1   **Revision 2**

2   **Trace element and isotopic (S, Pb) constraints on the formation of the giant**

3   **Chalukou porphyry Mo deposit, NE China**

4

5   Word Count: 11904

6

7   Qingqing Zhao[1], Degao Zhai[1, 2*], Anthony E. Williams-Jones[2], Jiajun Liu[1]

8

9   *[1]State Key Laboratory of Geological Processes and Mineral Resources, and School of*

10   *Earth Sciences and Resources, China University of Geosciences, Beijing, 100083,*

11   *China*

12   *[2]Department of Earth and Planetary Sciences, McGill University, Quebec, 3450,*

13   *Canada*

14

15

16   *E-mail: dgzhai@cugb.edu.cn*

17

18

22

23   **ABSTRACT**

24   Porphyry type Mo deposits have supplied most of the Mo to the world. However,

25   the source of the Mo and the controls on its enrichment in such deposits is still a

26   matter of great debate. In this study, we present in situ trace element and isotopic data

27   for a giant porphyry Mo deposit (the Chalukou Mo deposit in NE China) and use

28   these data to address these issues. Three primary paragenetic stages of mineralization

29   were recognized at Chalukou: (I) K-feldspar + quartz + minor pyrite (Py-I) + minor

30   molybdenite (Mol-I); (II) quartz + sericite + molybdenite (Mol-II) + pyrite (Py-II);

31   (III) quartz + chlorite + epidote + fluorite + pyrite (Py-III) + galena + sphalerite +

32   minor chalcopyrite. The bulk of the molybdenite was deposited in Stage II. In situ S

33   isotope analyses of the sulfide ores show that the $\delta^{34}S$ values vary from -5.2 to +7.8‰

34   (mean = +2.9‰), and correspond to $\delta^{34}S_{H2S}$ values from -2.4 to +3.3‰ (mean =

35   +1.1‰). These values are consistent with a magmatic source for the sulfur. In situ Pb

36   isotope compositions of the sulfide ores are almost identical to those of the local

37   Mesozoic granites and other magmatic-hydrothermal ore deposits in this region,

38   suggesting a close genetic association between the Mo mineralization and felsic

39   magmatism.

40   Pyrite from the three stages of mineralization differs significantly in its trace

41   element composition. The first generation, Py-I, has a high Cu content (8.7 ± 49.6

42   ppm; where the first value is the median and the second is the standard deviation) and

43   Mo content (6.9 ± 3.8 ppm). Pyrite-II has the lowest Cu concentration (1.3 ± 2.1 ppm)

44   and a relatively high Mo concentration (5 ± 128 ppm), and Py-III has a high Cu

2

45   content (8.7 ± 37.1 ppm) but the lowest Mo content (0.05 ± 5.7 ppm). From this, we

46   infer that pyrite recorded the chemical evolution in the Mo/Cu ratio of the ore fluid,

47   and that this ratio reached a maximum in Stage II, coinciding with the widespread

48   saturation of the fluid in molybdenite. The evolution of the Mo/Cu ratio in pyrite

49   implies that the fluid was undersaturated in chalcopyrite at the high temperature of

50   Stage I, despite the Cu concentration of the fluid apparently being at its high level,

51   and chalcopyrite only saturated later, at lower temperature. Molybdenite, however,

52   because of its lower solubility, saturated early (Stage I), and in the subsequent stage

53   (Stage II) was supersaturated in the fluid.

54   There is a significant enrichment of Mo in the syn-ore intrusions at Chalukou

55   compared to the pre-ore monzogranite. The very low Sr/Y ratios for the Chalukou

56   syn-ore intrusions, which are in sharp contrast to the high Sr/Y ratios of the pre-ore

57   monzogranite and those of porphyries related to Cu deposits, suggest that fractional

58   crystallization of plagioclase may have been a key factor in generating the syn-ore

59   magmas. Molybdenum is a highly incompatible metal and will concentrate in the

60   crust, and assimilation of old continental crust, therefore, may explain the Mo

61   enrichment of the syn-ore intrusions and ultimately the formation of the giant

62   Chalukou deposit.

63   **Keywords:** Sulfur and lead isotopes, trace element chemistry, porphyry Mo deposits,

64   magma and fluid evolution, metal source and enrichment

65

66   **INTRODUCTION**

3

67   The genesis of porphyry type deposits has been a subject of debate since their

68   discovery (Camus 1975; Carten et al. 1988; Clark et al. 1990; Mathur et al. 2000;

69   Sillitoe 2010; Richards 2003, 2011; Lee and Tang 2020). Much of this debate has

70   centered on the sources of the ore metals and the processes of enrichment, particularly

71   for the giant deposits (Audétat et al. 2000; Chiaradia 2013; Lee et al. 2012; Chang et

72   al. 2018; McFall et al., 2019). Early models for the formation of porphyry deposits

73   focused on processes relating to subduction (Clark et al. 1990; Blevin 2002; Richards

74   2003, 2011; Olson et al. 2017), but as some porphyry deposits form in post-collisional

75   settings, it has become clear that their genesis needs to be viewed through a wider lens

76   (Hou et al. 2015; Yang et al. 2015; Yang and Cooke 2019; Xu et al. 2021). Whether

77   porphyry-type deposits emplaced in different tectonic settings have different metal

78   sources is a point of contention (Zheng et al. 2019). Some studies of porphyry Cu

79   deposits have suggested that the Cu is derived from a mixture of oceanic crust and

80   mantle during subduction (Zhou et al. 2015). Others have concluded that, in arc

81   magmas, there is a negative correlation between crustal thickness and copper content

82   (Chiaradia 2013), which suggests that the required Cu may come from the deep

83   continental crust (Sillitoe 2010). It is thought, however, that in the unusually

84   well-endowed Colorado and Qinling Mo porphyry districts a large proportion of the

85   molybdenum came from recycling of ancient continental crust (Carten et al. 1993;

86   Mao et al. 2011).

87   The Great Hingan Range metallogenic belt, which lies in the eastern part of the

88   Central Asian orogenic belt (CAOB), hosts numerous porphyry Mo (-Cu), skarn Fe,

89   epithermal Au-Ag and polymetallic (Ag-Pb-Zn) vein deposits (Chen et al. 2012, 2017;

90   Zhai et al. 2014, 2017, 2019, 2020; Shu et al. 2016; Gao et al. 2016; Xing et al. 2020).

91   More than 80 Mo deposits have been discovered in northeast China (e.g., Chen et al.

92   2017; Xing et al. 2020), and among them, the Chalukou deposit is the largest

93   (reserves of 2.46 Mt @ 0.087 wt.% Mo; Zhao et al. 2021a). Previous studies have

94   discussed the deposit geology and its tectonic setting (Jin et al. 2014), the age of the

95   mineralization (Nie et al. 2011; Liu et al. 2014b; Zhang and Li 2017; Zhao et al.

96   2021a), the bulk rock geochemical and Sr-Nd-Hf isotope compositions (Li et al. 2014;

97   Liu et al. 2015a; Liu et al. 2017; Duan et al. 2018), the fluid inclusion characteristics

98   and the H-O-S-Pb isotope data (Liu et al. 2014a; Li et al. 2019). These studies have

99   concluded that the Chalukou deposit was the product of hydrothermal processes

100   related to a set of highly-fractionated magmatic rocks, including monzogranite,

101   granite porphyry, fine-grained porphyry and quartz porphyry, during the subduction of

102   the Mongol-Okhotsk Ocean (Nie et al. 2011; Li et al. 2014; Liu et al. 2017). Issues

103   relating to metal source and the processes of metal enrichment, however, have not

104   been fully addressed. Whether the Mo was supplied by old continental crust, as in the

105   Colorado and Qinling metallogenic belts, or a thickened lower crust enriched by

106   intracrustal magmatic processes in a subduction zone remains unresolved.

107   In this paper, we report results of a detailed study of the in situ trace element and

108   sulfur and lead isotopic composition of three generations of pyrite and molybdenite in

109   the Chalukou Mo deposit, and use them to determine the metal source, reconstruct

110   aspects of the fluid evolution and gain insight into the Mo enrichment process. The

5

111 new results indicate that in situ compositional (including isotopes and trace elements)

112 analyses of sulfides can provide valuable information on the environment of origin

113 and chemical evolution (including metal ratios) of the ore fluid.

REGIONAL GEOLOGY

115 The Chalukou porphyry Mo deposit is located in the Heilongjiang province in NE

116 China, and occurs within the Great Hingan Range metallogenic belt, which lies in the

117 eastern part of the CAOB (Fig. 1A). More than 80 Mo deposits have been discovered

118 in this area, with a combined reserve of 11.4 Mt Mo, making NE China one of the

119 World's most important Mo metallogenic provinces (Chen et al. 2017; Xing et al.

120 2020; Shu and Chiaradia 2021).

121 The rocks exposed in the vicinity of the Chalukou deposit comprise a Precambrian

122 basement, Paleozoic volcanic-sedimentary sequences and Mesozoic volcanic rocks

123 (Fig, 1B; Liu et al. 2017). The Precambrian basement has been subdivided into the

124 Xinghuadukou Group and Dawangzi Formation, with the former being composed of

125 migmatite, granulite, biotite-plagioclase gneiss, two-mica schist and marble. Zircon

126 U-Pb analyses provide an age of about 850 Ma for the Xinghuadukou group (Ge et al.

127 2015). This suite is overlain unconformably by greenschist facies quartz-chlorite

128 schist, quartz-biotite schist and minor marble of the Dawangzi Formation (Zhou et al.

129 2011; Liu et al. 2017). The Paleozoic volcano-sedimentary sequences comprise the

130 early Ordovician Tongshan and Duobaoshan Formations and the Devonian to early

131 Carboniferous Niqiuhe, Hongshuiquan and Baoligaomiao Formations (Li et al. 2018).

132   The Ordovician formations consist dominantly of tuffaceous sandstone, siltstone,

133   limestone, andesite, dacite, tuff, minor marble and slate, and were deposited between

134   490 and 470 Ma (Li et al. 2018). These rocks occur mainly in the eastern Hingan

135   Massif. The Devonian to early Carboniferous sedimentary sequences, which mainly

136   comprise sandstone, bioclastic limestone, shale and slate (Wu et al. 2015; Liu et al.

137   2017), are widely distributed from the Erguna block to the Hingan Massif. They are

138   overlain by Mesozoic volcanic rocks composed mainly of andesite, rhyolitic tuff and

139   rhyolitic pyroclastic rocks that are widespread in the region (Fig. 1B).

140   Northeast China is composed of several micro-blocks (Fig. 1B; Chen et al. 2017),

141   i.e., the Erguna, Hingan, Songliao, Lesser Hingan, and Jiamusi blocks. Multiple

142   subduction and collisional events involving these blocks resulted in widespread

143   magmatism (Chen et al. 2017). The Paleo-Asia Ocean that existed between the North

144   China Craton and the Siberian Craton finally closed in the late Permian-early Triassic,

145   leading to the assembly of several microcontinental blocks, i.e., the Lesser Hingan,

146   Jiamusi and Songliao blocks (Johnson et al. 2001; Zeng et al. 2013; Zhao et al. 2021b),

147   and the emplacement of numerous I-type granitoids (Zorin et al. 2001; Chen et al.

148   2017). The first episode of Mo mineralization in this region was during this period,

149   e.g., the emplacement of the Gaogangshan (~250 Ma, Zhang et al. 2017) and

150   Bilugangan (~237 Ma, Tang et al. 2012) porphyry Mo deposits.

151   After the closure of the Paleo-Asia Ocean, NE China gradually transformed into a

152   syn- to post-collisional extensional setting, characterized by the widespread

153   occurrence of Mesozoic S-type granitoids (Jahnson et al. 2001; Wu et al. 2011). The

154   second episode of regional Mo mineralization occurred at this time, and is

155   exemplified by the Wudaoling skarn (~194 Ma, Shi et al. 2012) and Luming porphyry

156   Mo deposit (~177 Ma, Chen et al. 2017). This was followed by the south to

157   southeastward subduction of the Mongol-Okhotsk oceanic plate at ~165 Ma (Wang et

158   al. 2017), which eventually led to the closure of the Mongol-Okhotsk Ocean, the

159   timing of which is still unresolved (Chen et al. 2017). Some researchers consider that

160   the Mongol-Okhotsk Ocean was closed in a scissor-like style from west to east

161   between the mid-Jurassic and early Cretaceous (Fritzell et al. 2016; Chen et al. 2017),

162   and associate this closure with the third regional Mo mineralization event (e.g.,

163   Chalukou, ~147 Ma, Nie et al. 2011, Caosiyao, ~148 Ma, Wang et al. 2017). Other

164   researchers, however, consider the third Mo mineralization event to be a product of

165   the westward subduction of the Paleo-Pacific oceanic plate (Chen et al. 2017 and

166   references therein).

