1   Revision 1

2

3   New insights into the metallogeny of the Nayongzhi MVT Zn-Pb deposit in

4   Guizhou Province (South China): Evidence from geology, bulk C-O-S and in

5   situ S-Pb isotopes

6

7

8   JIA-XI ZHOU[1, 2, *], XUAN-CE WANG[2], SIMON A. WILDE[2], KAI LUO[1, 3],

9   ZHI-LONG HUANG[1], TAO WU[4], ZHONG-GUO JIN[1]

10

11

12   [1] *Stake Key Laboratory of Ore Deposit Geochemistry, Institute of*

13   *Geochemistry, Chinese Academy Sciences, Guiyang 550081, China*

14   [2] *The Institute for Geoscience Research, Department of Applied Geology,*

15   *Curtin University, GPO Box U1987, Perth, WA 6845, Australia*

16   [3] *University of Chinese Academy Sciences, Beijing 100049, China*

17   [4] *School of Earth Sciences, Zhejiang University, Hangzhou 310027, China*

18

19

20   *Corresponding author, JIA-XI ZHOU, E-mail: zhoujiaxi@vip.gyig.ac.cn

21

22

ABSTRACT

23

24   The newly-discovered Nayongzhi Zn-Pb deposit (> 20 Mt ores @ 1.11-15.65

25   wt. % Zn and 0.59-0.97 wt. % Pb) in NW Guizhou province, South China, is

26   hosted by late Ediacaran and early Cambrian carbonate rocks. Ore body is

27   structurally controlled by a kilometer-scale reverse fault-anticline system and

28   occurs as stratiform, lentiform or steeply dipping veined. Its geological feature

29   can compare to that of the Mississippi Valley-type (MVT) Zn-Pb deposits. δ^{34}S

30   values (+11.8-+33.0‰) of sulfide minerals determined by NanoSIMS have a

31   larger range than those determined by conventional bulk analysis (δ^{34}S =

32   +18.12-+24.79‰). This suggests that S isotopes determined by in situ analysis

33   can reflect the nature of fractionation involved in mineralization. Further, cores

34   of sulfide crystals have higher δ^{34}S values (+26.1-+33.0‰) than their rims

35   (+11.8-+24.5‰). This implies a mixture of multiple S reservoirs or a Rayleigh

36   fractionation of S isotopes occurred during ore formation process. Additionally,

37   both S isotopic compositions determined by in situ and bulk analyses reflect

38   the enrichment of ^{34}S in hydrothermal fluid (δ^{34}S$_{fluid}$ > +11.8‰), a typical

39   characteristic of marine sulfate-derived S. Such S isotopic signatures also

40   show that thermochemical sulfate reduction (TSR) is the dominant mechanism

41   for the incorporation of S^{2-} from SO$_4^{2-}$. Pb isotopic ratios of galena obtained by

42   femtosecond LA-MC-ICPMS plot in the field that overlaps with the Pb evolution

43   curve of upper crust contributed to the orogeny and the field of modern lower

44   crust, and can be compared to the Proterozoic metamorphic rocks. The means

45 that the majority of Pb metal is sourced from the basement rocks. Although

46 $\delta^{13}C$ values (-4.1-+0.5‰) of calcite separates and corresponding fluids are

47 similar to both fresh limestone (-1.7-+1.3‰) and typical marine carbonate

48 rocks, the $\delta^{18}O$ values (+12.4-+14.1‰) are significantly lower than both

49 limestone (+24.1-+25.5‰) and marine carbonate rocks. Such C-O isotopic

50 characteristics suggest that the source of C is ore-hosting carbonate rocks,

51 whereas O has a mixed source of metamorphic fluids and carbonate rocks

52 resulting from water/rock (W/R) interaction. All in all, this study demonstrates

53 that (i) fluid mixing caused rapid sulfide precipitation, resulting in significant

54 fractionation of S isotopes; and (ii) both the W/R interaction and CO_2

55 degassing controlled local carbonate cyclic process of dissolution →

56 re-crystallization, which provided metastable physical and chemical conditions

57 for giant sulfide mineralization. These two processes are crucial in forming

58 MVT deposits.

59 **Key words:** In situ S-Pb isotopes; Fluid mixing; Buffer of carbonate; MVT

60 deposits; South China

61

62 **INTRODUCTION**

63 Zn-Pb deposits hosted by carbonate or siliciclastic rocks contain the world's

64 greatest Zn and Pb resources, and predominate the world production of these

65 metals (e.g., Leach et al. 2005). They are known as sediment-hosted types of

66 ore deposit and generally have no direct genetic association with igneous

3

67 activity (e.g., Leach et al. 2010). Carbonate-hosted Zn-Pb deposits, one of the

68 two major subtypes of sediment-hosted Zn-Pb deposits, occur in platform

69 carbonate sequences and are commonly named as the Mississippi Valley-type

70 (MVT) deposits (e.g., Leach et al. 2010). Extensive research on the MVT

71 deposits has dedicated greatly to our understanding of fluid flow and metal

72 transport in sedimentary basin (e.g., Heijlen et al. 2003; Leach et al. 2005;

73 Wilkinson et al. 2009). However, as the MVT deposits are the products of a

74 variety of ore formation processes in a wide range of geologic and tectonic

75 environments (e.g., Wilkinson et al. 2009; Leach et al. 2010), so their ore

76 genesis is still controversial, and the chemical and isotopic evolution of

77 hydrothermal fluids also needs to be careful constrained.

78 In China, carbonate-hosted Zn-Pb deposits are widely distributed in the

79 platform carbonate sequences surrounding the Yangtze Craton (e.g., Zaw et al.

80 2007; Wang et al. 2014; Hu et al. 2017). For example, more than 400 Zn-Pb

81 deposits in the western Yangtze Craton form the Sichuan-Yunnan-Guizhou

82 (SYG) Pb-Zn metallogenic province (Fig. 1A-B) with more than 200 Mt ores

83 grading 10-15 wt. % Zn + Pb (e.g., Zhou et al. 2013a, 2014a). Such a province

84 is an important part of the giant South China low-temperature metallogenic

85 domain (e.g., Hu et al. 2017), accounting for 27% of total Zn + Pb resources in

86 China (Zhang et al. 2015). Extensive investigation on the origin of the Zn-Pb

87 deposits in the SYG province has been carried out in the past two decades,

88 although they belong to epigenetic type is widely recognized, there is still a

89 struggle of ore genesis, such as MVT (e.g., Zheng and Wang 1991; Zhou et al.

90 2001; Wang et al. 2014; Zhang et al. 2015; Zhu et al. 2017), distal

91 magmatic-hydrothermal type (e.g., Xie, 1963; Huang et al. 2010; Bai et al.

92 2013; Xu et al. 2014) or unique SYG-type (e.g., Zhou et al. 2013b, 2014b; Li et

93 al. 2015, 2016; Zhu et al. 2016).

94 Micro-beam analytical techniques have potential to provide key in situ

95 elemental and isotopic information to constrain the sources of mineralizing

96 elements and associated fluids, as well as the metallogenic environments of

97 the hydrothermal system (e.g., Liu et al. 2008; Barker et al. 2009; Steinhoefel

98 et al. 2009; Ye et al. 2011; Zhang et al. 2014; Yuan et al. 2015; Jin et al. 2016).

99 Such information is crucial for understanding the metallogeny of hydrothermal

100 deposits. Secondary ion mass spectroscopy (SIMS) and laser-ablation

101 multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICPMS)

102 are techniques that can efficiently determine micro-scale isotopic compositions

103 of sulfide minerals in hydrothermal deposits (e.g., Peevler et al. 2003; Ikehata

104 et al. 2008; Chen et al. 2014; Bao et al. 2016).

105 Here we use the newly-discovered Nayongzhi MVT Zn-Pb deposit that situates

106 in the southeastern part of the SYG province as a case, and report a set of

107 NanoSIMS in situ S, femtosecond LA-MC-ICPMS in situ Pb, and conventional

108 whole-rock C and O isotopic data. Through integrating the newly obtained data

109 and detailed ore deposit geology, this study aims to reveal the origin and

110 evolution of hydrothermal fluids, and then to propose a new genetic model for

111 the Nayongzhi deposit. The outcomes are crucial for understanding the

112 formation and exploration of MVT deposits in general.

113

114 **GEOLOGICAL SETTING**

115 **General geology of the western Yangtze Craton**

116 The Yangtze Craton constitutes a significant part of the South China Block,

117 and is bounded by the Cathysia Block to the southeast, the Qinling-Dabie

118 Orogenic Belt to the north, the Songpan-Ganzê Orogenic Belt to the northwest,

119 and the Sanjiang Orogenic Belt to the southwest (Fig. 1A). The basement of

120 the western Yangtze Craton consists of late Paleoproterozoic to early

121 Neoproterozoic weakly metamorphic rocks, which were intruded by

122 widespread late Neoproterozoic igneous rocks (e.g., Qiu et al. 2000; Zhou et al.

123 2002, 2014c; Gao et al. 2011). The sedimentary succession of the western

124 Yangtze Craton is composed mainly of Cambrian to Triassic marine and

125 Jurassic to Cenozoic continental sedimentary rocks (e.g., Yan et al. 2003;

126 Zhou et al. 2013a; Hu et al. 2017). Sulfate-bearing evaporates are common in

127 the Cambrian to Triassic marine sedimentary strata, which are an important S

128 source for the sediment-hosted hydrothermal deposits in the western Yangtze

129 Craton (e.g., Bai et al. 2013; Zhou et al. 2014a; Chen et al. 2015). Faults in the

130 western Yangtze Craton are well-developed and have undergone multi-stage

131 activities (namely Hercynian, Indosinian, and Yanshanian orogenic events,

132 and even Himalayan Orogeny), which dominantly controlled the sedimentation,

6

133 magmatism and mineralization (e.g., Liu and Lin 1999), such as the regional

134 NW-trending Yiliang-Shuicheng and NS-trending Xiaojiang faults (Figs. 1B,

135 2-3).

136 A significant feature of the western Yangtze Craton is the occurrence of

137 Emeishan Large Igneous Province (ELIP) and its flood basalts (ca. 260 Ma)

138 with an area of more than 250,000 km^2 (e.g., Zhou et al. 2002; Jian et al. 2009).

139 After eruption of late Permian Emeishan basalts, the western Yangtze Craton

140 collided with the adjacent blocks (for example, Yidun Arc), resulting in the

141 closure of the Paleo-Tethys ocean (e.g., Reid et al. 2007; Hu and Zhou 2012;

142 Zhou et al. 2013a; Qiu et al. 2016; Hu et al. 2017). This event is named as the

143 Indosinian Orogeny (257-205 Ma) (e.g., Carter et al. 2001). After then, there is

144 the Yanshanian Orogeny that occurred during Jurassic-Cretaceous (205-135

145 Ma) time (e.g., Wong 1927). These two orogenic events resulted in faulting

146 and folding that significantly controlled the distribution of carbonate-hosted

147 Zn-Pb deposits in the western Yangtze Craton (e.g., Liu and Lin 1999; Huang

148 et al. 2010; Zhou et al. 2014b; Zhang et al. 2015).

149 Another significant feature of the western Yangtze Craton is the occurrence of

150 the SYG Zn-Pb mineralization province and its 408 Zn-Pb deposits with an

151 area of more than 170,000 km^2 (e.g., Liu and Lin 1999; Zhou et al. 2014a; Hu

152 et al. 2017). All the Zn-Pb deposits host in the late Ediacaran to middle

153 Permian carbonate rocks and are spatially associated with the late Permian

154 Emeishan basalts (Fig. 1B). Calcite/fluorite Sm-Nd, sphalerite/pyrite Rb-Sr and

7

155 bitumen Re-Os isotope geochronology studies suggest that these

156 carbonate-hosted Zn-Pb deposits formed between 226 Ma and 165 Ma (e.g.,

157 Li et al. 2007; Lin et al. 2010; Mao et al. 2012; Zhou et al. 2013a, 2013b, 2015;

158 Zhang et al. 2015; Hu et al. 2017). This indicates that the Zn-Pb mineralization

159 in the SYG province occurred during late Triassic-middle Jurassic, and related

160 to the Indosinian and Yanshanian two orogenic events.

161 **Regional geology of the NW Guizhou district**

162 The newly-discovered Nayongzhi carbonate-hosted Zn-Pb deposit is located

163 in NW Guizhou province (Figs. 1B, 2-3). In the NW Guizhou district, the

164 basement rocks of the western Yangtze Craton are not exposed (Figs. 2-3).

165 The cover sequences including late Ediacaran to Triassic marine and Jurassic

166 continental sedimentary rocks, as well as late Permian Emeishan continental

167 flood basalts. The late Ediacaran strata consist mainly of limestone and

168 dolostone. The Cambrian strata are composed dominantly of siltstone,

169 claystone, limestone, argillaceous dolostone and dolomitic sandstone. These

170 sedimentary rocks of late Ediacaran and Cambrian are unconformable overlain

171 by Devonian strata that consist predominantly of sandstone, siltstone, shale,

172 limestone and dolostone. The Devonian sedimentary rocks are conformably

173 overlain by Carboniferous strata, which are composed mainly of shale,

174 limestone and dolostone. The early-middle Permian sequence consists

175 dominantly of sandstone, shale, coal layers and limestone, all of which are

176 unconformable overlain by the late Permian Emeishan flood basalts. The

8

177   basalts, in turn, are overlain by sandstone, siltstone and coal measures of the

178   late Permian strata. The Triassic strata consist mainly of siltstone, sandstone,

179   dolostone and limestone, and the Jurassic strata are dominated by sandstone.

180   The Zn-Pb sulfide ores are hosted by the late Ediacaran to middle Permian

181   carbonate rocks and parts of them have a spatial association with late Permian

182   basalts (e.g., Jin 2008; Zhou et al. 2013a; Li et al. 2015; Figs. 1B, 2-3).

183   NW- and NE-striking faults and folds are well-developed in the NW Guizhou

184   district, for example, the NW-trending Yadu-Ziyun fault (Figs. 1B, 2-3), the

185   NE-trending Nayong-Kaiyang and Anshun-Pingba faults, and the NE-trending

186   Dayuan and Wuzhishan anticlines (Figs. 2-3). Among these structures, the

187   Yadu-Ziyun regional fault controlled the sedimentation and low temperature

188   mineralization (Zn-Pb, Au and fluorite deposits) in the studied region (Figs.

189   2-3). Mafic dykes (diabase), related to the ELIP (e.g., Jin 2008), also occur in

190   this district and spatially associate with parts of Zn-Pb deposits (Fig. 2).

191   More than 100 carbonate-hosted Zn-Pb deposits have been found in the NW

192   Guizhou district, such as the Tianqiao and Shanshulin deposits (Figs. 1B, 2-3;

193   Jin 2008; Zhou et al. 2013a, 2014b). The Nayongzhi Zn-Pb deposit,

194   discovered in 2011, occurs in the southeastern part of the NW Guizhou district

195   (Figs. 2-3) and is hosted by limestone and dolostone of late Ediacaran

196   Dengying Formation and early Cambrian Qingxudong Formation (Figs. 4-6).

197   This deposit is the largest and only large-scale (>0.5 Mt Zn + Pb metal reserve)

198   carbonate-hosted Zn-Pb deposit in the Guizhou part of the SYG province (Jin

199 et al. 2016), containing Zn + Pb metal reserve of more than 1.5 Mt with ore

200 grades of 1.11-15.65 wt. % Zn and 0.59-0.97 wt. % Pb.

201

202 **GEOLOGY OF THE NAYONGZHI ZN-PB DEPOSIT**

203 **Stratigraphy and lithology**

204 The Nayongzhi deposit is situated in the central part of the Wuzhishan

205 anticline (Figs. 2-4). In the Wuzhishan anticline area, the exposed strata are

206 late Ediacaran, Cambrian, early Carboniferous, early Permian and early

207 Triassic (Figs. 4-5). The late Ediacaran Dengying Formation consists mainly of

208 limestone and dolostone, which are conformable overlain by the early

209 Cambrian Jindingshan Formation that is composed dominantly of siltstone and

210 shale. Followed the Jindingshan Formation is the early Cambrian Qingxudong

211 Formation, which is mainly made up of limestone and dolostone. The middle

212 Cambrian Douposi Formation is composed predominantly of dolostone and

213 sandstone, and the late Cambrian Loushanguan Formation is dominated by

214 limestone and dolostone. The early Carboniferous strata comprise the

215 Xiangbai and Jiusi formations, which consist mainly of limestone and siltstone,

216 and shale and limestone, respectively. The early Permian Liangshan

217 Formation consists dominantly of shale and sandstone, and the early Triassic

218 Daye Formation is mainly made up of limestone. In the Nayongzhi mining area,

219 the exposed strata are Qingxudong Formation (Fig. 4) that can be subdivided

220 into three sections based on the lithological feature, of which the 1st and 2nd

10

sections have six and two lithological layers, respectively (Fig. 5). Zn-Pb ores

host in the limestone and dolostone of the Dengying Formation, and the 1st

section and the 1st layer of the 2nd section of the Qingxudong Formation (Figs.

