). This provides compelling evidence that the tellurium was not  
514 transported with the gold. We therefore propose, as have Cooke and McPhail (2001), that tellurium  
515 was introduced into the dominantly meteoric auriferous fluid at the site of ore deposition by a  
516 magmatic vapor derived from the coeval trachyandesite magma, which condensed on contact with  
517 the ore fluid. This instantly increased  $aHTe^-_{(aq)}$ , driving Reactions 6 and 7 to the right, thereby  
518 causing massive gold- and silver-telluride precipitation. Evidence of the potential importance of this  
519 process, particularly for gold, is illustrated by Figure 17, in which it can be seen that less than a log  
520 unit increase in  $aHTe^-_{(aq)}$  will lead to deposition of 99% of the dissolved gold and a four log unit  
521 increase in  $aHTe^-_{(aq)}$  will lead to deposition of 99% the silver.

522 In summary, we propose that condensation of H<sub>2</sub>Te vapor into the ore fluid was the principal  
523 control of ore deposition and that sulfidation played a subordinate role by lowering the activity of

524 HS- thereby destabilizing the bisulphide species that were responsible for silver and gold transport.  
525 We further propose that condensation of the H<sub>2</sub>Te vapor and sulfidation were considerably more  
526 efficient in depositing gold (Fig. 17a) than silver (Fig. 17b), which may help explain why much  
527 more gold-bearing telluride than silver-bearing telluride formed in the deposit.

528 The end of Stage III was marked by deposition of Cu-Zn and Pb-Zn-Cu alloys, implying that  
529 neither tellurium nor sulfur was available to act as depositional ligands as almost all the HS<sup>-</sup><sub>(aq)</sub> and  
530 HTe<sup>-</sup><sub>(aq)</sub> had been consumed in earlier reactions. The model of telluride-dominant ore formation  
531 proposed above for the Sandaowanzi deposit, is also likely other large epithermal Au-Ag-Te  
532 deposits (e.g., Emperor, Fiji; Porgera, Papua New Guinea; Acupan, Philippines; Cripple Creek,  
533 Colorado).

534

535

### Conclusions

536 The low-sulfidation Sandaowanzi Au-Ag-Te deposit in NE China is unusual because the bulk of the  
537 gold is present as coarse-grained tellurides within bonanza Au ores (up to 35,000 g/t). Fluid  
538 inclusion microthermometric data show that the gold-silver telluride ores deposited from an  
539 epithermal system emplaced at a depth of < 1 km that boiled intensely and cooled from a  
540 temperature in excess of 300 °C to a temperature less than 200 °C at a pressure that approached  
541 hydrostatic. The δ<sup>18</sup>O<sub>H<sub>2</sub>O</sub> and δD<sub>H<sub>2</sub>O</sub> isotopic values and importance of Ca<sup>2+</sup> and sulfur species in the  
542 fluid are consistent with a meteoric water-dominant hydrothermal system that underwent significant  
543 interaction with its host rocks. In contrast, the δ<sup>34</sup>S<sub>H<sub>2</sub>S</sub> isotopic composition of the fluids and the  
544 lead isotope ratios of the sulfides are indicative of a magmatic source for the sulfur and metals,  
545 which is interpreted to indicate that sulfur and metals were leached from the host trachyandesites.  
546 Although fluid boiling is commonly invoked to explain the genesis of adularia-sericite (low  
547 sulfidation) epithermal deposits, this mechanism cannot explain the genesis of the Sandaowanzi  
548 Au-Ag-Te deposit. Instead, we show that the deposit owes its origin to a H<sub>2</sub>Te vapor, which was  
549 derived from the coeval alkaline magma and condensed in the dominantly meteoric ore fluid;  
550 sulfidation of the host rocks contributed to the deposition by destabilizing the gold and silver  
551 bisulfide species. This study emphasizes the importance of fluid-rock interaction and the mixing of  
552 low density magmatic fluids with meteoric waters in producing World class Au- and Ag-telluride

553 deposits.

554

555

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## 760 **Figure Captions**

761 Fig. 1. (a): Map showing the location of the Sandaowanzi deposit in relation to the tectonic framework in the  
762 Great Hinggan Range Metallogenic Belt, northeastern China, and the distribution of Mesozoic volcanic rocks  
763 in eastern China (based on Wu et al. 2005). Abbreviations: NCC–North China Craton, YC–Yangtze Craton,  
764 SECOB–South East China Orogenic Belt; (b): Generalized geological map of the Great Hinggan Range  
765 (modified after Qi et al. 2005), (c): Map showing general geology of the Sandaowanzi area (modified after  
766 Lu et al. 2005).

767 Fig. 2. Detailed geological map of the Sandaowanzi gold-telluride deposit (modified after Lu et al. 2005).

768 Fig. 3. Geological cross section of the Sandaowanzi veins and gold-telluride orebody (modified after Lu et al.  
769 2005).

770 Fig. 4. Photographs showing Sandaowanzi quartz veins: (a). Sandaowanzi ore-bearing quartz veins hosted in  
771 trachyandesite; (b). Mineralized quartz veins were oxidized in outcrops in which the trachyandesite was  
772 intensively altered and brecciated; (c). Banded milky, grey and clear quartz veins; milky quartz shows  
773 colloform banding (enlarged square in dashed lines); stage II sulfide-telluride and stage III telluride  
774 mineralization are associated with grey quartz and clear quartz veins, respectively; (d). Banded milky, grey,  
775 clear and white quartz veins; milky quartz shows comb and vuggy textures; stage II sulfide-telluride and  
776 stage III telluride and native gold mineralization (enlarged square in dashed lines) are associated with grey  
777 quartz and clear quartz veins, respectively; (e). Banded milky, grey (with sulfide and telluride mineralization)  
778 and clear quartz (with telluride mineralization) veins; milky quartz may occur as breccias in grey quartz  
779 (associated with sulfide and telluride mineralization); clear quartz contains telluride mineralization; (f).  
780 Complex relationships between different quartz veins showing milky quartz contains abundant angular  
781 fragments of altered trachyandesite, and pyrite grains, and is commonly replaced by grey quartz, whereas

782 milky, grey and white quartz veins are occasionally intruded by clear quartz veins, mostly reflecting multiple  
783 episodes of quartz precipitation. Scale bar on c-f is 1 cm.

784 Abbreviations: CQ–clear quartz, GQ–grey quartz, MQ–milky quartz, Au–native gold, Py–pyrite,  
785 S-Te–sulfide-telluride, Te–telluride, T–trachyandesites, WQ–white quartz.

786 Fig. 5. Photomicrographs of representative sulfide and telluride mineralization at Sandaowanzi. (a):  
787 Intergrowth of petzite-calaverite with galena and sphalerite in stage II grey quartz veins (BSE), (b): Altaite  
788 coexisting with petzite from clear quartz veins in stage III (BSE), (c): Hessite and petzite intergrowth with  
789 anilite in stage III clear quartz veins (BSE), (d): Intergrowth of altaite, petzite, hessite and chalcopryrite in  
790 stage III, and stage IV native gold with crack-filling textures (reflected light), (e):  
791 Sylvanite-krennerite-calaverite assemblage replacing petzite-hessite assemblage and is intergrown with or  
792 replaced by native gold and chalcopryrite, and these assemblages occur in stage III clear quartz (reflected  
793 light), (f): Stage III sylvanite intergrown with chalcopryrite and replacing stage II sphalerite, which is  
794 replaced by tennantite (reflected light), (g): Stage III petzite and calaverite, which are associated with an  
795 assemblage calaverite-gold at nano-scale (BSE), (h): Stage III sylvanite containing inclusions of altaite and  
796 stage II sphalerite, and all three minerals are replaced by stage III tetrahedrite (BSE), (i): Stage III  
797 petzite-hessite assemblage replaces stage II chalcopryrite and sphalerite (BSE).

798 Abbreviations: Alt-altaite, Ani-anilite, Au-native gold, Cav-calaverite, Cp-chalcopryrite, Gn-galena,  
799 Hes-hessite, Kre-krennerite, Ptz-petzite, Qtz-quartz, Sp-sphalerite, Syl-sylvanite, Td-tetrahedrite,  
800 Tn-tennantite.

801 Fig. 6. SEM-CL textures in Sandaowanzi hydrothermal quartz. (a) Obvious oscillatory euhedral growth  
802 zones observed in hydrothermal vein quartz; (b) Quartz with oscillatory euhedral growth zones replaced by  
803 late stage quartz with growth zones; (c)-(d) Hydrothermal vein quartz grains with oscillatory euhedral  
804 growth zones destroyed and surrounded by late stage quartz; (e)-(f) Quartz with euhedral growth zones cut  
805 by fractures and replaced by late relatively homogenous quartz.

806 Fig. 7. Photomicrographs of fluid inclusion assemblages in Sandaowanzi quartz veins. (a) and (b): Primary  
807 L-V type inclusions occur in growth zones, whereas the secondary inclusions are arranged in parallel trails  
808 that are aligned along fractures and terminate at crystal growth surfaces. Figure (b) is an enlargement of the  
809 black square in (a), (c): Fluid inclusion assemblages with variable vapor-liquid ratios, (d): Coexisting of  
810 primary L-V and V-L type inclusions in one growth zone, (e): Primary L-V and L-V-S type inclusions, and (f)

811 and g): Primary L-V-S and L-V inclusions (vapor bubble occupies up to  $\approx 35$  vol. %). Photographed at +  
812 25°C in plane-polarized, transmitted light ( $L_{H_2O}$ = aqueous liquid,  $V_{H_2O}$  = vapor).

813 Fig. 8. Histograms of homogenization temperature and salinity of fluid inclusions from different stage quartz  
814 veins in the Sandaowanzi deposit.

815 Fig. 9. Homogenization temperature versus salinity plots in the NaCl-H<sub>2</sub>O system for different stage fluid  
816 inclusion assemblages from the Sandaowanzi deposit. Vertical line represents the boiling FIA.

817 Fig. 10. Histogram of  $\delta^{34}S_{H_2S}$  isotopic compositions of the Sandaowanzi ore fluids in isotopic equilibrium  
818 with pyrite and chalcopyrite. Most of the data are from Lu et al. (2005), Liu and Lu (2006) and Zhao et al.  
819 (2010).

820 Fig. 11  $^{206}Pb/^{204}Pb$  versus  $^{207}Pb/^{204}Pb$  uranogenic (a) and  $^{206}Pb/^{204}Pb$  versus  $^{208}Pb/^{204}Pb$  thorogenic (b) plots of  
821 pyrite and whole-rock samples (based on Zartman and Doe 1981).

822 Fig. 12.  $\delta^{18}O$  versus  $\delta D$  diagram showing mineralizing fluid compositions at Sandaowanzi. Fields of  
823 volcanic vapors, felsic magmas and magmatic water are based on Hedenquist and Lowenstern (1994). The  
824 metamorphic water boxes and the kaolinite weathering and meteoric water lines are adopted from  
825 Giggenbach (1992) and Hoefs (2009). D-O isotope patterns of Qtz-Cal-Ad±Sec±Illite and  
826 Qtz-Alun±Dick±Kao type epithermal deposits are based on Simmons et al. (2005). Some data are collected  
827 from Lu et al. (2009).

828 Fig. 13. Variations of  $\delta^{18}O_{H_2O}$ ,  $\delta D_{H_2O}$ , and  $\delta^{34}S_{H_2S}$  isotopic compositions of hydrothermal fluids with depth  
829 from the Sandaowanzi deposit.

830 Fig. 14. Activity-activity diagrams showing Sandaowanzi mineralizing fluids in equilibrium with alteration  
831 minerals at different temperatures. (a):  $\text{Log}(\alpha_K^+/\alpha_H^+)$  versus  $\text{log}(\alpha_{Na}^+/\alpha_H^+)$  in the K<sub>2</sub>O-Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O  
832 system; (b):  $\text{Log}(\alpha_K^+/\alpha_H^+)$  versus  $\text{log}[\alpha_{Ca}^{++}/(\alpha_H^+)^2]$  in the K<sub>2</sub>O-CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O system; (c):  $\text{Log}(\alpha_K^+/\alpha_H^+)$   
833 versus  $\text{log}[\alpha_{Mg}^{++}/(\alpha_H^+)^2]$  in the K<sub>2</sub>O-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O system; (d):  $\text{Log}[\alpha_{Mg}^{++}/(\alpha_H^+)^2]$  versus  
834  $\text{log}[\alpha_{Ca}^{++}/(\alpha_H^+)^2]$  in the CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O system. The blue, pink and green squares represent the  
835 equilibrium for stages I, II and III, respectively, and the thermodynamic data were derived from SUPCRT92  
836 database (Johnson 1992).

837 Fig. 15.  $\text{Log}/O_2$  versus pH diagrams showing stability relationships in the Fe-Cu-O-S system. (a): For stage I,  
838 at 330°C and 180 bars. Dotted lines represent the field boundaries of the principal aqueous sulfur species and  
839 thicker dashed lines represent the stability field boundaries for pyrite, pyrrotite, hematite and magnetite.

