**S, Pb, and Sr isotope geochemistry and genesis of Pb–Zn mineralization in the
Huangshaping polymetallic ore deposit of southern Hunan Province, China**

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Abstract: The Huangshaping Pb–Zn–W–Mo polymetallic deposit, located in southern Hunan Province, China, is one of the largest deposits in the region and is unique for its metals combination of Pb–Zn–W–Mo and the occurrence of significant reserves of all these metals. The deposit contains disseminated scheelite and molybdenite within a skarn zone located between Jurassic granitoids and Carboniferous sedimentary carbonate, and sulfide ores located within distal carbonate-hosted stratiform orebodies. The metals and fluids that formed the W–Mo mineralization were derived from granitoids, as indicated by their close spatial and temporal relationships. However, the source of the Pb–Zn mineralization in this deposit remains controversial.

Here, we present new sulfur, lead, and strontium isotope data of sulfide minerals (pyrrhotite, sphalerite, galena, and pyrite) from the Pb–Zn mineralization within the deposit, and these data are compared with those of granitoids and sedimentary carbonate in the Huangshaping deposit, thereby providing insights into the genesis of the Pb–Zn mineralization. These data indicate that the sulfide ores from deep levels in the Huangshaping deposit have lower and more consistent

$\delta^{34}\text{S}$ values (–96 m level: +4.4‰ to +6.6‰, n = 13) than sulfides within the shallow part of the deposit (20 m level: +8.3‰ to +16.3‰, n = 19). The $\delta^{34}\text{S}$ values of deep sulfides are compositionally similar to those of magmatic sulfur within southern Hunan Province, whereas the shallower sulfides most likely contain reduced sulfur derived from evaporite sediments. The sulfide ores in the Huangshaping deposit have initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.707662–0.709846) that lie between the values of granitoids (0.709654–0.718271) and sedimentary carbonate (0.707484–0.708034) in the Huangshaping deposit, but the ratios decreased with time, indicating that the ore-forming fluids were a combination of magmatic and formation-derived fluids, with the influence of the latter increasing over time. The lead isotopic compositions of sulfide ores do not correlate with sulfide type and define a linear trend in a $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram that is distinct from the composition of the disseminated pyrite within sedimentary carbonates and granitoids in the Huangshaping deposit, but is similar to the lead isotopic composition of sulfides within coeval skarn Pb–Zn deposits in southern Hunan Province. In addition, the sulfide ores have old signatures with relative high $^{207}\text{Pb}/^{206}\text{Pb}$ ratios, suggesting that the underlying Paleoproterozoic basement within southern Hunan Province may be the source of metals within the Huangshaping deposit.

The isotope geochemistry of sulfide ores in the Huangshaping deposit shows a remarkable mixed source of sulfur and ore-forming fluids, and the metals were derived from the basement. These features are not found in representative skarn-type Pb–Zn mineralization located elsewhere. The ore-forming elements (S, Pb, and Zn) from the granitoids made an insignificant contribution to sulfide precipitation in this deposit. However, the emplacement of granitoids did provide large amounts of heat and fluids to the hydrothermal system in this area and extracted metals from the

basement rocks, indicating that the Jurassic magmatism associated with the Huangshaping deposit was crucial to the Pb–Zn mineralization.

Keywords: Huangshaping, Pb–Zn mineralization, isotopic compositions, evaporitic sediments, granitoids, basement.

1. Introduction

The polymetallic Huangshaping Pb–Zn–W–Mo deposit (containing 152.9 kt WO₃ at a grade of 0.2%, 43.2 kt Mo at 0.2%, 761.3 Kt Pb at 3.55%, and 1.5291 Mt Zn at 7.13%; [Huang et al., 2013](#)) is located within the Cathaysia Block in southern Hunan Province, China. This area records intensive Mesozoic magmatism and hosts numerous coeval world-class polymetallic deposits, including the granite-related Shizhuyuan and Xintianling giant skarn W deposits, the Hehuaping and Furong large skarn Sn deposits, and the granodiorite porphyry-related Baoshan and Shuikoushan large skarn Pb–Zn deposits ([Yao et al., 2007](#); [Li et al., 2013](#); [Mao et al., 2013](#); [Xie et al., 2013](#); [Yao et al., 2014](#); [Zuo et al., 2014](#)). The polymetallic Huangshaping deposit hosts significant tungsten, molybdenum, and lead–zinc mineralization, a combination that is unique in the area.

Previous geochronological research suggests that the granitoids associated with the Huangshaping deposit formed in the Late Jurassic (generally around 161.6 ± 1.1 to 150.1 ± 0.4 Ma; [Yao et al., 2005](#); [Lei et al., 2010](#); [Quan et al., 2012](#); [Ai, 2013](#); [Li et al., 2014b](#); [Yuan et al., 2014](#)), and molybdenite disseminated within W–Mo-bearing skarns, which occur between the granitoids and sedimentary carbonate in the deposit, yield Re–Os isochron ages of 159.4 ± 3.3 to 153.8 ± 4.8

Ma (Ma et al., 2007; Yao et al., 2007; Lei et al., 2010; Qi et al., 2012), which is within analytical error of the ages of the Huangshaping granitoids. The W–Mo mineralization within the deposit has close spatial and temporal relationships with granitoids in this area, suggesting a genetic relationship between the two. However, the genesis of the Pb–Zn mineralization within the deposit remains ambiguous, primarily as these sulfide ores are located within distal carbonate-hosted stratiform orebodies of unknown age. Xi et al. (2009) suggested that the sulfur within these sulfide ores was a mixture of magmatic and sediment-derived sulfur and that the metals within the deposit were dominantly sourced from the mantle, with a minor contribution from the upper crust. However, Tong (1986) and Zhu et al. (2012) suggested that the granite porphyry, one of the granitoids associated with the Huangshaping deposit, was the source of both the sulfur and the metals within the deposit. In addition, Huang et al. (2013) concluded that the fluids that formed the W and Mo mineralization within the Huangshaping deposit were derived from a deep magma chamber; these fluids also formed the Pb–Zn mineralization in this area after evolving and mixing with meteoric fluids in the surrounding sediments. However, there has been no comprehensive analysis of the Pb–Zn mineralization in the Huangshaping deposit.