5, 6A-B).

Tectonics

In the Wuzhishan anticline area, the tectonics are well-developed and strictly

control the distribution of Zn-Pb deposits (Figs. 3-4). The Wuzhishan anticline,

a NE-trending asymmetric anticline, is 16 km long and 4 km wide with an axis

trending angle of 45° (Fig. 4). The Narun fault (F_1 in Fig. 4), a normal structure,

strikes NE and dips at SE. This fault intersects the Yadu-Ziyun regional fault to

the southwest (Fig. 3). The Dujiaqiao fault (F_2 in Fig. 4) is a reverse fault that

strikes 30° and dips at SE with a dipping angle of 60°-70°. Another important

fault, F_7 reverse fault (Fig. 4), trends north with a dipping angle of 51°-75°.

Studies suggest that the Wuzhishan anticline, and NE- and NW-trending faults

were active during the Yanshanian Orogeny (e.g., Chen et al. 2015). In the

Nayongzhi ore district, sulfide ore is structurally controlled by a reverse

fault-anticline system, namely the F_7 reverse fault and Wuzhishan anticline

(Figs. 4, 6A-B).

Ore body

In the Nayongzhi ore district, one steeply dipping veined and twenty stratiform

or lentiform ore bodies have been found in total until 2015 (Peng et al. 2016).

The steeply dipping veined ore body occurs along the F_7 reverse fault zone

11

243 (Figs. 6A, 7E), which is 20-50 m long, 0.5-3 m wide and 200 m thick. This ore

244 body contains high ore grade of Zn (> 10 wt. %), with less abundant Pb. The

245 stratiform or lentiform ore bodies (Figs. 6A-B, 7A) can be combined into three

246 groups (I, II and III) based on the lithological character of their ore-bearing

247 layers (Figs. 5, 6A-B). Ore bodies in these three groups are similar, of which

248 the Group II is the largest and occurs in the 5th layer of the 1st section of the

249 Qingxudong Formation (Figs. 5, 6A-B). Here we take the Group II as an

250 example to introduce the geology of ore body. Sulfide ore in this group is

251 hosted by limestone and dolostone, with argillaceous limestone and dolostone

252 as wall rocks. The ore bodies are stratiform or lentiform and have the same

253 orientation as the ore-hosting rocks, namely strike NE and dip SE with a

254 dipping angle of 8°-20°. The main ore body in the Group II is 2725 m long,

255 250-775 m wide and 1-29.6 m thick, containing 0.5-36.63 wt. % Zn (average

256 4.03 wt. %) and 0.04-4.05 wt. % Pb (average 0.45 wt. %). This ore body

257 contains Zn + Pb metal reserve of more than 0.5 Mt and is the largest one in

258 the Nayongzhi deposit.

259 **Texture and structure of sulfide ores**

260 Sulfide ore in the Nayongzhi deposit consists mainly of sphalerite, secondary

261 galena and pyrite, with calcite or dolomite as primary gangue minerals, and

262 rare quartz or barite as local associated minerals (Figs. 7-10).

263 Sulfide ore in veined, stratiform or lentiform ore bodies occurs as either veined

264 (Figs. 7B, D, G, J-K, M, O, 8H, J, L-P), massive (Figs. 7C, K, N, 8D-F, I), or

12

265   disseminated (Figs. 7H, 8A-C, G, L). Their general feature is as follows: (i)

266   Veined ore: sulfide minerals (sphalerite, galena and pyrite) occur as veinlet or

267   stockwork, and fill into fracture or cement carbonate solution collapse breccia

268   (such as Fig. 7B, D, G); (ii) Massive ore: sulfide minerals form massive

269   aggregation in wall rocks (for example, Figs. 7C, 8D-E); and (iii) Disseminated

270   ore: sulfide minerals present as speckle aggregation that densely or sparsely

271   distributes in wall rocks (e.g. Figs. 7H, 8A-C, G). Syn- or post-ore gangue

272   minerals occur as crumb or veined aggregation that fills into fracture or

273   cements carbonate breccia (such as Fig. 7B-C, F, H).

274   Sulfide minerals have granular, fragmented or replacement textures (Figs.

275   9-10), which have general feature as following: (i) Granular texture: sphalerite

276   presents as fine to coarse (0.01-10 mm) granular crystal that coexists with

277   pyrite (Figs. 9C, F-H, 10C-E, H-J), galena (Figs. 9D, F-G, J-K, N-O, 10B, G-H,

278   K-N), quartz (Fig. 9D), or calcite/dolomite (Figs. 9A, D, J-K, M-O, 10B, D, F, G-I,

279   L-P), and is enclosed by pyrite (Fig. 9B), galena (Fig. 9O, 10A) or

280   calcite/dolomite (Figs. 9A-C, E-F, 10C, G-J, L, N-O); galena occurs as fine to

281   medium (0.05-0.6 mm) granular crystal, coexisting with sphalerite (Figs. 9D,

282   F-G, J-K, N-O, 10B-C, G-H, L-N) and is enclosed by calcite/dolomite (Figs. 9F,

283   K, 10A, G-H, K-L, N), sphalerite (Fig. 10L, O) or pyrite (Fig. 10I); pyrite occurs

284   as fine (0.001-0.2 mm) granular crystal, coexisting with sphalerite (Figs. 9A-C,

285   F-H, 10C-F, H-J) and is enclosed by calcite/dolomite (Figs. 9C, 10J), galena

286   (Fig. 10A) or sphalerite (Fig. 10P). Diagenetic pyrite is fine-grained and

287 distributes in wall rocks (Fig. 8K) or is cemented by quartz (Fig. 9L) (ii)

288 Fragmented texture: fragmented sphalerite is enclosed by pyrite (Fig. 10D) or

289 calcite/dolomite (Fig. 10J) and is filled by galena (Fig. 10K) or calcite/dolomite

290 (Fig. 10P); and (iii) Replacement texture: sphalerite is replaced by galena (Fig.

291 9H) or replaces pyrite (Figs. 9M, 10F).

292 **Mineral paragenesis**

293 The Nayongzhi carbonate-hosted Zn-Pb deposit has experienced diagenetic,

294 hydrothermal and oxidized periods (Table 1), of which the hydrothermal period

295 can be further subdivided into sulfide + (quartz + calcite/dolomite) and quartz +

296 calcite/dolomite + (barite) stages (Figs. 7-10). There are two principal types of

297 sulfide ore formed during the sulfide stage: sphalerite-dominated + pyrite +

298 galena + quartz + calcite/dolomite, and sphalerite- and galena-dominated +

299 pyrite + quartz + calcite/dolomite. The spatial distribution of sulfide ore (Fig. 7)

300 shows the formation sequence is from sphalerite-dominated massive (Fig. 8D,

301 I) or dense disseminated ore (Fig. 8A-C, L), and sphalerite- and

302 galena-dominated massive (Fig. 8E-F) or spare disseminated ore (Fig. 8G), to

303 metasomatic, filled or cemented ore vein (Fig. 8H, J, L-P). Therefore, sulfide

304 minerals have two generations. Sphalerite-I is fine- to medium-grained

305 (0.02-0.6) mm, coexisting with pyrite-I (Figs. 8D, 9A, C, G-H, 10C, E, J) or

306 galena-I (Figs. 8C, 10C), and is enclosed by pyrite-II (Figs. 9B, 10D) or

307 galena-II (Figs. 9O, 10A), as well as is replaced by galena-II (Fig. 9H);

308 Sphalerite-II is medium to coarse granular crystal (0.5-10 mm) that coexists

14

309 with pyrite-II (Figs. 9B, F, 10D, H-I) or galena-II (Figs. 9D, F, J-K, N-O, 10B,

310 G-H, L-O), and is enclosed by calcite-II (Fig. 9E, 10G-I, N-O) and also replaces

311 pyrite-I (Figs. 9M, 10F). Galena-I is fine- to medium-grained (0.05-0.2 mm),

312 coexisting with pyrite-I or sphalerite-I (Figs. 8C, 10C), and is enclosed by

313 sphalerite-II (Figs. 9I, 10L), pyrite-II (Fig. 10I) or calcite-II (Fig. 10K); Galena-II

314 is medium to coarse granular crystal (0.1-0.6 mm) that coexists with

315 sphalerite-II (Figs. 9D, F, J-K, N-O, 10B, G-H, L-O) or pyrite-II (Fig. 10H), and

316 is enclosed by calcite-II (Fig. 10G, N), as well as replaces sphalerite-I (Fig. 9H).

317 Pyrite-I coexists with sphalerite-I (Figs. 8D, 9A, C, G-H, 10C, E, J) or pyrite-I

318 (Fig. 10C), and is enclosed by galena-II (Fig. 10A) or sphalerite-II (Fig. 10P),

319 and also is replaced by sphalerite-II (Figs. 9M, 10F); Pyrite-II coexists with

320 sphalerite-II (Figs. 9B, F, 10D, H-I) or galena-II (Fig. 10H), and encloses

321 sphalerite-I (Fig. 9B). In addition, calcite/dolomite-I is rare (Figs. 9A, H-I, 10E,

322 J-K); Calcite/dolomite-II fills or cements sphalerite-I, galena-I or pyrite-I (Figs.

323 9A-C, G, 10C, E, J-K), and coexists with pyrite-II, sphalerite-II or galena-II

324 (Figs. 9D-E, J-K, N-O, 10B, D, L-M); Calcite/dolomite-III occurs as crumb,

325 veinlet or stockwork that fills into fractures of sulfide ore (Figs. 7B-C, 8G, 9C)

326 or cements carbonate breccia (Fig. 7C, F, H).

327 **Wall rock alteration**

328 Wall rock alteration includes dolomitization (dolomite), calcitization (calcite),

329 silicification (quartz) and baratization (barite). These alteration styles can be

330 divided into two stages: (i) pre-ore stage of carbonatization that formed

15

331   re-crystallized Fe-/Mn-bearing dolostone (Fig. 7A), and silicification that

332   generated banded quartz or silicified dolostone (Fig. 7M); and (ii) post-ore

333   stage of carbonatization, silicification and baratization that formed carbonate

334   veinlet or stockwork (dolomite and calcite) (Fig. 7C, H-I, L), quartz and barite

335   vein (Fig. 7F, P), respectively. The pre-ore alteration is the result of water/rock

336   interaction between hydrothermal fluids and wall rocks, and then resulted in

337   elemental and isotopic exchange. This type of alteration occurs commonly

338   along the structure for fluid migration. The post-ore alteration is the result of

339   late evolution of hydrothermal fluids and is generally close to sulfide ore, and

340   thus can be used as a cue for ore exploration.

341

342   **SAMPLES AND ANALYTICAL METHODS**

343   **Samples**

344   Samples were collected from the exploration engineering of the Nayongzhi

345   Zn-Pb deposit, including drill holes and underground mining tunnels (Figs. 7-8).

346   Seven calcite and sixteen sulfide minerals (pyrite and sphalerite) separates

347   were handpicked from twenty-three sulfide ore samples by micro-drill and

348   binocular microscope. Five limestone whole-rock samples were also collected

349   for C and O isotope analyzing. Five polished thin sections of sulfide ore were

350   used for in situ S and Pb isotope analyzing. In situ S isotopic composition of

351   galena was not determined as no galena standard is available for comparison

352   (Zhang et al. 2014). In addition, in situ Pb isotopic composition of sphalerite

353   and pyrite was not determined, because of the high Hg content of them could

354   significantly affect the quality of the obtained Pb isotopic data (Chen et al.

355   2014).

356   **Analytical methods**

357   (I) Bulk C and O isotope analyses

358   Bulk C and O isotope analyses were completed by using a Finnigan MAT-253

359   mass spectrometer at the State Key Laboratory of Ore Deposit Geochemistry

360   (SKLODG), Institute of Geochemistry (IG), Chinese Academy Sciences (CAS).

361   Calcite and whole-rock limestone reacted with 100% phosphoric acid (H_3PO_4)

362   to produce CO_2. The analytical precision calculated from replicate analyses of

363   unknown samples is better than 0.2‰ (2σ) for $\delta^{13}C$ and 1‰ (2σ) for $\delta^{18}O$. The

364   C and O isotopic ratios are reported relative to Vienna Pee Dee Belemnite

365   (V-PDB).

366   (II) Bulk S isotope analysis

367   Bulk S isotopic composition was analyzed by using a Finnigan MAT-253 mass

368   spectrometer at the SKLODG, IGCAS. Powder of sulfide separate finer than

369   200 mesh was mixed with CuO powder, and then heated to extract SO_2 gas.

370   The $^{34}S/^{32}S$ ratios are expressed by the conventional $\delta^{34}S$ value in per mil

371   relative to the Vienna Canyon Diablo Troilite (V-CDT) standard. The analytical

372   error is better than 0.1‰ (1σ) calculated from replicate analyses of the IAEA

373   international standards: IAEA S1 (-0.3‰), IAEA S2 (+22.62‰) and IAEA S3

374   (-32.49‰). The precision calculated from replicate analyses of unknown

375   samples is better than 0.2‰ (2σ).

376   (III) In situ S isotope analysis

377   In situ S isotopic composition was performed by using a CAMECA NanoSIMS

378   50 L at the Key Laboratory of Earth and Planetary Physics, IGGCAS. The

379   measurement was made using three different settings of the Faraday cup (FC)

380   and/or electron multiplier (EM) detector, which meet different requirements for

381   spatial resolution. The effect of EM aging and quasi-simultaneous arrival was

382   corrected before the calibration of instrumental mass fractionation by a

383   standard-sample-standard bracketing method using the standards measured

384   together with the samples. Target spot of the most homogeneous isotopic

385   composition (such as ^{32}S, ^{34}S and ^{75}As in Fig. 15B) was selected for S isotope

386   analyzing in order to obtain the credible in situ S isotopic data. International

387   standards included Balmat (pyrite and sphalerite) and CAR 123 (pyrite), and

388   internal standards included PY-1117 (pyrite), CS01 (pyrite), JC-14 (sphalerite)

389   and MY09-12 (sphalerite). The analytical precision calculated from replicate

390   analyses of unknown samples is better than 0.2‰ (1s). The detail of

391   NanoSIMS in situ S isotope analysis and instrument parameter was described

392   in the reference of Zhang et al. (2014).

393   (IV) In situ Pb isotope analysis

394   In situ Pb isotopic ratio was determined by using a Nu II MC-ICPMS (Nu

395   Instruments, Wrexham, UK) combined with a 266 nm NWR UP Femto

396   femtosecond (fs) laser ablation system (ESI, USA) at the State Key Laboratory

18

397 of Continental Dynamics, Northwest University. The surface of the polished

398 thin section was cleaned with milli-Q water (18.2 MΩ·cm). Line scan ablation

399 consisted of background collection for 20 s followed by 50 s of laser ablation

400 for signal collection. Laser ablation parameter is as follows: (i) spot size: 15 μm

401 for galena; (ii) 100% output energy: > 600 μJ; (iii) 100% energy density: 6

402 J/cm^2; (iv) laser frequency: 5-50 Hz; and (v) ablation way: line 3 μm/s. This

403 ensures a strong enough Pb signal for the analyses of sulfide samples. The Tl

404 (20 ppb, NIST SRM 997, ^{205}Tl/^{203}Tl = 2.38890) and NIST SRM 610 glass were

405 served as internal and external standards, respectively. The repeated analyses

406 of NIST SRM 610 glass standard yielded highly reliable and reproducible

407 results during the whole analytical process with mean ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb

408 and ^{208}Pb/^{204}Pb ratios of 17.052 ± 0.003, 15.515 ± 0.003 and 36.980 ± 0.007

409 (1s, *n* = 183), respectively. The detail of fs LA-MC-ICPMS in situ Pb isotope

410 analysis and instrument parameter was described in the references of Chen et

411 al. (2014) and Bao et al. (2016).