840 The stability boundary for the orthoclase-illite equilibrium is also shown, and the square represents  
841 constrained physicochemical conditions for stage I mineralization, (b): For stage II, at 280°C and 120 bars.  
842 Solid thick line is the stability field boundary for the equilibrium bornite + pyrite = chalcopyrite, at 280°C.  
843 Dotted lines represent the field boundaries of the principal aqueous sulfur and tellurium species. Thicker  
844 dashed and dashed-dotted lines represent the stability field boundaries for Fe-O-S minerals and anglesite and  
845 galena, respectively. The stability boundaries for the orthoclase-illite-kaolinite equilibriums are also  
846 presented. The square represents constrained physicochemical conditions for stage II mineralization, and the  
847 left and right boxes are the stability fields of calaverite and hessite at 280°C, (c): For stage III, at 240°C and  
848 80 bars. Solid thick line is the stability field boundary for the equilibrium bornite + pyrite = chalcopyrite, at  
849 240°C. Dotted, thicker dashed and dashed-dotted lines represent same as in (b). The stability boundary for  
850 the albite-adularia equilibrium is also presented. The square represents constrained physicochemical  
851 conditions for stage III mineralization, and the upper and lower boxes are the stability fields of calaverite and  
852 hessite (after Zhang and Spry 1994), at 240°C, and (d): For stage IV, at 200°C and 50 bars. Dotted lines  
853 represent the field boundaries of the principal aqueous sulfur species. Thicker dashed line represents the  
854 stability field boundaries for pyrite and hematite. The dashed-dot-dotted lines are the  $\text{Au}(\text{HS})_2^-$  solubility  
855 contours. The square represents physicochemical conditions for stage IV. All phase diagrams were  
856 constructed assuming  $m_{\Sigma\text{S}} = 0.01$  and  $m_{\text{K}^+} = 0.01$ , and the thermodynamic data were derived from  
857 SUPCRT92 database (Johnson 1992).

858 Fig. 16.  $\log f\text{S}_2$  versus  $\log f\text{Te}_2$  equilibrium diagrams obtained from sulfides and tellurides at 280°C (a) and  
859 240°C (b), at vapor saturation. The enclosed areas indicate the approximate physicochemical conditions of  
860 stage II and III minerals precipitation. Diagrams are constructed based on data from Ahmad et al. (1987),  
861 Afifi et al. (1988) and Simon and Essene (1996). Abbreviations: Bn-bornite, Cp-chalcopyrite, Po-pyrrhotite,  
862 Py-pyrite, Te-native tellurium,  $\text{AuTe}_2$ -calaverite, Au-native gold, PbTe-altaite, PbS-galena, HgTe-coloradoite,  
863 HgS-cinnabar, Hg-native mercury,  $\text{Ag}_2\text{Te}$ -hessite,  $\text{Ag}_2\text{S}$ -argentite.

864 Fig. 17. Plots of the solubility of calaverite (a) and hessite (b) as a function of  $\alpha_{\text{HS}^-(\text{aq})}$  and  $\alpha_{\text{HTe}^-(\text{aq})}$  at 280  
865 and 240 °C. The star indicates an arbitrarily assumed starting composition, and three paths that could lead to  
866 deposition of these minerals. Path1 could represent the result of sulfidation, whereas Path 2 could reflect the  
867 condensation of a  $\text{H}_2\text{Te}$  vapor, and Path 3 a combination of the two processes. The diagrams were constructed  
868 using the program Unitherm (Shvarov 2011).



Table 1. Electron microprobe analyses of native metals, tellurides, sulfides and sulfosalts from the Sandaowanzi deposit

| Mineral                  | 1                 | 1                 | 2                 | 3                 | 4                 | 5                 | 6                 | 6                 | 7a                | 7b                | 8                 | 9                 | 9                 | 10                 | 11                | 12    | 13                | 14                | 15                | 16                | 17     | 18                |      |
|--------------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|--------------------|-------------------|-------|-------------------|-------------------|-------------------|-------------------|--------|-------------------|------|
| <i>Wt %</i>              |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                    |                   |       |                   |                   |                   |                   |        |                   |      |
| Se                       | 0.01              | 0.01              | 0.25              | 0.27              | 0.24              | 0.16              | 0.10              | 0.09              | 0.01              | bd                | 0.04              | bd                | bd                | bd                 | bd                | bd    | bd                | bd                | 0.33              | bd                | 0.02   | 0.02              |      |
| As                       | bd                | bd                | bd                | bd                | bd                | bd                | bd                | bd                | bd                | bd                | bd                | 3.48              | 4.37              | 21.06              | bd                | bd    | bd                | bd                | bd                | 0.03              | bd     | bd                |      |
| S                        | bd                | bd                | bd                | bd                | 0.01              | 0.02              | bd                | bd                | bd                | bd                | 0.02              | 24.65             | 25.58             | 28.38              | 22.00             | 33.66 | 24.56             | 20.36             | 13.05             | 31.90             | 53.32  | 0.01              |      |
| Pb                       | 61.91             | 62.08             | bd                | bd                | bd                | bd                | bd                | bd                | bd                | bd                | bd                | 0.22              | 0.12              | 0.00               | bd                | 0.10  | 0.16              | 6.01              | 86.47             | 0.24              | 0.03   | 0.01              |      |
| Bi                       | bd                | bd                | 0.71              | 0.83              | 0.60              | 0.05              | 0.65              | 1.17              | 0.70              | 1.53              | 0.40              | bd                | 0.01              | 0.09               | 0.04              | bd    | bd                | bd                | bd                | bd                | 0.04   | 0.01              |      |
| Ag                       | 0.10              | bd                | 5.63              | 0.81              | 6.07              | 62.59             | 4.01              | 4.04              | 12.21             | 6.64              | 47.84             | bd                | 0.03              | 0.04               | 0.10              | 0.04  | 0.25              | 0.09              | bd                | bd                | bd     | 0.02              |      |
| Fe                       | 0.03              | 0.04              | bd                | 0.04              | 0.02              | bd                | bd                | 0.02              | bd                | bd                | bd                | 0.27              | 0.19              | 3.02               | 2.00              | 30.29 | 10.44             | 3.40              | 0.03              | 0.29              | 46.78  | 0.12              |      |
| Cu                       | 0.12              | bd                | 0.24              | 0.05              | 0.02              | 0.01              | bd                | 0.01              | bd                | bd                | bd                | 37.76             | 38.03             | 46.28              | 75.71             | 34.46 | 63.54             | 69.61             | 0.03              | bd                | 0.10   | 59.33             |      |
| Zn                       | bd                | 0.01              | 0.05              | 0.02              | bd                | bd                | 0.01              | bd                | bd                | bd                | 0.01              | 7.63              | 7.45              | 2.48               | 0.06              | 0.08  | 0.03              | 0.06              | 0.02              | 65.65             | 0.00   | 40.69             |      |
| Au                       | bd                | 0.05              | 32.48             | 40.88             | 38.16             | 0.03              | 68.03             | 72.16             | 85.93             | 90.95             | 19.45             | 0.02              | 0.00              | 0.12               | 0.05              | 0.06  | 0.02              | 0.13              | 0.00              | 0.02              | bd     | 0.03              |      |
| Te                       | 37.45             | 38.46             | 59.37             | 58.01             | 55.74             | 38.01             | 25.98             | 22.02             | 0.08              | 0.14              | 34.06             | bd                | bd                | bd                 | 0.02              | 0.02  | 0.08              | bd                | 0.14              | bd                | bd     | 0.01              |      |
| Sb                       | bd                | bd                | bd                | bd                | bd                | bd                | bd                | bd                | bd                | bd                | bd                | 26.79             | 26.08             | 0.30               | 0.01              | bd    | bd                | bd                | bd                | bd                | 0.01   | bd                |      |
| Ni                       | bd                | bd                | bd                | bd                | bd                | bd                | bd                | bd                | bd                | bd                | bd                | bd                | bd                | bd                 | bd                | bd    | bd                | bd                | bd                | bd                | 0.01   | 0.21              |      |
| Co                       | bd                | bd                | bd                | bd                | bd                | bd                | bd                | bd                | 0.02              | bd                | bd                | bd                | bd                | 0.01               | bd                | 0.04  | 0.05              | bd                | bd                | bd                | 0.04   | bd                |      |
| Total                    | 99.60             | 100.65            | 98.72             | 100.90            | 100.85            | 100.86            | 98.78             | 99.51             | 98.95             | 99.26             | 101.81            | 100.82            | 101.85            | 101.78             | 99.98             | 98.73 | 99.12             | 99.66             | 100.06            | 98.14             | 100.33 | 100.44            |      |
| Number of atoms based on |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                    |                   |       |                   |                   |                   |                   |        |                   |      |
| Se                       | 0.00              | 0.00              | 0.03              | 0.02 <sup>d</sup> | 0.01 <sup>d</sup> | 0.01 <sup>e</sup> | 0.01 <sup>e</sup> | 0.01 <sup>e</sup> | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00               | 0.00              | 0.00  | 0.00              | 0.00              | 0.00              | 0.01 <sup>e</sup> | 0.00   | 0.00              | 0.00 |
| As                       | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.77 <sup>h</sup> | 0.95 <sup>h</sup> | 3.96 <sup>g</sup>  | 0.00              | 0.00  | 0.00              | 0.00              | 0.00              | 0.00              | 0.00   | 0.00              | 0.00 |
| S                        | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 13.00             | 13.00             | 13.00              | 4.00              | 2.00  | 4.00              | 6.00              | 0.98 <sup>e</sup> | 0.99 <sup>n</sup> | 2.00   | 0.00              |      |
| Pb                       | 0.99 <sup>a</sup> | 0.99 <sup>a</sup> | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.02 <sup>g</sup> | 0.01 <sup>g</sup> | 0.00               | 0.00              | 0.00  | 0.00              | 0.32 <sup>m</sup> | 1.00              | 0.00              | 0.00   | 0.00              |      |
| Bi                       | 0.00              | 0.00              | 0.06 <sup>b</sup> | 0.02 <sup>c</sup> | 0.01 <sup>c</sup> | 0.00              | 0.02 <sup>b</sup> | 0.03 <sup>b</sup> | 0.01 <sup>c</sup> | 0.01 <sup>c</sup> | 0.01 <sup>f</sup> | 0.00              | 0.00              | 0.01 <sup>g</sup>  | 0.00              | 0.00  | 0.00              | 0.00              | 0.00              | 0.00              | 0.00   | 0.00              | 0.00 |
| Ag                       | 0.00              | 0.00              | 0.90 <sup>b</sup> | 0.03 <sup>c</sup> | 0.24 <sup>c</sup> | 2.00              | 0.19 <sup>b</sup> | 0.19 <sup>b</sup> | 0.20 <sup>c</sup> | 0.12 <sup>c</sup> | 3.27 <sup>f</sup> | 0.00              | 0.00              | 0.01 <sup>g</sup>  | 0.01 <sup>i</sup> | 0.00  | 0.01 <sup>j</sup> | 0.01 <sup>l</sup> | 0.00              | 0.00              | 0.00   | 0.00              | 0.00 |
| Fe                       | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.08 <sup>g</sup> | 0.06 <sup>g</sup> | 0.79 <sup>g</sup>  | 0.22 <sup>i</sup> | 1.00  | 0.99 <sup>k</sup> | 0.68 <sup>m</sup> | 0.00              | 0.01 <sup>n</sup> | 1.00   | 0.01 <sup>o</sup> |      |
| Cu                       | 0.01 <sup>a</sup> | 0.01 <sup>a</sup> | 0.06 <sup>b</sup> | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 9.93 <sup>g</sup> | 9.71 <sup>g</sup> | 10.61 <sup>g</sup> | 6.76 <sup>i</sup> | 1.00  | 4.99 <sup>j</sup> | 9.97 <sup>l</sup> | 0.00              | 0.00              | 0.00   | 2.99 <sup>o</sup> |      |
| Zn                       | 0.00              | 0.00              | 0.02 <sup>b</sup> | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 1.97 <sup>g</sup> | 1.85 <sup>g</sup> | 0.55 <sup>g</sup>  | 0.01 <sup>i</sup> | 0.00  | 0.00              | 0.01 <sup>l</sup> | 0.00              | 0.99              | 0.00   | 1.99 <sup>o</sup> |      |