The sulfide ores that form skarn-type Pb–Zn mineralization are commonly either hosted by proximal skarns or by distal sedimentary carbonates, and this type of deposit is distinct from other types of carbonate-hosted Pb–Zn mineralization (e.g., MVT, Irish-type, SEDEX), as skarn-type Pb–Zn deposits are always associated with certain igneous rocks and the sulfides occur as mantos and chimney (pipe-shaped) orebodies (Megaw et al., 1988; Leach et al., 2005, 2010; Meinert, 2005; Wilkinson et al., 2005; Chang et al., 2008). All of these types of skarn-type Pb–Zn mineralization have similar characteristics, including highly variable temperatures of sulfide

deposition (500°C–100°C) and formation from magmatic- rather than basinal-dominated fluids (Megaw et al., 1988; Samson et al., 2008; Kalender, 2011). In addition, the sulfide ores typically have low and consistent $\delta^{34}\text{S}$ values (usually close to those of magmatic sulfur) and have Pb isotopic compositions that are very similar to the granitoids associated with this mineralization, both of which suggest that the metals and sulfur within the Pb–Zn mineralization were derived from coeval granitoids (Ault and Williams-Jones, 2004; Kalender et al., 2011; Li et al., 2012; Akiska et al., 2013; Shu et al., 2013; Wang et al., 2014a; Xie et al., 2015). The granitoid-related Huangshaping Pb–Zn mineralization is hosted by distal carbonate-hosted stratiform and chimney orebodies, and has sulfur and lead isotopic compositions that are significantly different from the skarn-type sulfide ores mentioned above, showing a wide range of $\delta^{34}\text{S}$ values and more radiogenic lead in sulfide ores compared with associated granitoids in the Huangshaping deposit (Tong, 1986; Xi et al., 2009; Zhu et al., 2012).

Isotope systematics is a powerful tool for the study of hydrothermal mineral deposits. The S and Sr isotopic systems are widely used to determine the source of sulfur and ore-forming hydrothermal fluids, and the flow pathways for fluids during mineralizing events (Ault and Williams-Jones, 2004; Goldfarb et al., 2005; Zhou et al., 2013; Tang et al., 2015; Zhao et al., 2015). In addition, Pb isotopic analysis is useful for constraining the origin of metals within mineral deposits (Zhou et al., 2001; Cunha et al., 2007; Zeng et al., 2014; Tessalina et al., 2016). There are no existing isotopic datasets for the polymetallic Huangshaping deposit, even though such data could provide important insights into the genesis of the Pb–Zn mineralization. Here, we present new S, Pb, and Sr isotopic data to identify the sources of sulfur, ore-forming fluids, and metals (Pb and Zn) within the Huangshaping deposit, and to further our understanding of the

111 formation processes of the skarn-type Huangshaping polymetallic Pb–Zn–W–Mo deposit.

112

113 2. Geological background

114 The Cathaysia Block amalgamated with the Yangtze Block as a result of the Jinning orogenic
115 event at 970 Ma (Li and McCulloch, 1996). It records intensive Mesozoic magmatism that
116 occurred between the Jurassic and the Cretaceous and this magmatism formed a belt of igneous
117 rocks that young towards the coast within the Cathaysia Block (Fig. 1a; Zhou et al., 2006). The
118 intrusive and volcanic rocks that formed during this magmatism include a belt of granites with
119 high Sm (>8 ppm) and Nd (>45 ppm) concentrations, $\epsilon_{\text{Nd}}(t)$ values greater than –8, and young Nd
120 model ages ($T_{\text{DM}} < 1.5$ Ga; Gilder et al., 1996). These granites form a belt that is approximately
121 parallel to two NE–SW-trending Mesozoic grabens between Hangzhou within Zhejiang Province
122 and Shiwandashan in Guangxi Province, and this belt has been termed the Shi–Hang zone (Fig.
123 1a). Various models have been proposed for the formation of the Shi–Hang zone, including the
124 commonly accepted models of shallow subduction and roll-back of the Paleo-Pacific Plate or the
125 foundering of a flat-subducted slab with subsequent slab roll-back during the Jurassic (Li et al.,
126 2007b; Jiang et al., 2009; Ding et al., 2015).

127 In addition, the area within Guangxi, Hunan, Jiangxi, and Guangdong provinces that contains
128 the W–Sn–Cu–Pb–Zn deposits associated with granitoids in China has been termed the Nanling
129 belt (Fig. 1a; Mao et al., 2013). The Huangshaping deposit is located in southern Hunan Province
130 where the Shi–Hang zone and Nanling belt meet (Fig. 1a). This area has a basement that is
131 dominated by Paleo- to Mesoproterozoic metamorphic rocks that are overlain by a sequence of
132 Neoproterozoic to Paleozoic continental and neritic marine sediments, mainly Devonian and

Carboniferous carbonates (Wang et al., 2007; Fig. 1b). The igneous rocks in southern Hunan Province can be divided into granites that formed by remelting of crustal material and granodiorite porphyries that formed from a mix of crustal- and mantle-derived material; the former are associated with W and Sn mineralization, including the Furong skarn Sn and Yaogangxian wolframite and skarn scheelite W deposits, whereas the latter are associated with skarn-type Pb–Zn deposits, such as the Baoshan deposit (Fig. 1b; Li et al., 2007b; Jiang et al., 2009; Mao et al., 2013; Xie et al., 2013; Yao et al., 2014). All of these deposits are hosted by Devonian and Carboniferous carbonates, and the significant endowment of the southern part of Hunan Province means that this area has been the focus of much geological and mineral exploration and research.