412

413   **ANALYTICAL RESULTS**

414 **Carbon and Oxygen isotopic composition**

415 Carbon and Oxygen isotopic data of limestone whole-rock samples and

416 syn-ore calcite separates are presented in Table 2, and are shown in Figures

417 11-13. Limestone samples have δ^{13}C and δ^{18}O values ranging from -1.7 to

418 +1.3‰ and +24.1 to +25.5‰, respectively. Calcite separates have δ^{13}C values

19

419   ranging from -4.1 to +0.5‰ and $\delta^{18}O$ values from +12.4 to +14.1‰. The

420   calcite-II separates have higher $\delta^{13}C$ values (-1.9-+0.5‰) and lower $\delta^{18}O$

421   values (+12.4-+13.6‰) than that of calcite-III separate ($\delta^{13}C$ = -4.1‰ and $\delta^{18}O$

422   = +14.1‰). A marked negative relationship between $\delta^{13}C$ and $\delta^{18}O$ values of

423   all the calcite separates is shown in Figure 11.

424   **Bulk and in situ S isotopic composition**

425   Bulk and in situ S isotopic data are listed in Table 3, and are shown in Figures

426   14-15. Sulfide separates have bulk $\delta^{34}S$ values ranging from +17.17 to

427   +24.79‰, of which pyrite and sphalerite separates have $\delta^{34}S$ values ranging

428   from +18.12 to +22.06‰ and +17.17 to +24.79‰, respectively. In addition,

429   bulk $\delta^{34}S$ values (+22.51-+24.79‰) of sphalerite-I overlap with those of

430   sphalerite-II ($\delta^{34}S$ = +17.17-+24.59‰). The NanoSIMS in situ $\delta^{34}S$ values of

431   sulfide crystals range from +11.8 to +33.0‰, of which pyrite and sphalerite

432   crystals have in situ $\delta^{34}S$ values ranging from +15.1 to +27.0‰ and +11.8 to

433   +33.0‰, respectively. As shown in Figure 14C, in situ S isotopic data have a

434   much wider range than bulk S isotopic data. A significant feature of both

435   sphalerite and pyrite crystals is that the in situ $\delta^{34}S$ values decrease from core

436   to rim (sphalerite: decreasing from +33.0 to +11.8‰; pyrite: decreasing from

437   +27.0 to +15.1‰; Fig. 15A).

438   **In situ Pb isotopic ratio**

439   In situ Pb isotopic ratios of galena are presented in Table 4, and are shown in

440   Figures 16-18. Galena crystals have in situ Pb isotopic ratios as follows:

441 $^{206}Pb/^{204}Pb$ = 17.83-17.87, $^{207}Pb/^{204}Pb$ = 15.65-15.67 and $^{208}Pb/^{204}Pb$ =

442 37.92-38.00 with μ ($^{238}U/^{204}Pb$) values of 9.64-9.67. The galena-I (fine-grained)

443 crystals have $^{206}Pb/^{204}Pb$ ratios of 17.83-17.84, $^{207}Pb/^{204}Pb$ ratios of

444 15.65-15.67 and $^{208}Pb/^{204}Pb$ ratios of 37.92-37.97, which are slightly lower

445 than those of galena-II crystals (coarse-grained) ($^{206}Pb/^{204}Pb$ = 17.84-17.87,

446 $^{207}Pb/^{204}Pb$ = 15.65-15.67, and $^{208}Pb/^{204}Pb$ = 37.93-38.00) (Fig. 17A-B).

447

448 **DISCUSSION**

449 **Source of mineralizing elements**

450 (I) Source of CO_2 and mechanism of calcite precipitation

451 (i) Source of CO_2

452 Carbon and oxygen isotopic composition of CO_2 of different origins are distinct.

453 For example, mantle-derived CO_2 has $δ^{13}C$ values ranging from -8 to -4‰ and

454 $δ^{18}O$ values from +6 to +10‰ (e.g., Taylor et al. 1967; Demény et al. 1998),

455 whereas marine carbonate rocks-derived CO_2 has $δ^{13}C$ = -4-+4‰ and $δ^{18}O$ =

456 +20-+30‰ (e.g., Veizer and Hoefs 1976), and the $δ^{13}C$ and $δ^{18}O$ values of

457 sedimentary organic matter-derived CO_2 range from -30 to -15‰ and +24 to

458 +30‰, respectively (e.g., Hoefs 2009).

459 Calcite and dolomite are the two main C-bearing hydrothermal minerals in the

460 Nayongzhi sulfide ore (Figs. 6-7). Therefore, H_2CO_3 [present as CO_2

461 (aqueous)] and HCO_3^- are two key C species in hydrothermal fluids as

462 evidenced by fluid inclusion observation (Zhu et al. 2016). Given that the C

21

463   isotope fractionation between H_2CO_3 or HCO_3^- (liquid) and CO_2 (gas) is

464   negligible, i.e. $\delta^{13}C_{fluid} \approx \delta^{13}C_{CO2}$ (Ohmoto 1972), we could obtain the

465   theoretical $\delta^{13}C_{fluid}$ value according to the calculated $\delta^{13}C_{CO2}$ value.

466   With an average homogenization temperature of 180°C (fluid inclusions in

467   quartz-II that formed synchronously with calcite-II; Zhu et al. 2016), the $\delta^{13}C_{CO2}$

468   values that range from -4.2 to +0.4‰ were calculated by using the function of

469    $1000ln\alpha_{(CO2-Calcite)} = -2.4612 + 7.663 \times 10^3 / (t + 273.15) - 2.988 \times 10^6 / (t +$

470    $273.15)^2$ (Bottinga 1968; t = 180°C). Similarly, the $\delta^{18}O_{H2O}$ values that vary

471   from +2.3 to +4.0‰ were calculated by using the function of $1000ln\alpha_{(Calcite-H2O)}$

472    $= 2.78 \times 10^6 / (t + 273.15)^2 - 3.39$ (O'Neil et al. 1969; t = 180°C).

473   As shown in Figure 11, the proposed $\delta^{13}C_{fluid}$ values (-4.2-+0.4‰) are higher

474   than those of the mantle and sedimentary organic matter, but are similar to

475   those of both fresh limestone and typical marine carbonate rocks. However,

476   the calculated $\delta^{18}O_{fluid}$ values (+2.3-+4.0‰) are different from the above three

477   geological reservoirs, but overlap with those of metamorphic water (+2-+25‰:

478   Hoefs 2009). Therefore, the theoretical $\delta^{13}C_{fluid}$ and $\delta^{18}O_{fluid}$ values suggest

479   that the source of C is the main ^{13}C-enriched limestone, while O is from a

480   mixed source of ^{18}O-depleted metamorphic water and ^{18}O-enriched limestone.

481   As suggested by in situ S and Pb isotopic evidence (Figs. 14-18), the

482   ore-hosting sedimentary rocks and underlying metamorphic rocks are the two

483   principal sources of mineralizing elements and associated fluids for the

484   Nayongzhi deposit (see below).

485   (ii) Mechanism of calcite precipitation

486   Because the solubility of calcite decreases with increasing of temperature (e.g.,

487   Zheng 1990; Barnes 1997), cooling of hydrothermal fluids themselves could

488   not result in calcite precipitation. In an open hydrothermal system, the major

489   mechanism that can cause calcite precipitation include fluid mixing, water/rock

490   (W/R) interaction and CO_2 degassing (e.g., Zheng 1990; Zheng and Hoefs

491   1993; Hoefs 2009; Du et al. 2017). The high and uniform C isotopic

492   composition of syn-ore calcite suggests a main limestone source for C (Fig. 11),

493   and so the fluid mixing cannot be the dominant mechanism resulting in calcite

494   precipitation. The W/R interaction can generate a circulating process between

495   dissolution and re-crystallization of local carbonate (e.g., Warren 2000). Such

496   a circulating process of carbonate precipitation → dissolution →

497   re-precipitation produced the metastable physical-chemical condition that is

498   requested for giant sulfide mineralization and contributed to calcite

499   precipitation. Further, using C and O isotope fractionation factors and

500   equations (e.g., O'Neil et al. 1969; Zheng and Hoefs 1993), we simulated the C

501   and O isotopic evolution curves of calcite precipitated by the interaction

502   between supposed metamorphic fluids ($\delta^{13}C_{fluid}$ = -2‰, $\delta^{18}O_{fluid}$ = +6‰) and

503   carbonate rocks (Fig. 12). The simulation result suggests that our C and O

504   isotopic data match well with the evolution curve of HCO_3^- as the dominant C

505   species (Fig. 12; Zheng and Hoefs 1993). Similarly, the C and O isotopic

506   compositions of calcite precipitated by CO_2 degassing (with 0.1, 0.2, 0.3 and

23

507   0.4 mol fraction of total C and O; $\delta^{13}C_{fluid}$ = -2‰, $\delta^{18}O_{fluid}$ = +6‰) were

508   simulated (Fig. 13A-B). The result shows that our C and O isotopic data still

509   match well with the evolution curve of HCO_3^- as the dominant C species (Fig.

510   13B). We thus propose that both the W/R interaction and CO_2 degassing are

511   the main mechanisms for calcite precipitation in the Nayongzhi deposit.

512   (II) Source of S, formation mechanism, and isotope fractionation

513   (i) Source of S

514   The fact that both in situ S isotopic data ($\delta^{34}S$ = +11.8-+33.0‰) and the bulk

515   ones ($\delta^{34}S$ = +17.17-+24.79‰) (Table 3) reflect the enrichment of ^{34}S in

516   hydrothermal fluids, a typical characteristic of marine sulfate-derived S. In

517   additional, it has been well-documented that $\delta^{34}S_{barite}$ > $\delta^{34}S_{fluid}$ > $\delta^{34}S_{sulfide}$ if

518   the hydrothermal minerals contain barite (e.g., Ohmoto 1972; Ohmoto et al.

519   1990). Thus, the $\delta^{34}S_{fluid}$ value should be higher than the minimum or average

520   $\delta^{34}S_{sulfide}$ value determined by in situ and bulk analyses (Figs. 14-15) as

521   recorded by the paragenetic association of barite in post-ore phase (Table 1;

522   Peng et al. 2016), i.e. $\delta^{34}S_{fluid}$ > +11.8 or +17.17‰ (minimum in situ and bulk

523   $\delta^{34}S_{sulfide}$ values, respectively) or +21.7‰ (mean value of all measured data).

524   Such S isotopic signatures differ from mantle-derived S (0 ± 3‰: Chaussidon

525   et al. 1989), but overlap with those of the sulfate-bearing (barite/gypsum)

526   evaporates within Cambrian to Triassic marine sedimentary strata in the

527   studied region (Fig. 14B; $\delta^{34}S$ = +22-+28‰: Jin 2008; Zhou et al. 2013a) and

528   the Ediacaran to Cambrian seawater (Fig. 14A-B; $\delta^{34}S$ = +25-+35‰: Claypool

24

529   et al. 1980; Seal 2006). As $\Delta^{34}S_{sulfate\text{-}sulfide}$ can be high up to +15‰ in the

530   process of thermochemical sulfate reduction (Ohmoto et al. 1990; Machel et al.

531   1995; Worden et al. 1995; Ohmoto and Goldhaber 1997), so the theoretical

532   $\delta^{34}S_{sulfide}$ value could down to +7‰ or +10‰, if the reduced S was completely

533   derived from evaporates or seawater. The theoretically predicted $\delta^{34}S_{sulfide}$

534   values sourced from both of the above two reservoirs can match well with the

535   observed $\delta^{34}S$ values (> +11.8‰; Fig. 14C). This suggests multiple S

536   reservoirs for S^{2-} in the studied deposit. Previous studies showed that the S in

537   the nearby carbonate-hosted Zn-Pb deposits, such as Shaojiwan (hosts in

538   Permian), Tianqiao, Qingshan and Shanshulin (hosts in Carboniferous) (Figs.

539   2, 14A-B), is also derived from multiple S reservoirs (Zhou et al. 2013a, 2014b;

540   Li et al., 2015).

541   (ii) Formation mechanism of reduced S

542   Two mechanisms, including bacterial sulfate reduction (BSR) and

543   thermochemical sulfate reduction (TSR), have been employed to explain the

544   formation of S^{2-} from SO_4^{2-} (e.g., Seal 2006; Basuki et al. 2008; Zhou et al.

545   2014a). These two reduction processes are temperature-dependent. BSR

546   occurs at a relatively low T (< 110°C: Jørgenson et al. 1992; Basuki et al. 2008).

547   The homogenization temperature of fluid inclusions in quartz (113-232°C; Zhu

548   et al. 2016) is too high for bacteria to survive. So BSR played an insignificant

549   role in the formation of S^{2-}. TSR occurs at a relatively high T (> 100-140°C:

550   Machel et al. 1995; Worden et al. 1995) and can produce a large amount of S^{2-},

25

551   with relatively stable δ^{34}S values (e.g., Ohmoto et al. 1990; Seal 2006).

552   Moreover, the mixed process of hot and cold ore-forming fluids could form S^{2-}

553   from SO_4^2 by TSR through the reactions of SO_4^{2-} + 2C = S^{2-} + 2CO$_2$, SO_4^{2-} +

554   CH_4 = H_2S + CO_3^{2-} + H^2O or SO_4^{2-} + 2CH$_2$O = H_2S + HCO$_3^-$ (e.g., Worden et al.

555   1995; Leach et al., 2005). We thus propose that the TSR has played a key role

556   in the formation of S^{2-} in the Nayongzhi deposit.

557   (iii) S isotope fractionation

558   The similarity of bulk S isotopic composition between pyrite (δ^{34}S =

559   +18.12-+22.06‰) and sphalerite (δ^{34}S = +17.17-+24.79‰) precipitated at

560   different ore-forming stages (Table 2; Fig. 14C) indicates that the bulk S

561   isotopic data could not reflect the real S isotope fractionation. The imparity of in

562   situ δ^{34}S values between pyrite (+15.1-+27.0‰) and sphalerite (+11.8-+33.0‰)

563   crystals suggests that in situ determined S isotopes can reflect the nature of

564   fractionation involved in mineralization. As shown in Figure 15A, rims of pyrite

565   crystal have δ^{34}S values (+15.1-+15.3‰) higher than those of rims of

566   paragenetic sphalerite crystal (δ^{34}S = +11.8-+11.9‰). Such S isotopic

567   signatures suggest that S isotope fractionation between pyrite and paragenetic

568   sphalerite has reached thermodynamic equilibrium (e.g. Ohmoto et al. 1990;

569   Seal 2006). We thus propose an equilibrium S isotope fractionation between

570   paragenetic sulfide minerals, at least locally.

571   In addition, the in situ S isotopic ratios decrease from the core to rim of both

572   pyrite and sphalerite crystals (Fig. 15A), which can be explained by (a)

26

573   variation of physical-chemical condition (T, pH, f_{O2}, etc.) in single S reservoir

574   (Seal 2006); (b) mixture of multiple S reservoirs (Ohmoto et al. 1990); or (c)

575   dynamic fractionation of S isotopes (Hoefs 2009). Previous studies suggested

576   that the change of physical-chemical condition can cause significant variation

577   of S isotopes in hydrothermal system (e.g., Seal 2006; Hoefs 2009). However,

578   the circulating process of carbonate dissolution → re-precipitation can provide

579   a metastable environment for giant mineralization (see above), so the variation

580   of physical-chemical condition is indistinctive, and thus plays an insignificant

581   role in the decreasing $\delta^{34}S$ values from core to rim of sulfide crystals. The

582   mixed process of the heavy S isotope-enriched fluid and the ^{34}S-depleted fluid

583   can cause significant variation of S isotopes (e.g., Seal 2006). Both bulk and in

584   situ S isotopic data in this study suggests multiple S reservoirs for S^{2-} in the

585   Nayongzhi deposit, so the observed decrease of S isotopes from core to rim of

586   sulfide crystals (Fig. 15A) may be the result of a mixture of multiple S

587   reservoirs. Alternatively, the rapid precipitation of sulfide minerals can cause a

588   strong Rayleigh fractionation of S isotopes during the process of fluid mixing.

589   As a consequence of the dynamic fractionation, ^{34}S is expected to be more

590   enriched in the core of sulfide crystals than their rim (Fig. 15A).

591   (III) Source of ore-forming metal

592   Because of extremely low contents of U and Th in sulfide minerals (especially

593   galena), time-integrated effect of U and Th on radiogenic Pb isotopes in

594   sulfides is negligible (e.g., Carr et al, 1995; Muchez et al. 2005; Pass et al.