ORE DEPOSIT GEOLOGY

167

168   The Chalukou ore district is 8 km long and 5 km wide, and is divided into the

169   eastern and western exploration zones, which are separated by the Duobukuer River.

170   Exploration has focused mainly on the eastern exploration zone, where the main

171   molybdenum resource is located (Nie et al. 2011).

172   **Local rocks**

173   The tectonostratigraphic sequence exposed in the vicinity of the Chalukou deposit

174   comprises rocks ranging in age from Neoproterozoic to Mesozoic (Fig. 2A; Xiong et

8

175   al. 2015). Neoproterozoic metamorphic rocks of the Dawangzi Formation crop out in

176   the center of the ore district and discontinuously to the northeast. These rocks

177   comprise quartz-chlorite schist, quartz-biotite schist, meta-sandstone, and minor

178   marble; a recent zircon U-Pb analysis of quartz-chlorite schist collected from this

179   formation yielded an age of 684.4 ± 9.5 Ma, which represents the formation age of the

180   protolith (Li et al. 2018). The main hosts to the ores are volcano-sedimentary rocks

181   that have been considered to be part of the thick, late Jurassic Guanghua Formation

182   (Liu et al. 2015a). They comprise tuffs of rhyolitic, dacitic and andesitic composition

183   and are particularly well-exposed in the eastern exploration zone where they have a

184   thickness of > 1500 m. Recent zircon U-Pb data for three drill core samples (rhyolite,

185   dacite and tuff) returned ages ranging from 473.9 ± 3.7 to 470.7 ± 2.4 Ma,

186   constraining their formation to the early Ordovician. These ages coincide with those

187   of the regional Duobaoshan Formation (from 490 Ma to 470 Ma, Li et al. 2018).

188   Widespread late Jurassic to early Cretaceous volcano-sedimentary rocks generated

189   from the eruption of the Jinsong caldera (Li et al. 2014), namely those of the

190   Baiyingaolao Formation, comprise andesite, dacite, rhyolite, breccia, tuff and lava;

191   the tuff breccia yielded a zircon U-Pb age of 135 ± 1 Ma (Nie et al. 2011; Liu et al.

192   2017).

193   **Intrusions**

194   There were three episodes of intrusions in the Chalukou area, i.e., pre-, syn- and

195   post-ore intrusions, as revealed by detailed core logging and cross-cutting

196   relationships (Fig. 2A, B; Liu et al. 2014b). The principal pre-ore intrusion is a

197 monzogranite, which is only observed in drill core at depths > 600 m below the

198 southeast part of the Chalukou deposit and crops out over an area of > 80 km^2 outside

199 the ore district (Fig. 2B). A zircon U-Pb radiometric determination yielded an age for

200 the monzogranite of 166 ± 2 Ma (Liu et al. 2014b; Zhao et al. 2021a).

201   The syn-ore intrusions comprise granite porphyry, quartz porphyry and fine-grained

202 porphyry. The granite porphyry occurs as apophyses or small stocks that intrude the

203 Ordovician volcano-sedimentary rocks and have widths ranging from 3 to 80 m. The

204 quartz porphyry was emplaced in the shallow parts of the deposit as small stocks

205 intruding the Ordovician volcano-sedimentary rocks (~100 m; Fig. 2B), and is

206 compositionally similar to the granite porphyry. A single fine-grained porphyry

207 intruded the Ordovician volcano-sedimentary rocks in the central part of the ore

208 district. This intrusion is only encountered at a depth >600 m (Fig. 2B). Based on

209 zircon U-Pb radiometric determinations, the granite porphyry, quartz porphyry, and

210 fine-grained porphyry are coeval with ages of 152.1 ± 2.2, 148.2 ± 2.2, and 148.1 ±

211 2.6 Ma, respectively (Li et al. 2014, Liu et al. 2014b; Zhang and Li 2017; Duan et al.

212 2018, Zhao et al. 2021a).

213   The post-ore intrusions comprise diorite porphyry and quartz monzonite porphyry,

214 and occur mainly as small dikes (Fig. 2B) that cross-cut the earlier intrusions as well

215 as the Mo orebodies (Li et al. 2014). Zircon from the diorite porphyry and quartz

216 monzonite porphyry yielded U-Pb ages of 132.7 ± 2.5 and 128.4 ± 2.1 Ma,

217 respectively (Li et al. 2014; Liu et al. 2017).

10

Alteration and mineralization types

218

219   The various rock-types exposed in the mine area, including quartz-chlorite schist of

220   the Dawangzi Formation, volcano-sedimentary rocks of the Ordovician Duobaoshan

221   Formation and the Jurassic monzogranite, all experienced intense hydrothermal

222   alteration related to the emplacement of the syn-ore intrusions (granite porphyry,

223   quartz porphyry and fine-grained porphyry). An elliptical alteration zone with a long

224   axis of ~1800 m and a short axis of 400-800 m is observed on the surface, and is

225   characterized by a central silicic core that passes outwards through potassic, phyllic

226   and argillic alteration to propylitic alteration (Fig. 2C; Li et al. 2019). Potassic and

227   phyllic alteration are closely associated with Mo mineralization. Silicification is

228   restricted to the apex of the fine-grained porphyry, where it is spatially associated

229   with unidirectional solidification textures (UST). Only minor disseminated or veinlet

230   Mo mineralization could be observed in this zone (Fig. 3A, B). Potassic alteration

231   developed along the contact between the fine-grained porphyry and Ordovician

232   volcano-sedimentary rocks, and/or between the granite porphyry and Ordovician

233   volcano-sedimentary rocks at depths of >400 m (Jin et al. 2014), in a zone that

234   reaches a width of 1200 m in cross-section. Mineralogically, this zone is identified by

235   the abundance of K-feldspar and quartz (Fig. 3 C, D; Nie et al. 2011; Jin et al. 2014).

236   Phyllic alteration is present mainly in the lower Ordovician volcano-sedimentary

237   rocks and overprinted the earlier potassic alteration (Fig. 3E). It forms a zone

238   measuring 1200 m in length, 300-400 m in width and ~800 m in depth (Liu et al.

239   2017). Phyllic alteration is characterized by the mineral assemblage, quartz + sericite

11

240   + fluorite + pyrite ± molybdenite ± calcite. Abundant sericite is observed as halos

241   (2-10 mm wide) along quartz veins. The argillic alteration is developed irregularly at

242   the margin of the phyllic zone (Liu et al. 2017) and consists of quartz, calcite and

243   pyrite with minor galena, sphalerite and chalcopyrite. Propylitic alteration is observed

244   mainly in the Dawangzi Formation, the lower Ordovician rocks and the monzogranite,

245   and is manifested by the assemblage epidote-chlorite-calcite.

246   The economic mineralization in the Chalukou deposit has been subdivided into a

247   lower Mo mineralized zone and an upper zone of Pb-Zn mineralization (Li et al. 2014;

248   Liu et al. 2014b; Duan et al. 2018). The Pb-Zn mineralization occurs as quartz-sulfide

249   veins in Ordovician volcano-sedimentary rocks and is associated with propylitic and

250   argillic alteration (Jin et al. 2014). This mineralization constitutes a resource of 0.143

251   Mt Pb @ 0.6 wt.% and 0.013 Mt Zn @ 0.3 wt.% (Liu et al. 2017; Duan et al. 2018).

252   The Pb-Zn mineralized veins vary in width from 0.2 to 2 m, occur above the Mo

253   orebodies and locally cross-cut the Mo-bearing veins, indicating a relatively late

254   timing of emplacement (Liu et al. 2014b). The Mo mineralization, most of which

255   occurs as stockwork or veins (Figs. 3 and 4 A-C), is hosted by fine-grained porphyry,

256   granite porphyry, breccia pipes and lower Ordovician volcano-sedimentary rocks. It is

257   zoned vertically in terms of grade from a thin, low-grade (<0.06 wt.% Mo) domain in

258   the upper part of the deposit through a thicker, medium-grade (0.06-0.26 wt.% Mo)

259   intermediate domain, to a thick, high-grade (0.08-0.53 wt.% Mo) domain in the lower

260   part of the deposit (Fig. 2D; Nie et al. 2011; Zhang and Li 2017).

261   **Mineralization stages**

262   The ore minerals in the Chalukou deposit comprise molybdenite, pyrite and minor

263   sphalerite, galena, chalcopyrite and hematite, and the main gangue minerals are quartz,

264   K-feldspar, plagioclase, sericite, fluorite, calcite, epidote and chlorite. Based on

265   cross-cutting relationships among the different vein-types, and the mineral

266   assemblages, the Chalukou mineralization has been subdivided into three ore stages.

267   Stage I mineralization consists of quartz veins and minor disseminated

268   mineralization and is represented by the mineral assemblage quartz + K-feldspar +

269   minor pyrite + minor molybdenite ± magnetite ± hematite ± fluorite. The veins (0.5-2

270   mm) in this stage generally have halos of strong silicification or potassic alteration.

271   Numerous quartz veinlets are observed to cross-cut the USTs that are associated with

272   this stage (Zhao et al. 2021a). Magnetite occurs as subhedral to euhedral grains with

273   obvious growth zones and was replaced by hematite (martite) (Fig. 4D, E). The

274   magnetite and hematite occur as veinlets (Liu et al. 2015a) or irregularly shaped

275   masses in association with quartz. The vein-hosted and disseminated molybdenite

276   (Mol-I) of Stage I occurs as euhedral plate-like crystals (Fig. 5A, B) in potassically

277   altered granite porphyry. The pyrite (Py-I) is in the form of subhedral to euhedral

278   crystals (Figs. 4F, G and 5A, B), and is generally cross-cut and replaced by later

279   molybdenite (Mol-II, Fig. 4F).

280   The main ore stage (Stage II) is composed of mineralized veins and breccias, which

281   contain molybdenite and minor pyrite, accompanied by quartz, K-feldspar, sericite

282   and fluorite. Veins (0.2-5 cm) in this stage can be subdivided into quartz +

283   molybdenite ± fluorite, quartz + K-feldspar + molybdenite (Fig. 3C), quartz + sericite

13

284   + molybdenite ± pyrite and molybdenite-dominant types. Molybdenite (Mol-II)

285   usually occurs along the edges of the quartz + K-feldspar veins, and locally delineates

286   a suture in the vein-center (Fig. 5A, B). These veins are surrounded by sericite halos.

287   In some cases, the vein consists dominantly of molybdenite and contains only minor

288   quartz (Zhao et al. 2021a). The major modes of occurrence of Mol-II are as

289   fine-grained aggregates (Figs. 4F and 5D) and wispy lamellae (Fig. 5 E-G) that vary

290   from 20 to 250 μm in width and 50 to 500 μm in length. These aggregates are

291   associated with pyrite (Py-II), which is coarse-grained, cross-cuts Mol-II or contains

292   inclusions of Mol-II (Fig. 4H).

293   Stage III veins are composed of quartz, pyrite, galena, sphalerite, chlorite, epidote,

294   fluorite and minor chalcopyrite. Pyrite (Py-III) is coarse-grained and is associated

295   with quartz, galena, sphalerite, and fluorite (Fig. 4B, C, J, K). Chalcopyrite is rarely

296   observed and occurs only as inclusions in sphalerite (Fig. 4I). It may also coexist with

297   galena and/or sphalerite and was replaced by pyrite (Liu et al. 2015a). Galena and

298   sphalerite occur at the margins of pyrite crystals (Fig. 4J).

SAMPLES AND ANALYTICAL METHODS

299

300   **In situ trace element analyses**

301   The trace element concentrations of pyrite and molybdenite were analyzed in situ

302   using an Agilent 7500a ICP-MS, equipped with a New Wave 193 nm laser at the State

303   Key Laboratory of Geological Processes and Mineral Resources, China University of

304   Geosciences, Beijing. The laser ablation included a pre-ablation period of 5 s to clean

14

305   the surface of the samples, 20 s for background measurement, and 45 s for signal

306   collection. The repetition rate of the laser was 10 Hz and the spot diameter was 36 μm.

307   The external standard NIST 610 was used for calibration, NIST 612 was used as the

308   monitoring standard and MASS-1 was used as a blind sample. The integration time

309   was 8 ms for ^{57}Fe, ^{63}Cu, ^{66}Zn, 15 ms for ^{51}V, ^{55}Mn, ^{59}Co, ^{60}Ni, ^{71}Ga, 20 ms for ^{82}Se,

310   ^{111}Cd, ^{115}In, ^{116}Sn, ^{121}Sb, ^{205}Tl, ^{209}Bi, 30 ms for ^{75}As, ^{95}Mo, ^{182}W, ^{208}Pb, ^{238}U, and 80

311   ms for ^{107}Ag, ^{197}Au and other elements. Details of the analytical method can be found

312   in Zhang et al. (2019).