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|    |      |      |                   |                   |                   |                   |                   |                   |                   |                   |      |                   |                   |                   |      |      |                   |                   |                   |      |      |                   |
|----|------|------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|------|-------------------|-------------------|-------------------|------|------|-------------------|-------------------|-------------------|------|------|-------------------|
| Au | 0.00 | 0.00 | 0.96 <sup>b</sup> | 0.92 <sup>c</sup> | 0.75 <sup>c</sup> | 0.00              | 1.79 <sup>b</sup> | 1.78 <sup>b</sup> | 0.79 <sup>c</sup> | 0.87 <sup>c</sup> | 1.00 | 0.00              | 0.00              | 0.01              | 0.00 | 0.00 | 0.00              | 0.01 <sup>l</sup> | 0.00              | 0.00 | 0.00 | 0.00              |
| Te | 1.00 | 1.00 | 4.03              | 1.98 <sup>d</sup> | 1.99 <sup>d</sup> | 0.99 <sup>c</sup> | 0.99 <sup>c</sup> | 0.99 <sup>c</sup> | 0.00              | 0.00              | 2.00 | 0.00              | 0.00              | 0.00              | 0.00 | 0.00 | 0.00              | 0.00              | 0.01 <sup>c</sup> | 0.00 | 0.00 | 0.00              |
| Sb | 0.00 | 0.00 | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00 | 3.64 <sup>h</sup> | 3.48 <sup>h</sup> | 0.04 <sup>h</sup> | 0.00 | 0.00 | 0.00              | 0.00              | 0.00              | 0.00 | 0.00 | 0.00              |
| Ni | 0.00 | 0.00 | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00 | 0.00              | 0.00              | 0.00              | 0.00 | 0.00 | 0.00              | 0.00              | 0.00              | 0.00 | 0.00 | 0.01 <sup>o</sup> |
| Co | 0.00 | 0.00 | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00              | 0.00 | 0.00              | 0.00              | 0.00              | 0.00 | 0.00 | 0.01 <sup>k</sup> | 0.00              | 0.00              | 0.00 | 0.00 | 0.00              |

<sup>a</sup>Pb+Cu = 1, Te = 1

<sup>b</sup>Ag + Au + Bi + Cu + Zn = 2, Te = 4

<sup>c</sup>Au + Ag + Bi = 1, <sup>d</sup>Te + Se = 2

<sup>e</sup>Te + Se + S = 1

<sup>f</sup>Ag + Bi = 3.28, Au = 1, Te = 2

<sup>g</sup>Cu + Zn + Fe + Pb + Ag + Bi = 2, <sup>h</sup>Sb + As = 2, S = 13

<sup>i</sup>Cu + Fe + Ag + Zn = 7, S = 4

<sup>j</sup>Cu + Fe + Ag + Zn = 7, S = 4

<sup>k</sup>Cu + Ag = 7, <sup>l</sup>Fe + Co = 1, S = 4

<sup>m</sup>Cu + Ag + Au + Zn = 10, <sup>n</sup>Pb + Fe = 1, S = 6

<sup>o</sup>Zn + Fe = 1, S = 1

<sup>p</sup>Cu + Zn + Ni + Fe = 6

1 = altaite from stage III (CM13/170m)

2 = sylvanite from stage III (CM13/170m)

3 = calaverite from stage III (CM23/130m)

4 = krennerite from stage III (CM23/130m)

5 = hessite from stage III (CM23/130m)

6 = unnamed telluride (Au<sub>1.8</sub>Ag<sub>0.2</sub>Te) from Stage III (CM23/130m)

7a = electrum from stage II (CM28/130m)

7b = native gold from stage III (CM17/90m)

8 = petzite from stage III (CM17/90m)

9 = Zn-tetrahedrite from stage III (CM13/170m)

10 = tennantite from stage III (CM13/170m)

11 = anilite from stage III (CM23/130m)

12 = chalcopyrite from stage II (CM28/130m)

13 = bornite from stage II (CM23/130m)

14 = betekhtinite from stage II (CM23/130m)

15 = galena from stage II (CM28/130m)

16 = sphalerite from stage II (CM28/130m) with X<sub>FeS</sub> = 0.49%

17 = pyrite from stage I (CM37/90m)

18 = brass from stage III (CM28/130m)

Abbreviations: bd: Below detection limit and CM: The transverses drifts used at the mine.

Table 2. Microthermometric data of primary fluid inclusions in quartz veins from the Sandaowanzi deposit

| Sample    | Location  | N  | Stage | Mineral      | Phases      | T <sub>m<sub>ice</sub></sub><br>(°C) | Th<br>(°C) | T <sub>m<sub>halite</sub></sub><br>(°C) | Salinity<br>(wt.% NaCl equiv) |
|-----------|-----------|----|-------|--------------|-------------|--------------------------------------|------------|---|-------------------------------|
| sdwz-12   | 279 line  | 22 | I     | Milky quartz | L-V and V-L | -2.5 to -0.3                         | 240 to 385 | -                                       | 0.53 to 4.18                  |
| sdwz-13   | CM17/90m  | 30 | I     | Milky quartz | L-V and V-L | -2.1 to -0.6                         | 256 to 381 | -                                       | 1.05 to 3.55                  |
| sdwz-36   | CM17/90m  | 30 | II    | Grey quartz  | L-V and V-L | -3.6 to -0.2                         | 230 to 345 | -                                       | 0.35 to 5.86                  |
| sdwz-43   | CM28/130m | 17 | II    | Grey quartz  | L-V and V-L | -10.2 to -0.2                        | 160 to 400 | -                                       | 0.35 to 14.15                 |
| sdwz-49   | CM25/130m | 49 | II    | Grey quartz  | L-V and V-L | -1.8 to -0.4                         | 177 to 306 | -                                       | 0.70 to 3.06                  |
| sdwz-49-2 | CM25/130m | 4  | II    | Grey quartz  | L-V-S       | -                                    | 307 to 365 | 384 to 430                              | 45.3 to 51.9                  |
| sdwz-52   | CM33/130m | 34 | III   | Clear quartz | L-V and V-L | -1.8 to -0.2                         | 160 to 360 | -                                       | 0.35 to 3.06                  |
| sdwz-47   | CM23/130m | 25 | III   | Clear quartz | L-V         | -4.0 to -0.5                         | 157 to 365 | -                                       | 0.88 to 6.45                  |
| sdwz-48   | CM23/130m | 29 | III   | Clear quartz | L-V and V-L | -3.6 to -0.3                         | 195 to 285 | -                                       | 0.53 to 5.86                  |
| sdwz-56   | CM28/50m  | 38 | IV    | White quartz | L-V and V-L | -3.2 to -0.1                         | 128 to 243 | -                                       | 0.18 to 5.26                  |
| sdwz-57   | CM28/50m  | 21 | IV    | White quartz | L-V and V-L | -3.9 to -0.2                         | 135 to 265 | -                                       | 0.35 to 6.30                  |

T<sub>m<sub>ice</sub></sub> = final ice-melting temperature, T<sub>m<sub>halite</sub></sub> = halite dissolution temperature, Th = homogenization temperature, - = not analyzed, N = the number of analyzed fluid inclusions.

Table 3. Compositions of vapor and liquid for fluid inclusions from the Sandaowanzi deposit ( $\mu\text{g/g}$ )

| Sample   | Mineral                | CH <sub>4</sub> | C <sub>2</sub> H <sub>2</sub> +<br>C <sub>2</sub> H <sub>4</sub> | C <sub>2</sub> H <sub>6</sub> | CO <sub>2</sub> | H <sub>2</sub> O | O <sub>2</sub> | N <sub>2</sub> | Na <sup>+</sup> | K <sup>+</sup> | Mg <sup>2+</sup> | Ca <sup>2+</sup> | F <sup>-</sup> | Cl <sup>-</sup> | Br <sup>-</sup> | NO <sub>3</sub> <sup>-</sup> | SO <sub>4</sub> <sup>2-</sup> |
|----------|------------------------|-----------------|--|-------------------------------|-----------------|------------------|----------------|----------------|-----------------|----------------|------------------|------------------|----------------|-----------------|-----------------|------------------------------|-------------------------------|
| sdwz-22  | Milky quartz (stage I) | 0.42            | 0.10   | bd                            | 97.43           | 545.28           | 11.21          | 60.61          | 1.77            | 6.86           | 1.55             | 24.07            | 1.38           | 0.72            | bd              | 0.19                         | 8.82                          |
| sdwz-27a | Milky quartz (stage I) | 0.27            | 0.06   | bd                            | 80.18           | 282.69           | 10.92          | 57.48          | 1.40            | bd             | bd               | 36.12            | 0.28           | 0.97            | bd              | 0.15                         | 3.84                          |
| sdwz-35  | Grey quartz (stage I)  | 0.47            | 0.11   | bd                            | 146.16          | 529.04           | 25.40          | 123.05         | 1.79            | 4.42           | 0.90             | 32.02            | 0.31           | 1.36            | 0.12            | 0.11                         | 3.03                          |
| sdwz-43  | Grey quartz (stage I)  | 0.79            | 0.21   | 0.01                          | 139.49          | 535.26           | 10.75          | 67.27          | 2.92            | 7.11           | 0.32             | 1.92             | 0.20           | 1.32            | bd              | 0.29                         | 9.66                          |
| sdwz-36  | Grey quartz (stage I)  | 0.40            | 0.14   | 0.01                          | 164.44          | 291.05           | 22.32          | 113.98         | 2.26            | 11.93          | 0.76             | 28.74            | 0.28           | 0.98            | bd              | 0.06                         | 11.39                         |
| sdwz-47  | Clear quartz (stage I) | 0.27            | 0.12   | 0.01                          | 84.33           | 432.31           | 13.74          | 70.32          | 1.84            | 4.54           | 0.24             | 13.32            | 0.68           | 0.52            | 0.07            | 0.10                         | 6.65                          |
| sdwz-53  | Clear quartz (stage I) | 0.38            | 0.14   | 0.01                          | 103.58          | 483.24           | 13.04          | 68.97          | 1.81            | 6.90           | 0.83             | 17.64            | 14.52          | 1.18            | bd              | 0.10                         | 3.08                          |
| sdwz-56  | White quartz (stage I) | 0.62            | 0.15   | 0.01                          | 124.19          | 866.18           | 6.75           | 44.10          | 1.37            | 3.79           | 0.65             | 2.79             | 0.34           | 0.58            | bd              | 0.06                         | 8.24                          |

Abbreviations: bd: Below detection limit



Table 4. Sulfur isotopic compositions of pyrite and chalcopyrite from the Sandaowanzi deposit

| Sample  | Location  | Occurrence     | Stage | Mineral      | Temperature <sup>A</sup><br>(°C) | $\delta^{34}\text{S}_{\text{CDT}}$<br>(per mil) | $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ <sup>B</sup><br>(per mil) |
|---------|-----------|----------------|-------|--------------|----------------------------------|---|--|
| sdwz-26 | CM13/170m | Trachyandesite | -     | Pyrite       | 330                              | -0.5  | -1.6   |
| sdwz-38 | CM37/90m  | Trachyandesite | -     | Pyrite       | 330                              | -0.4  | -1.5   |
| sdwz-39 | 238 line  | Trachyandesite | -     | Pyrite       | 330                              | 0.3   | -0.8   |
| sdwz-55 | CM35/130m | Trachyandesite | -     | Pyrite       | 330                              | 0.9   | -0.2   |
| sdwz-32 | CM27/90m  | Grey quartz    | II    | Pyrite       | 280                              | 0.6   | -0.7   |
| sdwz-50 | CM23/130m | Grey quartz    | II    | Pyrite       | 280                              | -0.9  | -2.2   |
| sdwz-43 | CM28/130m | Grey quartz    | II    | Chalcopyrite | 280                              | -1.8  | -1.6   |
| sdwz-47 | CM23/130m | Clear quartz   | III   | Chalcopyrite | 240                              | -2.2  | -2.0   |

<sup>A</sup>Average homogenization temperatures of fluid inclusions from grey (stage II) and clear quartz (stage III)

<sup>B</sup>Utilizing H<sub>2</sub>S-sulfide equations of Grootenboer and Schwarcz (1969) and Ohmoto and Rye (1979)

Table 5. Oxygen and hydrogen isotopic compositions for samples from the Sandaowanzi deposit

| Sample   | Location  | Stage | Mineral/Rock | Temperature <sup>A</sup><br>(°C) | $\delta^{18}\text{O}_{\text{SMOW}}$<br>(per mil) | $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ <sup>B</sup><br>(per mil) | $\delta\text{D}_{\text{H}_2\text{O}}$<br>(per mil) |
|----------|-----------|-------|--------------|----------------------------------|--|--|--|
| sdwz-22  | CM7/170m  | I     | Milky quartz | 330                              | -2.5   | -10.6  | -123   |
| sdwz-35  | CM15/90m  | II    | Grey quartz  | 280                              | -0.4   | -8.3   | -116   |
| sdwz-53  | CM33/130m | II    | Grey quartz  | 280                              | -0.3   | -10.1  | -111   |
| sdwz-36  | CM17/90m  | II    | Grey quartz  | 280                              | -1.9   | -9.7   | -98  |
| sdwz-47  | CM23/130m | III   | Clear quartz | 240                              | -3.3   | -12.9  | -107   |
| sdwz-27a | CM13/170m | III   | Clear quartz | 240                              | -1.8   | -9.8   | -96  |
| sdwz-04  | 296 line  | III   | Clear quartz | 240                              | -3.9   | -12.0  | -123   |
| sdwz-43  | CM28/130m | III   | Clear quartz | 240                              | -0.3   | -7.6   | -101   |
| sdwz-56  | CM33/50m  | IV    | White quartz | 200                              | -3.5   | -13.6  | -109   |
| sdwz-58  | CM35/50m  | IV    | White quartz | 200                              | -2.6   | -10.9  | -127   |