27

2014; Zhou et al. 2014b). Therefore, the Pb isotopic ratios of galena from the Nayongzhi deposit can represent those of hydrothermal fluids. The narrow range of in situ Pb isotopic data suggests a single source or else a well-mixed source of Pb (Table 4; Fig. 16A-B). In the plot of $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ (Fig. 16A), all the Pb isotopic data plot in the field that overlaps with the Pb evolution curve of the upper crust contributed to the orogeny and the field of modern lower crust (Zartman and Doe 1981). Similarly, in the $^{208}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ diagram (Fig. 16B), all the Pb isotopic data also plot into the field of modern lower crust (Zartman and Doe 1981). This suggests that the source of Pb is the deep continental crust (e.g., Zartman and Doe 1981). Again, the μ values ($^{238}U/^{204}Pb$ = 9.64-9.67) of the galena are slightly higher than that of the mean value of the continental crust (μ = 9.58), also indicating a deep-seated crustal source for Pb (e.g., Carr et al. 1995).

As shown in Figure 16A, at a given $^{207}Pb/^{204}Pb$ ratio, the galena displays significantly lower $^{206}Pb/^{204}Pb$ ratios than those of the Permian Emeishan flood basalts, and Ediacaran carbonate rocks. Such Pb isotopic signatures rule out the main contribution of Pb metal from mantle-derived magmatic rocks and ore-hosting sedimentary rocks. On the contrary, in situ Pb isotopic ratios of the galena are similar to those of the Proterozoic metamorphic rocks (Fig. 16A). This further suggests a continental crustal origin for Pb in hydrothermal fluids and the basement rocks provided the majority of Pb metal.

The in situ Pb isotopic ratios gradually increase from galena-I (fine-grained) to

28

617   galena-II (coarse-grained) in both $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ (Fig. 17A) and

618    $^{208}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ diagrams (Fig. 17B). There are two possibilities: (i)

619   U and Th contents of galena-II are relatively higher than those of galena-I; or (ii)

620   high radiogenic Pb-enriched source provides more Pb for galena-II than

621   galena-I. Trace elements determined by LA-ICPMS show that there is no

622   significant difference of both U and Th contents between two generations of

623   galena (Ye Lin et al. 2011 and unpublished data). Furthermore, Pb isotopic

624   data of galena-I overlap with those of galena-II in the diagram of $^{208}Pb/^{206}Pb$ vs.

625    $^{207}Pb/^{206}Pb$ (Fig. 18), suggesting that both of them have the same contents of

626   U and Th. On the contrary, in both $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ (Fig. 17A),

627    $^{208}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ (Fig. 17B), and $^{208}Pb/^{206}Pb$ vs. $^{207}Pb/^{206}Pb$

628   diagrams (Fig. 18), the Pb isotopic compositions of two generations of galena

629   form two distinct evolution curves. This implies that the high radiogenic

630   Pb-enriched source (most likely the ore-hosting sedimentary rocks) provides

631   more Pb for the ore-forming fluids at the late phase than the early phase, and

632   thus slightly changes the evolution curve of Pb isotopes.

633   **Timing of mineralization**

634   The occurrence of ore body (Fig. 6) and sulfide ore (Figs. 7-8), and the

635   evidence of mineralogy (Figs. 9-10) and isotope geochemistry (Figs. 11-18)

636   show that the Nayongzhi deposit belongs to epigenetic type. This means that

637   the formation of the Nayongzhi deposit should posterior to the ore-hosting late

638   Ediacaran and early Cambrian strata. In addition, the Nayongzhi deposit is

29

639   located at the northern margin of the Triassic Youjiang Basin and is structurally

640   controlled by the Wuzhishan fold-fault system (Figs. 2-4), all of which were

641   active during the Yanshanian Orogeny (e.g., Chen et al. 2015). Such an

642   ore-controlling structure feature suggests that the Nayongzhi deposit was most

643   likely formed in the Yanshanian period. Moreover, isotope geochronology

644   studies suggest that the ages of carbonate-hosted Zn-Pb deposits in the SYG

645   province are 226-165 Ma (e.g., Mao et al. 2012; Zhou et al. 2013a; Zhang et al.

646   2015). Therefore, we propose that the Nayongzhi deposit formed in the early

647   Yanshanian (late Triassic) and related to the evolution of the Triassic Youjiang

648   Basin, and was most likely to be the product of basin-orogeny coupling.

649

650   **IMPLICATIONS**

651   **Ore genesis type**

652   Ore body in the Nayongzhi deposit occurs as stratiform or lentiform (Figs. 6A-B,

653   7A), with a clear strata-bound feature. This led some researchers to classify it

654   as a SEDEX-type or sedimentation reworking type (e.g., Chen et al. 2015; Jin

655   et al. 2015). In fact, with the exception of stratiform or lentiform Zn-Pb ore body,

656   the steeply dipping veined one is also developed (Figs. 6A, 7E). Furthermore,

657   the ore-hosting rocks are late Ediacaran and early Cambria carbonate rocks,

658   which differ from the siliciclastic rocks that host sulfide ore of the SEDEX-type

659   (e.g., Leach et al. 2005, 2010). The newly-obtained bulk C-O and S isotopes,

660   and in situ S and Pb isotopes, together with ore deposit geology and

661   mineralogy, suggesting an epigenetic origin for the Nayongzhi deposit.

662   Extensive studies have suggested that the carbonate-hosted Zn-Pb deposits in

663   the SYG province are epigenetic SYG-type and are characterized by: (a) ore

664   body has a closely spatial association with the Emeishan mafic magmatism

665   (Fig. 1B); (b) sulfide ore has a high grade, i.e. > 10 wt. % Zn + Pb, and rich in

666   Ag, Cu, Cd, Ge and Ga (e.g., Ye et al. 2011; Zhou et al. 2013a; Zhu et al. 2017);

667   (c) ore-forming fluids having low-medium temperature (120-280°C) and low

668   salinity (2-10 wt. % NaCl equiv.) (e.g., Li et al. 2007; Zhou et al. 2014a; Zhu et

669   al. 2016); and (d) a mixed metal source of overlying basalts, ore-hosting

670   sedimentary rocks and underlying metamorphic rocks (e.g., Huang et al. 2010;

671   Zhou et al. 2014b; Li et al. 2015, 2016). However, the Nayongzhi deposit is

672   distinct from the nearby Zn-Pb deposits (Table 5) in: (a) ore body has no

673   directly genetic   association with igneous activity (Fig. 4); (b) sulfide ore

674   having low ore grade, namely average 8-10 wt. % Zn + Pb; (c) ore-forming

675   fluids are characterized by low temperature (113-232°C) and moderate salinity

676   (10-15 wt. % NaCl equiv.) (Zhu et al. 2016); (d) basement-derived metals are

677   dominant in hydrothermal fluids (Fig. 16A); and (e) carbonate solution collapse

678   breccia is well-developed (Figs. 7-8). These mineralized features of the

679   Nayongzhi deposit can be compared to those of typical MVT deposits (e.g.,

680   Leach et al. 2005, 2010). So we interpret the Nayongzhi deposit to be an

681   epigenetic MVT deposit.

682   **Ore formation process**

683 Through integrating all the information, this paper proposes a new working

684 model to explain the Zn-Pb mineralization in the Wuzhishan anticline area (Fig.

685 19) as follows: The basement-derived metal-bearing metamorphic fluids (as

686 suggested by C-O and Pb isotopes; Figs. 12-13, 16-18) were driven upward

687 along the regional Yadu-Ziyun fault (Figs. 2-3) by the late Indosinian Orogeny

688 (226-205 Ma) and Triassic Youjiang Basining (e.g., Zhou et al. 2013a; Zhang

689 et al. 2015), and then released into secondary structural units (such as the

690 Wuzhishan anticline; Figs. 2-3) when the tectonic regimes shift from

691 compression to extension at the early Yanshanian period (205-165 Ma) (e.g.,

692 Qiu et al. 2016). These fluids were trapped into the platform carbonate

693 sequences, where the evaporitic salt structure and sedimentary organic matter

694 are well-developed (Fig. 19). This process resulted in the formation of S^{2-} from

695 SO_4^{2-} by TSR and the extraction of parts of mineralizing elements from the

696 ore-hosting strata via the W/R interaction (as evidenced by C-O, S and Pb

697 isotopes; Figs. 12-18). The rapid sulfide precipitation caused by mixing

698 multiple S reservoirs with associated fluids results in significant fractionation of

699 S isotopes (Figs. 14A-C, 15A). During the ore formation process, local

700 carbonate acted as a buffer through repeated dissolution and re-precipitation,

701 providing the metastable metallogenic environment for massive sulfide

702 mineralization. According to our new model, some potential and buried ore

703 bodies may be found in the future (Fig. 19).

704 From the above, this study implies that the extensional setting (Youjiang Basin)

705 facilitated the excretion of hydrothermal fluids, the fold structure (Wuzhishan

706 anticline) was beneficial to trap fluids, the carbonate platform sequences

707 supplied an S source and organic reducers, and the fluids then mixed and the

708 carbonate buffer caused rapid and continued precipitation of sulfide minerals,

709 all of which are crucial for the formation and exploration of MVT deposits in

710 general.

711

712 **ACKNOWLEDGEMENTS**

722

723 **REFERENCES CITED**

724 Bai, J., Huang, Z., Zhu, D., Yan, Z., and Zhou, J. (2013) Isotopic compositions

725 of sulfur in the Jinshachang lead-zinc deposit, Yunnan, China, and its

726 implication on the formation of sulfur-bearing minerals. Acta Geologica

727   Sinica (English Edition), 87, 1355–1369.

728 Bao, Z., Yuan, W., Yuan, H., Liu, X., Chen, K., and Zong, C. (2016)

729   Non-matrix-matched determination of lead isotope ratios in ancient bronze

730   artifacts by femtosecond laser ablation multi-collector inductively coupled

731   plasma mass spectrometry. International Journal of Mass Spectrometry,

732   402, 12–19.

733 Barnes, H.L. (1997) Geochemistry of hydrothermal ore deposits. John Wiley &

734   Sons, v. 1.

735 Barker, S.L., Hickey, K.A., Cline, J.S., Dipple, G.M., Kilburn, M.R., Vaughan,

736   J.R., and Longo, A.A. (2009) Uncloaking invisible gold: Use of nanoSIMS

737   to evaluate gold, trace elements, and sulfur isotopes in pyrite from

738   Carlin-type gold deposits. Economic Geology, 104, 897–904.

739 Basuki, N.I., Taylor, B.E., and Spooner, E.T.C. (2008) Sulfur isotope evidence

740   for thermo-chemical reduction of dissolved sulfate in Mississippi valley

741   type zinc-lead mineralization, Bongara area, northern Peru. Economic

742   Geology, 103, 183–799.

743 Bottinga, Y. (1968) Calculation of fractionation factors for carbon and oxygen

744   isotopic exchange in the system calcite-carbon dioxide-water. The Journal

745   of Physical Chemistry, 72, 800–808

746 Carr, G.R., Dean, J.A., Suppel, D.W., and Heithersay, P.S. (1995) Precise lead

747   isotope fingerprinting of hydrothermal activity associated with Ordovician

748   to Carboniferous metallogenic events in the Lachlan fold belt of New

749   South Wales. Economic Geology, 90, 1467–1505.

750 Carter, A., Roques, D., Bristow, C., and Kinny, P. (2001). Understanding

751   Mesozoic accretion in Southeast Asia: significance of Triassic

752   thermotectonism (Indosinian orogeny) in Vietnam. Geology 29, 211–214.

753 Chaussidon, M., Albarède, F., and Sheppard, S.M.F (1989) Sulphur isotope

754   variations in the mantle from ion microprobe analyses of micro-sulphide

755   inclusions. Earth and Planetary Science Letters, 92, 144–156.

756 Chen, G.Y., Wang, L., Fan, Y.M., and Zheng, W. (2015) Ore-search prospect of

757   the deep subsurface in the Wuzhishan Pb-Zn ore field, Guizhou province.

758   Geology and Exploration, 51, 859–869 (in Chinese with English abstract).

759 Chen, K.Y., Yuan, H.L., Bao, Z.A., Zong, C.L., and Dai, M.N. (2014) Precise

760   and accurate in situ determination of lead isotope ratios in NIST, USGS,

761   MPI-DING and CGSG glass reference materials using femtosecond laser

762   ablation MC-ICP-MS. Geostandards and Geoanalytical Research, 38, 5–

763   21.

764 Chen, M., Zhang, Z., Santosh, M., Dang, Y., and Zhang, W. (2015). The

765   Carlin-type gold deposits of the "golden triangle" of SW China: Pb and S

766   isotopic constraints for the ore genesis. Journal of Asian Earth Sciences,

767   103, 115–128.

768 Claypool, G.E., Holser, W.T., Kaplan, I.R., Sakai, H., and Zak, I. (1980) The

769   age curves of sulfur and oxygen isotopes in marine sulfate and their

770   mutual interpretation. Chemical Geology, 28, 199–260.

771   Demény, A., Ahijado, A., Casillas, R., and Vennemann, T.W. (1998) Crustal

772   contamination and fluid/rock interaction in the carbonatites of

773   Fuerteventura (Canary Islands, Spain): A C, O, H isotope study. Lithos, 44,

774   101–115.

775   Du, L.J., Li, B., Huang, Z.L., Zhou, J.X., Zou, G.F., and Yan, Z.F. (2017)

776   Carbon-oxygen isotopic geochemistry of the Yangla Cu skarn deposit, SW

777   China: Implications for the source and evolution of hydrothermal fluids.

778   Ore Geology Reviews, 88, 809–821.

779   Friedman, I., and O'Neil, J.R. (1977) Compilation of stable isotope fractionation

780   factors of geochemical interest. Data of Geochemistry, U.S. Geological

781   Survey Professional Paper, 440-KK, p. 1–12.

782   Gao, S., Yang, J., Zhou, L., Li, M., Hu, Z.C., Guo, J.L., Yuan, H.L., Gong, H.J.,

783   Xiao, G.Q., and Wei, J.Q. (2011) Age and growth of the Archean Kongling

784   terrain, South China, with emphasis on 3.3 Ga granitoid gneisses.

785   American Journal of Sciences, 311, 153–182.

786   Gustafson, L.B., and Williams, N. (1981) Sediment-hosted stratiform deposits

787   of copper, lead and zinc. Economic Geology, 75, 139–178.

788   Heijlen, W., Muchez, P., Banks, D., Schneider, J., Kucha, H., and Keppens, E.

789   (2003) Carbonate-hosted Zn-Pb deposits in Upper Silesia, Poland: Origin

790   and Evolution of Mineralizing fluids and constraints on genetic models.

791   Economic Geology, 98, 911–932.

792   Hoefs, J. (2009) Stable isotope geochemistry (sixth edition). Springer-Verlag

793   Berlin Heidelberg doi: 10.1007/978-3-540-70708-0

794   Hu, R.Z., and Zhou, M.F. (2012) Multiple Mesozoic mineralization events in

795   South China-an introduction to the thematic issue. Mineralium Deposita,

796   47, 579–588.

797   Hu, R., Fu, S., Huang, Y., Zhou, M., Fu, S., Zhao, C., Wang, Y., Bi, X., and Xiao,

798   J. (2017) The giant South China Mesozoic low-temperature metallogenic

799   domain: Reviews and a new geodynamic model. Journal of Asian Earth

800   Sciences, 137, 9–34.

801   Huang, Z., Li, X., Zhou, M., Li, W., and Jin, Z. (2010) REE and C-O isotopic

802   geochemistry of calcites from the word-class Huize Pb-Zn deposits,

803   Yunnan, China: Implication for the ore genesis. Acta Geologica Sinica

804   (English edition), 84, 597–613.

805   Ikehata, K., Notsu, K., and Hirata, T. (2008) In situ determination of Cu isotope

806   ratios in copper-rich materials by NIR femtosecond LA-MC-ICPMS.

807   Journal of Analytical Atomic Spectrometry, 23, 1003–1008.

808   Jian, P., Li, D.Y., Kröner, A., Zhang, Q., Wang, Y.Z., Sun, X.M., and Zhang, W.

809   (2009) Devonian to Permian plate tectonic cycle of the Paleo-Tethys

810   Orogen in southwest China (II): Insights from zircon ages of ophiolites,

811   arc/back-arc assemblages and within-plate igneous rocks and generation

812   of the Emeishan CFB province. Lithos, 113, 767–784.