In situ sulfur and lead isotope analyses

314   In situ sulfur and lead isotopic analyses of sulfides (molybdenite, pyrite, galena and

315   sphalerite) were carried out at the State Key Laboratory of Continental Dynamics,

316   Northwest University, China. Detailed descriptions of the methods employed in the

317   analyses can be found in Yuan et al. (2017). The sulfur isotopic measurements were

318   made using a Nu Plasma 1700 MC-ICP-MS (Nu instruments, UK) coupled to a

319   RESOlution M-50 laser ablation system (ASI, Australia) equipped with a 193 nm ArF

320   CompexPro102 excimer laser (Coherent, USA). A spot size of 37 μm was adopted

321   with a laser repetition rate of 3-4 Hz and an energy density of 3.5-4.0 J/cm^2. Each

322   sample acquisition consisted of background collection for 30 s, followed by ablation

323   signal collection for 50 s. A standard-sample bracketing method was used to correct

324   the mass discrimination and instrumental drift. The external standards for sphalerite,

325   pyrite and galena were NIST NBS123, PY-4, and CBI-3, respectively. The analytical

326   precision calculated from replicate analyses of unknown samples was better than 0.2‰

15

327 (1σ). In situ lead isotopic analyses were conducted with a Nu Plasma II MC-ICP-MS

328 instrument (Nu Instruments, UK) coupled to a 266 nm NWR UP Femto laser ablation

329 system (ESI, USA). The laser ablation employed a spot size of 15 μm for galena and

330 50 μm for pyrite and molybdenite, a maximum energy density of 6 J/cm^2, and a laser

331 frequency of 5-50 Hz. A NIST SRM 997 Tl dry aerosol (50 ng/g, $^{205}Tl/^{203}Tl = 2.3889$)

332 standard was used in conjunction with the standard-sample bracketing method to

333 correct for the mass discrimination of the mass spectrometer. Repeated analyses of the

334 NIST SRM 610 glass standard yielded reproducible results with mean $^{206}Pb/^{204}Pb$,

335 $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios of 17.052 ± 0.003, 15.515 ± 0.003 and 36.980 ±

336 0.007 (1σ, n = 183), respectively.

337 **Whole-rock lead isotope analyses**

338 Whole-rock lead isotope analyses of the intrusive rocks were conducted at the

339 Beijing Research Institute of Uranium Geology, China National Nuclear Corporation.

340 The samples were cleaned in deionized water and leached in hot 6 N HCl for 15 to 20

341 minutes. Then, the samples were dissolved using HF and $HClO_4$, and treated with a

342 basic anion exchange resin to purify Pb. The Pb isotopes were measured by thermal

343 ionization mass spectrometry using a mass spectrometer (Thermo Finnigan); the

344 measurement accuracy was better than 0.005%. The measured Pb isotope ratios of the

345 Pb standard reference NBS 981 were $^{206}Pb/^{204}Pb = 16.937 ± 0.002$, $^{207}Pb/^{204}Pb =$

346 $15.457 ± 0.002$ and $^{208}Pb/^{204}Pb = 36.611 ± 0.004$, respectively, and are consistent with

347 the reference values (Todt et al. 1993).

348   **RESULTS**

349   **Trace elements**

350   Molybdenite samples from the Chalukou deposit have highly variable trace element

351   concentrations (Table 1; Fig. 6). However, the concentrations are generally lower in

352   Mol-I than in Mol-II (Fig. 6). The median concentrations of V, Cu, Zn, Ag, Sb, and W

353   in Mol-I are < 10 ppm, but the concentrations of some of these metals can range to

354   very high values, e.g., Zn (1250 ppm) (Table 1; Fig. 6), due to the presence of

355   sub-microscopic inclusions. Compared to Mol-I, Mol-II is enriched in almost all the

356   metals analyzed and the median concentrations of V, Cu, Zn, Ag, Sb and W in Mol-II

357   are all over 10 ppm. The median content of Ti in Mol-II is 312 ppm. There is a strong

358   correlation of Ti with Fe. Analysis of some Mol-II crystals yielded anomalously high

359   Ti contents (Fig. 7A), due probably to the presence of submicroscopic ilmenite and/or

360   rutile inclusions.

361   Both Mol-I and Mol-II have high concentrations of Fe and Pb with median values

362   of 894, 7570 ppm and 269, 4519 ppm, respectively (Table 1). The Co and Ni contents

363   of Mol-I and Mol-II are relatively low, with median values of 0.2, 1.9 ppm and 3.8,

364   4.4 ppm, respectively. Though Mol-II contains slightly more Co and Ni than Mol-I,

365   both have a Co/Ni ratio <1. There are strong correlations (Fig. 7 B-E) between Fe and

366   Cu ($R^2 = 0.77$), Bi and Pb ($R^2 = 0.97$), Bi and Ag ($R^2 = 0.74$), W and As ($R^2 = 0.73$),

367   and a weak correlation between Sb and Au ($R^2 = 0.35$; Fig. 7F).

368   Trace element concentrations in pyrite are variable and lower than in molybdenite

369   (Table 1; Figs. 8, 9). There is a progressive decrease in the contents of Ti, Mn, Zn, Cd,

370   Sn and W from Py-I through Py-II, to Py-III (Fig. 8). The Cu content decreases from a

371   median of 8.7 ppm in Py-I, to a median of 1.3 ppm in Py-II but increases in Py-III to a

372   median of 8.7 ppm. The Py-I samples have the highest Mo contents (6.9 ± 3.8 ppm,

373   where the first value is the median and the second value is the standard deviation,

374   S.D.; Table 1). The Py-II samples have a relatively high Mo content (5.0 ± 128.1 ppm)

375   and the lowest Cu content (1.3 ± 2.1 ppm) of the three pyrite types, whereas the Py-III

376   sample is generally enriched in Cu (8.7 ± 37.1 ppm) and extremely depleted in Mo

377   (0.05 ± 5.7 ppm) (Table 1; Fig. 8).

378   There are good correlations among Pb, Ag and Bi (Fig. 9A, B) and weaker

379   correlations among Zn, Ti and Mn (Fig. 9C, D). Most elements (e.g., As, Co, Ni and

380   Se, Fig. 10A) show relatively smooth curves in the time-resolved depth profiles. For

381   Pb, Ag and Bi, the spikes could be found in the time-resolved depth profiles of sample

382   C142Q2-3 (Fig. 10B). Samples of Py-I and Py-II have relatively high Co (median

383   values of 12 and 10 ppm, respectively) and Ni (median values of 19 and 5 ppm,

384   respectively) concentrations, and Co/Ni ratios ranging between 0.04 and 7.71 (Fig.

385   9E). The Py-III samples, however, have much lower Co (median = 0.2 ppm) and Ni

386   (median = 0.6 ppm) contents than Py-I and Py-II, and the Co/Ni ratios are all < 1 (Fig.

387   9E).

388   **Sulfur and lead isotope ratios**

389   The results of the in situ sulfur isotope analyses are reported in Table 2 and

390   illustrated in Figure 11A. The full dataset has $\delta^{34}S_{V\text{-}CDT}$ values in the range from -5.2

391   to +7.8‰; the mean is +2.9‰. The molybdenite is characterized by relatively high

392      $\delta^{34}S$ values (+4.2 to +7.8‰) compared to the other sulfides. The 17 spots for Py-I,

393   Py-II and Py-III all yielded similar values, which range from +3.2 to +4.2‰ (mean =

394   3.7‰), +1.4 to +2.5‰ (mean = 2.1‰) and +1.1 to +4.6‰ (mean = 3.0‰),

395   respectively. Within single pyrite crystals, there is a small but significant $\delta^{34}S$

396   variation from +1.1 to +3.3‰; the cores have typically ~2‰ isotopically heavier

397   values than mantles (Fig. 11A). The sphalerite yielded $\delta^{34}S$ values of +0.2 to +2.4‰.

398   Two spots for galena returned $\delta^{34}S$ values of -5.2 and -5.0‰.

399   The lead isotope compositions of the sulfides are reported in Table 3 and illustrated

400   in Figure 12. The $^{206}Pb/^{204}Pb$ ratios vary from 18.274 to 18.386, $^{207}Pb/^{204}Pb$ from

401   15.518 to 15.597, and $^{208}Pb/^{204}Pb$ from 38.097 to 38.308. Significantly, the sulfides

402   from Stages I and II (Mol-I, Mol-II, Py-I and Py-II) contain more radiogenic lead than

403   the Stage III sulfides (i.e., Py-III, galena and sphalerite).

404   **Whole-rock lead isotope ratios**

405   The whole rock Pb isotope compositions of the syn-ore (granite porphyry, quartz

406   porphyry and fine-grained porphyry) intrusions are similar, with $^{206}Pb/^{204}Pb$,

407      $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ values of 18.442-18.570, 15.549-15.591, and

408   38.323-38.482, respectively (Table 4; Fig. 12). These values are also similar to those

409   of sulfides, especially the ratios of $^{207}Pb/^{204}Pb$, which completely overlap with sulfides

410   in the Chalukou deposit.

<div align="center">

DISCUSSION

</div>

411

412   **Sulfur and lead sources**

413   **Sulfur sources**. As reported above, the sulfur isotope compositions of the Chalukou

414   sulfides have $\delta^{34}S$ values ranging from -5.2 to +7.8‰, which decrease in the order

415   molybdenite, pyrite, sphalerite and galena (Fig. 11A; Table 2). In order to calculate

416   the corresponding $\delta^{34}S$ for H_2S in equilibrium with each sulfide, we used the

417   homogenization temperatures of fluid inclusions from previous studies, which are 320

418   to 480 °C for the early quartz + K-feldspar stage, 260 to 410 °C for the

419   quartz-molybdenite   stage,   and   200   to   250   °C   for   the   late

420   quartz-pyrite-galena-sphalerite stage (Liu et al. 2014a; Li et al. 2019). The

421   corresponding range and mean $\delta^{34}S_{H2S}$ values of the different stages are from +2.3 to

422   +3.3‰ (mean = 2.8‰; T= 400°C) for Stage I, from +0.4 to +1.5‰ (mean = 1.1‰; T=

423   350°C) for Stage II, and from -2.7 to +2.8‰ (mean = 0.8‰; T= 225°C) for Stage III.

424   The narrow range of $\delta^{34}S_{H2S}$ values centered on 0‰ (-2.7 to +3.3‰, mean = 1.0‰)

425   indicates a magmatic sulfur source (Seal 2006). However, the sulfur isotope

426   fractionation of over 6‰ between coexisting galena and sphalerite in Stage III implies

427   a temperature of 101 °C, which is much lower than the homogenization temperature

428   described above, indicating that the two minerals were not in isotopic equilibrium

429   (Seal 2006).

430   The $\delta^{34}S_{H2S}$ values for Chalukou are similar to those reported for other

431   magmatic-hydrothermal ore deposits in the region (Appendix Table A1; Ma 1984;

<div align="center">20</div>

432   Zhao et al. 2016), e.g., the Daheishan porphyry Mo deposit (-0.8 to +3.0‰; Hu et al.

433   2014), the Badaguan porphyry Cu-Mo deposit (-1.8 to +2.4‰; Mi et al. 2017; Hou

434   2014; Kang 2015; Gao et al. 2016), and the Wunugetushan porphyry Cu-Mo deposit

435   (-0.1 to +2.8‰; Chen et al. 2011; Zhang et al. 2016). All of these deposits are close to

436   the Derbugan fault, which is the boundary between the Erguna block and the Hingan

437   block and the locus of a large number of Mesozoic granites (Fig. 1B). In contrast,

438    $\delta^{34}S_{H2S}$ values for deposits in the Duobaoshan ore district, which is located to the east

439   of the Derbugan fault area and characterized by widely distributed Paleozoic rocks

440   (Fig.1B), are generally negative (Fig. 11B), e.g., the Zhengguang gold deposit (-14.2

441   to +1.6‰; Fu et al. 2014; Gao et al. 2017), the Tongshan Cu deposit (-1.1 to -0.2‰;

442   Liu et al. 2015b), the Sankuanggou skarn Fe-Cu deposit (-4.5 to -0.5‰; Deng et al.

443   2018), and the Duobaoshan porphyry Cu deposit (-3.2 to -0.5‰; Fu et al. 2014).

444   However, some deposits in the Duobaoshan ore district also have positive $\delta^{34}S_{H2S}$

445   values, e.g., the Yongxin gold deposit (+2 to +3.9‰; Yuan et al. 2018).