3. Geology of the Huangshaping deposit

3.1 Stratigraphy and structure

The Huangshaping deposit is located in the northwestern part of the Qitianling granite batholith (Fig. 1b). The exposed sedimentary rocks associated with the Huangshaping deposit are dominantly neritic marine sediments that can be subdivided into a number of different units. The Upper Devonian Xikuangshan Formation crops out within the southeast of the deposit and consists of a lower section of thickly bedded limestones interbedded with chert (>100 m thickness) and an upper section of calcareous sandstone (~45 m). The lower Carboniferous Douling'ao Formation also crops out in the southeast of the deposit and is dominated by thickly bedded limestones interbedded with minor dolomite and chert (~109 m). The lower Carboniferous Shidengzi Formation consists of thickly bedded limestone that is interbedded with minor dolomite or carbonaceous limestone; this formation hosts the majority of the mineralization in the study

area and has a thickness of >500 m (Fig. 2b, c). The lower Carboniferous Ceshui Formation is dominated by calcareous sandstones that contain small faulted coal horizons (~38 m) and forms one of the major hangingwall units to the mineralization in the Huangshaping deposit, with the Pb–Zn orebodies that lie beneath this formation hosting the majority of the Pb–Zn reserves within this deposit (Fig. 2b, c). The lower Carboniferous Zimenqiao Formation contains thickly bedded dolomite with chert (100–150 m). The structure of the study area is dominated by the N–S trending Guanyindazuo–Baoling reverse anticline, which has a core that consists of the Shidengzi Formation and limbs that are formed from the Ceshui and Zimenqiao formations (Fig. 2b, c). Three N–S-trending thrust faults (F1, F2, and F3) are present within the anticlinal axis and limbs (Fig. 2a), and these control the location of the majority of the Pb–Zn reserves, especially true of the F3 fault (Fig. 2b, c). Several E–W- and WNW–ENE-trending normal faults (F0, F6, F7, and F9) are also present within the deposit (Fig. 2a). The combination of the reverse anticline and these faults form a “#”-shaped structure that controls both the outcrop of the granitoids and the location of the associated Pb–Zn–W–Mo mineralization within the deposit.

3.2 Granitoids

The granitoids associated with the Huangshaping deposit include quartz porphyry, granite porphyry, and felsite phases based on mineral assemblages and geochemistry. The granite porphyry contains potash feldspar, plagioclase, quartz, and minor biotite phenocrysts, whereas the quartz porphyry unit only contains quartz phenocrysts, whereas the felsite is aphyric, containing no obvious phenocrysts. All three types of granitoids contain similar accessory minerals, including primary zircon and apatite, and secondary sulfides and fluorite. The quartz porphyry and

177 weathered felsite units are exposed in the Huangshaping deposit, whereas the granite porphyry lies
 178 beneath the southeastern part of this deposit (Figs 2 and 3). All of these rocks have SiO₂
 179 concentrations of >70% wt.%, indicating that they are acidic intrusions. They have aluminum
 180 saturation index (ASI) values of 0.67–1.62, which indicate these rocks are metaluminous or
 181 peraluminous. These rocks have K₂O concentrations of 4%–7% and are high-K calc-alkaline to
 182 shoshonitic (Yao et al., 2005; Li et al., 2014a). Previous geochronological research suggests that
 183 these rocks formed during the Late Jurassic (161.6 ± 1.1 to 150.1 ± 0.4 Ma) and all were formed as
 184 a result of partial melting of crustal material, although the quartz porphyry may contain minor
 185 amounts of mantle-derived material (Yao et al., 2005; Lei et al., 2010; Ai, 2013; Li et al., 2014a;
 186 Yuan et al., 2014). Our new zircon laser ablation–inductively coupled plasma–mass spectrometry
 187 (LA–ICP–MS) U–Pb data indicate that the quartz porphyry, felsite, and granite porphyry formed
 188 at 160.5 ± 1.3 , 156.6 ± 1.4 , and 155.3 ± 1.6 Ma, respectively. In addition, the Sr–Nd–Hf–Pb
 189 isotopic compositions of these units suggest that the felsite and granite porphyry are comagmatic,
 190 with both forming from magmas generated by the partial melting of metamorphic basement rocks
 191 in the upper crust, whereas the quartz porphyry intrusion associated with the Huangshaping
 192 deposit was formed from a magma generated by partial melting of Paleoproterozoic metamorphic
 193 basement rocks within the lower crust in a process that involved some input from a coeval basaltic
 194 magma (our unpublished data).

195 Scanning electron microscope (SEM) observations show that fluorite is present in both the
 196 granite porphyry and quartz porphyry units, indicating that both of these units are fluorine-rich;
 197 this is especially true of the granite porphyry (Fig. 4a–e). The quartz porphyry unit contains pyrite,
 198 sphalerite, and chalcopyrite; the latter is only present within this unit and either coexists with

fluorite or replaces pyrite (Fig. 4a, b). In comparison, wolframite, molybdenite, and columbite are found in the granite porphyry. Wolframite is hosted by quartz veins and is associated with fluorite whereas molybdenite is present within quartz veins and fluorite contact zones (Fig. 4c–e). This indicates that the granite porphyry is W–Mo-enriched, a fact that is consistent with the location of W–Mo skarn mineralization along the contact between the granite porphyry and the host rocks. The felsite hosts a sulfide assemblage that includes pyrite, sphalerite, and galena, all of which either replace potash feldspar or are present as disseminated sulfides within the matrix; pyrite veins also occur in the matrix or in the contact zone between potash feldspar and the matrix (Fig. 4f–h). All of the sulfides within the granitoids appear to be secondary and may have formed as a result of late-stage magmatism or post-magmatic hydrothermal activity.

3.3 Alteration and mineralization

The alteration within the Huangshaping deposit consists of skarn and sulfide–carbonate alteration; the former generally occurs along the contact between granitoids and Shidengzi Formation limestones whereas the latter is generally located within distal sedimentary carbonates.

Most of the skarn associated with the Huangshaping deposit are located at the contact zone between granitoids and Shidengzi Formation limestones, with skarns preferentially developed around the granite porphyry (Figs 2 and 3). The skarn alteration is zoned from the granite porphyry outwards to the distal limestone, with potassic alteration present within the granite porphyry adjacent to the skarn. The proximal skarn consists of garnet–diopside adjacent to the potassic-altered granite porphyry; this assemblage is dominated by garnet with minor amounts of diopside, and the former has a composition of $\text{andradite}_{84.0}\text{grossularite}_{15.1}\text{almandite}_{0.9}$ and is

commonly zoned (Internal Report of Huangshaping Company, 2011). Scheelite and molybdenite are commonly disseminated within the garnet–diopside skarn, which is also cut by later magnetite and fluorite veins (Figs 5a–c and 6a, c–e). The garnet–diopside skarn also hosts significant W resources, including the No. W216 orebody which is located close to the granite porphyry and hosts 88% of the known scheelite reserves within the deposit. The other 12% of the reserves are hosted within the No. W1 orebody that is located close to the quartz porphyry intrusion (Fig. 3a and b). Fluid inclusions in garnet homogenize at temperatures of 528°C–600°C, and inclusions in disseminated scheelite and fluorite homogenize at temperatures of 400°C–460°C and 250°C–303°C, respectively (Huang et al., 2013).