813   Jin, C.H., Li, K., Huang, L., Zhang, Y., and Shen, Z.W. (2015) Characteristics of

814   sulfur and lead isotope composition and metallogenic material source of

815   the Nayongzhi Pb-Zn deposit, northwestern Guizhou province. Journal of

816   Mineralogy and Petrology, 35, 81–88 (in Chinese with English abstract).

817 Jin, Z.G. (2008) The ore-control factors, ore-forming regularity and ore

818   forecasting of Pb-Zn deposits in NW Guizhou province. Engine Industry

819   Press, Beijing, pp. 1–105 (in Chinese).

820 Jin, Z.G., Zhou, J.X., Huang, Z.L., Luo, K., Gao, J.G., Peng, S., Wang, B., and

821   Chen, X.L. (2016). Ore genesis of the Nayongzhi Pb-Zn deposit, Puding

822   city, Guizhou Province, China: Evidences from S and in situ Pb isotopes.

823   Acta Petrologica Sinica, 32, 3441–3455.

824 Jørgenson, B.B., Isaksen, M.F., and Jannasch, H.W. (1992) Bacterial sulfate

825   reduction above 100°C in deep sea hydrothermal vent sediments.

826   Science, 258, 1756–1757.

827 Wilkinson, J.J., Stoffell, B., Wilkinson, C.C., Jeffries, T.E., and Appold, M.S.

828   (2009) Anomalously metal-rich fluids form hydrothermal ore deposits.

829   Science, 323, 764–767.

830 Leach, D.L., Bradley, D.C., Huston, D., Pisarevsky, S.A., Taylor, R.D., and

831   Gardoll, S.J. (2010) Sediment-hosted lead-zinc deposits in Earth history.

832   Economic Geology, 105, 593–625.

833 Leach, D.L., Sangster, D., Kelley, K.D., Large, R.R., Garven, G., Allen, C.,

834   Gutzmer, J., and Walters, S. (2005) Sediment-hosted lead-zinc deposits:

835   A global perspective. Economic Geology, 100th Ann 561–607.

836 Li, B., Zhou, J.X., Huang, Z.L., Yan, Z.F., Bao, G.P., and Sun, H.R. (2015)

837   Geological, rare earth elemental and isotopic constraints on the origin of

838   the Banbanqiao Zn-Pb deposit, southwest China. Journal of Asian Earth

839   Sciences, 111, 100–112.

840 Li, B., Zhou, J., Li, Y., Chen, A., and Wang, R. (2016) Geology and Isotope

841   Geochemistry of the Yinchanggou-Qiluogou Pb-Zn Deposit, Sichuan

842   Province, Southwest China. Acta Geologica Sinica (English Edition), 90,

843   1768–1779.

844 Li, W.B., Huang, Z.L., and Yin, M.D. (2007) Dating of the giant Huize Zn-Pb ore

845   field of Yunnan province, southwest China: Constraints from the Sm-Nd

846   system in hydrothermal calcite. Resource Geology, 57, 90–97.

847 Liao, W. (1984) Mineralization model and the characters of isotope

848   composition of S and Pb in the Pb-Zn metallic area in the East and West

849   Yunnan Province, China. Geology and Prospecting, 1, 1–6 (in Chinese

850   with English abstract).

851 Lin, Z.Y., Wang, D.H., and Zhang, C.Q. (2010) Rb-Sr isotopic age of sphalerite

852   from the Paoma lead-zinc deposit in Sichuan Province and its implications.

853   Geology of China, 37, 488–196 (in Chinese with English abstract).

854 Liu, H.C., and Lin, W.D. (1999) Study on the law of Pb-Zn-Ag ore deposit in

855   northeast Yunnan, China. Kunming, Yunnan University Press, pp. 1–468

856   (in Chinese).

857 Liu, Y., Hu, Z., Gao, S., Günther, D., Xu, J., Gao, C., and Chen, H. (2008) In

858   situ analysis of major and trace elements of anhydrous minerals by

859   LA-ICP-MS without applying an internal standard. Chemical Geology, 257,

860   34–43.

861 Mao, J.W., Zhou, Z.H., Feng, C.Y., Wang, Y.T., Zhang, C.Q., Peng, H.J., and

862   Miao, Y. (2012) A preliminary study of the Triassic large-scale

863   mineralization in China and its geodynamic setting. Geology of China, 39,

864   1437−1471 (in Chinese with English abstract).

865 Machel, H.G., Krouse, H.R., and Sassen, R. (1995) Products and

866   distinguishing criteria of bacterial and thermo-chemical sulfate reduction.

867   Applied Geochemistry, 10, 373−389.

868 Muchez, P., Heijlen, W., Banks, D., Blundell, D., Boni, M., and Grandia, F.

869   (2005) Extensional tectonics and the timing and formation of basin-hosted

870   deposits in Europe. Ore Geology Reviews, 27, 241−267.

871 Ohmoto, H., and Goldhaber, M.B. (1997) Sulfur and carbon isotopes, in

872   Barnes HL (Editor), Geochemistry of hydrothermal ore deposits, 3rd edition.

873   Wiley, New York pp. 517–611

874 Ohmoto, H., Kaiser, C.J., and Geer, K.A. (1990) Systematic of sulfur isotopes

875   in recent marine sediments and ancient sediment-hosted base metal

876   deposits In H.K Herbert and S.E. Ho (Editors), Stable isotopes and Fluid

877   Processes in Mineralisation. Geol Dep Univ Extens, University of Western

878   Australia 23: 70–120

879 Ohmoto, H. (1972) Systematics of Sulfur and Carbon Isotopes in Hydrothermal

880   Ore Deposits. Economic Geolog, 67, 551–579.

881 O'Neil, J.R., Clayton, R.N., and Mayeda, T.K. (1969) Oxygen isotope

882   fractionation in divalent metal carbonates. Journal of Chemical Physics,

883   51, 5547–5558.

884 Pass, H.E., Cookem, D.R., Davidson, G., Maas, R., Dipple, G., Rees, C.,

885   Ferreira, L., Taylor, C., and Deyell, C.L. (2014) Isotope geochemistry of

886   the northeast zone, Mount Polley alkalic Cu-Au-Ag porphyry deposit,

887   British Columbia: A case for carbonate assimilation. Economic Geology,

888   109, 859–890.

889 Peevler, J., Fayek, M., Misra, K.C., and Riciputi, L.R. (2003) Sulfur isotope

890   microanalysis of sphalerite by SIMS: constraints on the genesis of

891   Mississippi valley-type mineralization, from the Mascot-Jefferson City

892   district, East Tennessee. Journal of Geochemical Exploration, 80, 277–

893   296.

894 Peng, S., Jin, Z.G., Lin, G.S., Zhu, Y.Q., and Wang, B (2016) Analysis of

895   ore-controlling factors and metallogenic model of Wuzhishan Pb-Zn

896   deposit, Guizhou: A case study of Nayongzhi deposit. Mineral Exploration,

897   7, 463−470 (in Chinese with English abstract).

898 Qiu, L., Tang, S.L., Wang, Q., Yang, W.X., Tang, X.L., and Wang, J.B. (2016)

899   Mesozoic geology of southwestern China: Indosinian foreland

900   overthrusting and subsequent deformation. Journal of Asian Earth

901   Sciences, 122, 91–105.

902 Qiu, Y.M., Gao, S., McNaughton, N.J., Groves, D.I., and Ling, W.L. (2000) First

903   evidence of >3.2 Ga continental crust in the Yangtze craton of south China

904   and its implications for Archean crustal evolution and Phanerozoic

905   tectonics. Geology, 28, 11–14.

906   Reid, A., Wilson, C.J.L., Shun, L., Pearson, N., and Belousova, E. (2007)

907   Mesozoic plutons of the Yidun Arc, SW China: U-Pb geochronology and

908   Hf isotopic signature. Ore Geology Reviews, 31, 88–106.

909   Steinhoefel, G., Horn, I., and von Blanckenburg, F. (2009) Micro-scale tracing

910   of Fe and Si isotope signatures in banded iron formation using

911   femtosecond laser ablation. Geochimica et Cosmochimica Acta, 73,

912   5343–5360.

913   Seal, I.R. (2006) Sulfur isotope geochemistry of sulfide minerals. Review of

914   Mineralogy and Geochemistry, 61, 633–677.

915   Taylor, H.P., Frechen, J., and Degens, E.T. (1967) Oxygen and carbon isotope

916   studies of carbonatites from the Laacher See District, West Germany and

917   the Alnö District, Sweden. Geochimica et Cosmochimica Acta, 31, 407–

918   430.

919   Tu GZ (1984) Geochemistry of Strata-bound Ore Deposits in China (Volumes

920   I). Science Press, Beijing, pp. 13–69 (in Chinese with English abstract)

921   Veizer, J., and Hoefs, J. (1976) The nature of O^{18}/O^{16} and C^{13}/C^{12} secular

922   trends in sedimentary carbonate rocks. Geochimica et Cosmochimica

923   Acta, 40, 1387–1395

924   Warren, J. (2000) Dolomite: occurrence, evolution and economically important

925   associations. Earth Science-Review, 52, 1–81.

926 Wang, C.M., Deng, J., Carranza, E.J.M., and Lei, X.R. (2014) Nature, diversity

927   and temporal-spatial distributions of sediment-hosted Pb-Zn deposit in

928   China. Ore Geology Reviews, 56, 327–351.

929 Wang, L.J. (1994) Geological and geochemical features of lead-zinc deposits

930   in northwestern, Guizhou Province, China. Journal of Guilin College of

931   Geology, 14, 125–130 (in Chinese with English abstract).

932 Wei, A.Y., Xue, C.D., Xiang, K., Li, J., Liao, C., and Akhter, Q.J. (2015) The

933   ore-forming process of the Maoping Pb-Zn deposit, northeastern Yunnan,

934   China: Constraints from cathodoluminescence (CL) petrography of

935   hydrothermal dolomite. Ore Geology Reviews, 70, 562–577.

936 Wong, W.H. (1927) Crustal movements and igneous activities in eastern China

937   since Mesozoic time. Bulletin Geol Association China, 6, 9–37.

938 Worden, R.H., Smalley, P.C., and Oxtoby, N.H. (1995) Gas souring by the

939   thermo chemical sulfate reduction at 140°C. AAPG Bulletin 79, 854–863.

940 Xie, J.R. (1963) Introduction of the Chinese Ore Deposits. Scientific Books

941   Publishing House, Beijing, pp. 1–71 (in Chinese).

942 Xu, Y., Huang, Z., Zhu, D., and Luo, T. (2014) Origin of hydrothermal deposits

943   related to the Emeishan magmatism. Ore Geology Reviews, 63, 1–8.

944 Yan, D.P., Zhou, M.F., Song, H.L., Wang, X.W., and Malpas, J. (2003) Origin

945   and tectonic significance of a Mesozoic multilayer overthrust system

946   within the Yangtze Block (South China). Tectonophysics, 361, 239–254.

947   Yan, Z.F., Huang, Z.L., Xu, C., Chen, M., and Zhang, Z.L. (2007) Signatures of

948   the source for the Emeishan flood basalts in the Ertan area: Pb isotope

949   evidence. Chinese Journal of Geochemistry, 26, 207–213.

950   Ye, L., Cook, N.J., Ciobanu, C.L., Liu, Y.P., Zhang, Q., Liu, T.G., Gao, W., Yang,

951   Y.L., and Danyushevsky, L. (2011) Trace and minor elements in sphalerite

952   from base metal deposits in South China: a LA–ICPMS study. Ore

953   Geology Reviews, 39, 188–217.

954   Yuan, H.L., Yin, C., Liu, X., Chen, K.Y., Bao, Z.A., Zong, C.L., Dai, M.N., Lai,

955   S.C., Wang, R., and Jiang, S.Y. (2015) High precision in-situ Pb isotopic

956   analysis of sulfide minerals by femtosecond laser ablation multi-collector

957   inductively coupled plasma mass spectrometry. Science China Earth

958   Science, 58, 1713–1721.

959   Zartman, R.E., and Doe, B.R. (1981) Plumbotectonics-the model.

960   Tectonophysics, 75, 135–162.

961   Zaw, K., Peters, S.G., Cromie, P., Burrett, C., and Hou, Z.Q. (2007) Nature,

962   diversity of deposit types and metallogenic relations of South China. Ore

963   Geology Reviews, 31, 3–47.

964   Zhang, C., Wu, Y., Hou, L., and Mao, J. (2015) Geodynamic setting of

965   mineralization of Mississippi Valley-type deposits in world-class

966   Sichuan-Yunnan-Guizhou Zn-Pb triangle, southwest China: Implications

967   from age-dating studies in the past decade and the Sm-Nd age of the

968   Jinshachang deposit. Journal of Asian Earth Sciences, 103, 103–114.

969 Zhang, J., Lin, Y., Yang, W., Shen, W., Hao, J., Hu, S., and Cao, M. (2014)

970   Improved precision and spatial resolution of sulfur isotope analysis using

971   NanoSIMS. Journal of Analytical Atomic Spectrometry, 29, 1934–1943.

972 Zheng, M.H., and Wang, X.C. (1991) Genesis of the Daliangzi Pb-Zn deposit in

973   Sichuan, China. Economic Geology, 86, 831–846.

974 Zheng, Y.F. (1990) Carbon-oxygen isotopic covariation in hydrothermal calcite

975   during degassing of CO_2. Mineralium Deposita, 25, 246–250.

976 Zheng, Y.F., and Hoefs, J. (1993) Carbon and oxygen isotopic covariations in

977   hydrothermal calcites. Mineralium Deposita, 28, 79–89.

978 Zhou, C.X., Wei, C.S., and Guo, J.Y. (2001) The source of metals in the

979   Qilingchang Pb-Zn deposit, Northeastern Yunnan, China: Pb-Sr isotope

980   constraints. Economic Geology, 96, 583–598.

981 Zhou, J.X., Huang, Z.L., Lv, Z.C., Zhu, X.K., Gao, J.G., and Mirnejad, H.

982   (2014b) Geology, isotope geochemistry and ore genesis of the Shanshulin

983   carbonate-hosted Pb-Zn deposit, southwest China. Ore Geology Reviews,

984   63, 209–225.

985 Zhou, J., Huang, Z., and Yan, Z. (2013b) The origin of the Maozu

986   carbonate-hosted Pb-Zn deposit, southwest China: Constrained by

987   C-O-S-Pb isotopic compositions and Sm-Nd isotopic age. Journal of Asian

988   Earth Sciences, 73, 39–47.

989 Zhou, J., Huang, Z., Zhou, M., Li, X., and Jin, Z. (2013a) Constraints of

990   C-O-S-Pb isotope compositions and Rb-Sr isotopic age on the origin of

the Tianqiao carbonate-hosted Pb-Zn deposit, SW China. Ore Geology Reviews, 53, 77–92.

Zhou, J.X., Huang, Z.L., Zhou, M.F., Zhu, X.K., and Muchez, P. (2014a) Zinc, sulfur and lead isotopic variations in carbonate-hosted Pb-Zn sulfide deposits, southwest China. Ore Geology Reviews, 58, 41–54.

Zhou, J.X., Bai, J.H., Huang, Z.L., Zhu, D., Yan, Z.F., and Lv, Z.C. (2015) Geology, isotope geochemistry and geochronology of the Jinshachang carbonate-hosted Pb-Zn deposit, southwest China. Journal of Asian Earth Sciences, 98, 272–284.

Zhou, M.F., Yan, D.P., Kennedy, A.K., Li, Y.Q., and Ding, J. (2002) SHRIMP zircon geochronological and geochemical evidence for Neo-Proterozoic arc-related magmatism along the western margin of the Yangtze Block, South China. Earth and Planetary Science Letters, 196, 1–67.

Zhou, M.F., Zhao, X.F., Chen, W.T., Li, X.C., Wang, W., Yan, D.Y., and Qiu, H.N. (2014c) Proterozoic Fe-Cu metallogeny and supercontinental cycles of the southwestern Yangtze Block, southern China and northern Vietnam. Earth Science-Review, 139, 59–82.

Zhu, C.W., Wen, H.J., Zhang, Y.X., Fu, S.H., Fan, H.F., and Cloquet, C. (2017) Cadmium isotope fractionation in the Fule Mississippi Valley-type deposit, Southwest China. Mineralium Deposita, 52, 675–686.