446   The above observations indicate that there are differences in the sulfur isotope

447   composition of the fluids forming deposits close to the Derbugan fault and those in

448   the Duobaoshan ore district, although all the deposits in both regions are of

449   magmatic-hydrothermal origin. Moreover, the sulfur isotope values are independent

450   of the ore deposit type, and mineral paragenesis (Chen et al. 2011; Hu et al. 2014; Mi

451   et al. 2017; Yuan et al. 2018). Geologically, the two regions differ significantly.

452   Whereas Paleozoic sedimentary strata are common in the Duobaoshan district,

453   Mesozoic volcanics and granites are dominant in the Derbugan fault area (Fig. 1B).

21

454   Furthermore, sulfur isotope data for the Palaeozoic sedimentary rocks in this area

455   show that the δ^{34}S values range from -43.8 to -8.5‰ (mean = -35.48‰; Huang et al.

456   2018). We therefore infer that there was a considerable contribution of sulfur from the

457   Paleozoic strata in the Duobaoshan area, leading to negative δ^{34}S$_{H2S}$ values (as low as

458   -14.2‰) in several deposits (e.g., the Zhengguang gold deposit; Fu et al. 2014),

459   whereas the dominance of the Derbugan fault area by igneous rocks ensured that

460   deposits in this area had δ^{34}S$_{H2S}$ values close to zero.

461   **Lead sources.** In order to identify the source of lead and, by extension, the other

462   metals, we have compared the lead isotope compositions of the Chalukou sulfides

463   with those for sulfides from numerous ore deposits in the region, the Mesozoic granite,

464   basalt and trachyte, and the Duobaoshan Formation andesitic tuff (Fig. 12). In general,

465   the in situ lead isotope data are similar to those of previous studies of sulfides using

466   mineral separates at Chalukou and other Mesozoic ore deposits in the region

467   (Appendix Table A2; Guo et al. 2010; Chu et al. 2012; Zhao et al. 2016), all of which

468   plot in a field between the mantle and orogen evolutionary curves (Fig. 12; Zartman

469   and Doe 1981). The Paleozoic deposits, however, tend to have lower ^{208}Pb/^{204}Pb and

470   ^{207}Pb/^{204}Pb ratios at a given value of ^{206}Pb/^{204}Pb, whereas those for the Mesozoic

471   deposits completely overlap the Chalukou data (e.g., Liu et al. 2015b), suggesting that

472   the Chalukou deposit and the other Mesozoic deposits had the same metal source (Hu

473   et al. 2014; Yuan et al. 2018). Moreover, the Pb isotope data for the Chalukou ore

474   minerals are very similar to those for Mesozoic granites in the region (Fig. 12), further

475   indicating a Mesozoic magmatic source for the metals (Hu et al. 2014; Liu et al.

476   2014a, 2015a). It is also important to note that, compared to the Chalukou sulfides,

477   the Pb isotopic data for the Mesozoic basalt and trachyte show distinctly higher

478    $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios (Fig. 12), making these rocks less plausible

479   candidates for significant sources of metals for the Chalukou deposit.

480   **Metal signature of the fluid**

481   **Trace elements in pyrite.** Our results show that the trace element concentrations in

482   pyrite vary widely, underscoring the complexity of the ore-forming fluids (Cook et al.

483   2013; Mavrogonatos et al. 2020). The Mo contents of Py-I (6.9 ± 3.8 ppm) and Py-II

484   (5 ± 128 ppm) are higher than those of Py-III (0.05 ± 5.7 ppm). The highest Mo

485   content was recorded by pyrite in Stage I and was high enough for the fluid to saturate

486   with molybdenite at high temperature (390-480°C; Li et al. 2019). The high solubility

487   of molybdenite at this temperature, however, ensured that its precipitation was limited,

488   thereby explaining the small proportion of molybdenite deposited during this stage.

489   Although the Cu content of pyrite was high in Stage I, the fluid did not saturate with a

490   Cu mineral (e.g., chalcopyrite). We attribute this to the fact that at the relatively high

491   temperature of Stage I, the solubility of copper minerals like chalcopyrite is too high

492   for them to saturate in the fluid (Landtwing et al. 2005; Williams-Jones and Migdisov

493   2014). The Mo content of Py-II is slightly lower than that of Py-I, but was high

494   enough in the corresponding fluid for molybdenite to have been strongly

495   oversaturated and deposit the bulk of the molybdenite in Stage II (Fig. 13). This

496   reflects the fact that with decreasing temperature, the solubility of molybdenite

497   decreases sharply (Williams-Jones and Migdisov 2014). The low content of Cu in

23

498   pyrite of Stage II is consistent with the observation that the fluid did not saturate with

499   a Cu-bearing sulfide during this stage. The Mo/Cu ratio recorded by pyrite reached its

500   maximum in Stage II. By Stage III, however, the combination of a sharply higher Cu

501   content in the fluid and lower temperature allowed the fluid to saturate with

502   chalcopyrite. The extremely low Mo content in Py-III precluded precipitation of

503   molybdenite and the Mo/Cu ratio of the ore fluid reached its minimum (Fig. 9F).

504   From the observations discussed above, we conclude that pyrite recorded the chemical

505   evolution in the Mo/Cu ratio of the ore fluid, and that, in reaching its maximum

506   Mo/Cu ratio in Stage II, pyrite recorded the onset of main stage of molybdenite

507   deposition. We also conclude that the absolute content of metal in the fluid is not the

508   key factor affecting metal precipitation, but that ore mineral saturation controlled by

509   the system temperature is the real key.

510   **Trace elements in molybdenite.** Several studies have investigated the uptake of

511   trace elements by molybdenite and its use in predicting the trace element signature of

512   ore fluids (e.g., Ciobanu et al. 2013; Huang et al. 2014; Ren et al. 2018; McFall et al.

513   2019). Molybdenum is present in molybdenite as Mo^{4+}, which has a large ionic radius

514   that, together with its high charge, makes it difficult for trace metals such as Fe, Cu,

515   Zn, As, Pb, Co and Ni to substitute for it in concentrations of more than a few tens of

516   ppm (Ren et al. 2018). Because of the relatively high crystallization temperature of

517   molybdenite, the trace element composition of molybdenite could be, nevertheless,

518   important in recording the signature of the mineralizing fluid (Huang et al. 2014).

519   The trace element contents of Mol-I and Mol-II in the Chalukou deposit are clearly

520   different. Whereas Mol-I contains up to several hundred ppm of Ti, Mn, Fe, Pb and

521   several tens of ppm of Cu, As, Se, Ag, Sn, and Bi (Fig. 6), Mol-II contains thousands

522   of ppm of Ti, Fe, and Pb, and concentrations of several other trace metals are in the

523   range of tens to hundreds of ppm (Fig. 6). The observation that Mol-II is more

524   enriched in trace metals than Mol-I is consistent with greater metal enrichment in the

525   ore fluid in Stage II compared to Stage I. Given that the bulk of the molybdenite was

526   deposited in Stage II, the high metal content of Mol-II is an important signature of the

527   mineralizing fluid at Chalukou and potentially at other deposits.

528   **The role of magma Mo content**

529   The mechanism of metal enrichment in giant porphyry deposits has been a

530   contentious issue because of the large amounts of metal required to form these

531   deposits (Audétat et al. 2000, 2008; Richards 2003, 2011; Heinrich 2005; Pettke et al.

532   2010; Hou et al. 2015; Chang et al. 2018). Such large amounts of metal could be

533   extracted from a very large volume of magma with a low metal content, or a smaller

534   volume of magma with a high metal content (Core et al. 2006; Yang et al. 2016).

535   Which of these possibilities reflects reality, however, is still debated (Carten et al.

536   1988; Stern et al. 2007; Audétat 2010). In the case of Cu, the presence of

537   anhydrite-bearing intrusive rocks in the El Teniente Cu-Mo deposit containing >0.5%

538   Cu supports the argument that the source magma was unusually enriched in this metal

539   (Stern et al. 2007). Thus, the availability of a fertile magma (metal enriched) could be

540   an essential step in forming porphyry deposits (Nadeau et al. 2010; Chiaradia 2013).

541   In the case of Mo, which is a highly incompatible element and, thus, is preferentially

542   concentrated in the continental crust, a contribution of metal from this source could

543   lead to a fertile magma and thereby help explain the formation of giant porphyry Mo

544   deposits.

545   Audétat (2010), noting that the Mo content in the initial magma recorded by melt

546   inclusion data is relatively low (5-6 ppm), has argued that the magmas and fluids in

547   mineralized Mo systems are not unusually Mo-rich. Thus, in this model, a large

548   amount of magma would be needed to form a large porphyry Mo deposit. Similar

549   conclusions have been reached by Wang et al. (2014) and Zhang and Audétat (2017).

550   The processes by which metals form giant ore deposits from magmas containing a

551   very low Mo content, however, are still unclear.

552   In principle, the magmas forming the pre-ore monzogranite or those forming the

553   syn-ore intrusions could have been the source of Mo for the Chalukou deposit. The

554   two analyzed samples of monzogranite have Mo contents of 0.2 ppm, which is lower

555   than that of the average upper continental crust (0.8 ppm, Rudnick and Gao 2014). In

556   contrast, the unaltered syn-ore granite porphyry, quartz porphyry and fine-grained

557   porphyry contain 1-68 ppm (median, 18 ppm), 5-110 ppm (median, 9 ppm) and 3-96

558   ppm (median, 25 ppm) Mo, respectively (Li et al. 2014). This enrichment of the

559   syn-ore granites in Mo by a factor of 45 to 125 relative to the pre-ore monzogranite

560   and the extremely low Mo content of the latter makes it extremely unlikely that the

561   pre-ore monzogranite magmas were the source of the Mo for the Chalukou deposit

562   (Fig. 13). Thus, although the Mo content of the magmas forming some giant Mo

563   deposits may have been relatively low (Audétat 2010; Zhang and Audétat 2017), our

26

564   data leave little doubt that the Mo-rich syn-ore magmas at Chalukou were the source

565   of the Mo for this deposit.

566   A feature of the whole-rock geochemical data is the very low Sr/Y ratio (Sr/Y from

567   0.4 to 37; mean, 7) of the Mo-enriched syn-ore intrusions compared to the pre-ore

568   monzogranite (Sr/Y from 14 to 69; mean, 37) (Li et al. 2014; Liu et al. 2015a). This

569   could indicate that the magmas forming the syn-ore intrusions were derived from the

570   magma after an unusually high degree of fractional crystallization of plagioclase.

571   Such fractional crystallization would have greatly reduced the Sr content of the

572   residual magma (Kobylinski et al. 2020), thereby explaining the very low Sr/Y ratios

573   of the syn-ore intrusions. In turn, this could also explain the extremely strong negative

574   Eu anomalies of the syn-ore intrusions. Indeed, according to Li et al. (2014),

575   fractional crystallization of the main rock-forming minerals could have reached up to

576   50%, which could have significantly enriched the residual magma in Mo. However,

577   even considering the very high melt/silicate mineral partition coefficients reported for

578   Mo (35-1080 at 2.61 GPa and 600-800 °C; Bali et al. 2012), the Mo enrichment due

579   to fractional crystallization would only have increased the concentration of Mo in the

580   magma to 0.4 ppm.

581   Although the pre-ore monzogranite and syn-ore intrusions at Chalukou have similar

582   Sr-Nd-Hf isotope compositions, which permit them being genetically related (Liu et al.

583   2015a), the negative initial Hf isotope signature (εHf) of the syn-ore intrusions (-1.4

584   to +0.5) indicates that their magmas assimilated old continental crust, which was not

585   the case for the pre-ore barren monzogranite (+0.9 to +3.0). As Mo is a highly

27

586   incompatible element and, therefore, concentrates in the crust, assimilation of old

587   continental crust likely explains the high Mo concentration of Mo in the syn-ore

588   intrusions (Zhang and Li 2017).

589   **IMPLICATIONS**

590   The trace element chemistry of pyrite and S and Pb isotopic compositions have

591   made it possible to interpret the evolution of hydrothermal fluids during the formation

592   of the Chalukou porphyry Mo deposit. This evolution occurred in three paragenetic

593   stages characterized by distinctive mineral assemblages. The composition of the fluid

594   as recorded by pyrite indicates that the fluids in Stage I and Stage II were enriched in

595   Mo, whereas the fluid in Stage III was highly depleted in Mo. The combination of a

596   relatively high Mo content of the fluid in Stage II (compared to the fluid in Stage III)

597   and lower temperature (compared to Stage I), caused the fluid to be highly

598   oversaturated with respect to molybdenite, and explains why molybdenite was

599   deposited mainly in Stage II. This leads to the conclusion that the absolute content of

600   metal in the ore fluid was not the key factor controlling metallic mineral deposition,

601   and that molybdenite saturation was controlled by the system temperature. Another

602   important conclusion of the study is that magmas that were unusually enriched in Mo

603   due to crustal contamination, and crystallized the syn-ore intrusions, were the most

604   plausible source of Mo for the Chalukou deposit. This shows, contrary to previous

605   studies, that magma fertility (enrichment in Mo) may play an essential role in

606   generating large porphyry Mo deposits. Finally, the study highlights the importance of

607   in situ compositional analyses (including S and Pb isotopes and trace elements) of ore

28

608 sulfides as tools for constraining the origin and chemical evolution of ore fluids that

609 should find widespread application well beyond porphyry Mo ore genesis.