The garnet–diopside zone is followed by the tremolite skarn zone, which hosts long columnar or radial polycrystalline textured tremolite (Figs 5c and 6b), abundant disseminated molybdenite, and late-stage calcite veins and disseminated scheelite (Figs 5c and 6c–d). Sulfide–quartz mineralization is weakly developed within the Huangshaping deposit and is generally present as veins that cross-cut early-formed skarn. These veins include molybdenite–quartz veins within fractures in the granite porphyry (Fig. 5d) and sulfide veins (including chalcopyrite, pyrite, and molybdenite) that cut early-formed garnet and scheelite (Fig. 6c–e). These veins host quartz with fluid inclusions that homogenize at temperatures of 300°C–340°C, lower than for the inclusions within garnet and scheelite in the more proximal skarn (Huang et al., 2013). The most distal skarn zone is a marble zone that is adjacent to the surrounding limestones (Fig. 5e).

The Pb–Zn mineralization formed during a sulfide–carbonate stage of mineralization; this stage hosts nearly all of the pyrrhotite, sphalerite, galena, and pyrite within the Huangshaping deposit. These sulfides are hosted by distal sedimentary carbonate and are present as vein-type,

stratiform, and lens-shaped zones of mineralization that are generally located within the Shidengzi Formation limestones, the Ceshui Formation sandstones, and the Zimenqiao Formation dolomite limestones (Fig. 5f). The sulfide orebodies are located beneath hangingwall rocks of the Ceshui Formation sandstone and the quartz porphyry intrusion within the upper section of the Huangshaping deposit (Fig. 2b, c). The Pb–Zn orebodies within the same level of the deposit are not in contact (Fig. 3a, b), but instead are located along faults that acted as conduits for ore-forming fluids (Fig. 2a, b). Sulfide ores within the deposit are dominated by galena and sphalerite with pyrrhotite and pyrite in a calcite and fluorite gangue (Fig. 5f–i). The Huangshaping deposit is zoned vertically, with pyrrhotite abundance decreasing and pyrite abundance increasing upward within the deposit. In addition, early stage pyrrhotite is cut by sphalerite and galena veins (Figs 5i and 6f), with sphalerite replaced by galena (Fig. 6f), indicating that pyrrhotite formed before sphalerite, which in turn formed before the galena in the deposit. Calcite and fluorite gangue minerals host fluid inclusions that homogenize at 160°C–240°C, with no obvious evidence of boiling (Huang et al., 2013). This paragenesis is based on the textures and replacement relationships between sulfides and previously determined fluid-inclusion homogenization temperatures, and it is summarized in Fig. 7.

4. Sampling and analytical methods

The sulfide ore samples analyzed during this study were taken from various levels within the Huangshaping deposit, mainly sampled from the –96 and 20 m levels (Fig. 3; Table 1). The granitoids and sedimentary carbonates are fresh and unaltered, and were sampled from the locations shown in Tables 1–3. The sulfide ore, granitoid, and carbonate samples were crushed to

pass 80 mesh before the sulfides were concentrated using heavy liquid separation techniques that yielded pure and clear sulfides that were then handpicked under a binocular microscope before being rinsed in deionized water and ground to powder (passing 200 mesh) for S–Pb–Sr isotope analyses. The fresh granitoids and carbonate samples were directly ground to powder for whole-rock Pb–Sr isotope analyses.

Sulfur isotope analyses were undertaken at the Key Laboratory of Nuclear and Resources and Environment, East China Institute of Technology, Nanchang, China. This analysis used 20–100 mg of sulfide powder (passing 200 mesh) that was heated at 1020°C to extract SO₂ that was then analyzed using combined Flash-EA and MAT-253 mass spectrometer instruments. The resulting ³⁴S/³²S ratios are expressed using conventional δ³⁴S per mil values relative to the Canyon Diablo Troilite (CDT) standard with analytical precision within 0.2‰.

Lead isotope compositions were determined using ~100 mg sulfide or whole-rock powder that was dissolved in concentrated HF + HNO₃ for 48 hours. Lead was separated and purified using diluted HBr before isotopic compositions were determined using an ISOPROBE-T mass spectrometer at the Analytical Laboratory of the Beijing Research Institute of Uranium Geology, Beijing, China. Analytical accuracy was monitored by analysis of the NBS981 standard, yielding the following values: ²⁰⁸Pb/²⁰⁴Pb = 36.602 (0.0039%), ²⁰⁷Pb/²⁰⁴Pb = 15.459 (0.0038%), and ²⁰⁶Pb/²⁰⁴Pb = 16.911 (0.0041%).

Sr isotopic compositions were determined using thermal ionization mass spectrometry and a Triton Ti instrument at the State Key Laboratory for Mineral Deposits Research, Nanjing University, Nanjing, China. Measured ⁸⁷Sr/⁸⁶Sr ratios were adjusted to the NBS SRM 987 standard with ⁸⁷Sr/⁸⁶Sr = 0.71025 ± 0.00013. For details of the analytical procedure, see [Pu et al. \(2005\)](#).