Zhu, L.Y., Su, W.C., Shen, N.P., Dong, S.D., Cai, J.L., Zhang, Z.W., Zhao, H., and Xie, P. (2016) Fluid inclusion and sulfur isotopic studies of lead-zinc

46

1013   deposits, northwestern Guizhou, China. Acta Petrologica Sinica, 32,

1014   3431–3440 (in Chinese with English abstract).

1015

1016   Figure captions

1017   FIGURE 1. A: Regional geological setting of South China, highlighting the

1018   general study area; B: Geological sketch map of the Sichuan-Yunnan-Guizhou

1019   (SYG) Pb-Zn metallogenic province (modified from Liu and Lin 1999 and Yan

1020   DP unpublished map), which shows the distribution of Zn-Pb deposit, strata,

1021   fault and Emeishan basalts.

1022

1023   FIGURE 2. Geological sketch map of the NW Guizhou Zn-Pb metallogenic

1024   district (modified from Zhou et al. 2013a), which shows the distribution of

1025   Zn-Pb deposit, strata, fault and mafic dykes.

1026

1027   FIGURE 3. Geological sketch map of the southeastern part of the NW Guizhou

1028   district (modified from Chen et al. 2015), which displays the fault, strata,

1029   ore-controlling structure, and Zn-Pb, Au, phosphate and fluorite deposits.

1030

1031   FIGURE 4. Geological sketch map of the Wuzhishan anticline area (modified

1032   from Peng et al. 2016), which reveals the ore-controlling structure, strata and

1033   Zn-Pb deposit.

1034

1035   FIGURE 5. A generalized stratigraphic map of the Nayongzhi mining area,

1036   which shows the lithology of ore-hosting strata and location of Zn-Pb ore body.

1037

1038   FIGURE 6. A: Cross-section map of No. 17 exploration line (modified from

1039   Peng et al. 2016); B: Cross-section map of No. 23 exploration line (modified

1040   from Chen et al. 2015). Strata, lithology, ore body and fault are shown in both

1041   maps.

1042

1043   FIGURE 7. The picture of sulfide ore and post-ore hydrothermal vein, which

1044   shows the geometry feature of ore body and aggregate structural feature of

1045   hydrothermal minerals. A: Stratiform and lentiform ore bodies; B: Sulfide and

1046   carbonate mineral veins; C: Massive sulfide and two phases of calcite/dolomite;

1047   D: Sulfide vein cements dolostone breccia; E: Steeply dipping veined ore body

1048   occurs along F_7 reverse fault; F: Post-ore quartz and barite vein fills into

1049   fracture of wall rocks; G: Sulfide vein fills and cements dolostone breccia; H:

1050   Disseminated sphalerite and post-ore calcite/dolomite fills into fracture of wall

1051   rocks; I: Post-ore calcite/dolomite vein fills and cements dolostone breccia; J;

1052   Sulfide vein cements dolostone breccia; K: Massive sulfide and veined sulfide

1053   cements dolostone breccia; L: Post-ore calcite/dolomite vein fills and cements

1054   dolostone breccia; M: Sulfide vein fills into fracture of silicified dolostone; N:

1055   Massive sulfide; O: Sulfide vine cements dolostone breccia and post-ore

1056   calcite/dolomite vein fills into fracture of wall rocks; P: Post-ore barite vein fills

48

1057   into fracture of wall rocks.

1058

1059   FIGURE 8. The structural feature of sulfide ore in the Nayongzhi deposit. A-B:

1060   Sphalerite-I occurs as dense disseminated; C: Sphalerite-I occurs as dense

1061   disseminated and galena-I presents as sparse disseminated; D: Sphalerite-I

1062   and pyrite-I form massive ore; E: Sphalerite-II and galena-II form massive ore;

1063   F: Sphalerite-II, galena-II and pyrite-II form massive ore; G: Sphalerite-II

1064   presents as spare disseminated and calcite-III vein fills into fracture of ore; H:

1065   Sphalerite-II vein cements dolostone breccia and calcite-III vein fills into

1066   fracture of ore; I: Sphalerite-I forms massive ore; J: Sphalerite-II vein cements

1067   dolostone breccia; K: Diagenetic pyrite in wall rocks; L: Sphalerite-II presents

1068   as disseminated or veined; M: Sphalerite-II replaces wall rocks and forms

1069   metasomatic vein; N: Sphalerite-II fills and cements carbonate breccia; O:

1070   Sphalerite-II fills into fracture of wall rocks; P: Sphalerite-II cements carbonate

1071   breccia.

1072

1073   FIGURE 9. The textural feature of hydrothermal minerals in the Nayongzhi

1074   deposit under microscope. A: Fine-grained calcite-I (Cal-I) is enclosed by

1075   sphalerite-I (Sp-I) that coexists with pyrite-I (Py-I), both of which are cemented

1076   by dolomite-II (dol-II); B: Sp-I is enclosed by Py-II that coexists with Sp-II and

1077   Dol-II; C: Sp-I and Py-I are cemented by Dol-II, Cal-III fills into the fracture; D:

1078   Quartz-I (Qtz-I) is enclosed by galena-II (Gn-II) that coexists with Sp-II, Dol-II

49

1079 and Qtz-II; E: Coarse-grained Sp-II coexists with or is cemented by Cal-II; F:

1080 Sp-II coexists with Gn-II and Py-II, both of which are cemented by Dol-III; G:

1081 Fine-grained Gn-I and veined Py-I and Sp-I are enclosed by Dol-II; H:

1082 Fine-grained Py-I and Cal-I are enclosed by Sp-I that are replaced by Gn-II; L:

1083 Diagenetic Py is cemented by Qtz; M: Py-I is replaced by Sp-II that coexists

1084 with Cal-II; N: Coarse-grained Gn-II coexists with Sp-II and Cal-II; P:

1085 Fine-grained Sp-I is enclosed by Gn-II that coexists with Sp-II and Cal-II.

1086

1087 FIGURE 10. The textural feature of hydrothermal minerals in the Nayongzhi

1088 deposit under scanning electron microscope (SEM). A: Fine-grained

1089 sphalerite-I (Sp-I) and pyrite-I (Py-I) are enclosed by galena-II (Gn-II) that is

1090 cemented by dolomite-II (Dol-II); B: Sp-II coexists with Gn-II and Dol-II; C:

1091 Paragenetic Sp-I, Gn-I, Py-I and Dol-I are enclosed by calcite-II (Cal-II); D:

1092 Fine-grained Sp-I is enclosed by Py-II that coexists with Sp-II, Cal-II fills into

1093 the fracture; E: Dol-I is enclosed by Cal-II that fills into the boundary of Sp-I

1094 and Py-I; F: Sp-II replaces Py-I and coexists with Cal-II; G: Paragenetic Sp-II

1095 and Gn-II are enclosed by Cal-II; H: Paragenetic Sp-II, Py-II and Gn-II are

1096 enclosed by Cal-II; I: Py-II encloses Gn-I and coexists with Sp-II, both of which

1097 are enclosed by Cal-II; J: Paragenetic Sp-I and Py-I are enclosed by Cal-II; K:

1098 Fine-grained Gn-I and Dol-I are enclosed by Cal-II; Gn-II and Cal-II fill into the

1099 fracture of sphalerite-I; L: Sp-II encloses fine granular Gn-I and coexists with

1100 Gn-II and Cal-II; M: Paragenetic Sp-II, Gn-II and Cal-II; N: Cal-II cements Sp-II

1101 and Gn-II; O: Call-II fills and cements Sp-II that contains Gn-I; P: Sp-II

1102 encloses granular Py-I and coexists with Cal-II.

1103

1104 FIGURE 11. Plot of $\delta^{13}C$ versus $\delta^{18}O$ values. C-O isotopic data for mantle,

1105 marine carbonate rocks and sedimentary organic matter are sourced from

1106 Taylor et al. (1967), Demény et al. (1998), Veizer and Hoefs (1976) and Hoefs

1107 (2009).

1108

1109 FIGURE 12. Plot of $\delta^{13}C$ vs. $\delta^{18}O$ for the calcite precipitated by W/R interaction

1110 with variation of R/W ratio and temperature (400-50°C) for either HCO_3^- or

1111 H_2CO_3 as the dominant dissolved C species (Zheng and Hoefs, 1993). Initial

1112 metamorphic fluids: $\delta^{13}C$ = -2‰, $\delta^{18}O$ = +6‰. $\Delta = \delta^i_{rock} - \delta^f_{rock}$; I: $\Delta^{13}C$ = +0.2‰,

1113 $\Delta^{18}O$ = +2‰; II: $\Delta^{13}C$ = +1‰, $\Delta^{18}O$ = +6‰; III: $\Delta^{13}C$ = +2‰, $\Delta^{18}O$ = +10‰.

1114

1115 FIGURE 13. Plots of $\delta^{13}C$ vs. $\delta^{18}O$ for calcite precipitated by CO_2 degassing

1116 with H_2CO_3 (A) or HCO_3^- (B) as the dominant dissolved C species. The batch

1117 (solid line) and Rayleigh (dashed line) degassing-precipitation models change

1118 with temperature (400-50°C) and mol fraction of C in the degassed CO_2 (0.1 to

1119 0.4) (after Zheng, 1990). The $\delta^{13}C$ and $\delta^{18}O$ values of the initial ore-forming

1120 fluids were taken as -2‰ and +6‰, respectively.

1121

1122

51

1123   FIGURE 14. A: S isotopic composition for seawater sulfate, and the Nayongzhi

1124   and nearby Zn-Pb deposits; B: S isotopic composition for the Nayongzhi

1125   deposit and a brief comparison with the nearby Zn-Pb deposits,

1126   sulfate-bearing evaporites, seawater and mantle-derived S; C: Histogram of

1127   bulk and in situ S isotopic composition for the Nayongzhi deposit. S isotopic

1128   data for the nearby Zn-Pb deposits and evaporites are taken from Jin (2008),

1129   Zhou et al (2013a, 2014b) and Li et al (2015), for the mantle-derived S are

1130   taken from Chaussidon et al (1989), for the seawater are taken from Claypool

1131   et al. (1980) and Seal (2006).

1132

1133   FIGURE 15. A: In situ δ^{34}S value in sphalerite and paragenetic pyrite crystals

1134   from core to rim; B: The best target selected for in situ S isotope analysis that

1135   has homogeneous isotopic composition (such as ^{32}S, ^{34}S, ^{75}As and ^{63}Cu^{32}S).

1136

1137   FIGURE 16. Plots of ^{207}Pb/^{204}Pb vs. ^{206}Pb/^{204}Pb (A) and ^{208}Pb/^{204}Pb vs.

1138 ^{206}Pb/^{204}Pb (B) that present a brief comparison of the modern MORB, Pelagic

1139   sediment, Oceanic island volcanic rocks, Upper Crust and Lower Crust Pb

1140   (Zartman and Doe 1981), and whole-rock of Ediacaran carbonate rocks,

1141   Permian Emeishan basalts and Proterozoic metamorphic rocks (Li et al. 2007;

1142   Yan et al. 2007; Zhou et al. 2013a, 2014a). Solid lines enclose 80% of all data

1143   points for each field, and dashed lines enclose probable average values.

1144   Mantle (A), Orogeny (B), Upper crust contributed to the orogeny (C), and

1145   Lower crust contributed to the orogeny (D).

1146

1147   FIGURE 17. Plots of $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ (A) and $^{208}Pb/^{204}Pb$ vs.

1148 $^{206}Pb/^{204}Pb$ that reveal the variation in Pb isotopes from the early phase

1149   galena-I to the late phase galena-II.

1150

1151   FIGURE 18. Diagram of $^{208}Pb/^{206}Pb$ vs. $^{207}Pb/^{206}Pb$ that shows the relationship

1152   and evolution of two generations of galena.

1153

1154   FIGURE 19. An integrated working and ore exploration model of the

1155   carbonate-hosted Zn-Pb deposits in the Wuzhishan anticline area.

Fig. 1

Fig. 2

Fig.3

Legend:

- Jurassic-Triassic
- Late-middle Permian
- Early Permian-late Carboniferous
- Early Carboniferous-late Devonian
- Cambrian-Ediacaran
- Fault
- Anticlinal axis
- <0.2 Mt Pb-Zn deposit
- 0.2-0.5 Mt Pb-Zn deposit
- >0.5 Mt Pb-Zn deposit
- Fluorite deposit
- Au deposit
- Phosphate deposit
- City