<sup>A</sup>Average homogenization temperatures from milky (stage I), grey (stage II), clear (stage III) and white quartz (stage IV) and the maximum temperature obtained from fluid inclusions

<sup>B</sup>Utilizing the quartz-H<sub>2</sub>O equations of Zheng (1993)

Table 6. Lead isotope ratios for pyrite, the host trachyandesite and monzogranite from the Sandaowanzi deposit

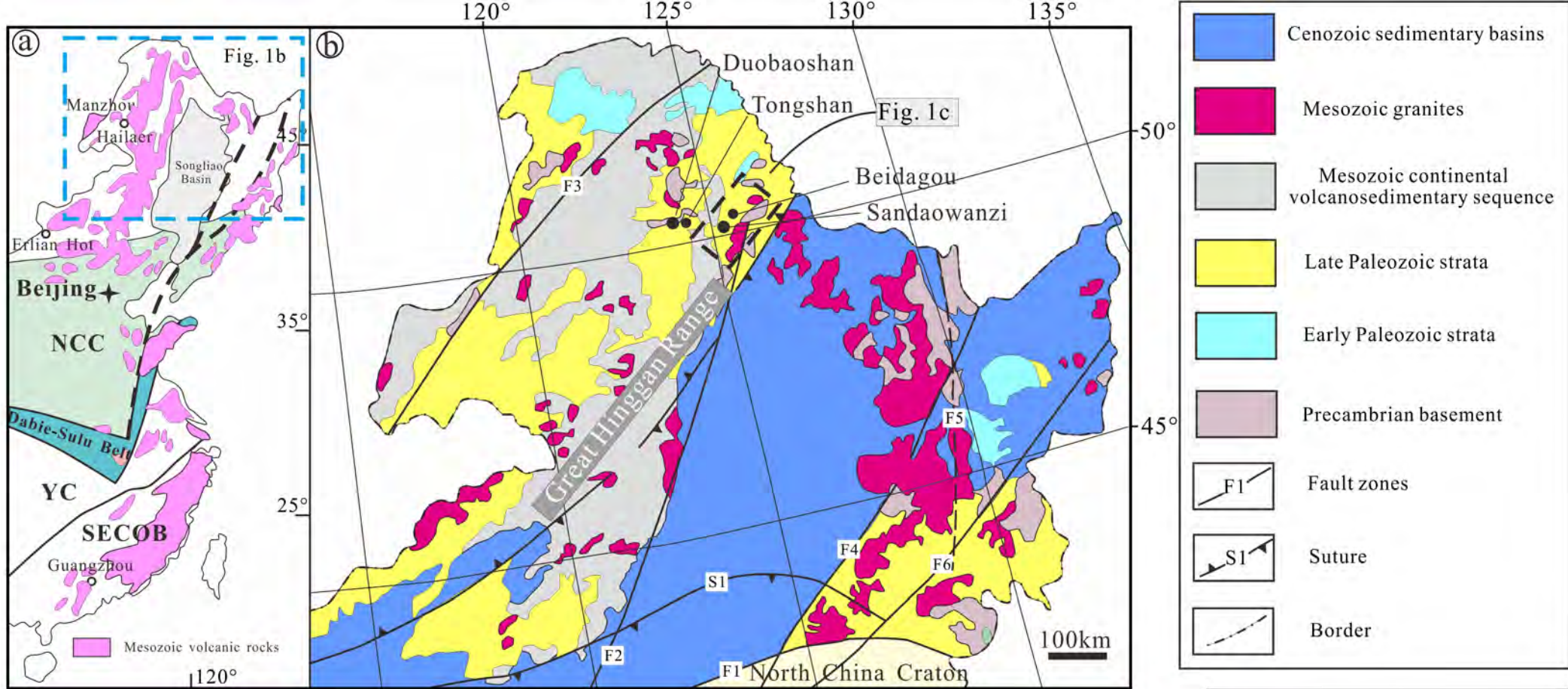
| Sample       | Mineral/Rock   | $^{208}\text{Pb}/^{204}\text{Pb}$ | $^{207}\text{Pb}/^{204}\text{Pb}$ | $^{206}\text{Pb}/^{204}\text{Pb}$ | $^{208}\text{Pb}/^{206}\text{Pb}$ | $^{207}\text{Pb}/^{206}\text{Pb}$ |
|--------------|----------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| 09sdwz-26    | Pyrite         | 38.0901                           | 15.5404                           | 18.2366                           | 2.0887                            | 0.8522                            |
| 09sdwz-32    | Pyrite         | 38.2293                           | 15.5624                           | 18.3146                           | 2.0873                            | 0.8497                            |
| 09sdwz-38    | Pyrite         | 38.1919                           | 15.557                            | 18.3119                           | 2.0856                            | 0.8496                            |
| 09sdwz-39    | Pyrite         | 38.0982                           | 15.5409                           | 18.2433                           | 2.0884                            | 0.8519                            |
| 09sdwz-50    | Pyrite         | 38.1499                           | 15.5465                           | 18.2776                           | 2.0873                            | 0.8506                            |
| 09sdwz-55    | Pyrite         | 38.1863                           | 15.555                            | 18.2726                           | 2.0898                            | 0.8513                            |
| 09sdwz-61    | Monzogranite   | 38.2882                           | 15.5658                           | 18.2729                           | 2.0954                            | 0.8519                            |
| 09sdwz-62    | Monzogranite   | 38.6944                           | 15.5863                           | 18.8377                           | 2.0541                            | 0.8274                            |
| 09sdwz-55(2) | Trachyandesite | 38.2400                           | 15.6255                           | 18.2138                           | 2.0995                            | 0.8579                            |
| 09sdwz-26(2) | Trachyandesite | 38.2066                           | 15.5487                           | 18.3296                           | 2.0844                            | 0.8483                            |
| 09sdwz-38(2) | Trachyandesite | 38.2277                           | 15.6188                           | 18.2093                           | 2.0994                            | 0.8577                            |

All errors are reported at  $\pm 2\sigma$  (minimum of 0.00001 and maximum of 0.0035)

Table 7. Calculated physicochemical parameters of the Sandaowanzi mineralizing fluid

| Physicochemical Parameter                 | Stage I        | Stage II       | Stage III      | Stage IV     |
|---|----------------|----------------|----------------|--------------|
| pH  | 3.0 to 3.2     | 4.0 to 4.3     | 4.5 to 5.1     | 5.9 to 6.0   |
| $\log(\alpha_{K^+}/\alpha_{H^+})$         | 3.7            | 2.3            | 4.9            | -            |
| $\log(\alpha_{Na^+}/\alpha_{H^+})$        | 2.4            | 4.0 to 4.4     | 5.9            | -            |
| $\log[\alpha_{Ca^{++}}/(\alpha_{H^+})^2]$ | 5.1            | 6.0            | 9.5            | -            |
| $\log[\alpha_{Mg^{++}}/(\alpha_{H^+})^2]$ | 4.3            | 6.8            | 5.2 to 5.3     | -            |
| $\log f_{S_2}$                            | -9.5 to -8.4   | -12.1 to -9.2  | -14.1 to -10.6 | -            |
| $\log f_{Te_2}$                           | -              | -12.6 to -9.9  | -15.2 to -7.9  | -            |
| $\Delta \log f_{O_2}$ (HM)                | -2.6 to -2.2   | -2.1 to -1.0   | -0.6 to -0.4   | +1.9         |
| $\log f_{H_2S(g)}$                        | -0.9 to -0.1   | -1.5 to -1.4   | -2.6 to -1.8   | -            |
| $\log \alpha_{H_2S(aq)}$                  | -3.2           | -4.0           | -4.3           | -            |
| $\log \alpha_{HS^-(aq)}$                  | -1.7 to -1.6   | -1.6 to -1.2   | -1.3 to -1.2   | -            |
| $\log f_{H_2S(g)}/f_{SO_2(g)}$            | -10.7 to -10.3 | -12.1 to -11.0 | -7.8 to -8.6   | 5.3          |
| $\log f_{H_2Te(g)}$                       | -              | -2.1 to -1.7   | -1.6 to -1.5   | -            |
| $\log \alpha_{H_2Te(aq)}$                 | -              | -5.6 to -4.4   | -3.9 to -3.5   | -            |
| $\log \alpha_{HTe^-(aq)}$                 | -              | -3.8 to -3.6   | -1.7 to -1.5   | -            |
| $\log f_{H_2S(g)}/f_{H_2Te(g)}$           | -              | 0.6 to 0.3     | -0.3 to -1.0   | -            |
| $\log \alpha_{Au(HS)_2(aq)^-}$            | -13.4 to -13.0 | -11.4 to -10.6 | -9.7 to -9.3   | -9.1 to -8.8 |
| $\log \alpha_{Fe^{++}(aq)}$               | -3.7 to -3.5   | -5.8 to -5.2   | -              | -            |
| $\log \alpha_{Zn^{++}(aq)}$               | -9.10          | -7.80          | -              | -            |
| $\log \alpha_{Cu(HS)_2^-(aq)}$            | -8.5 to -8.4   | -7.3 to -7.1   | -              | -            |
| $\log \alpha_{Pb^{++}(aq)}$               | -              | -3.9 to -3.7   | -4.2 to -4.2   | -            |