5. Results

5.1 Sulfur isotopes

The S isotopic compositions of samples from the Huangshaping deposit are summarized in [Table 1](#). These sulfides have $\delta^{34}\text{S}$ values that are consistent across different types of mineralization, although they vary with depth in the deposit. Sulfides from the -96 m level have $\delta^{34}\text{S}$ values that range from +4.4‰ to +6.6‰ (n = 13), whereas those from the -56 m level have values of +9.7‰ to +13.9‰ (n = 4). In comparison, sulfides from the 20 m level have highly variable $\delta^{34}\text{S}$ values (+8.3‰ to +16.3‰; n = 19). These data indicate that sulfide $\delta^{34}\text{S}$ values increase with height within the deposit. In addition, disseminated pyrite within the Shidengzi Formation limestones contains isotopically depleted sulfur with $\delta^{34}\text{S}$ values of -22.6‰ to -2.5‰ (n = 6), whereas pyrite within granitoids ($\delta^{34}\text{S}$ of +0.2‰ to +16.5‰; n = 12) has consistent $\delta^{34}\text{S}$ values that are similar to those of the sulfide ores and are independent of rock type or sampling location.

5.2 Lead isotopes

The Pb isotopic compositions of sulfides and granitoids from the Huangshaping deposit are summarized in [Tables 1 and 2](#). The sulfide ores from the deposit have $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ values of 18.525–18.652, 15.686–15.845, and 38.821–39.345, respectively; disseminated pyrite within the Shidengzi Formation limestones has values of 18.370–18.484, 15.607–15.645, and 38.122–38.233, respectively; disseminated pyrite within granitoids has values of 18.525–18.567, 15.695–15.740, and 38.887–38.989, respectively; and the whole-rock analysis of granitoids in the study area yielded initial Pb isotopic compositions of 17.737–18.789,

15.607–15.727, and 38.048–39.003, respectively.

310

5.3 Strontium isotopes

The Sr isotopic compositions ($^{87}\text{Sr}/^{86}\text{Sr}$) of samples from the Huangshaping deposit are summarized in Table 3. The Shidengzi Formation limestone and Zimenqiao Formation dolomite samples have the most depleted initial Sr isotopic compositions (I_{Sr} ; 0.707484–0.708034 with an average of 0.707801), whereas the granitoids in the study area are enriched in ^{87}Sr and have I_{Sr} values of 0.709654–0.718271 (average of 0.713273) and the sulfide ore (0.707662–0.709846) and calcite gangue (0.708774–0.709278) samples yield I_{Sr} values that lie between the compositions of the sedimentary carbonates and granitoids, with averages of 0.708204 and 0.708980, respectively. In addition, the sulfides have I_{Sr} values that decrease from early to late within the sulfide paragenetic sequence.

6. Discussion

6.1 S isotopes and the source of sulfur within the Huangshaping deposit

The sulfide ores within the Huangshaping deposit are dominated by pyrrhotite, sphalerite, galena, and pyrite, and the lack of sulfate within the deposit indicates that the $\delta^{34}\text{S}$ compositions of the sulfide ores are indicative of the $\delta^{34}\text{S}$ values of the ore-forming fluids (Ohmoto, 1972). Although pyrrhotite, sphalerite, and galena coexist within the deposit, galena formed after the other two sulfides and sphalerite postdates pyrrhotite (Fig. 6f), suggesting that these minerals were not in equilibrium during ore formation. This is exemplified by the fact that galena has lower $\delta^{34}\text{S}$ values than pyrite from the same sample but yields calculated mineralization temperatures (based

on the isotopic equilibrium equation $\Delta^{34}\text{S}_{\text{pyrite-galena}} = 1.15 \times 10^6/T^2$; [Smith et al., 1977](#)) of 452°C–752°C, much higher than the temperature of mineralization indicated by fluid inclusion microthermometry (160°C–240°C; [Huang et al., 2013](#)). This suggests that the sulfur within these sulfides was distributed by kinetic equilibrium rather than as a result of thermodynamics, indicating that fractionation between the hydrothermal fluids and these sulfide minerals was minimal, and that the composition of these sulfides may reflect the $\delta^{34}\text{S}$ values of the ore-forming fluids ([Ohmoto, 1972](#); [Burnard et al., 1993](#)).

The sulfide ores within the deposit have a wide range of $\delta^{34}\text{S}$ values that increase with height, from +4.4‰ at the –96 m level to +17.5‰ at the 273 m level ([Fig. 8a–b](#)). As mentioned above, the majority of the Pb–Zn sulfide reserves are located within the upper parts of the Huangshaping deposit beneath the Ceshui Formation sandstone and part of the quartz porphyry intrusion, meaning that the majority of the sulfide ores within the Huangshaping deposit are enriched in heavy sulfur. These characteristics differ from other skarn Pb–Zn deposits associated with granitoids that have $\delta^{34}\text{S}$ values that usually lie within ranges typical of magmatic sulfur ([Ault and Williams-Jones, 2004](#); [Kalender et al., 2011](#); [Li et al., 2012](#); [Akiska et al., 2013](#); [Shu et al., 2013](#); [Wang et al., 2014a](#); [Xie et al., 2015](#); [Zuo, 2015](#)). The wide range of $\delta^{34}\text{S}$ values within the Huangshaping deposit is indicative of a mixed source of sulfur, a characteristic that is always present within the large fluid systems located along large-scale shear zones ([Goldfarb et al., 2005](#); [Zeng et al., 2014](#)).

The sulfide ores within the upper part of the Huangshaping deposit are enriched in ^{34}S , yielding $\delta^{34}\text{S}$ values of +8.3‰ to +16.3‰ for the 20 m level and +2.3‰ to +17.5‰ (110 out of 137 samples yielded values of >8‰) for the 273 m level ([Fig. 8a–b](#)), both of which are similar to

the $\delta^{34}\text{S}$ values of Devonian and Carboniferous seawater (about 15‰–25‰; Holser, 1977). This indicates that the sulfur within the upper parts of the Huangshaping deposit was generated by the thermodynamic reduction of evaporite horizons within the surrounding sediments. No sulfates were found in the study area, thereby preventing direct measurement of marine sulfate isotope compositions, but evaporite horizons are known to be present within the lower Carboniferous Zimenqiao Formation in adjacent areas of central Hunan Province (Jin et al., 2006), a sedimentary sequence that hosts a significant proportion of the Pb–Zn mineralization within the Huangshaping deposit. Previous research indicates that reactions between carbonates and hydrothermal fluids can produce methane (McCollom and Seewald, 2006), with sulfates and methane reacting at temperatures of $>140^\circ\text{C}$ as follows: $\text{SO}_4^{2-} + \text{CH}_4 = \text{H}_2\text{S} + \text{CO}_3^{2-} + \text{H}_2\text{O}$. No differentiation of sulfur isotopes takes place during this process, meaning that the sulfur can maintain the same isotopic composition as the original sulfate (Ohmoto, 1972; Worden et al., 1995). This thermodynamic reduction may have been the source of the majority of the dominant heavy sulfur within the Pb–Zn sulfide ores in the upper parts of the Huangshaping deposit, as abundant CH_4 gas was identified during Raman spectroscopic analysis of fluid inclusions (Huang et al., 2013).