620   **REFERENCES CITED**

621 Audétat, A., Gunther, D., and Heinrich, C.A. (2000) Causes for large-scale metal

622   zonation around mineralized plutons: Fluid inclusion LA-ICP-MS evidence from

623   the Mole Granite, Australia. Economic Geology, 95, 1563–1581.

624 Audétat, A., Pettke, T., Heinrich, C.A., and Bodnar, R.J. (2008) The composition of

625   magmatic-hydrothermal fluids in barren and mineralized intrusions. Economic

626   Geology, 103, 877–908.

627 Audétat, A. (2010) Source and evolution of molybdenum in the porphyry-Mo(-Nb)

628   deposit at Cave Peak, Texas. Journal of Petrology, 51, 1739–1760.

29

629   Bali, E., Keppler, H., and Audétat, A. (2012) The mobility of W and Mo in subduction

630   zone fluids and the Mo-W-Th-U systematics of island arc magmas. Earth and

631   Planetary Science Letters, 351–352, 195–207.

632   Blevin, P.L. (2002) The petrographic and compositional character of variably

633   K-enriched magmatic suites associated with Ordovician porphyry Cu-Au

634   mineralisation in the Lachlan Fold Belt, Australia. Mineralium Deposita, 37, 87–

635   99.

636   Camus, F. (1975) Geology of the El Teniente orebody with emphasis on wallrock

637   alteration. Economic Geology, 70, 1341−1372.

638   Carten, R.B., Geraghty, E.P., Walker, B.M., and Shannon, J.R. (1988) Cyclic

639   development of igneous features and their relationship to high-temperature

640   hydrothermal features in the Henderson porphyry molybdenum deposit,

641   Colorado. Economic Geology, 83, 266–296.

642   Carten, R.B., White, W.H., and Stern, H. (1993) High-grade granite-related

643   molybdenum systems: Classification and origin. Geological Association of

644   Canada - Special Paper, 40, 521–554.

645   Chang, J., Li, J.W., and Audétat, A. (2018) Formation and evolution of multistage

646   magmatic-hydrothermal fluids at the Yulong porphyry Cu-Mo deposit, Eastern

647   Tibet: Insights from LA-ICP-MS analysis of fluid inclusions. Geochimica et

648   Cosmochimica Acta, 232, 181–205.

649   Chen, Z.G., Zhang, L.C., Wan, B., Wu, H.Y., and Cleven, N. (2011) Geochronology

650   and geochemistry of the Wunugetushan porphyry Cu-Mo deposit in NE China,

651   and their geological significance. Ore Geology Reviews, 43, 92–105.

652   Chen, Y.J., Zhang, C., Li, N., Yang, Y.F., and Deng, K. (2012) Geology of the Mo

653   deposits in northeast China. Journal of Jilin University (Earth Science Edition),

654   42, 1224–1268 (in Chinese with English abstract).

655   Chen, Y.J., Zhang, C., Wang, P., Pirajno, F., and Li, N. (2017) The Mo deposits of

656   northeast China: A powerful indicator of tectonic settings and associated

657   evolutionary trends. Ore Geology Reviews, 81, 602–640.

658   Chiaradia, M. (2013) Copper enrichment in arc magmas controlled by overriding

659   plate thickness. Nature Geoscience, 7, 43–46.

660   Chu, S.X., Liu, J.M., Xu, J.H., Wei, H., Chai, H., and Tong, K.Y. (2012) Zircon U-Pb

661   dating, petrogenesis and tectonic significance of the granodiorite in the

662   Sankuanggou skarn Fe-Cu deposit, Heilongjiang Province. Acta Petrologica

663   Sinica, 28, 433–450 (in Chinese with English abstract).

664   Ciobanu, C.L., Cook, N.J., Kelson, C.R., Guerin, R., Kalleske, N., and Danyushevsky,

665   L. (2013) Trace element heterogeneity in molybdenite fingerprints stages of

666   mineralization. Chemical Geology, 347, 175–189.

667   Clark, A.H., Farrar, E., Kontak, D.J., Langridge, R.J., Arenas, M., France, L.J.,

668   McBride, S.L., Woodman, P.I., Wasteneys, H.A., Sandeman, H.A., and Archibald,

669   D.A. (1990) Geologic and geochronologic constraints on the metallogenic

670   evolution of the Andes of southeastern Peru. Economic Geology, 85, 1520–1583.

671   Cook, N.J., Ciobanu, C.L., Meria, D., Silcock, D., and Wade, B. (2013)

672   Arsenopyrite-pyrite association in an orogenic gold ore: Tracing mineralization

673   history from textures and trace elements. Economic Geology, 108, 1273–1283.

674 Core, D.P., Kesler, S.E., and Essene, E.J. (2006) Unusually Cu-rich magmas

675   associated with giant porphyry copper deposits: Evidence from Bingham, Utah.

676   Geology, 34, 41–44.

677 Deng, K., Liu, Q.G., Chen, Y.J., Zhang, C., Zhu, X.F., and Xu, Q.W. (2018)

678   Geochronology geochemistry and Sr-Nd-Pb-Hf isotopes of the Early Jurassic

679   granodiorite from the Sankuanggou intrusion, Heilongjiang Province,

680   Northeastern China: Petrogenesis and geodynamic implications. Lithos, 296–299,

681   113–128.

682 Duan, P.X., Liu, C., Mo, X.X., Deng, D.F., Qin, J.H., Zhang, Y., and Tian, S.P. (2018)

683   Discriminating characters of ore-forming intrusions in the super-large Chalukou

684   porphyry Mo deposit, NE China. Geoscience Frontiers, 9, 1417–1431.

685 Fritzell, E.H., Bull, A.L., and Shephard, G.E. (2016) Closure of the Mongol–Okhotsk

686   Ocean: Insights from seismic tomography and numerical modelling. Earth and

687   Planetary Science Letters, 445, 1–12.

688 Fu, J.J., Zhao, Y.Y., Zeng, H., and Li, Y. (2014) Chronological and isotopic

689   characteristics of Zhengguang gold deposit in Heilongjiang Province, China.

690   Acta Geologica Sinica-English Edition, 88, 718–719.

691 Gao, B.Y., Zhang, L.C., Jin, X.D., Li, W.J., Chen, Z.G., and Zhu, M.T. (2016)

692   Geochronology and geochemistry of the Badaguan porphyry Cu-Mo deposit in

693   Derbugan metallogenic belt of the NE China, and their geological significances.

694   International Journal of Earth Sciences, 105, 507–519.

695 Gao, Y.Z., Xue, C.J., Lv, X.B., Zhao, X.B., Yang, Y.S., and Li, C.C. (2017) Genesis of

696   the Zhengguang gold deposit in the Duobaoshan ore field, Heilongjiang Province,

697   NE China: Constraints from geology, geochronology and S-Pb isotopic

698   compositions. Ore Geology Reviews, 84, 202–217.

699 Ge, W.C., Chen, J.S., Yang, H., Zhao, G.C., Zhang, Y.L., and Tian, D.X. (2015)

700   Tectonic implications of new zircon U-Pb ages for the Xinghuadukou Complex,

701   Erguna Massif, northern Great Xing'an Range, NE China. Journal of Asian Earth

702   Sciences, 106, 169–185.

703 Guo, F., Fan, W.M., Gao, X.F., Li, C.W., Miao, L.C., Zhao, L., and Li, H.X. (2010)

704   Sr-Nd-Pb isotope mapping of Mesozoic igneous rocks in NE China: Constraints

705   on tectonic framework and Phanerozoic crustal growth. Lithos, 120, 563–578.

706 Heinrich, C.A. (2005) The physical and chemical evolution of low-salinity magmatic

707   fluids at the porphyry to epithermal transition: A thermodynamic study.

708   Mineralium Deposita, 39, 864–889.

709 Hou, Z.Q., Yang, Z.M., Lu, Y.J., Kemp, A., Zheng, Y.C., Li, Q.Y., Tang, J.X., Yang,

710   Z.S., and Duan, L.F. (2015) A genetic linkage between subduction- and

711   collision-related porphyry Cu deposits in continental collision zones. Geology,

712   43, 247–250.

713 Hou, Z.S. (2014) Ore genesis and tectonic setting of Badaguan copper-molybdenum

714   deposit in Erguna region, Inner Mongolia, 66 p. Master's thesis, Jilin University,

715   Changchun (in Chinese with English abstract).

716 Hu, X.L., Yao, S.Z., He, M.C., Ding, Z.J., Liu, M., Cui, Y.B., and Shen, J. (2014)

717   Sulfur and lead isotopic characteristics of Chalukou and Daheishan porphyry Mo

718   deposits in northern segment of Da Hinggan Mountains. Mineral Deposits, 33,

719   776–784 (in Chinese with English abstract).

720 Huang, F., Wang, D.H., Chen, Y.C., Wang, C.H., Tang, J.X., Chen, Z.H., Wang, L.Q.,

721   Liu, S.B., Li, J.K., Zhang, C.Q., Ying, L.J., Wang, Y.L., Li, L.X., and Li, C.

722   (2014) Trace elements characteristics of molybdenites from endogenous

723   molybdenum deposits in China. Mineral Deposits, 33, 1193–1212 (in Chinese

724   with English abstract).

725 Huang, Q.H., Cheng, H.G., Han, M.X., Jin, X.Y., and Zhou, W.J. (2018) Sulfur

726   isotope characteristics of the late Paleozoic strata in No. D101 well at western

727   Songliao Basin. Joint meetings on the 12th National Congress of the

728   Palaeontological Society of China (PSC) and the 29th Annual Conference of PSC,

729   S11–04 (in Chinese).

730 Jin, L.Y., Qin, K.Z., Meng, Z.J., Li, G.M., Song, G.X., Li, Z.Z., Lv, K.P., Kan, X.S.,

731   and Zhao, C. (2014) Vein features and occurrences in Chalukou giant

732   molybdenum-zinc-lead deposit, northern Great Xing'an Range, and its

733   indications for mineralization. Mineral Deposits, 33, 742–760 (in Chinese with

734   English abstract).

735 Johnson, M.F., Wang, C.Y., and Wang, P. (2001) Continental island from the Upper

736   Silurian (Ludfordian Stage) of Inner Mongolia: Implications for eustasy and

737   paleogeography. Geology, 29, 955–958.

738 Kang, Y.J. (2015) The Ore-forming processes and mineralization of Badaguan

739   porphyry Cu-Mo deposit, Inner Mongolia, 112 p. Master's thesis, Chinese

740   Academy of Geological Sciences, Beijing (in Chinese with English abstract).

741 Kobylinski, C., Hattori, K., Smith, S., and Plouffe, A. (2020) Protracted magmatism

742   and mineralized hydrothermal activity at the Gibraltar porphyry

743   copper-molybdenum deposit, British Columbia. Economic Geology, 115, 1119–

744   1136.

745 Landtwing, M.R., Pettke, T., Halter, W.E., Heinrich, C.A., Redmond, P.B., Einaudi,

746   M.T., and Kunze, K. (2005) Copper deposition during quartz dissolution by

747   cooling magmatic-hydrothermal fluids: The Bingham porphyry. Earth and

748   Planetary Science Letters, 235, 229–243.

749 Lee, C-T.A., Luffi, P., Chin, E.J., Bouchet, R., Dasgupta, R., and Morton, D.M. (2012)

750   Copper systematics in arc magmas and implications for crust-mantle

751   differentiation. Science, 336, 64–68.

752 Lee, C-T.A., and Tang, M. (2020) How to make porphyry copper deposits. Earth and

753   Planetary Science Letters, 529, 115868.

754 Li, Z.Z., Qin, K.Z., Li, G.M., Ishihara, S., Jin, L.Y., Song, G.X., and Meng, Z.J. (2014)

755   Formation of the giant Chalukou porphyry Mo deposit in northern Great Xing'an

756   Range, NE China: Partial melting of the juvenile lower crust in intra-plate

757   extensional environment. Lithos, 202, 138–156.