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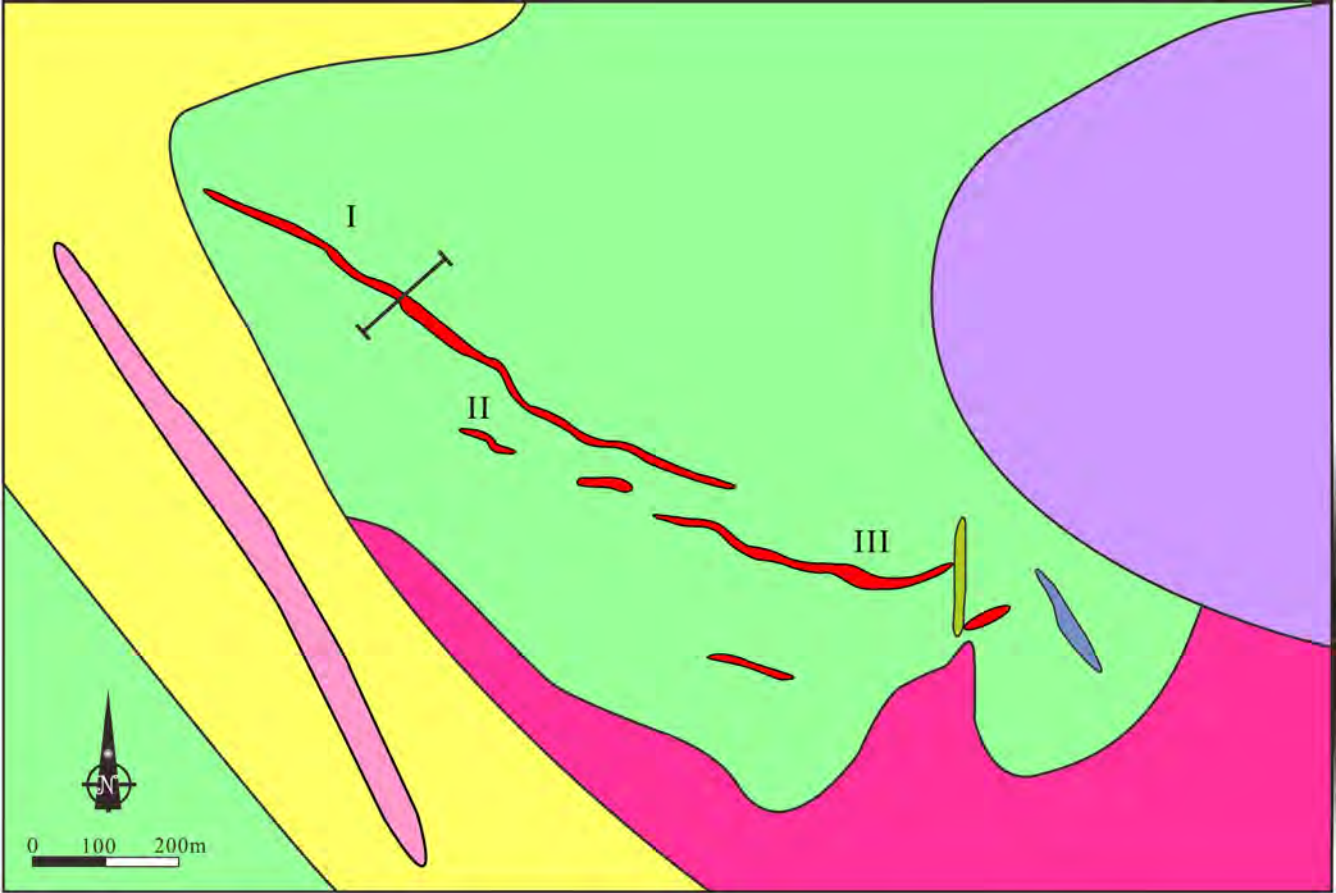
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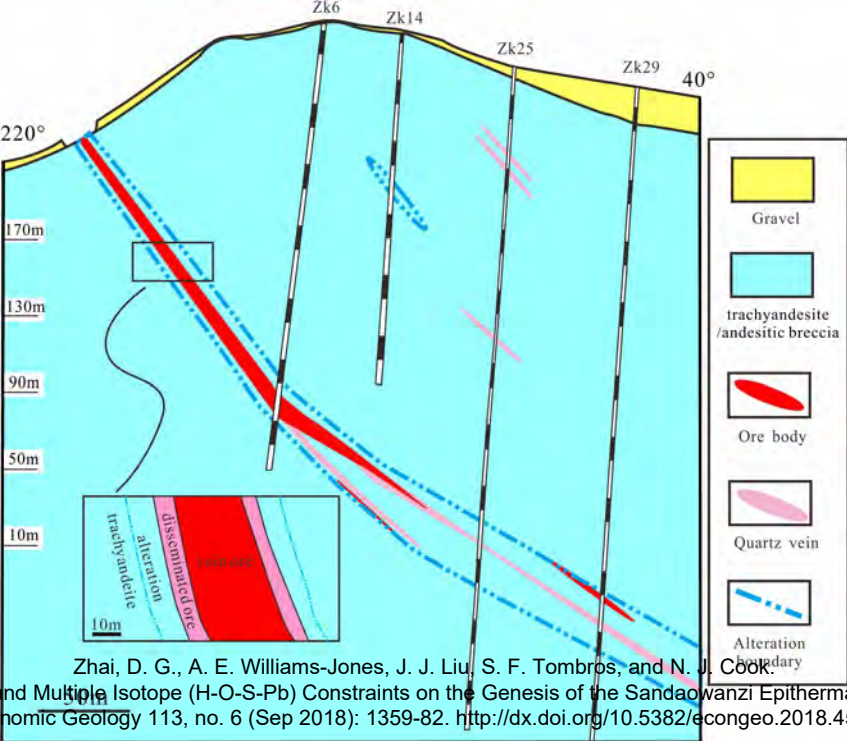
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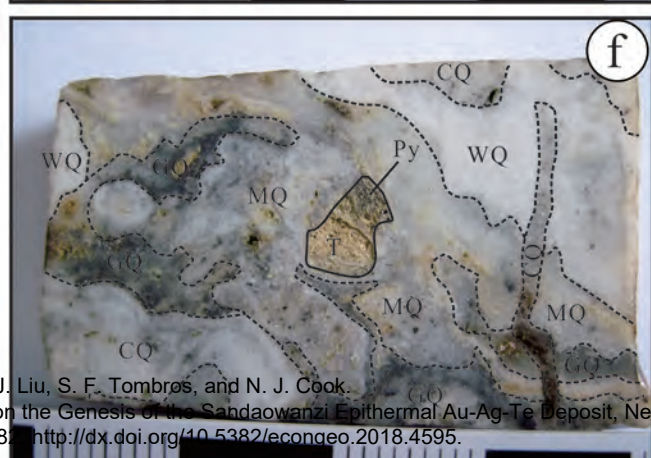
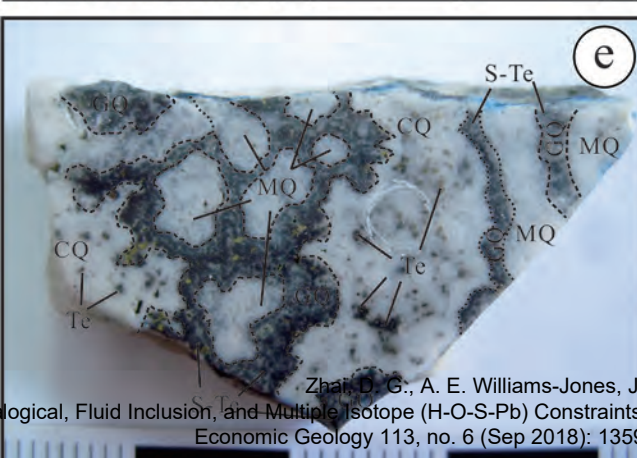
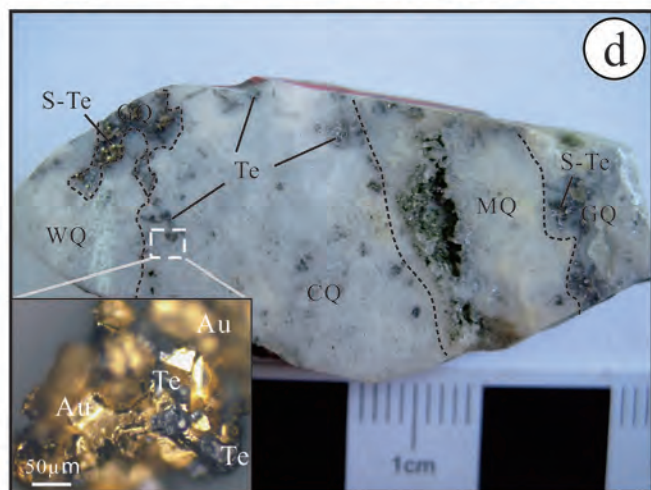
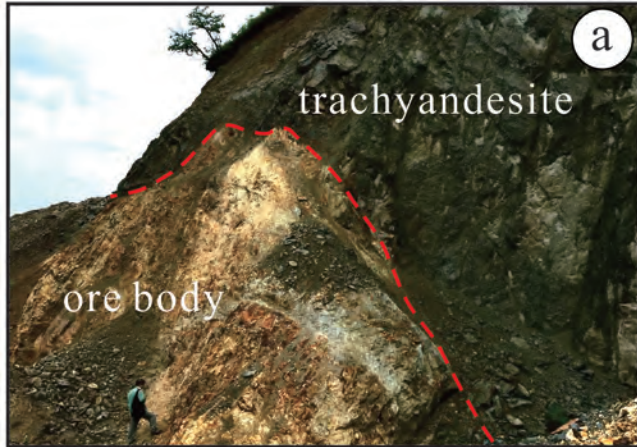
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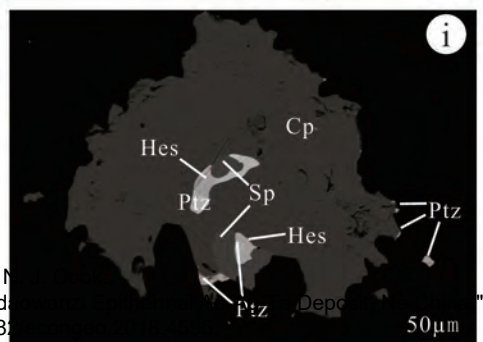
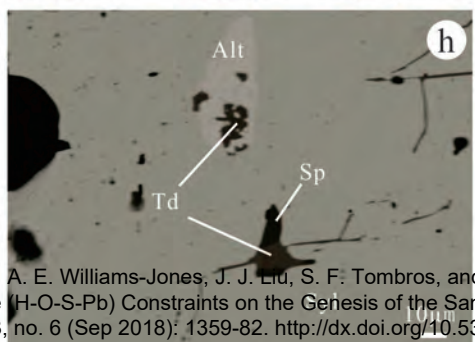
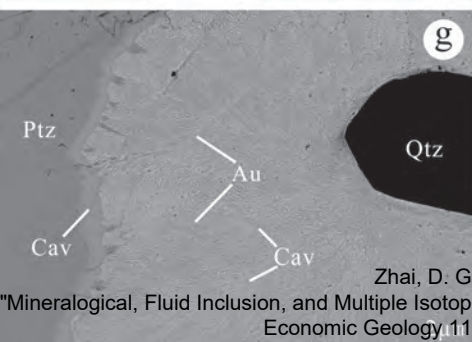
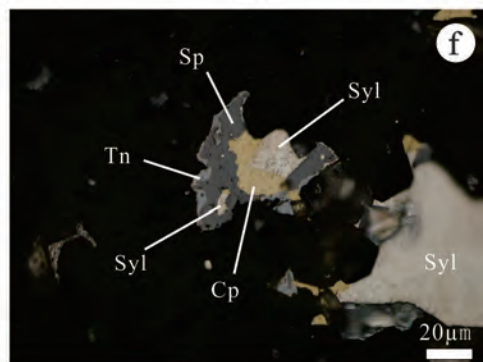
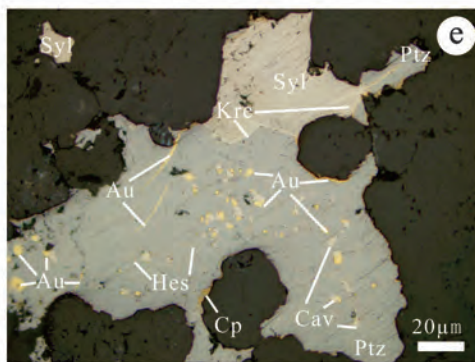
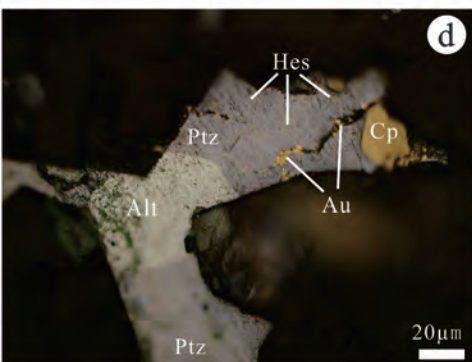
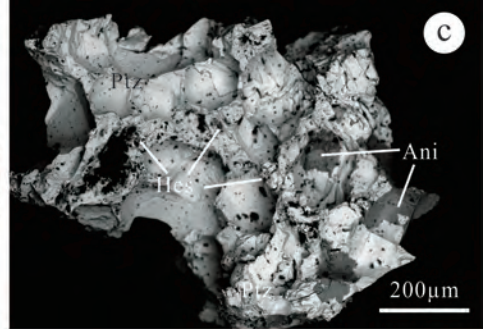
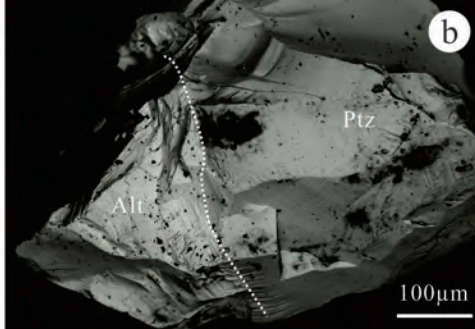
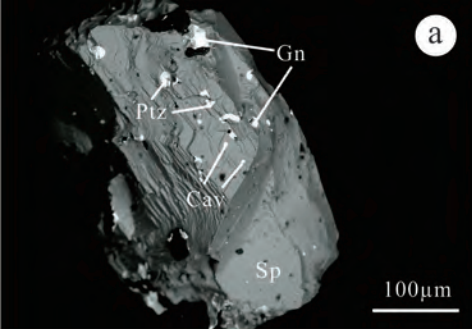
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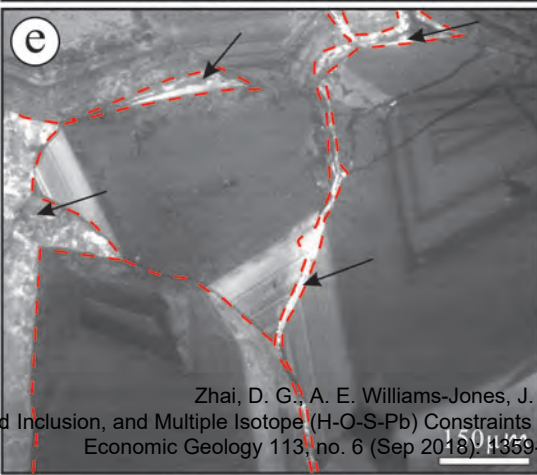
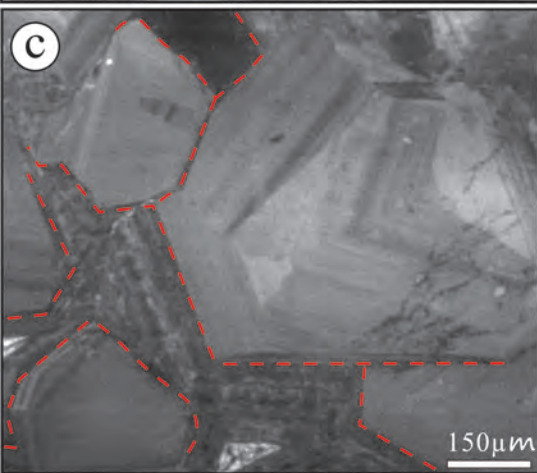
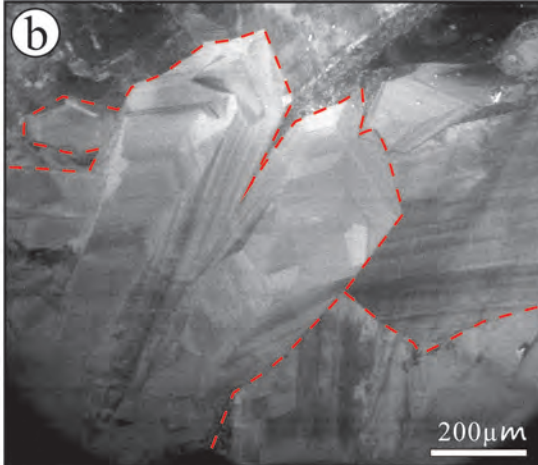
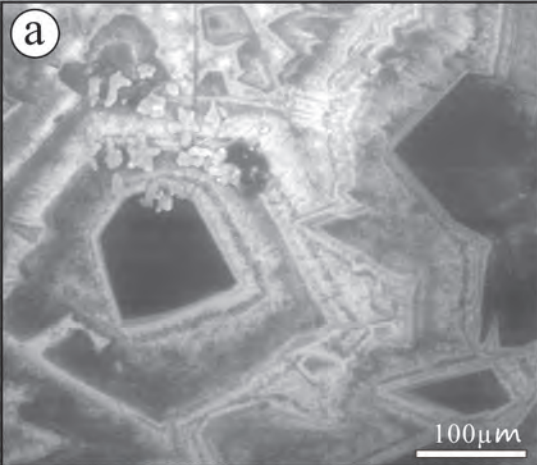