The pyrite within Jurassic granitoids associated with the Huangshaping deposit has a similar wide range of $\delta^{34}\text{S}$ values compared to the sulfide ores in the deposit (Fig. 8a, c), but this pyrite is generally present as later veins or as replacements after potash feldspar within these granitoids (Fig. 4f–g). This suggests that these pyrites were not homogenized during magmatism but instead were formed during post-magmatism hydrothermal activity, meaning that although these pyrites cannot provide any information on the magmatic source of sulfur within the Pb–Zn mineralization in the Huangshaping deposit, they may still provide evidence of the $\delta^{34}\text{S}$ composition of the

ore-forming hydrothermal fluids.

The sulfide within the Pb–Zn ores within the lower part of the Huangshaping deposit have lower and consistent $\delta^{34}\text{S}$ values, as exemplified by sulfide ores from the –96 m level that have $\delta^{34}\text{S}$ values of +4.4‰ to +6.7‰ (Fig. 8a). These sulfur isotopic characteristics are different to those of disseminated pyrite within the ore-hosting Shidengzi Formation limestone (–22.6‰ to –2.5‰; Fig. 8c), but are closer to the values of sulfides within quartz vein-type wolframite deposits in southern Hunan Province and adjacent areas, such as the Yaogangxian, Xihuashan, and Xiangdong deposits (–2.6‰ to +3.9‰; Cai et al., 2012; Zhu et al., 2012 and references therein). The $\delta^{34}\text{S}$ values of sulfides from classic skarn-type Pb–Zn deposits in these areas, such as the Baoshan, Shuikoushan, and Kangjiawan deposits, range from –2.7‰ to +6.46‰ (Xie et al., 2015; Zuo, 2015). This result suggests that the sulfur within sulfide ores in the lower part of the Huangshaping deposit was dominantly derived from a magmatic source. The fact that the $\delta^{34}\text{S}$ values of sulfides within the deposit increase with height may reflect an increase in the presence of heavy sulfur derived from evaporite horizons within the sediments that surround the upper parts of the deposit. A mixed sulfur source has also been suggested for Pb–Zn deposits elsewhere, such as the Nampundwe sulfide deposit in Zambia (Burnard et al., 1993) and the El Mochito skarn Zn–Pb–Ag deposit in Honduras (Ault and Williams-Jones, 2004).

6.2 Sr isotopes and the evolution of ore-forming fluids

The sulfur isotopic compositions of the sulfides within the Huangshaping deposit are indicative of a mixture of two sulfur end-member sources within the Pb–Zn mineralization: the uppermost evaporite horizon and the lowermost lower magma chamber sources. Sulfur isotopic

compositions can also reflect the evolution of ore-forming fluids (Ault and Williams-Jones, 2004), and in the present case these provide evidence of the mixing of ore-forming fluids during formation of the Huangshaping deposit. More evidence of mixing of ore-forming fluids is provided by Rb and Sr contents and Sr isotopic data in sulfides. For example, sulfide ores from the –96 m level have high Rb concentrations and Rb/Sr ratios compared with samples from the 20 m level (Fig. 9). The distribution of Rb and Sr is generally controlled by kinetic equilibrium rather than by any thermodynamic balance between sulfides and hydrothermal fluids, as the radii of Rb and Sr are markedly different from the radii of major elements within sulfides (S, Pb, and Zn; Shannon, 1976; Zhou et al., 2001), previous research suggests that Rb and Sr are generally present as inclusions within sulfides (Mao et al., 2009), meaning that the concentrations of Rb and Sr in sulfides can reflect the characteristics of ore-forming fluids. Sulfides from the –96 m level have Rb and Sr concentrations that are similar to those of the granitoids in the Huangshaping deposit, whereas sulfides from the 20 m level have Rb and Sr concentrations that are similar to those of the surrounding sedimentary carbonate (Fig. 9). This observation suggests that the ore-forming fluids that precipitated sulfides within the lower part of the deposit were dominantly magmatic fluids, whereas those that precipitated sulfides in the upper part of the deposit were significantly affected by formational fluids. In addition, the sulfide ores within the lower part of the deposit formed at higher temperatures than did the sulfides in the upper part of the deposit (Huang et al., 2013). Furthermore, the dominant Fe-sulfide changes from pyrrhotite within sulfide ores on the –96 m level by an increase in pyrite abundance and a decrease in pyrrhotite abundance with increasing height, until the vast majority of the Fe-sulfides are pyrite at the 273 m level (Xi et al., 2009). This change in Fe-sulfide phases is indicative of a decrease in temperature and an increase in sulfur

fugacity, suggesting that the higher temperatures deeper in the deposit may reflect the influence of magmatic fluids and that the lower temperature fluids within the upper part of the deposit may reflect the addition of externally derived low-temperature fluids that extracted the heavy sulfur that provided the majority of the sulfur within the Pb–Zn mineralization in the Huangshaping deposit.