Fig. 4

Fig. 5
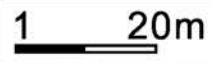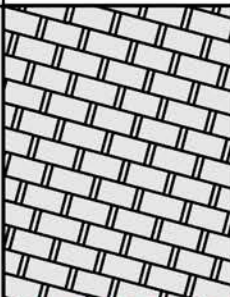
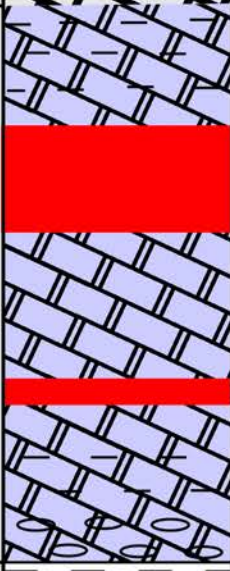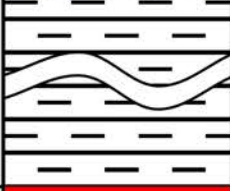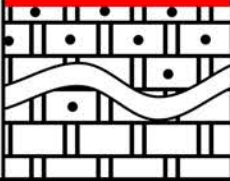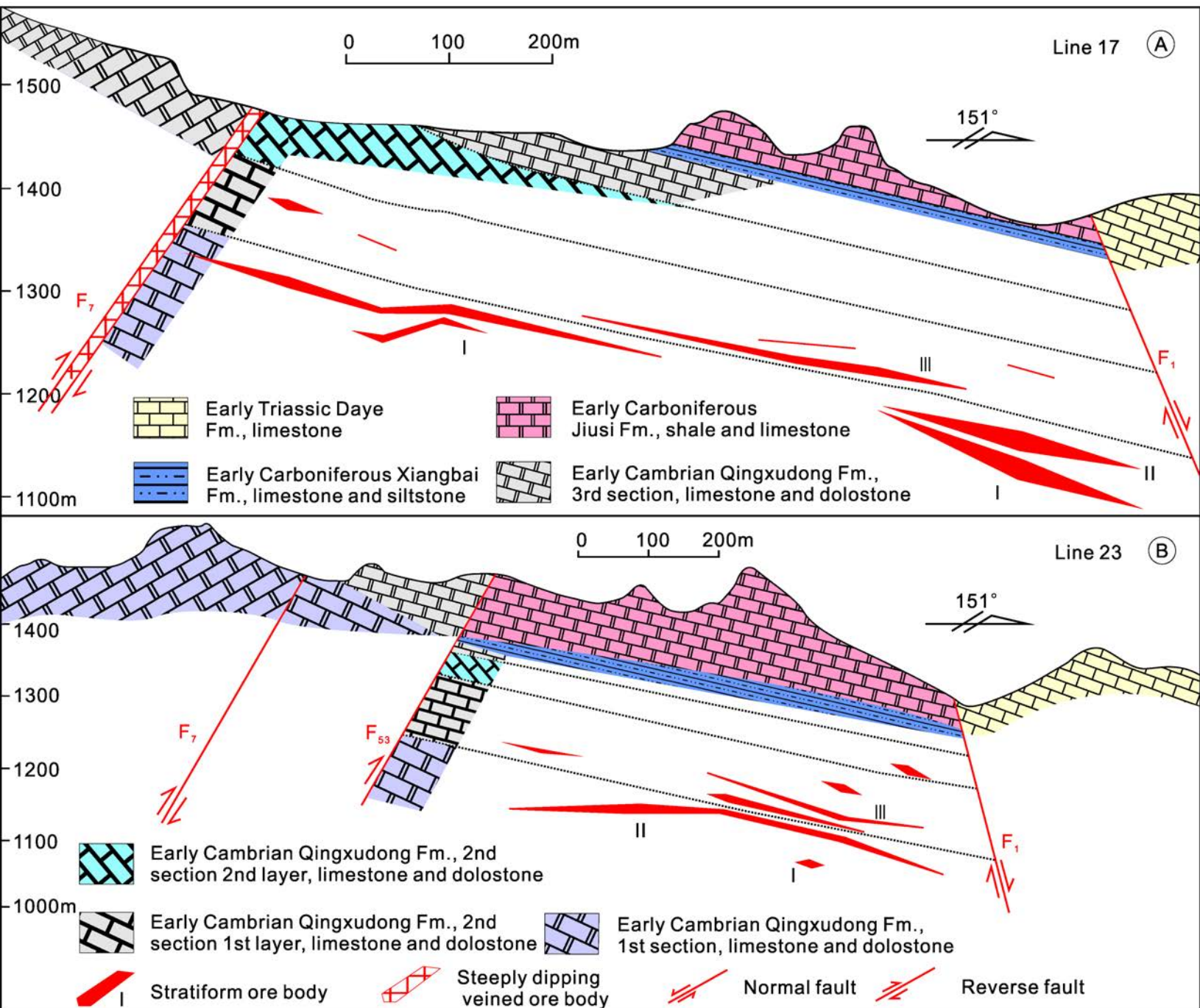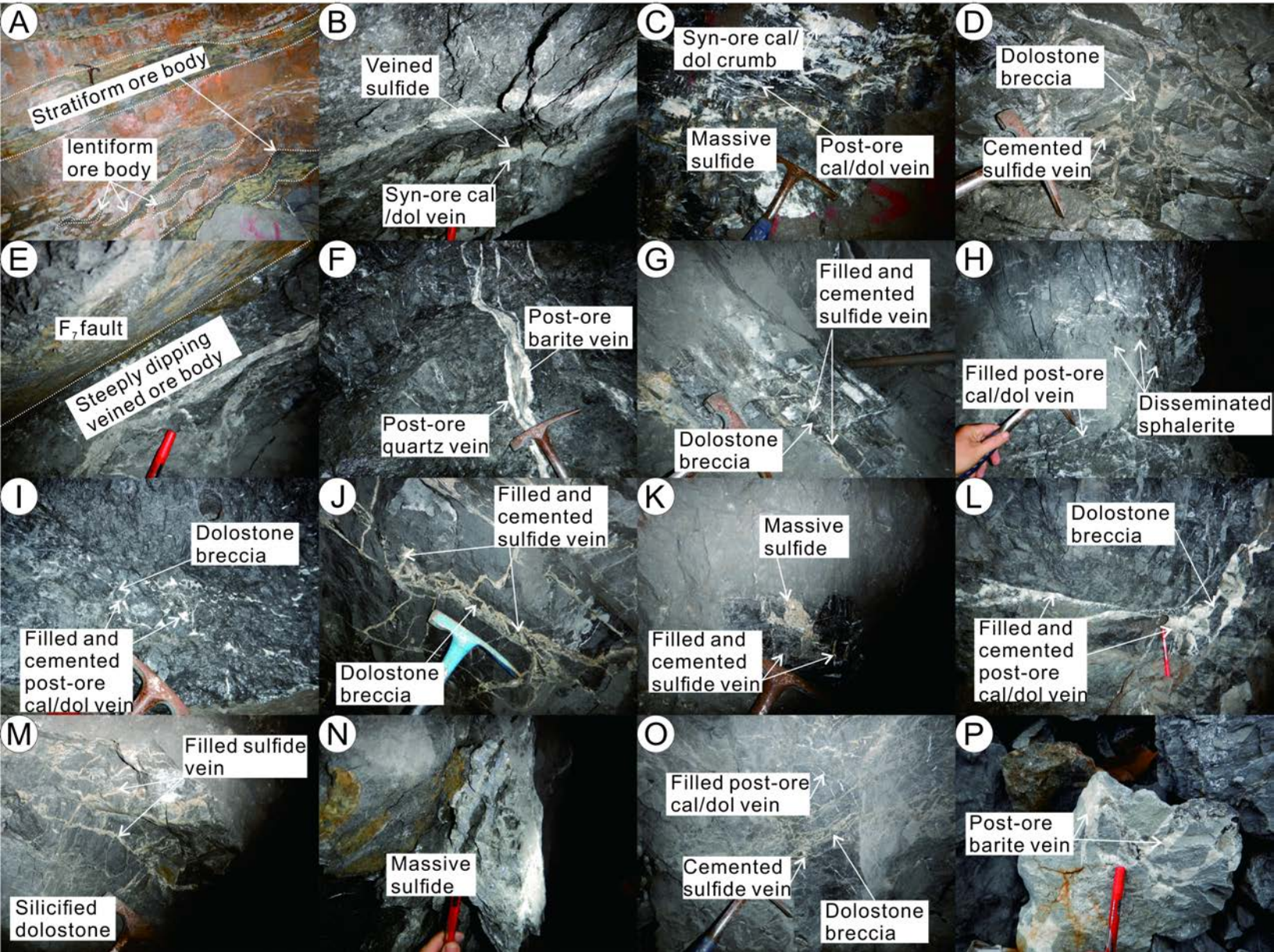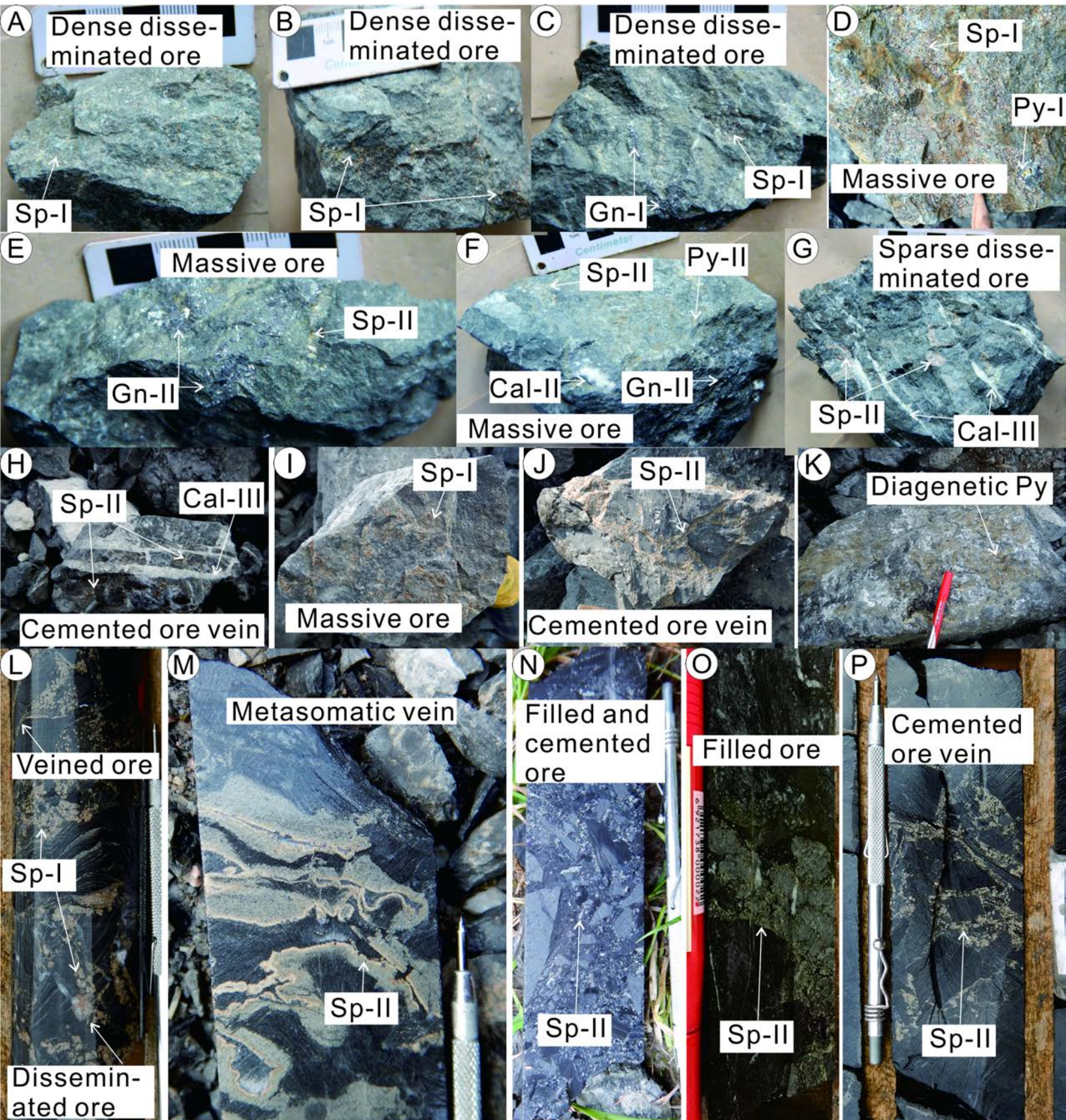| Strata	1　　20m	m	Petrology
Early Cambrian Qingxu-dong Fm., 3rd section		40-80	Gray fine-layer fine-grained argillaceous limestone and dolostone with rare light gray fine-grained limestone and dolostone.
Early Cambrian Qingxu-dong Fm., 2nd section 2nd layer		70-90	Gray thick-layer fine- to medium-grained limestone and dolostone with rare olite and tumor dolostone. Gray medium- to thick-layer powder- to medium-crystal dolostone with rare argillaceous limestone and dolostone. Group III ore bodies.
Early Cambrian Qingxu-dong Fm., 2nd section 1st layer		60-80	(6th) dark gray medium- to thick-layer fine-grained limestone and dolostone with irregular carbon argillaceous stripes, 20-40 m thick; (5th) gray thick-layer medium- to coarse -grained silty limestone and dolostone, 20 m thick;
Early Cambrian Qingxu-dong Fm., 1st section		105-160	(4th) gray thick-layer coarse-grained limestone and dolos-tone with geode, 0-10 m thick; (3rd) gray thick-layer oolite and tumor dolostone, 20-30 m thick; (2nd) dark gray thick-layer argillaceous limestone and dolostone, 30-50 m thick; (1st) gray middle- to thick-layer oolite and tumor dolostone, 5-10 m thick. Group I and II ore bodies.
Early Cambrian Jinding-shan Fm.		> 100	Dark gray, greyish-green fine- to medium-grained argillaceous siltstone and shale.
Late Ediacaran Dengying Fm.		> 100	Gray medium- to thick-layer dolarenite, algae-bearing dolostone and powder crystal limestone and dolostone.

Fig. 6

A Line 17

0 100 200m

151°

1500
1400
1300
F7
1200
1100m

I

III

I

II

F1

Early Triassic Daye Fm., limestone

Early Carboniferous Jiusi Fm., shale and limestone

Early Carboniferous Xiangbai Fm., limestone and siltstone

Early Cambrian Qingxudong Fm., 3rd section, limestone and dolostone

B Line 23

0 100 200m

151°

1400
1300
F7
1200
F53
1100
1000m

II

III

I

F1

Early Cambrian Qingxudong Fm., 2nd section 2nd layer, limestone and dolostone

Early Cambrian Qingxudong Fm., 2nd section 1st layer, limestone and dolostone

Early Cambrian Qingxudong Fm., 1st section, limestone and dolostone

Stratiform ore body

Steeply dipping veined ore body

Normal fault

Reverse fault

Fig. 7

Fig. 8

A Dense disse-
minated ore
Sp-I

B Dense disse-
minated ore
Sp-I

C Dense disse-
minated ore
Sp-I
Gn-I

D Sp-I
Py-I
Massive ore

E Massive ore
Sp-II
Gn-II

F Sp-II Py-II
Cal-II Gn-II
Massive ore

G Sparse disse-
minated ore
Sp-II Cal-III

H Sp-II Cal-III
Cemented ore vein

I Sp-I
Massive ore

J Sp-II
Cemented ore vein

K Diagenetic Py

L Veined ore
Sp-I
Dissemin-
ated ore

M Metasomatic vein
Sp-II

N Filled and
cemented
ore
Sp-II

O Filled ore
Sp-II

P Cemented
ore vein
Sp-II

Fig.9

Fig. 10

Fig.11

Fig. 12

Fig. 13

(A) Calcite-II (purple filled triangle), Calcite-III (cyan open triangle). Temperature contours from 50°C to 400°C with ratio labels 0.1, 0.2, 0.3, 0.4. H$_2$CO$_3$ as the dominant C species. Axes: δ^{18}O$_{SMOW}$/‰ (x), δ^{13}C$_{PDB}$/‰ (y).

(B) HCO$_3^-$ as the dominant C species. Temperature contours from 50°C to 400°C with ratio labels 0.1, 0.2, 0.3, 0.4. δ^{13}C$_{fluid}$ = −2‰, δ^{18}O$_{fluid}$ = +6‰. Axes: δ^{18}O$_{SMOW}$/‰ (x), δ^{13}C$_{PDB}$/‰ (y).

Fig. 14

Fig. 15

A

Dol

W-1 (+33.0‰)

W-5 (+11.9‰)

W-2 (+32.5‰)

W-6 (+11.8‰)

W-3 (+12.0‰)

W-4 (+12.3‰)

Sp

Py

W-10 (+24.5‰) W-7 (+15.3‰)

W-11 (+26.1‰)

W-8 (+15.1‰)

W-9 (+24.4‰)

W-12 (+27.0‰)

200μm

B

^{32}S

^{75}As

^{34}S

$^{63}Cu^{32}S$

Fig. 16

Fig. 17

Fig. 18

Fig. 19

Early Triassic Daye Fm.

Early Permian Liangshan Fm.

Early Carboni-ferous Jiusi Fm.

Late Cambrian Loushanguan Fm.

Middle Cambrian Douposi Fm.

Early Cambrian Qingxudong Fm.

Early Cambrian Jindingshan Fm.

Late Ediacaran Dengying Fm.

Neo- to Meso-Proterozoic

Limestone

Argillaceous limestone

Dolostone

Shale and mudstone

Stratiform ore body

Steeply dipping veined ore body

Predicted two types of ore body

Hydrothermal fluids migration direction

Table 1 Mineral paragenesis in the Nayongzhi Zn-Pb deposit

Period	Diagenetic	Hydrothermal			Oxidized
Stage		Sulfide-(quartz-carbonates)		Quartz-carbonates-barite	
Mineral assemblage	Pyrite + quartz + dolomite	**Sphalerite** + pyrite + galena + quartz + calcite/dolomite	**Sphalerite** + **galena** + pyrite quartz + calcite/dolomite	Quartz + calcite/dolomite + barite	Oxidized Leached
Phase		I	II	III	
Pyrite					
Sphalerite					
Galena					
Quartz					
Calcite					
Dolomite					
Barite					
Limonite					
Cerussite					
Smithsonite					
Hemimorphite					

Table 2 C-O isotopic compositions of calcite and limestone in the Nayongzhi deposit

No.	Mineral/Rock	$\delta^{13}C_{PDB}$/‰	$\delta^{18}O_{PDB}$/‰	$\delta^{18}O_{SMOW}$/‰	$\delta^{13}C_{CO2}$/‰ [1]	$\delta^{18}O_{H2O}$/‰ [2]
H06-6	Calcite-III	-4.1	-16.2	+14.1	-4.2	+4.0
H06-17	Calcite-II	-0.7	-17.9	+12.4	-0.8	+2.3
1290F-4	Calcite-II	-1.9	-16.7	+13.6	-2.0	+3.5
1390Cal	Calcite-II	-0.2	-17.3	+13.0	-0.3	+2.9
1390JP-4	Calcite-II	-1.4	-16.8	+13.6	-1.5	+3.5
1390JP-6	Calcite-II	-1.1	-17.5	+12.9	-1.2	+2.8
1390JP-7	Calcite-II	+0.5	-17.6	+12.7	+0.4	+2.6
YH1220-1	Limestone	+0.2	-6.5	+24.2		
YH1220-2	Limestone	+0.6	-6.2	+24.5		
YH1220-3	Limestone	+0.8	-5.2	+25.5		
YH1220-4	Limestone	+1.3	-6.6	+24.1		
YH1220-5	Limestone	-1.7	-5.7	+25.0		

$\delta^{18}O_{SMOW}$ = 1.03086 × $\delta^{18}O_{PDB}$ + 30.86 (Friedman and O'Neil 1977); the error is ±0.2‰ (2σ) for $\delta^{13}C$ and ±1‰ (2σ) for $\delta^{18}O$;

[1] $1000\ln\alpha_{(CO2 - Calcite)}$ = -2.4612 + 7.663 × 10^3 / (t +273.15) - 2.988 × 10^6 / (t +273.15)^2 (Bottinga, 1968);

[2] $1000\ln\alpha_{(Calcite - H2O)}$ = 2.78 × 10^6 / (t +273.15)^2 - 3.39 (O'Neil et al., 1969);

t = 180°C, based on temperature analysis of fluid inclusion in quartz-II (Zhu et al., 2016b).