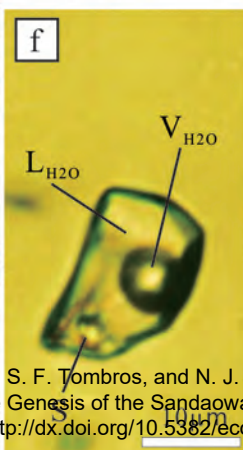
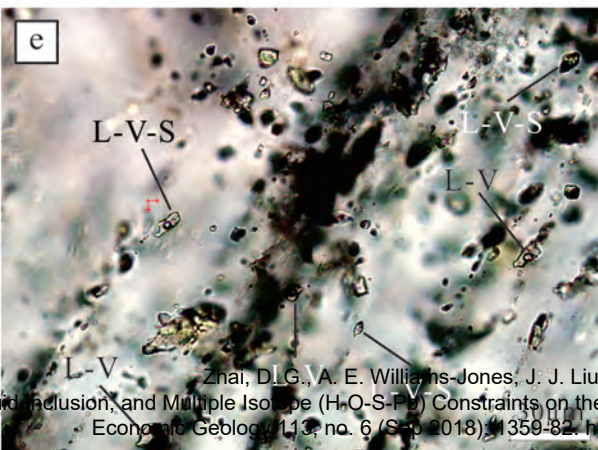
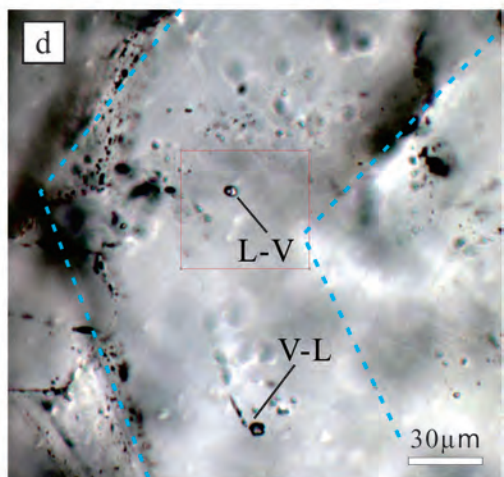
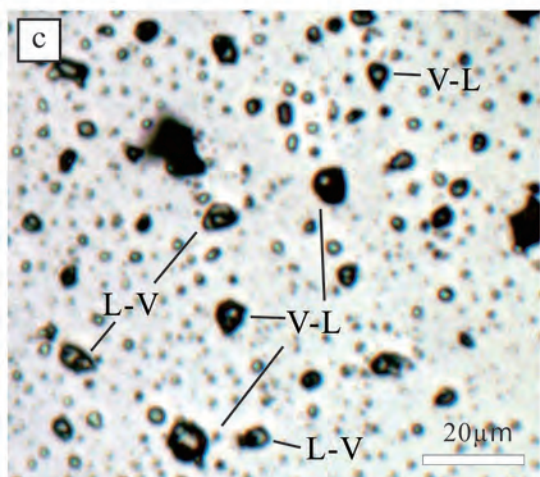
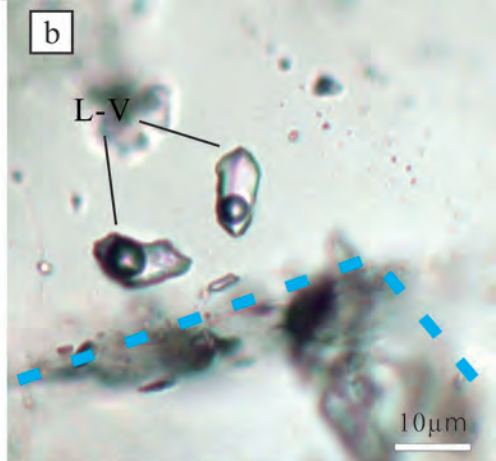
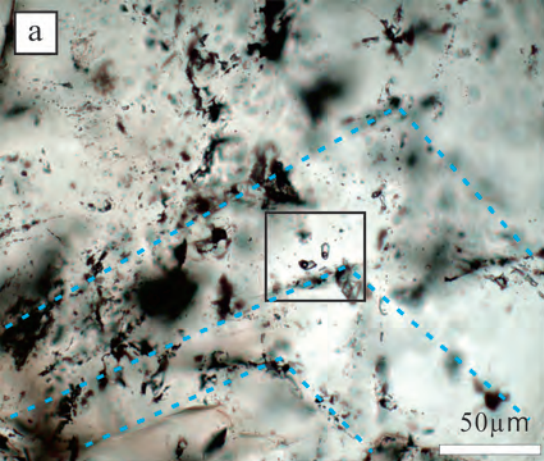




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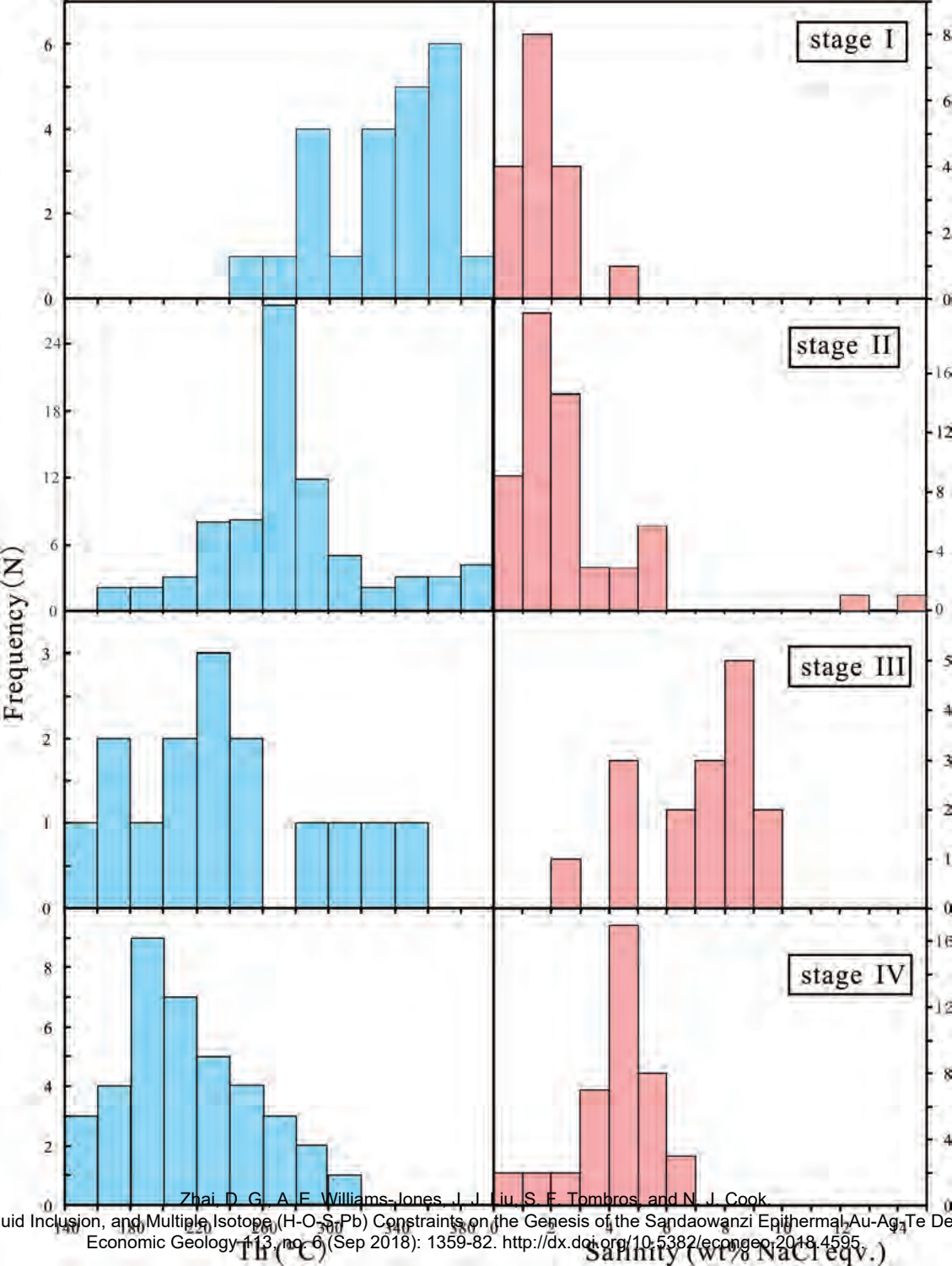