Strontium isotopes have been widely used to trace the evolution of ore-forming fluids, as these isotopes are not differentiated during fluid migration (Brannon et al., 1992; Zhou et al., 2001; Samson et al., 2008; Shen et al., 2010; Gromek et al., 2012; Zhou et al., 2013). The $^{87}\text{Sr}/^{86}\text{Sr}$ compositions of sulfide ores with relatively low Rb/Sr ratios (mainly from the 20 m level) were determined during this study and are summarized in Table 3. Sulfide ores and gangue calcites have initial $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic compositions (I_{Sr}) that fall between the compositions of granitoids in the Huangshaping deposit (excluding the granite porphyry, as it has extremely high Rb/Sr ratios that would inevitably result in highly uncertain $^{87}\text{Sr}/^{86}\text{Sr}$ values) and the hosting sedimentary carbonate (Fig. 10). Combining these data with the paragenesis of sulfides in the study area indicates that I_{Sr} values decrease with ongoing sulfide precipitation; for example, the pyrrhotite within the deposit has the most enriched ^{87}Sr isotope compositions whereas the galena is the most depleted sulfide; the values for these sulfides approach the compositions of the granitoids and the sedimentary carbonates in the Huangshaping deposit, respectively (Fig. 10). These Sr isotopic characteristics are generally indicative of the mixing of ore-forming fluids, although increased interaction with wall rocks is also expected, as observed in numerous other deposits (Zhou et al., 2001 and references therein; Samson et al., 2008), and that suggest that the fluids that formed the Huangshaping deposit were likely a mixture of magmatic and formation fluids, with the influence

of the latter increasing with ongoing sulfide precipitation.

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6.3 Pb isotopes and the source of metals

The Jurassic granitoids in the Huangshaping deposit, disseminated pyrite within Shidengzi Formation limestones, pyrite within granitoids, and Pb–Zn sulfide ores from the Huangshaping deposit all have a different ranges of Pb isotopic compositions (Fig. 11a–c). The Pb isotope compositions of the sulfide ores analyzed during this study are similar to those of the Pb–Zn ores within the Huangshaping deposit (Xi et al., 2009; Zhu et al., 2012), with all of these samples plotting well above the average upper crustal Pb evolution curves of Zartman and Doe (1981; Fig. 11a–b), indicating that the Pb–Zn mineralization in the Huangshaping deposit contains crustal-derived material. These sulfide ores also plot well above the two-stage Pb growth evolution curve of Stacey and Kramers (1975; Fig. 11d). These Pb isotope data define a clear linear trend but without any age constraints (Fig. 11a–b), these steep slopes are probably indicative of mixing of Pb derived from two end-members or alternatively the leaching of a single source of Pb (Cunha et al., 2007; Zeng et al., 2014).

Sulfide ores within the Huangshaping deposit are generally more enriched in radiogenic lead (^{206}Pb , ^{207}Pb , and ^{208}Pb) than is the pyrite disseminated within the Shidengzi Formation limestone (Fig. 11a–b), indicating that the former are derived from a source enriched in both U and Th. The extreme depletions in radiogenic lead of the pyrite in the Shidengzi Formation limestone also indicate that this unit cannot be the source of the Pb–Zn mineralization in the study area, even though these pyrites plot along the same trend as the sulfide ores (Fig. 11a–b). Similarly, the sulfide ores are generally more enriched in radiogenic lead (^{206}Pb , ^{207}Pb , ^{208}Pb) than is indicated

by the initial Pb isotopic compositions of the quartz porphyry, granite porphyry, and felsite intrusions, suggesting that the metals within these sulfides were derived from a U- and Th-enriched source that is not either of these intrusions (Fig. 11a–b), indicating only a minimal contribution of these granitoids to the ore-forming system. In addition, the initial Pb isotopic compositions of Jurassic granitoids also define a different evolutionary trend than the sulfide ores (Fig. 11a–b), that is indicative of different sources for the sulfide ores and the granitoids. In summary, it seems that neither the sedimentary limestones that host the mineralization nor the granitoids in the Huangshaping deposit are the source of metals within the Pb–Zn mineralization in the study area.

The Pb isotopic composition of pyrite (samples 1212HSP14 Py, 1212HSP27 Py, and 1212HSP30 Py) from the quartz porphyry and felsite intrusions in the Huangshaping deposit are different than the whole-rock initial Pb isotopic compositions of their hosting granitoids (samples 1212HSP14 WR, 1212HSP27 WR, and 1212HSP30 WR; Fig. 11c), but are similar to the compositions of the sulfide ores within this deposit, with all of these sulfides plotting along a single linear trend (Fig. 11a–c). This suggests that the pyrite within these granitoids has the same source of Pb as the sulfide ores, which is different to the source of Pb within the granitoids, meaning that the latter did not provide the Pb for the sulfide ores or the sulfides in the granitoids. The sulfides in the granitoids probably precipitated during the migration of ore-forming fluids through these hangingwall units, a conclusion that consistent with the SEM observations of pyrite occurrences (Fig. 4f–g) and the sulfur isotopic features discussed above.

The Pb isotopic compositions of sulfides from the Huangshaping deposit are similar to the compositions of sulfides from other coeval skarn Pb–Zn deposits within southern Hunan Province,

including the Hehuaping and Baoshan deposits (Fig. 11d). This suggests that these deposits may contain lead derived from the same source underlying this region. ^{207}Pb and ^{206}Pb are the decay daughters of ^{235}U and ^{238}U , indicating that $^{207}\text{Pb}/^{206}\text{Pb}$ ratios can be used to determine whether the Pb within a sample is derived from an old or new source, primarily as the half-life of ^{235}U is much shorter than the half-life of ^{238}U (0.7038 Ga for ^{235}U and 4.468 Ga for ^{238}U ; Faure, 1986; Zhou et al., 2001). Sulfide ores from mineral deposits in southern Hunan Province have $^{207}\text{Pb}/^{206}\text{Pb}$ ratios (0.835–0.861) that are significantly higher than in the majority of Pb–Zn deposits elsewhere, such as the $^{207}\text{Pb}/^{206}\text{Pb}$ values of galena from the Viburnum Trend (0.708–0.774) and the $^{207}\text{Pb}/^{206}\text{Pb}$ values of samples from Mississippi Valley-Type deposits in the southern and central Appalachians (0.800–0.830 and 0.815–0.845, respectively; Zhou et al., 2001 and references therein). This suggests that basement material beneath southern Hunan Province with an old Pb isotopic signature was the source of the metals within these deposits. This inference is consistent with the fact that the Mesozoic magmatism within Hunan Province was the result of remelting of Paleoproterozoic metamorphic basement material (Li et al., 2007b; Jiang et al., 2009; Xie et al., 2013; Yao et al., 2014; Zuo et al., 2014), and the Pb isotopic compositions of sulfide ores from the Huangshaping deposit plot in the field of Pb isotopic compositions that are typical of the Cathaysian metamorphic basement (Fig. 11a–b). The leaching of metals such as Pb and Zn by fluid flow during regional metamorphism or from crystalline basement material is thought to be one of the most important process during the formation of significant Pb–Zn deposits (Haack et al., 1984; Oliver et al., 2006), with the calculated Pb and Zn losses associated with this process in high-grade metamorphic zones reaching values of 2.7 and 27 Mt, respectively (Hammerli et al., 2015). The sharing of similar Pb isotopic compositions between multiple mineral deposits in the

same area has also been observed elsewhere, including within the Vazante Group Pb–Zn field in Brazil (Cunha et al., 2007) and the Aysen Pb–Zn field in southeastern Chile (Townley and Godwin, 2001). These Pb isotopic compositions indicate that the metals were all derived from the same basement.