758 Li, Z.Z., Qin, K.Z., Li, G.M., Jin, L.Y., and Song, G.X. (2018) Neoproterozoic and

759   early Paleozoic magmatic records from the Chalukou ore district, northern Great

760   Xing'an Range, NE China: Implications for tectonic evolution and Mesozoic Mo

35

761   mineralization. Journal of Asian Earth Sciences, 165, 96–113.

762   Li, Z.Z., Qin, K.Z., Li, G.M., Jin, L.Y., and Song, G.X. (2019) Incursion of meteoric

763   water triggers molybdenite precipitation in porphyry Mo deposits: A case study

764   of the Chalukou giant Mo deposit. Ore Geology Reviews, 109, 144–162.

765   Liu, J., Mao, J.W., Wu, G., Wang, F., Luo, D.F., Hu, Y.Q., and Li, T.G. (2014a) Fluid

766   inclusions and H-O-S-Pb isotope systematics of the Chalukou giant porphyry Mo

767   deposit, Heilongjiang Province, China. Ore Geology Reviews, 59, 83–96.

768   Liu, J., Mao, J.W., Wu, G., Wang, F., Luo, D.F., and Hu, Y.Q. (2014b) Zircon U-Pb

769   and molybdenite Re-Os dating of the Chalukou porphyry Mo deposit in the

770   northern Great Xing'an Range, China and its geological significance. Journal of

771   Asian Earth Sciences, 79, 696–709.

772   ——— (2015a) Geochemical signature of the granitoids in the Chalukou giant

773   porphyry Mo deposit in the Heilongjiang Province, NE China. Ore Geology

774   Reviews, 64, 35–52.

775   Liu, J., Zhou, Z.H., He, Z.F., and Ouyang, H.G. (2015b) Zircon U-Pb dating and

776   geochemistry of ore-bearing tonalite in Tongshan copper deposit, Heilongjiang

777   Province. Mineral Deposits, 34, 289–308 (in Chinese with English abstract).

778   Liu, Y.F., Bagas, L., Jiang, S.H., and Wang, F.X. (2017) The Chalukou deposit in the

779   North Great Xing'an Range of China: A protracted porphyry Mo ore-forming

780   system in a long-lived magmatic evolution cycle. Ore Geology Reviews, 89,

781   171–186.

782   Ma, D.Y. (1984) Isotope geology of the Duobaoshan copper ore field. Mineral

36

783   Deposits, 3, 47–57 (in Chinese with English abstract).

784 Mao, J.W., Pirajno, F., Xiang, J.F., Gao, J.J., Ye, H.S., Li, Y.F., and Guo, B.J. (2011)

785   Mesozoic molybdenum deposits in the east Qinling-Dabie orogenic belt:

786   Characteristics and tectonic settings. Ore Geology Reviews, 43, 264–293.

787 Mathur, R., Ruiz, J., Titley, S., Gibbins, S., and Margotomo, W. (2000) Different

788   crustal sources for Au-rich and Au-poor ores of the Grasberg Cu-Au porphyry

789   deposit. Earth and Planetary Science Letters, 183, 7–14.

790 Mavrogonatos, C., Voudouris, P., Zaccarini, F., Klemme, S., Berndt, J., Tarantola, A.,

791   Melfos, V., and Spry, P.G. (2020) Multi-stage introduction of precious and

792   critical metals in pyrite: A case study from the Konos Hill and Pagoni Rachi

793   porphyry/epithermal prospects, NE Greece. Minerals, 10, 784.

794 McFall, K., Roberts, S., McDonald, I., Boyce, A.J., Naden, J., and Teagle, D. (2019)

795   Rhenium enrichment in the Muratdere Cu-Mo (Au-Re) porphyry deposit, Turkey:

796   Evidence from stable isotope analyses (δ^{34}S, δ^{18}O, δD) and laser

797   ablation-inductively coupled plasma-mass spectrometry analysis of sulfides.

798   Economic Geology, 114, 1443–1466.

799 Mi, K.F., Liu, Z.J., Li, C.F., Liu, R.B., Wang, J.P., and Peng, R.M. (2017) Origin of

800   the Badaguan porphyry Cu-Mo deposit, Inner Mongolia, Northeast China:

801   Constraints from geology isotope geochemistry and geochronology. Ore Geology

802   Reviews, 81, 154–172.

803 Nadeau, O., Williams-Jones, A.E., and Stix, J. (2010) Sulphide magma as a source of

804   metals in arc-related magmatic hydrothermal ore fluids. Nature Geoscience, 3,

37

805 501–505.

806 Nie, F.J., Sun, Z.J., Li, C., Liu, Y.F., Lv, K.P., Zhang, K., and Liu, Y. (2011) Re-Os

807   isotopic dating of molybdenite separates from Chalukou porphyry Mo

808   polymetallic deposit in Heilongjiang Province. Mineral Deposits, 30, 828–836

809   (in Chinese with English abstract).

810 Olson, N.H., Dilles, J.H., Kent, A.J.R., and Lang, J.R. (2017) Geochemistry of the

811   Cretaceous Kaskanak Batholith and genesis of the Pebble porphyry Cu-Au-Mo

812   deposit, Southwest Alaska. American Mineralogist, 102, 1597–1621.

813 Pettke, T., Oberli, F., and Heinrich, C.A. (2010) The magma and metal source of giant

814   porphyry-type ore deposits based on lead isotope microanalysis of individual

815   fluid inclusions. Earth and Planetary Science Letters, 296, 267–277.

816 Ren, Z., Zhou, T.F., Hollings, P., White, N.C., Wang, F.Y., and Yuan, F. (2018) Trace

817   element geochemistry of molybdenite from the Shapinggou super-large porphyry

818   Mo deposit, China. Ore Geology Reviews, 95, 1049–1065.

819 Richards, J.P. (2003) Tectono-magmatic precursors for porphyry Cu- (Mo) deposit

820   formation. Economic Geology, 98, 1515–1531.

821 ——— (2011) High Sr/Y arc magmas and porphyry Cu ± Mo ± Au deposits: Just add

822   water. Economic Geology, 106, 1075–1081.

823 Rudnick, R.L., and Gao, S. (2014) Composition of the continental crust. In R.L.

824   Rudnick, Eds., Treatise on geochemistry, 1–51. Elsevier, Amsterdam.

825 Seal, R.R. (2006) Sulfur isotope geochemistry of sulfide minerals. Reviews in

826   Mineralogy and Geochemistry, 61, 633–677.

827   Shi, P.H., Yang, Y.C., Ye, S.Q., and Han, S.J. (2012) Geological and geochemical

828   characteristics and genesis of ferromolybdenum deposit in Wudaoling,

829   Heilongjiang Province. Global Geology, 31, 262–270 (in Chinese with English

830   abstract).

831   Shu, Q.H., Chang, Z.S., Lai, Y., Zhou, Y.T., Sun, Y., and Yan, C. (2016) Regional

832   metallogeny of Mo-bearing deposits in northeastern China with new Re-Os dates

833   of porphyry Mo deposits in the northern Xilamulun district. Economic Geology,

834   111, 1783–1798.

835   Shu, Q.H., and Chiaradia, M. (2021) Mesozoic Mo mineralization in northeastern

836   China did not require reginal-scale pre-enrichment. Economic Geology, 116,

837   1227–1237.

838   Sillitoe, R.H. (2010) Porphyry copper systems. Economic Geology, 105, 3–41.

839   Stern, C.R., Funk, J.A., Skewes, M.A., and Alejandra, A. (2007) Magmatic anhydrite

840   in plutonic rocks at the El Teniente Cu-Mo deposit, Chile, and the role of sulfur-

841   and copper-rich magmas in its formation. Economic Geology, 102, 1335–1344.

842   Tang, W.L., Zeng, W., Ran, H., Zhou, Y., and Sun, W.L. (2012) Geological features

843   and ore prospecting of Biligangan deposit, Abaga, Inner Mongolia. Geological

844   Survey and Research, 35, 161–166 (in Chinese with English abstract).

845   Todt, W., Cliff, R.A., Hanser, A., and Hofmann, A.W. (1993) Recalibration of NBS

846   lead standards using a $^{207}Pb/^{205}$ Pb double spike. Terra Abstracts, 5, 396.

847   Wang, G.G., Ni, P., Yu, W., Chen, H., Jiang, L.L., Wang, B.H., Zhang, H.D., and Li,

848   P.F. (2014) Petrogenesis of Early Cretaceous post-collisional granitoids at

849   Shapinggou, Dabie Orogen: Implications for crustal architecture and porphyry

850   Mo mineralization. Lithos, 184–187, 393–415.

851 Wang, G.R., Wu, G., Xu, L.Q., Li, X.Z., Liu, J., Zhang, T., Quan, Z.X., Wu, H., Li,

852   T.G., and Chen, Y.C. (2017) Molybdenite Re-Os age, H-O-C-S-Pb isotopes and

853   fluid inclusion study of the Caosiyao porphyry Mo deposit in Inner Mongolia,

854   China. Ore Geology Reviews, 81, 728–744.

855 Williams-Jones, A.E., and Migdisov, A.A. (2014) Experimental constraints on the

856   transport and deposition of metals in ore-forming hydrothermal systems. Society

857   of Economic Geologists, Special Publication, 18, 77–95.

858 Wu, F.Y., Sun, D.Y., Ge, W.C., Zhang, Y.B., Grant, M.L., Wilde, S.A., and Jahn, B.M.

859   (2011) Geochronology of the Phanerozoic granitoids in northeastern China.

860   Journal of Asian Earth Sciences, 41, 1–30.

861 Wu, G., Chen, Y.C., Sun, F.Y., Liu, J., Wang, G.R., and Xu, B. (2015) Geochronology

862   geochemistry and Sr-Nd-Hf isotopes of the early Paleozoic igneous rocks in the

863   Duobaoshan area, NE China, and their geological significance. Journal of Asian

864   Earth Sciences, 97, 229–250.

865 Xing, K., Shu, Q., Lentz, D.R., and Wang, F.Y. (2020) Zircon and apatite geochemical

866   constraints on the formation of the Huojihe porphyry Mo deposit in the Lesser

867   Xing'an Range, NE China. American Mineralogist, 105, 382–396.

868 Xiong, S.F., He, M.C., Yao, S.Z., Cui, Y.B., Shi, G.Z., Ding, Z.J., and Hu, X.L. (2015)

869   Fluid evolution of the Chalukou giant Mo deposit in the northern Great Xing'an

870   Range, NE China. Geological Journal, 50, 720–738.

871   Xu, B., Hou, Z.Q., Griffin, W.L., Lu, Y.J., Belousova, E., Xu, J.F., and O'Reilly S.Y.

872   (2021) Recycled volatiles determine fertility of porphyry deposits in collisional

873   settings. American Mineralogist, 106, 656–661.

874   Yang, L.Q., Deng, J., Gao, X., He, W.Y., Meng, J.Y., Santosh, M., Yu, H.J., Yang, Z.,

875   and Wang, D. (2016) Timing of formation and origin of the Tongchanggou

876   porphyry-skarn deposit: Implications for late Cretaceous Mo-Cu metallogenesis

877   in the southern Yidun Terrane, SE Tibetan Plateau. Ore Geology Reviews, 81,

878   1015–1032.

879   Yang, Z.M., Lu, Y.J., Hou, Z.Q., and Chang, Z.S. (2015) High-Mg diorite from

880   Qulong in southern Tibet: Implications for the genesis of adakite-like intrusions

881   and associated porphyry Cu deposits in collisional orogens. Journal of Petrology,

882   56, 227–254.

883   Yang, Z.M., and Cooke, D.R. (2019) Porphyry copper deposits in China. Society of

884   Economic Geologists, Special Publication, 22, 133–187.

885   Yuan, H., Liu, X., Chen, L., Bao, Z., Chen, K., and Zong, C. (2017) Simultaneous

886   measurement of sulfur and lead isotopes in sulfides using nanosecond laser

887   ablation coupled with two multi-collector inductively coupled plasma mass

888   spectrometers. Journal of Asian Earth Sciences, 154, 386–396.

889   Yuan, M.W., Li, S.R., Li, C.L., Santosh, M., Alam, M., and Zeng, Y.J. (2018)

890   Geochemical and isotopic composition of auriferous pyrite from the Yongxin

891   gold deposit, Central Asian Orogenic Belt: Implication for ore genesis. Ore

892   Geology Reviews, 93, 255–267.

41

893   Zartman, R.E., and Doe, B.R. (1981) Plumbotectonics. The model Tectonophysics, 75,

894   135–162.

895   Zeng, Q.D., Liu, J.M., Qin, K.Z., Fan, H.R., Chu, S.X., Wang, Y.B., and Zhou, L.L.

896   (2013) Types characteristics and time-space distribution of molybdenum deposits

897   in China. International Geology Review, 55, 1311–1358.