Table 3 Bulk S and in situ S isotopic compositions of sulfide minerals in the Nayongzhi deposit

No.	Obj.	Stage	$\delta^{34}S_{CDT}$/‰	Note
2015HT-2-0	Pyrite	Stage I	+22.06	
2015JP-1-1	Pyrite	Stage I	+18.12	
2015HT-2-1	Yellow sphalerite	Stage II	+21.04	
2015HT-2-2	Brown-yellow sphalerite	Stage II	+22.42	
2015HT-2-3	Brown sphalerite	Stage I	+22.51	
2015HT-1-1	Yellow sphalerite	Stage II	+24.59	
2015HT-1-2	Brown-yellow sphalerite	Stage II	+23.60	
2015HT-1-3	Brown-red sphalerite	Stage I	+24.73	Whole-
2015HT-1-3	Brown-red sphalerite	Stage I	+24.79	mineral
2015HT-5-1	Yellow sphalerite	Stage II	+23.57	
2015HT-5-2	Brown-yellow sphalerite	Stage II	+23.64	
2015HT-5-3	Brown-red sphalerite	Stage I	+23.27	
2015HT-4-1	Yellow sphalerite	Stage II	+17.17	
2015HT-4-2	Brown-yellow sphalerite	Stage II	+21.95	
2015HT-4-3	Brown sphalerite	Stage I	+24.17	
2015HT-4-3	Brown sphalerite	Stage I	+24.20	
W-1	Sphalerite-I	Core	+33.0	
W-2	Sphalerite-I	Core	+32.5	
W-3	Sphalerite-I	Rim	+12.0	
W-4	Sphalerite-I	Rim	+12.3	
W-5	Sphalerite-I	Rim	+11.9	
W-6	Sphalerite-I	Rim	+11.8	In situ
W-7	Pyrite-I	Rim	+15.1	
W-8	Pyrite-I	Rim	+15.3	
W-9	Pyrite-I	Rim	+24.4	
W-10	Pyrite-I	Rim	+24.5	
W-11	Pyrite-I	Core	+26.1	
W-12	Pyrite-I	Core	+27.0	

The error is ±0.2‰ (2σ) for bulk $\delta^{34}S$ and ±0.2‰ (1s) for in situ $\delta^{34}S$.

Table 4 In situ Pb isotopic compositions of galena in the Nayongzhi deposit

Spot	Stage	$^{206}Pb/^{204}Pb$	1s	$^{207}Pb/^{204}Pb$	1s	$^{208}Pb/^{204}Pb$	1s	μ	$^{208}Pb/^{206}Pb$	1s	$^{207}Pb/^{206}Pb$	1s
K-2-01	Galena-I	17.830	0.002	15.654	0.003	37.934	0.007	9.65	2.1274	0.0001	0.87786	0.00003
K-2-02	Galena-I	17.833	0.003	15.656	0.003	37.949	0.008	9.65	2.1278	0.0001	0.87792	0.00004
K-2-03	Galena-I	17.829	0.002	15.654	0.003	37.935	0.007	9.65	2.1275	0.0001	0.87795	0.00003
K-2-04	Galena-I	17.828	0.002	15.648	0.003	37.922	0.007	9.64	2.1270	0.0001	0.87774	0.00003
K-2-05	Galena-I	17.831	0.003	15.655	0.003	37.941	0.009	9.65	2.1277	0.0002	0.87794	0.00004
K-2-06	Galena-I	17.828	0.002	15.649	0.002	37.926	0.007	9.64	2.1274	0.0001	0.87780	0.00003
K-2-07	Galena-I	17.834	0.003	15.657	0.003	37.946	0.008	9.65	2.1278	0.0001	0.87793	0.00004
K-2-08	Galena-I	17.838	0.003	15.661	0.003	37.958	0.009	9.66	2.1279	0.0001	0.87793	0.00004
K-2-09	Galena-I	17.837	0.003	15.663	0.003	37.968	0.009	9.67	2.1284	0.0001	0.87809	0.00004
K-2-10	Galena-I	17.828	0.003	15.654	0.003	37.939	0.008	9.65	2.1279	0.0001	0.87803	0.00004
K-2-11	Galena-I	17.835	0.003	15.661	0.003	37.959	0.008	9.66	2.1282	0.0001	0.87803	0.00004
K-2-12	Galena-I	17.839	0.003	15.664	0.003	37.963	0.008	9.67	2.1279	0.0001	0.87801	0.00004
K-2-13	Galena-I	17.833	0.003	15.658	0.003	37.952	0.009	9.66	2.1281	0.0002	0.87802	0.00004
K-2-14	Galena-I	17.835	0.003	15.659	0.003	37.953	0.008	9.66	2.1278	0.0001	0.87796	0.00003
K-2-15	Galena-I	17.841	0.003	15.666	0.003	37.971	0.009	9.67	2.1281	0.0002	0.87806	0.00004
K-2-16	Galena-I	17.832	0.003	15.657	0.004	37.951	0.01	9.65	2.1279	0.0001	0.87801	0.00004
HA1-5-06	Galena-I	17.838	0.002	15.656	0.002	37.955	0.006	9.65	2.1277	0.0001	0.87770	0.00003
HA1-5-07	Galena-I	17.836	0.003	15.655	0.003	37.951	0.008	9.65	2.1279	0.0001	0.87770	0.00003
HA1-5-08	Galena-I	17.832	0.002	15.652	0.003	37.943	0.007	9.64	2.1269	0.0001	0.87700	0.00003
HA1-5-09	Galena-I	17.834	0.002	15.654	0.002	37.948	0.006	9.65	2.1269	0.0001	0.87705	0.00002
HA1-5-10	Galena-I	17.833	0.002	15.652	0.003	37.944	0.007	9.64	2.1265	0.0001	0.87691	0.00002
HA1-5-11	Galena-I	17.835	0.002	15.655	0.002	37.951	0.007	9.65	2.1263	0.0001	0.87656	0.00002
HA1-5-12	Galena-I	17.838	0.002	15.655	0.002	37.954	0.006	9.65	2.1277	0.0001	0.87761	0.00002
HA1-5-13	Galena-I	17.838	0.003	15.655	0.003	37.950	0.008	9.65	2.1275	0.0001	0.87760	0.00003
HA1-5-14	Galena-I	17.835	0.002	15.655	0.003	37.952	0.007	9.65	2.1280	0.0001	0.87783	0.00003
HA1-5-15	Galena-I	17.830	0.002	15.653	0.003	37.940	0.007	9.65	2.1278	0.0001	0.87781	0.00003
HA1-5-16	Galena-I	17.831	0.002	15.651	0.002	37.937	0.006	9.64	2.1277	0.0001	0.87775	0.00002
H2A5-4-01	Galena-II	17.837	0.002	15.659	0.003	37.952	0.007	9.66	2.1277	0.0001	0.87786	0.00003
H2A5-4-02	Galena-II	17.840	0.003	15.663	0.003	37.963	0.009	9.66	2.1280	0.0001	0.87795	0.00004
H2A5-4-03	Galena-II	17.840	0.002	15.662	0.003	37.964	0.007	9.66	2.1280	0.0001	0.87795	0.00003
H2A5-4-04	Galena-II	17.846	0.002	15.665	0.002	37.971	0.007	9.67	2.1277	0.0001	0.87779	0.00003
H2A5-4-05	Galena-II	17.846	0.003	15.661	0.003	37.960	0.008	9.66	2.1271	0.0001	0.87747	0.00003
H2A5-4-06	Galena-II	17.842	0.002	15.655	0.003	37.945	0.007	9.65	2.1269	0.0001	0.87747	0.00003
H2A5-4-07	Galena-II	17.842	0.002	15.661	0.002	37.954	0.007	9.66	2.1272	0.0001	0.87776	0.00003
H2A5-4-08	Galena-II	17.843	0.002	15.662	0.002	37.957	0.007	9.66	2.1275	0.0001	0.87781	0.00003
H2A5-4-09	Galena-II	17.848	0.002	15.658	0.002	37.955	0.007	9.65	2.1265	0.0001	0.87732	0.00003
H2A5-4-10	Galena-II	17.846	0.002	15.656	0.002	37.947	0.007	9.65	2.1263	0.0001	0.87729	0.00003
H2A5-4-11	Galena-II	17.849	0.003	15.659	0.003	37.960	0.007	9.66	2.1267	0.0001	0.87736	0.00003
H2A5-4-12	Galena-II	17.848	0.003	15.66	0.003	37.960	0.007	9.66	2.1269	0.0001	0.87744	0.00003
H2A5-4-13	Galena-II	17.848	0.003	15.66	0.003	37.957	0.007	9.66	2.1267	0.0001	0.87742	0.00003
H2A5-4-14	Galena-II	17.846	0.002	15.657	0.003	37.951	0.007	9.65	2.1266	0.0001	0.87735	0.00003
H2A5-4-15	Galena-II	17.853	0.002	15.665	0.003	37.971	0.007	9.67	2.1270	0.0001	0.87745	0.00003

H2A5-4-16	Galena-II	17.851	0.002	15.661	0.003	37.965	0.007	9.66	2.1268	0.0001	0.87738	0.00003
HA1-5-01	Galena-II	17.860	0.002	15.664	0.003	37.991	0.007	9.66	2.1271	0.0001	0.87745	0.00003
HA1-5-02	Galena-II	17.857	0.002	15.662	0.002	37.979	0.006	9.66	2.1276	0.0001	0.87763	0.00003
HA1-5-03	Galena-II	17.856	0.002	15.659	0.002	37.974	0.005	9.65	2.1276	0.0001	0.87768	0.00003
HA1-5-04	Galena-II	17.870	0.002	15.665	0.002	37.998	0.006	9.66	2.1277	0.0001	0.87771	0.00003
HA1-5-05	Galena-II	17.835	0.003	15.65	0.003	37.937	0.008	9.64	2.1276	0.0001	0.87767	0.00003
1390-JP-12-01	Galena-II	17.851	0.002	15.662	0.002	37.970	0.006	9.66	2.1269	0.0001	0.87734	0.00003
1390-JP-12-02	Galena-II	17.848	0.003	15.659	0.003	37.962	0.008	9.66	2.1269	0.0001	0.87739	0.00003
1390-JP-12-03	Galena-II	17.843	0.003	15.657	0.003	37.951	0.007	9.65	2.1268	0.0001	0.87742	0.00003
1390-JP-12-04	Galena-II	17.840	0.002	15.651	0.002	37.934	0.006	9.64	2.1263	0.0001	0.87727	0.00003
1390-JP-12-05	Galena-II	17.853	0.003	15.662	0.003	37.968	0.008	9.66	2.1267	0.0001	0.87730	0.00003
1390-JP-12-06	Galena-II	17.844	0.003	15.660	0.003	37.959	0.008	9.66	2.1272	0.0001	0.87763	0.00003
1390-JP-12-07	Galena-II	17.851	0.003	15.662	0.003	37.968	0.007	9.66	2.1268	0.0001	0.87735	0.00003
1390-JP-12-08	Galena-II	17.853	0.003	15.662	0.003	37.974	0.007	9.66	2.1270	0.0001	0.87726	0.00003
1390-JP-12-09	Galena-II	17.848	0.003	15.66	0.003	37.961	0.008	9.66	2.1269	0.0001	0.87743	0.00004
1390-JP-12-10	Galena-II	17.857	0.003	15.666	0.003	37.979	0.007	9.67	2.1269	0.0001	0.87733	0.00003
1390-JP-12-11	Galena-II	17.846	0.002	15.66	0.002	37.960	0.007	9.66	2.1271	0.0001	0.87752	0.00003
1390-JP-12-12	Galena-II	17.837	0.002	15.659	0.003	37.951	0.007	9.66	2.1277	0.0001	0.87790	0.00003
1390-JP-12-13	Galena-II	17.838	0.003	15.661	0.003	37.955	0.008	9.66	2.1277	0.0001	0.87790	0.00003
1390-JP-12-14	Galena-II	17.860	0.002	15.662	0.003	37.976	0.007	9.66	2.1263	0.0001	0.87693	0.00003
1390-JP-12-15	Galena-II	17.849	0.002	15.663	0.003	37.968	0.007	9.66	2.1271	0.0001	0.87749	0.00003
1390-JP-12-16	Galena-II	17.857	0.003	15.662	0.003	37.975	0.008	9.66	2.1266	0.0001	0.87705	0.00003

$\mu = {}^{238}U/{}^{204}Pb$

Table 5 A comparison between the Nayongzhi and the Huize, Tianqiao, and typical MVT deposits

Characteristics	Tianqiao	Huize	MVT	Nayongzhi
Grade	Pb + Zn: 6.92-20.51 wt. %, Zn/(Zn + Pb): 0.75±	Pb + Zn: 25-35 wt. %, Zn/(Zn + Pb): 0.9±	Pb + Zn: average < 10 wt. %, Zn/(Zn + Pb): 0.8±	Pb + Zn: average 8-10 wt. %, Zn/(Zn + Pb): 0.9±
Tonnage	Pb + Zn total reserve: > 0.2 Mt	Pb + Zn reserve: single ore body ~ 1 Mt, total > 5 Mt	Pb + Zn reserves: single ore body < 1 Mt	Pb + Zn reserves: single ore body < 0.5 Mt, total > 1 Mt
Acreage	The SYG province covers 170, 000 km^2	The SYG province covers 170, 000 km^2	Hundreds square kilometers	The Wuzhishan area covers 20 km^2
Host rocks	Late Devonian and early Carboniferous coarse-grained dolostone	Early Carboniferous coarse-grained dolostone	Cambrian to Carboniferous carbonate rocks	Late Ediacaran and early Cambrian dolostone
Depth of Mineralization	>400 m	>2000 m	<1500 m	<400 m
Tectonic setting	Western Yangtze Block, controlled by the NW fold-thrust fault	Western Yangtze Block, controlled by NE fold-thrust fault	Generally related to extensional basin	Northern Youjiang Basin, controlled by the Wuzhishan anticline
Relation with magmatic activity	Spatially associated with late Permian Emeishan basalts and Mesozoic mafic (diabase) dykes	Spatially associated with late Permian Emeishan basalts	Generally no genetic connection with magmatic activity	No genetic relationship with magmatic activity
Ore-controlled factors	Controlled by thrust fault-fold structure and lithology	Controlled by thrust fault-fold structure and lithology	Mainly controlled by structure and lithology	Mainly controlled by structure and lithology
Age	192 Ma	222-226 Ma	From Proterozoic to Cretaceous	Early Yanshanian
Ore texture and structure	Mainly exhibiting massive structures, and fine-, medium- and coarse-grained textures	Mainly exhibiting massive structures, and fine-, medium- and coarse-grained textures	Exhibiting disseminated, fine granular, branched, colloidal and massive structures and colloidal, skeleton coarse-crystalline textures	Veined, disseminated, and brecciated structures and colloidal, cataclastic, granular textures
Mineral compositions	Sphalerite, galena, pyrite, calcite and dolomite	Sphalerite, galena, pyrite and calcite	Sphalerite, galena, pyrite, barite, fluorite, calcite and dolomite, etc.	Sphalerite, galena, pyrite, calcite, dolomite, quartz and barite
Fluid inclusions	<10 wt. % NaCl equiv.; $Cl^--Na^+-Ca^{2+}-F^--SO_4^{2-}$; 150-280°C	<10 wt. % NaCl equiv.; $Cl^--Na^+-Ca^{2+}-F^--SO_4^{2-}$; 150-300°C	10-30wt. % NaCl equiv.; $Cl^--Na^+-Ca^{2+}-K^+-Mg^{2+}$; 50-200°C	10-15 wt. % NaCl equiv.; $Cl^--Na^+-Ca^{2+}-K^+-Mg^{2+}$; 113-232°C
Associated metals	Ag, Cu, Ge, Ga, Cd and In	Ag, Cu, Ge, Ga, Cd and In	Ag	Ag
S isotopes	+8- +15‰	+11-+17‰	+10-+25‰	+11-+33‰
Pb isotopes	Normal Pb isotopes	Normal Pb isotopes	Complicated Pb isotope ratios and regional zonation	Uniform Pb isotope ratios
References	Zhou et al. 2013a, 2014a	Li et al. 2007; Huang et al. 2010	Leach et al. 2005, 2010	Zhu et al. 2016; Jin et al. 2016; This paper