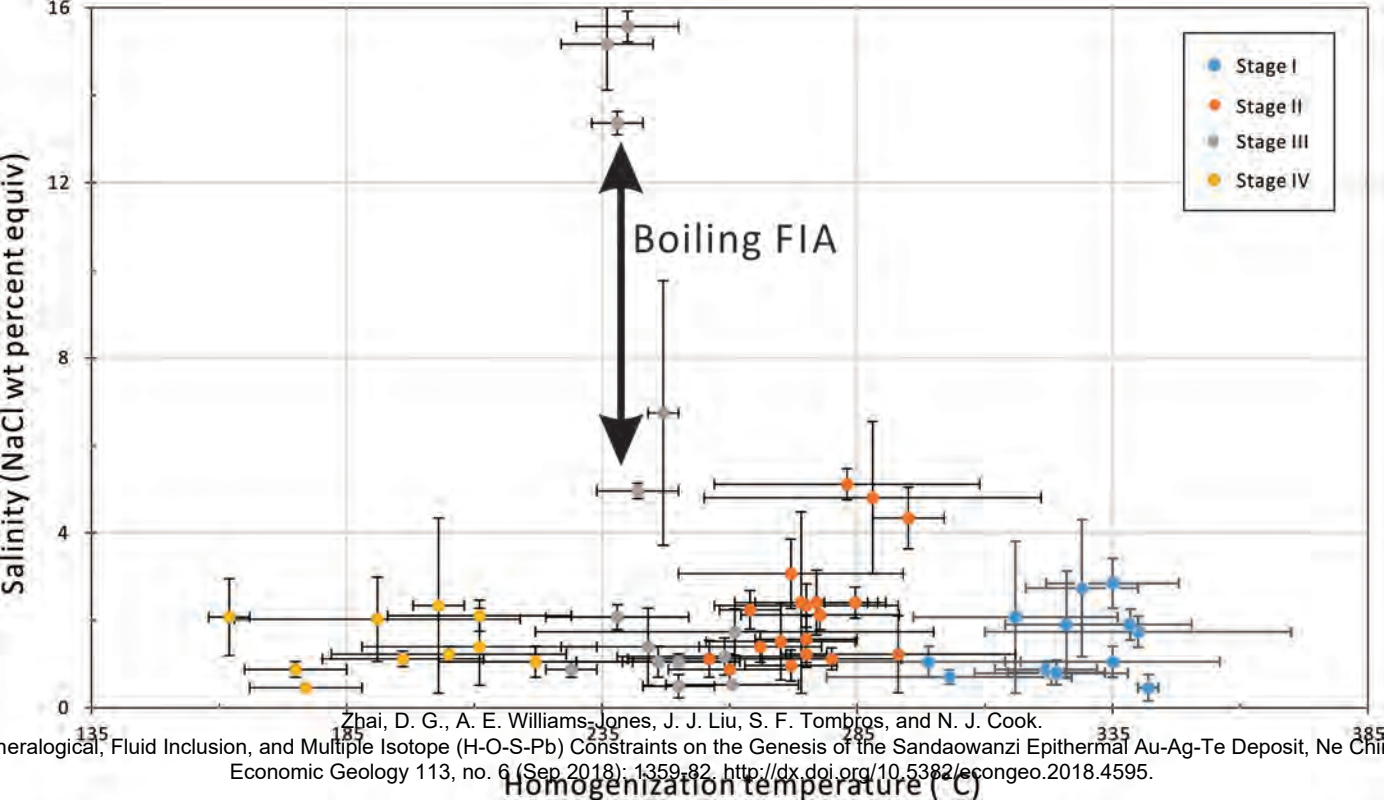
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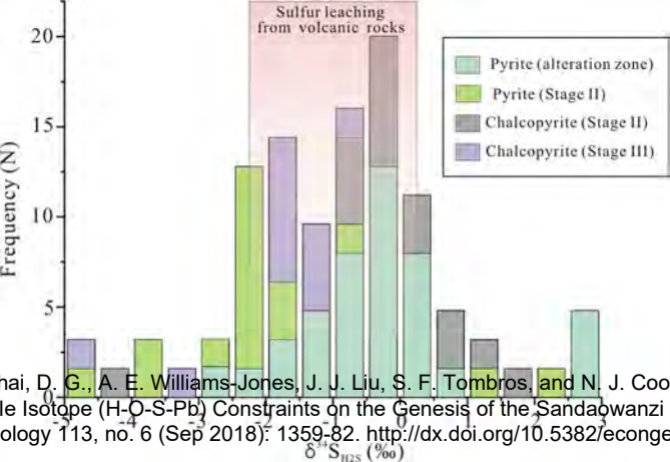
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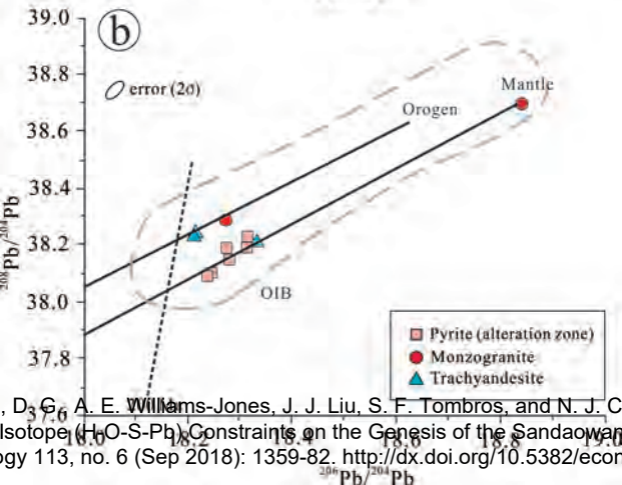
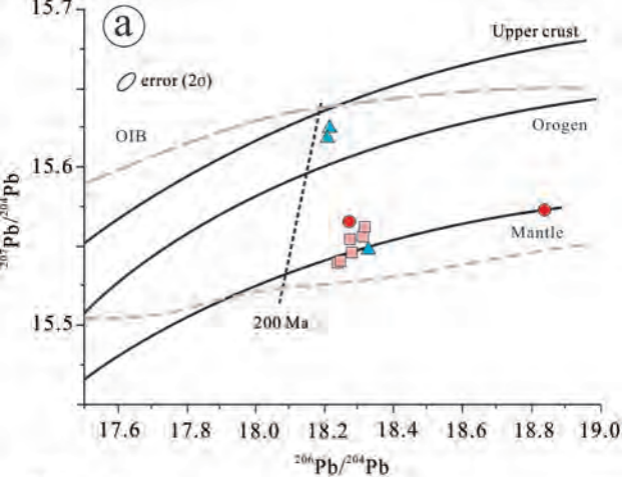


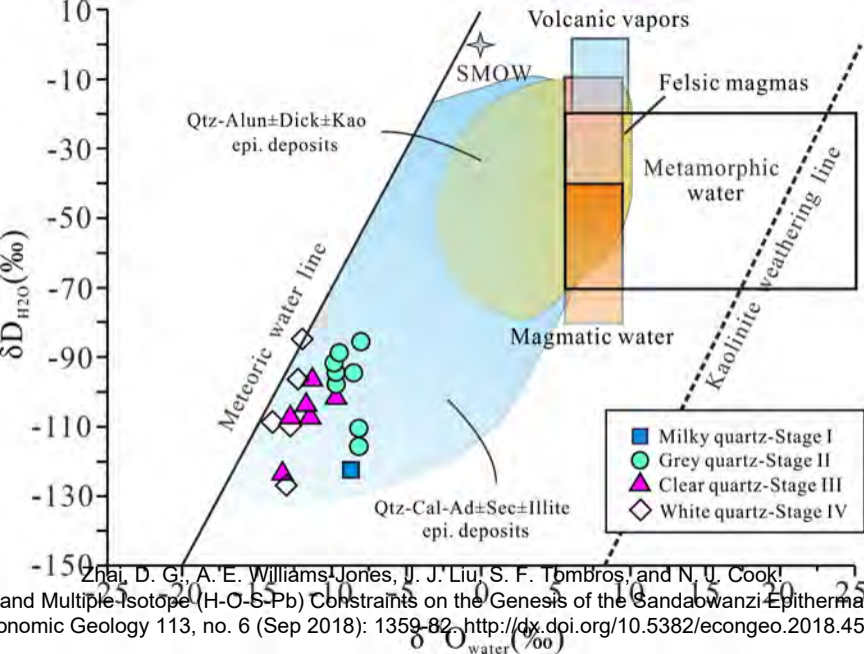
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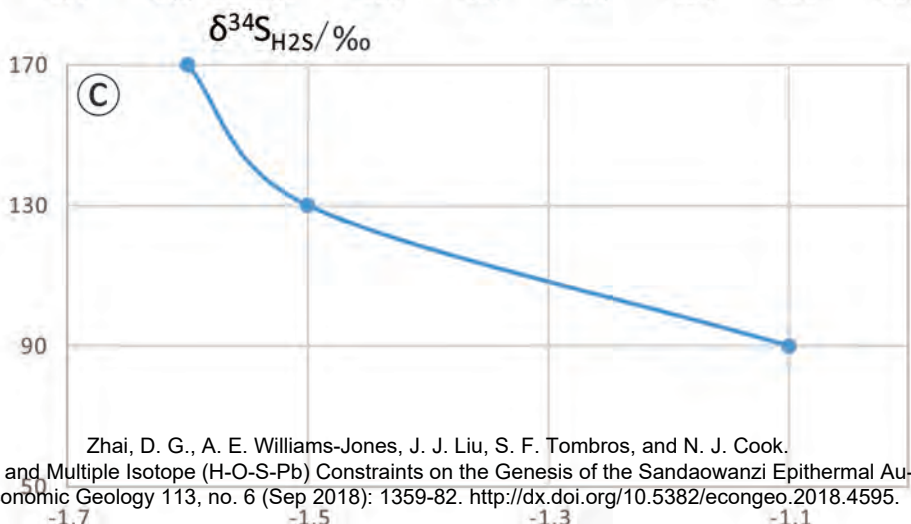
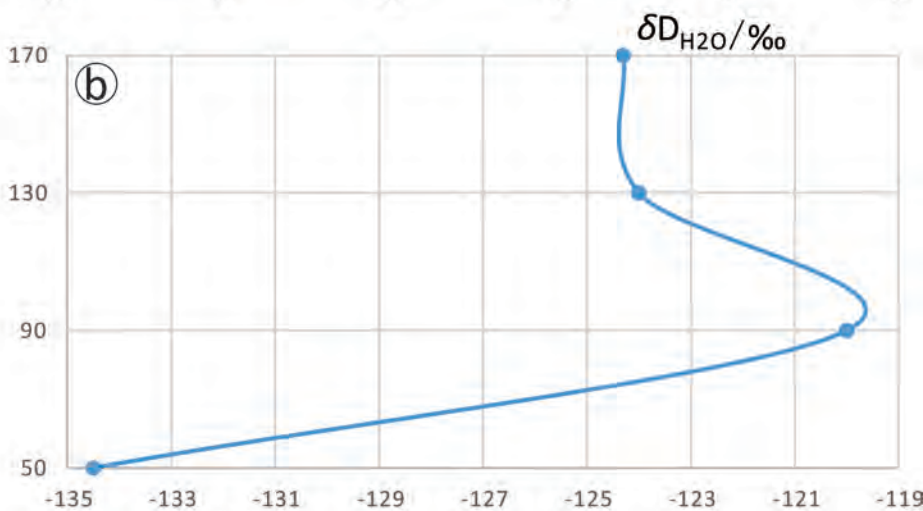
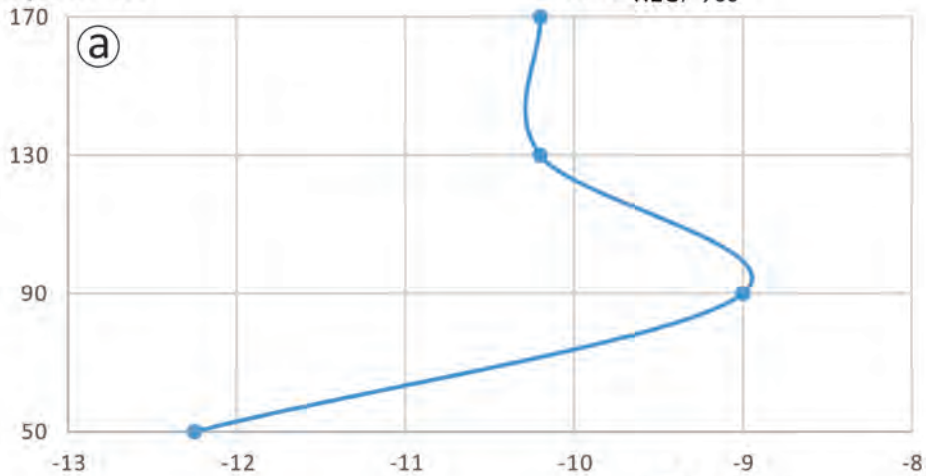