898   Zhai, D.G., Liu, J.J., Zhang, H.Y., Yao, M.J., Wang, J.P., and Yang, Y.Q. (2014) S-Pb

899   isotopic geochemistry, U-Pb and Re-Os geochronology of the Huanggangliang

900   Fe-Sn deposit, Inner Mongolia, NE China. Ore Geology Reviews, 59, 109–122.

901   Zhai, D.G., Liu, J.J., Zhang, A.L., and Sun, Y.Q. (2017) U-Pb, Re-Os and ^{40}Ar/^{39}Ar

902   geochronology of porphyry Sn ± Cu ± Mo and polymetallic (Ag-Pb-Zn-Cu) vein

903   mineralization at Bianjiadayuan, Inner Mongolia, NE China: Implications for

904   discrete mineralization events. Economic Geology, 112, 2041–2059.

905   Zhai, D.G., Liu, J.J., Cook, N.J., Wang, X.L., Yang, Y.Q., Zhang, A.L., and Jiao, Y.C.

906   (2019) Mineralogical, textural, sulfur and lead isotope constraints on the origin

907   of Ag-Pb-Zn mineralization at Bianjiadayuan, Inner Mongolia, NE China.

908   Mineralium Deposita, 54, 47–66.

909   Zhai, D.G., Williams-Jones, A.E., Liu, J.J., Selby, D., Voudouris, P.C., Tombros, S., Li,

910   K., Li, P.L., and Sun, H.J. (2020) The genesis of the giant Shuangjianzishan

911   epithermal Ag-Pb-Zn deposit, Inner Mongolia, Northeastern China. Economic

912   Geology, 115, 101–128.

913   Zhang, F.F., Wang, Y.H., Liu, J.J., Wang, J.P., Zhao, C.B., and Song, Z.W. (2016)

914   Origin of the Wunugetushan porphyry Cu-Mo deposit, Inner Mongolia, NE

42

915   China: Constraints from geology, geochronology, geochemistry, and isotopic

916   compositions. Journal of Asian Earth Sciences, 117, 208–224.

917 Zhang, C., and Li, N. (2017) Geochronology and zircon Hf isotope geochemistry of

918   granites in the giant Chalukou Mo deposit, NE China: Implications for tectonic

919   setting. Ore Geology Reviews, 81, 780–793.

920 Zhang, D.H., and Audétat, A. (2017) Chemistry mineralogy and crystallization

921   conditions of porphyry Mo-forming magmas at Urad-Henderson and Silver

922   Creek, Colorado, USA. Journal of Petrology, 58, 277–296.

923 Zhang, Y.M., Gu, X.X., Liu, R.P., Sun, X., Li, X.L., and Zheng, L. (2017) Geology,

924   geochronology and geochemistry of the Gaogangshan Mo deposit: A newly

925   discovered Triassic collision-type Mo mineralization in the Lesser Xing'an

926   Range, NE China. Ore Geology Reviews, 81, 672–688.

927 Zhang, H.Y., Su, L., Yang, L.M., Wang, D.C., Hu, X.L., Song, Y.T., and Xiong, L.

928   (2019) Study on LA-ICP-MS determination of trace elements in sulfide minerals.

929   Hans Journal of Chemical Engineering and Technology, 9, 401–409 (in Chinese

930   with English abstract).

931 Zhao, Y., Lv, J.C., Chen, J., Zhang, P., Xu, J., and Bi, Z.W. (2016) Geological and

932   S-Pb geochemical characteristics of Xinzhangfang molybdenum deposit in the

933   northern Greater Khingan Mountains region. Nonferrous Metals, 68, 18–23 (in

934   Chinese with English abstract).

935 Zhao, Q.Q., Zhai, D.G., Mathur, R., Liu, J.J., Selby, D., and Williams-Jones, A.E.

936   (2021a) The giant Chalukou porphyry Mo deposit, Northeast China: The product

937   of a short-lived, high flux mineralizing event. Economic Geology, 116, 1209–

938   1225.

939   Zhao, Q.Q., Zhai, D.G., Wang, J.P., Liu, J.J., and Williams-Jones, A.E. (2021b) The

940   geochemistry and geochronology of Permian granitoids from central Inner

941   Mongolia, NE China: Petrogenesis and tectonic implications. Lithos, 404–405,

942   106489.

943   Zheng, Y.F., Mao, J.W., Chen, Y.J., Sun, W.D., Ni, P., and Yang, X.Y. (2019)

944   Hydrothermal ore deposits in collisional orogens. Science Bulletin, 64, 67–74.

945   Zhou, J.B., Wilde, S.A., Zhang, X.Z., Zhao, G.C., Liu, F.L., Qiao, D.W., Ren, S.M.,

946   and Liu, J.H. (2011) A >1300 km late Pan-African metamorphic belt in NE

947   China: New evidence from the Xing'an block and its tectonic implications.

948   Tectonophysics, 509, 280–292.

949   Zhou, X., Fei, G.C., Zhou, Y., Wen, C.Q., Zhang, Y., and Yue, X.Y. (2015)

950   Chronology and crust-mantle mixing of ore-forming porphyry of the Bangongco:

951   Evidence from zircon U-Pb age and Hf isotopes of the Naruo porphyry

952   copper-gold deposit. Acta Geologica Sinica-English Edition, 89, 217–228.

953   Zorin, Y.A., Zorina, L., and Spiridonov, A.M. (2001) Geodynamic setting of gold

954   deposits in eastern and central Trans–Baikal (Chita Region Russia). Ore Geology

955   Reviews, 17, 215–232.

956

957   **Figure captions**

958   Fig. 1. (A) A schematic map of the Central Asian orogenic belt (CAOB; modified

44

959 from Shu et al. 2016; Zhai et al. 2019); (B) A geological map of the northern Great

960 Hinggan Range showing the locations of major ore deposits (modified from Chen et

961 al. 2017).

962 Fig. 2. (A) A geological map of the Chalukou porphyry Mo deposit (modified from

963 Xiong et al. 2015); (B) A representative cross-section showing the local intrusions,

964 dikes and hydrothermal breccias (modified from Li et al. 2014); (C) A representative

965 cross-section showing the vertical distribution of different hydrothermal alteration

966 zones, and (D) A representative cross-section showing the vertical distribution of

967 Mo-bearing orebodies (modified from Li et al. 2019).

968 Fig. 3 Field and hand-specimen photographs of alteration in the Chalukou deposit. (A

969 and B) Field and hand-specimen photographs of silicic alteration; (C and D)

970 Molybdenite-quartz veins associated with potassic alteration; (E) Phyllic alteration

971 overprinting the earlier potassic alteration.

972 Fig. 4. (A) A photograph showing the stockwork ores; (B and C) The mode of

973 occurrence of molybdenite-pyrite-quartz-fluorite veins; (D) Martite after magnetite;

974 (E) Magnetite replaced by hematite; (F) Molybdenite (Mol-II) cross-cutting

975 early-formed pyrite (Py-I); (G) An early-formed pyrite (Py-I) vein; (H) Molybdenite

976 (Mol-II) cut by a pyrite (Py-II) vein; (I) Sphalerite intergrown with galena, pyrrhotite

977 and pyrite; (J) Pyrite (Py-III) associated with galena and sphalerite; (K) The

978 occurrence of molybdenite (Mol-III) in pyrite interstices.

979 Fig. 5. (A) A hand specimen showing two generations of molybdenite; (B)

45

980   Molybdenite (Mol-I) associated with pyrite (Py-I); (C) A molybdenite-quartz vein; (D)

981   An occurrence of molybdenite (Mol-II) as fine-grained aggregates; (E, F, G) An

982   occurrence of molybdenite (Mol-II) as wispy veinlets.

983   Fig. 6. Box and whisker plots showing the concentrations of trace elements in

984   different molybdenite generations analyzed by LA-ICP-MS.

985   Fig. 7. Binary plots of (A) Fe vs. Ti, (B) Fe vs. Cu, (C) Bi vs. Pb, (D) Bi vs. Ag, (E)

986   W vs. As and (F) Sb vs. Au for different molybdenite generations. Two samples show

987   anomalously high Ti contents (dashed ellipse), due probably to the presence of

988   mineral inclusions (e.g., ilmenite and rutile).

989   Fig. 8. Box and whisker plots showing the concentrations of trace elements in

990   different pyrite generations analyzed by LA-ICP-MS.

991   Fig. 9. Binary plots of (A) Pb vs. Ag, (B) Bi vs. Pb, (C) Mn vs. Zn, (D) Ti vs. Zn, (E)

992   Ni vs. Co and (F) Mo vs. Cu for different pyrite generations. See text for additional

993   explanation.

994   Fig. 10. Representative pyrite samples selected for in situ trace element analyses. (A)

995   Pyrite (Py-II) from stage II (A1 A hand specimen photo of Py-II bearing

996   mineralization; A2 A reflected light image of pyrite showing the spots of a

997   LA-ICP-MS analytical profile; A3 Time-resolved depth profiles of selected elements

998   for the spot shown in A2; A4 Concentrations of selected trace elements along the

999   profile shown in A2); (B) Pyrite (Py-III) from stage III (B1 A hand specimen

1000   photograph of Py-III bearing mineralization; B2 A reflected light image of pyrite

46

1001   showing the spots of a LA-ICP-MS analytical profile; B3 Time-resolved depth

1002   profiles of selected elements for the spot shown in B2; B4 Concentrations of selected

1003   trace elements along the profile shown in B2).

1004   Fig. 11. (A) A histogram of sulfur isotopic compositions ($\delta^{34}S_{V\text{-}CDT}$) for sulfides from

1005   the Chalukou porphyry Mo deposit; (B) A comparison of the sulfur isotopic

1006   compositions ($\delta^{34}S_{H2S}$) of sulfide minerals from deposits in the Derbugan and

1007   Duobaoshan ore fields (data from Ma 1984; Chen et al. 2011; Fu et al. 2014; Hou

1008   2014; Hu et al. 2014; Kang 2015; Liu et al. 2015b; Zhang et al. 2016; Zhao et al. 2016;

1009   Gao et al. 2017; Mi et al. 2017; Yuan et al. 2018).

1010   Fig. 12. Lead isotope compositions of sulfides from the Chalukou porphyry Mo

1011   deposit compared to local early Paleozoic volcano-sedimentary rocks, Mesozoic

1012   granite, basalt and trachyte, and local early Paleozoic to Mesozoic ore deposits (data

1013   from Guo et al. 2010; Chu et al. 2012; Hu et al. 2014; Liu et al. 2015b; Zhao et al.

1014   2016; Gao et al. 2017; Mi et al. 2017; Deng et al. 2018; Yuan et al. 2018). (A)

1015 $^{206}Pb/^{204}Pb$ vs. $^{208}Pb/^{204}Pb$ plots; (B) $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ plots. The arrows in

1016   the inset figures show that Moly-I, Moly-II and Py-II have more radiogenic Pb isotope

1017   compositions than those of the Stage III sulfides. The Pb isotope curves for the mantle,

1018   orogen, and crust were taken from Zartman and Doe (1981).

1019   Fig. 13. A summary plot showing bulk igneous rock Mo concentrations as well as Mo

1020   concentrations in different pyrite generations; The Mo contents of local intrusions are

1021   from Li et al. (2014) and Liu et al. (2015a) and the Mo contents of the sulfides are

1022   from this study. Spot with anomaly high element content (pink dotted line) is

1023   excluded.

1024

1025   Table 1. In situ trace element compositions of sulfides from the Chalukou porphyry

1026   Mo deposit

1027   Table 2. In situ sulfur isotopic compositions of sulfides from the Chalukou porphyry

1028   Mo deposit

1029   Table 3. In situ lead isotopic compositions of sulfides from the Chalukou porphyry

1030   Mo deposit

1031   Table 4. Whole rock lead isotopic compositions of intrusions from the Chalukou

1032   porphyry Mo deposit

1033

1034   Appendix Table 1A. S isotope data of sulfides from ore deposits in NE China

1035   Appendix Table 2A. Pb isotope data of sulfides from local ore deposits, Mesozoic

1036   granite, basalt, tracyte, and Duobaoshan Formation volcano-sedimentary rocks in NE

1037   China

1038

Table 1. In situ trace element compositions of sulfides from the Chalukou porphyry Mo deposit

Element (ppm)	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Ag	Cd	Sn	Sb	W	Pb	Bi
Mol-I (n=6)																		
Max	152	31.8	88	296	4555	0.3	6.8	40.9	1250	6.6	70	22.5	54.9	20.6	3.2	207	424	106
Min	85	3.3	26.2	16	517	0.1	1.0	2.9	2.8	1.4	55	0.6	48.7	11.2	0.3	1.7	45	7
Mean	114	11.8	40.3	101	1570	0.2	3.8	18.1	217.1	3.4	63	8.4	51.5	13.3	1.3	53.8	261	55
Median	113	4.2	30.1	72	894	0.2	3.8	9.8	6.4	2.4	64	3.4	51.2	12	0.7	3	269	46
S.D.	28	12.8	23.8	109	1530	0.1	2.3	16.4	506.2	2.2	7	9.1	2.2	3.6	1.3	85.6	130	39
Mol-II (n=7)																		
Max	34247	103	308	560	11462	19	50	393	133	162	542	181	122	250	30.6	586	6041	1309
Min	187	6.2	37.5	67	1655	0.8	2.4	22.1	8.0	16.4	52	7.1	94.4	17.0	3.4	24.7	1239	159
Mean	5482	58.3	119.5	248	7298	4.4	11.3	153.1	37.3	105.2	143	90.1	104.1	70.4	21.7	321.5	4535	892
Median	312	59.9	74.9	233	7570	1.9	4.4	119	25.5	119.8	78	77.5	101.5	33.8	25.7	348.9	4519	910
S.D.	12718	29.6	97.3	152	3219	6.5	17.3	117.1	43.4	45.3	177	55.7	9.7	84.3	9.9	184.5	1622	373

Element (ppm)	Ti	V	Mn	Mo	Co	Ni	Cu	Zn	As	Se	Ag	Cd	Sn	Sb	W	Pb	Bi	U
Py-I (n=5)																		
Max	49.4	4.4	898	10627	19.2	744	118.7	3911	1845	11.5	15.2	22.8	22.8	8.4	10.1	344	74.2	5.7
Min	5.1	0.1	0.4	2.4	1.7	4	1.7	1	0.3	3.2	0.3	0.1	0.5	0.1	0.1	7	9.3	0.1
Mean	22.4	1.1	220.2	5.9	10.4	175	33.9	920	372	5.8	4.2	5.1	5.2	1.8	2.4	117	27.0	1.9
Median	13.8	0.3	75.3	6.9	12	19	8.7	26	1.6	5.0	2.3	0.2	0.9	0.1	0.5	24	15.5	0.9
S.D.	20.3	1.9	382.2	3.8	7.2	320.7	49.6	1696	823	3.2	6.2	9.9	9.9	3.7	4.3	151	27	2.4
Py-II (n=12)																		
Max	13.0	1.31	12.3	8075	87.8	63.7	7.3	5.7	8.0	35.3	1.68	1.5	1.3	0.45	6.47	65.2	13.9	0.81
Min	2.1	0.02	0.1	0.04	0.3	0.7	0.2	0.3	0.7	3.7	0.01	0.2	0.4	0.10	0.04	0.0	0.1	0.01
Mean	5.5	0.19	4.0	49.0	19.7	12.8	2.1	1.8	2.9	9.9	0.35	0.6	0.8	0.21	1.03	9.8	4.3	0.12
Median	3.1	0.06	3	5	10.1	5.3	1.3	1.4	1.4	7.3	0.11	0.3	0.5	0.15	0.2	4	1.3	0.03

S.D.	3.9	0.37	4.5	128.1	25.7	18.3	2.1	1.8	2.7	8.3	0.51	0.5	0.4	0.12	1.99	18.1	5.3	0.22
Py-III (n=31)																		
Max	5.5	0.09	7.75	31.19	43.5	277.8	2592	5.8	37	19.4	21	0.6	1.2	0.39	1.02	2243	44.2	0.21
Min	2.2	0.01	0.09	0.02	0.0	0.1	0.3	0.2	0.2	1.2	0.01	0.1	0.2	0.07	0.03	0.04	0.02	0.01
Mean	3.2	0.02	1.01	1.42	4.7	10.0	24.0	0.8	2.3	9.2	1.80	0.2	0.5	0.11	0.10	88.6	5.8	0.03
Median	3	0.02	0.14	0.05	0.1	0.6	8.7	0.4	0.5	8.1	0.05	0.2	0.4	0.1	0.06	0.17	0.3	0.02
S.D.	0.8	0.02	1.9	5.7	10.3	49.7	37.1	1.1	6.5	5.9	5.2	0.1	0.2	0.1	0.2	403.1	12	0.04

Note: S.D. = standard deviation values

Table 2 In situ sulfur isotopic compositions of sulfides from the Chalukou porphyry Mo deposit

No.	Sample No.	Depth (m)	Description	Mineral	$\delta^{34}S_{V-CDT}$ (‰)
1	16CLK-26-3-1	380	Py-Fl and Qz-Py-Mol veins	Py-I	4.2
2	16CLK-26-3-2	380	Py-Fl and Qz-Py-Mol veins	Py-I	3.2
3	16CLK-27-1--1	380	Mol-Py vein	Py-II	2.5
4	16CLK-27-2-1	380	Mol-Py vein	Py-II	2.1
5	16CLK-27-2-2	380	Mol-Py vein	Py-II	1.4
6	16CLK-27-2-3	380	Mol-Py vein	Py-II	2.4
7	16CLK-26-1-1	380	Py-Fl and Qz-Py-Mol veins	Py-III	4.0
8	16CLK-26-1-2	380	Py-Fl and Qz-Py-Mol veins	Py-III	2.9
9	16CLK-154-1-1	320	Py with minor Sp-Gn	Py-III	4.6
10	16CLK-154-1-2	320	Py with minor Sp-Gn	Py-III	3.9
11	16CLK-154-2-1	320	Py with minor Sp-Gn	Py-III	3.2
12	16CLK-154-3-1	320	Py with minor Sp-Gn	Py-III	2.0
13	16CLK-154-3-2	320	Py with minor Sp-Gn	Py-III	1.5
14	16CLK-154-3-3	320	Py with minor Sp-Gn	Py-III	1.1
15	16CLK-154-3-4	320	Py with minor Sp-Gn	Py-III	3.3
16	16CLK-154-3-5	320	Py with minor Sp-Gn	Py-III	3.0
17	16CLK-154-3-10	320	Py with minor Sp-Gn	Py-III	3.2
18	16CLK-26-2-1	380	Py-Fl and Qz-Py-Mol veins	Mol-I	7.2
19	16CLK-26-3-1	380	Py-Fl and Qz-Py-Mol veins	Mol-I	7.2
20	16CLK-154-1-3	320	Py with minor Sp-Gn	Mol-I	7.8
21	16CLK-27-1-1	380	Mol-Py vein	Mol-II	4.7
22	16CLK-27-1-2	380	Mol-Py vein	Mol-II	5.1
23	16CLK-27-2-4	380	Mol-Py vein	Mol-II	4.2
24	16CLK-27-2-5	380	Mol-Py vein	Mol-II	6.8
25	16CLK-154-2-2	320	Py with minor Sp-Gn	Sp	0.2
26	16CLK-154-2-3	320	Py with minor Sp-Gn	Sp	1.9
27	16CLK-154-3-8	320	Py with minor Sp-Gn	Sp	2.4
28	16CLK-154-3-9	320	Py with minor Sp-Gn	Sp	2.2
29	16CLK-154-3-6	320	Py with minor Sp-Gn	Gn	-5.0
30	16CLK-154-3-7	320	Py with minor Sp-Gn	Gn	-5.2

Abbreviations: Fl = fluorite, Gn = galena, Mol = molybdenite, Py = pyrite, Qz = quartz, Sp = sphalerite.

Table 3 In situ lead isotopic compositions of sulfides from the Chalukou porphyry Mo deposit

No.	Sample No.	Depth (m)	Description	Mineral	$^{206}Pb/^{204}Pb$	1σ	$^{207}Pb/^{204}Pb$	1σ	$^{208}Pb/^{204}Pb$	1σ
1	16CLK-26-1-1	380	Py-Fl and Qz-Py-Mol veins	Py-III	18.319	0.008	15.552	0.007	38.171	0.019
2	16CLK-26-1-2	380	Py-Fl and Qz-Py-Mol veins	Py-III	18.312	0.006	15.541	0.006	38.146	0.015
3	16CLK-26-2-2	380	Py-Fl and Qz-Py-Mol veins	Mol-I	18.370	0.007	15.570	0.006	38.218	0.015
4	16CLK-27-1-1	380	Mol-Py vein	Py-II	18.366	0.007	15.574	0.006	38.222	0.016
5	16CLK-27-1-3	380	Mol-Py vein	Mol-II	18.364	0.006	15.563	0.006	38.190	0.014
6	16CLK-27-1-4	380	Mol-Py vein	Mol-II	18.367	0.002	15.566	0.003	38.201	0.007
7	16CLK-27-1-5	380	Mol-Py vein	Mol-II	18.356	0.002	15.569	0.002	38.211	0.005
8	16CLK-27-2-1	380	Mol-Py vein	Py-II	18.365	0.007	15.559	0.007	38.180	0.017
9	16CLK-27-2-6	380	Mol-Py vein	Mol-II	18.347	0.017	15.550	0.018	38.153	0.049
10	16CLK-27-2-7	380	Mol-Py vein	Mol-II	18.364	0.006	15.576	0.007	38.226	0.018
11	16CLK-27-2-8	380	Mol-Py vein	Mol-II	18.386	0.009	15.597	0.009	38.282	0.023
12	16CLK-35-1-1	335	Qz-Py-Fl vein	Gn	18.338	0.007	15.569	0.007	38.206	0.020
13	16CLK-35-1-2	335	Qz-Py-Fl vein	Gn	18.335	0.007	15.566	0.007	38.196	0.020
14	16CLK-35-1-3	335	Qz-Py-Fl vein	Gn	18.336	0.007	15.568	0.007	38.200	0.020
15	16CLK-154-1-1	320	Py with minor Sp-Gn	Py-III	18.364	0.008	15.587	0.007	38.308	0.018
16	16CLK-154-1-2	320	Py with minor Sp-Gn	Mol-II	18.349	0.001	15.573	0.002	38.267	0.283
17	16CLK-154-2-2	320	Py with minor Sp-Gn	Sp	18.274	0.013	15.518	0.011	38.113	0.029
18	16CLK-154-3-1	320	Py with minor Sp-Gn	Py-III	18.312	0.005	15.542	0.006	38.180	0.023
19	16CLK-154-3-3	320	Py with minor Sp-Gn	Gn	18.346	0.007	15.573	0.007	38.258	0.019
20	16CLK-154-3-6	320	Py with minor Sp-Gn	Sp	18.278	0.015	15.518	0.015	38.099	0.039
21	16CLK-154-3-7	320	Py with minor Sp-Gn	Sp	18.310	0.006	15.535	0.006	38.097	0.018

Abbreviations: Fl = fluorite, Gn = galena, Mol = molybdenite, Py = pyrite, Qz = quartz, Sp = sphalerite.

Table 4 Whole rock lead isotopic compositions of intrusions from the Chalukou porphyry Mo deposit

No.	Sample No.	Depth (m)	Rock	$^{206}Pb/^{204}Pb$	1σ	$^{207}Pb/^{204}Pb$	1σ	$^{208}Pb/^{204}Pb$	1σ
1	16CLK-69	985	fine-grained porphyry	18.479	0.002	15.559	0.002	38.336	0.006
2	16CLK-88	443	quartz porphyry	18.442	0.002	15.561	0.002	38.323	0.005
3	16CLK-130	627	granite porphyry	18.544	0.002	15.549	0.002	38.342	0.004
4	16CLK-136	1185	fine-grained porphyry	18.570	0.002	15.591	0.002	38.482	0.007

Fig. 1

A

Russia
Siberian Craton
Fig. 1B
NE China
Kazakhstan
CAOB
Mongolia
NW China
Kyrgyzstan
Tarim Craton
North China Craton
500 km

B

120° 125° 130°
Mongol-Okhotsk Suture
100 km
Russia
Mohe
Erguna Massif
Chalukou
Tayuan
Xing'a
Daheishan
Taipingchuan
Russia
Sankuanggou
Heihe
Duobaoshan
Tongshan
50°
Erguna
Zhengguang
Hadatumuchang
Yongxin
Badaguan
Hingan Massif
50°
Baojiagou
Wunugetushan
Shiqigongli
Harar
Luming
Zhongshishan
Taipinggou
Songliao Basin
Houlinjiu
Mongolia
Derbugan Fault

Cenozoic sediments
Jurassic-Cretaceous volcanic rocks
Mesozoic granites
Late Paleozoic rocks
Early Paleozoic rocks
Precambrian rocks
Ophiolite suite
Fault (suture)

Deposit
● Mo porphyry
▲ Mo quartz vein
● Cu-Mo porphyry
● Au epithermal

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Fig. 12

Fig. 13