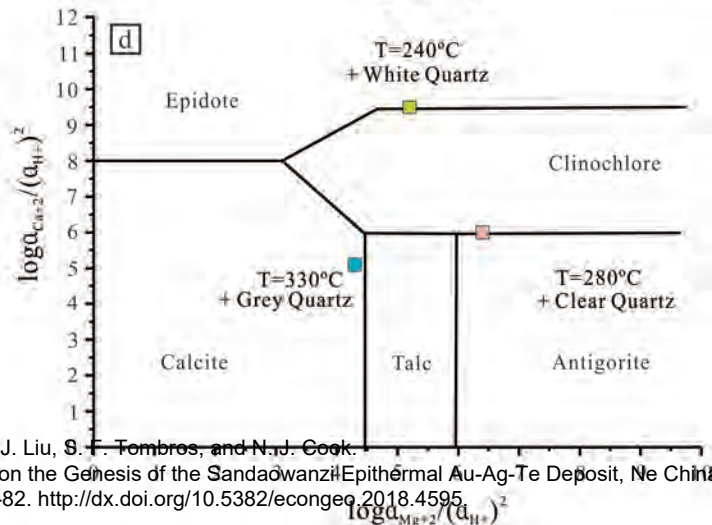
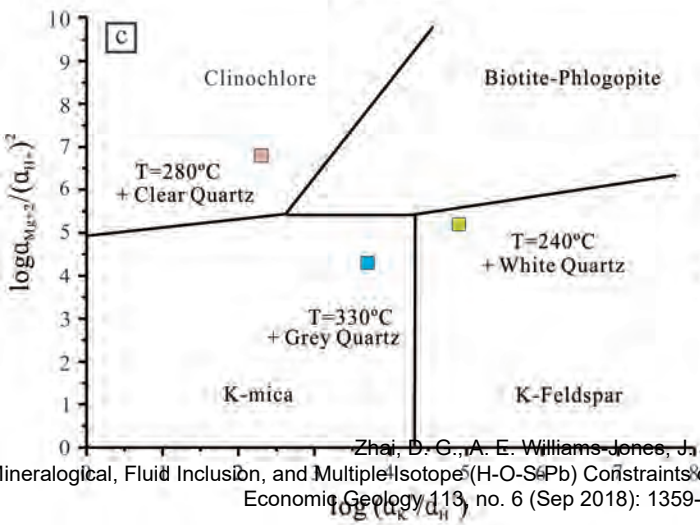
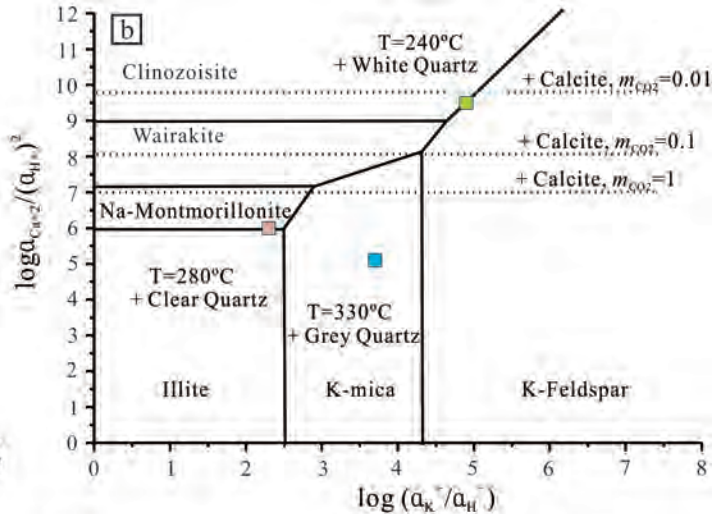
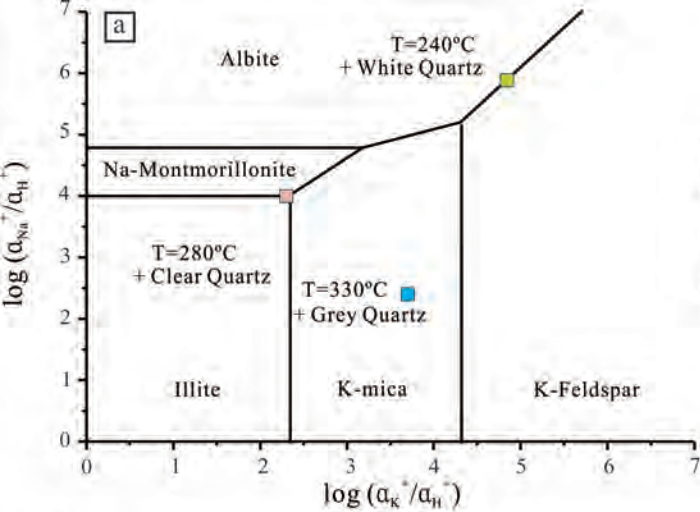


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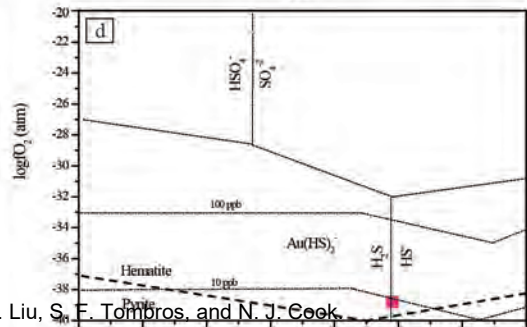
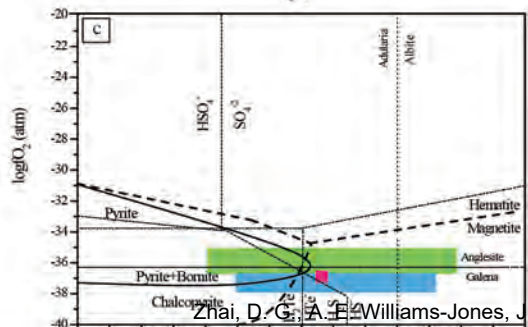
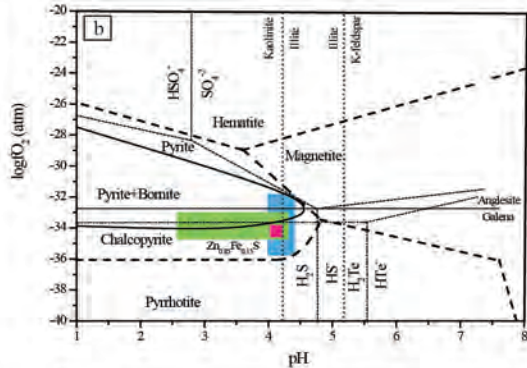
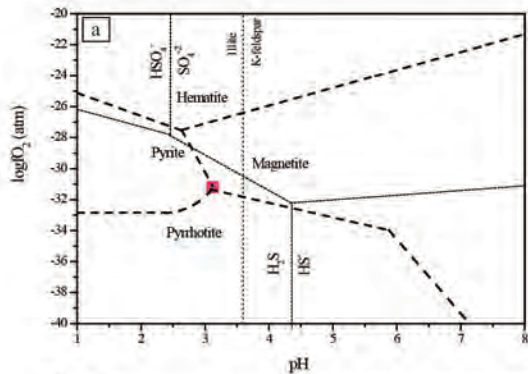


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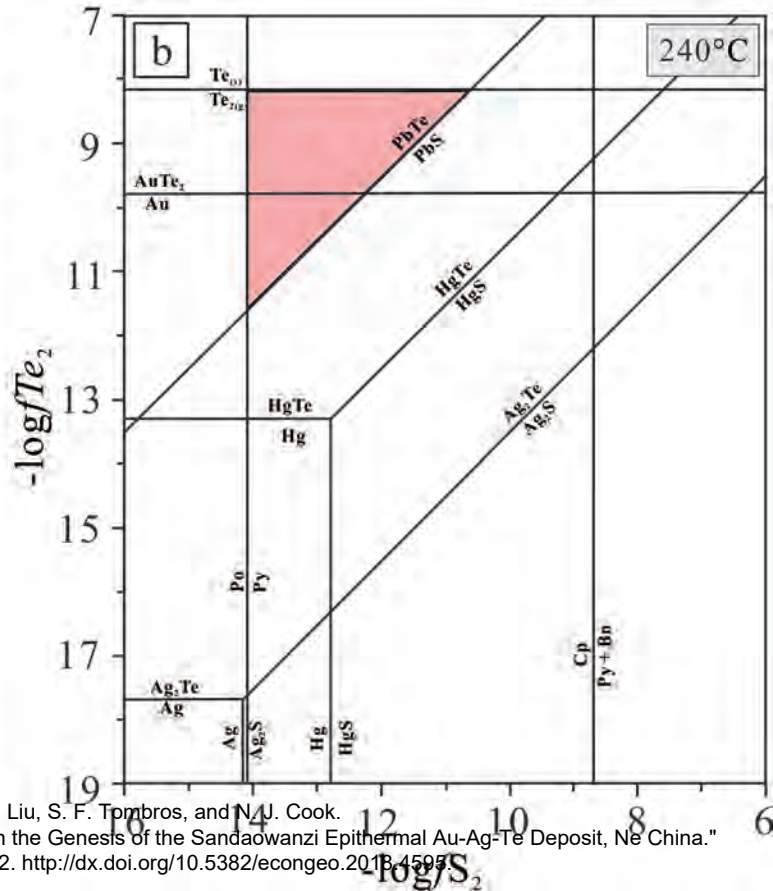
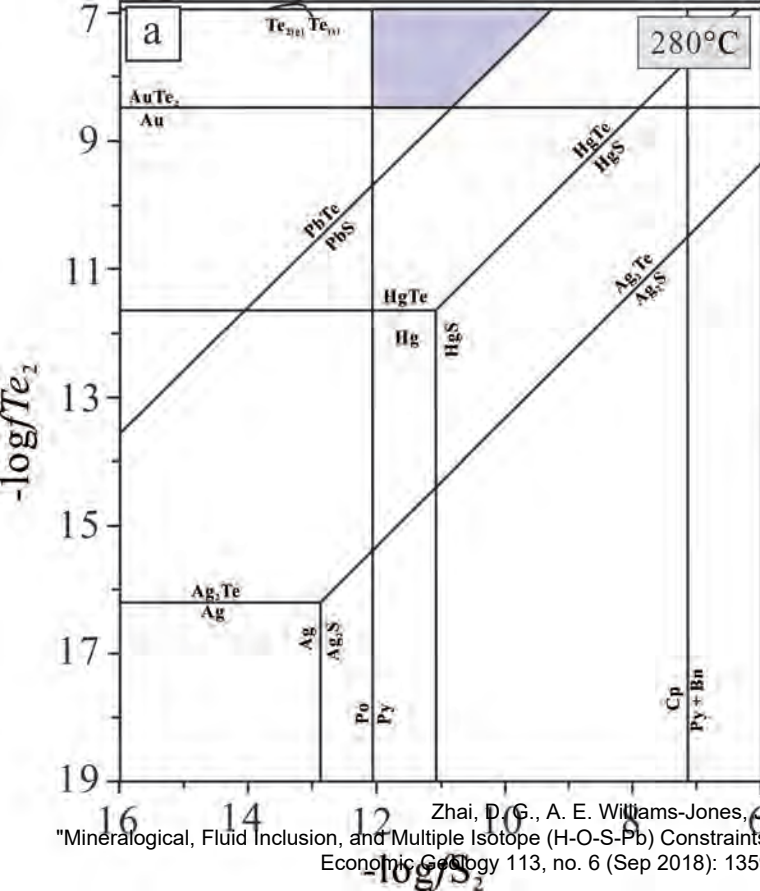


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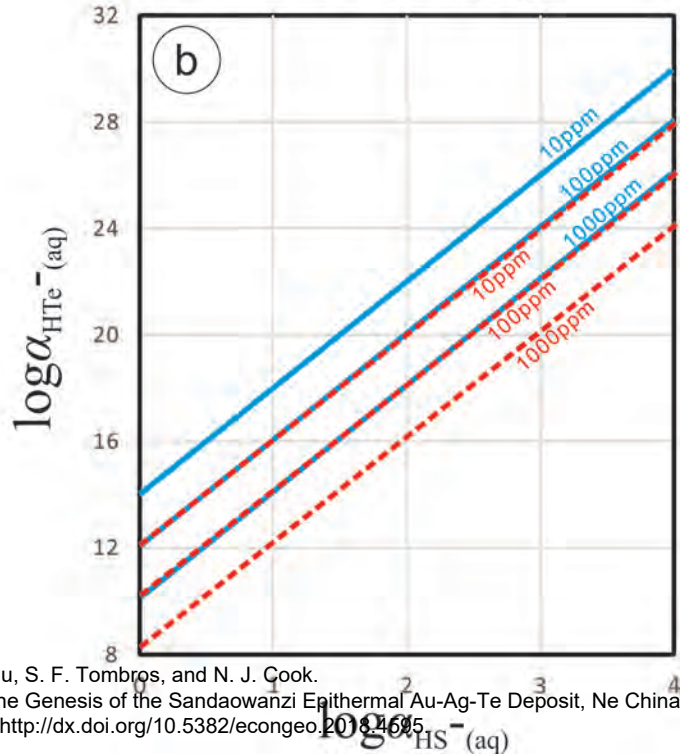
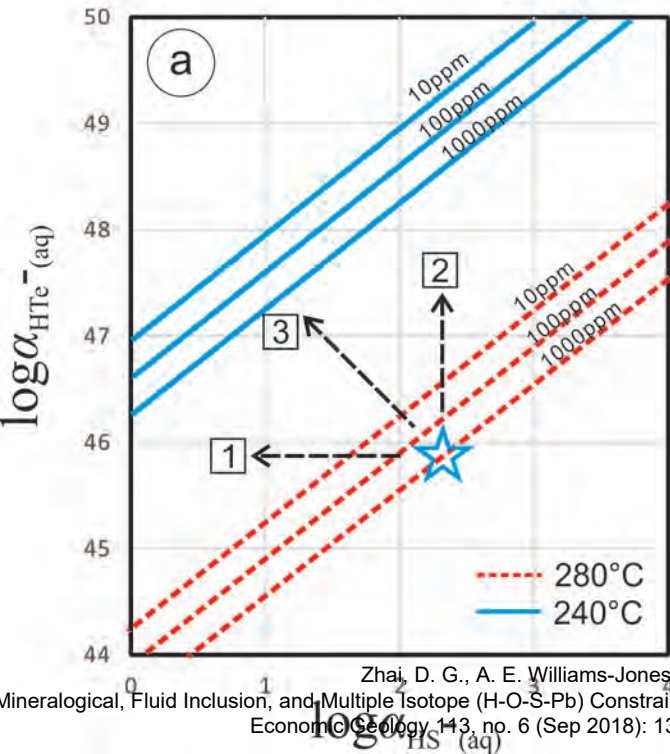


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