6.4 Relationship between granitoids and mineralization

The Jurassic granitoids associated with the Huangshaping deposit are enriched in fluorine, as exemplified by the occurrence of fluorite in these granitoids and the fact that biotite within the granite porphyry associated with the Huangshaping deposit contains >4% F (our unpublished data), higher than the majority of the granites elsewhere within southern Hunan Province (Li et al., 2007a). The presence of F means that melts retain W rather than preferentially losing this element to aqueous fluids (Keppler and Wyllie, 1991; Bai and Koster van Groos, 1999), a process that promoted the generation of the W mineralization within the Huangshaping deposit. In addition, fluorine can dramatically reduce the solidus temperature of granitic melts (Manning, 1981; Webster et al., 1987), meaning that the exsolution of magmatic fluids can be sustained for a long period (Chang et al., 2008). Granitoids can provide huge amounts of heat and fluid, both of which are fundamental to hydrothermal activity and the extraction of metals from basement material (Heinrich, 2005). However, Burnham (1979) suggested that only limited amounts of fluids and metals could be exsolved from small-volume felsic intrusions. In addition, a significant amount of research has invoked the involvement of deep magma chambers and related magmato-hydrothermal metal fluxes during the formation of world-class mineral deposits (Shinohara and Hedenquist, 1997; Heinrich, 2005; Klemm et al., 2007). This process is likely to

1 529 have played an important role in the formation of the Pb–Zn mineralization in the Huangshaping
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3 530 deposit in a process that is similar to that of other world-class mineral deposits associated with
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6 531 intrusive bodies in China and elsewhere (Amelin and Naldrett, 1999; Tang and Li, 2006; Chen,
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9 532 2012; Wang et al., 2014b).

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11 533 The processes that formed the Pb–Zn mineralization associated with magmatism and the
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14 534 sulfide-bearing basement material were as follows: (1) magmatism only provided heat that drove
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17 535 hydrothermal circulation but did not provide sulfur, fluids or metals, or (2) sulfide-bearing
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20 536 basement material was added to the magma by remelting or contamination, with this mingling
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23 537 causing the formation of sulfides and the later-formed orebodies (Vikre et al., 2011). The
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26 538 formation of the Huangshaping deposit is similar to the first of these models, as is evidenced by
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29 539 the isotopic data presented above, where ore sulfur and lead isotope compositions differ
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32 540 significantly from the compositions of granitoids. The formation of the Huangshaping deposit can
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35 541 be summarized as follows: a highly evolved magma (e.g., the granite porphyry) reacted with
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38 542 carbonates to form a W–Mo-bearing skarn. Contemporaneous magmatism in this area provided
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41 543 the Huangshaping mineralizing system with huge amounts of heat and fluid. The magmatic fluids
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44 544 extracted metals from basement material and deposited them within the main Pb–Zn orebodies by
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47 545 mixing and reaction with the formation fluids that contained large amounts of heavy sulfur
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50 546 reduced from evaporite horizons within sediments associated with the upper parts of the deposit.
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53 547 The formation of proximal W–Mo and distal Pb–Zn mineralization during a single Late Jurassic
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56 548 magmatic event resulted in the unique polymetallic Huangshaping deposit.

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58 550 7. Conclusions

1 551 1. The sulfur within Pb–Zn mineralization in the Huangshaping deposit was derived from a
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3 552 mixture of two end-members: heavy sulfur reduced from evaporite horizons and to a lesser extent
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6 553 relatively depleted magmatic sulfur.
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9 554 2. The fluids that formed the deposit were a combination of magmatic and formation fluids,
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11 555 with the influence of the latter increasing over time and with progression through the paragenetic
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14 556 sequence of the sulfide minerals within the deposit.
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17 557 3. Lead isotopic data indicate that the metals within the deposit were extracted from
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20 558 basement material beneath southern Hunan Province, with only minimal contributions from the
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23 559 hosting sedimentary carbonate and granitoids in the area.
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25 560 4. The granitoids associated with the Huangshaping deposit were the source of metals for the
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28 561 W–Mo mineralization and also provided significant amounts of heat and fluid, both of which were
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31 562 fundamental to the formation of hydrothermal circulation systems and the extraction of metals that
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34 563 were deposited in the Pb–Zn mineralization.
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Table Captions

Table 1. Sulfur and lead isotopic composition of sulfides from the Huangshaping deposit.

Table 2. Lead isotopic composition of granitoids from the Huangshaping deposit.

Table 3. Strontium isotopic composition of samples from the Huangshaping deposit.

Figure Captions

Fig. 1. (a) Distribution of Mesozoic intrusive and volcanic rocks in southeast China, adapted from Zhou et al., 2006. The locations of the Shi–Hang and Nanling belts are after Jiang et al., 2009; Li et al., 2013, and Mao et al., 2013. (b) Distribution of Jurassic igneous rocks and associated polymetallic mineral deposits in southern Hunan Province, including the location of the Huangshaping deposit.

Fig. 2. (a) Geological map of the Huangshaping deposit and (b–c) cross-sections through the Huangshaping deposit.

Fig. 3. Simplified geological maps of the Huangshaping deposit at the (a) 20 m and (b) –96 m levels.

Fig. 4. Back-scattered electron images showing typical accessory mineral assemblages within granitoids associated with the Huangshaping deposit. (a–b) quartz porphyry; (c–e) granite porphyry; (f–h) felsite. (a) chalcopyrite coexisting with fluorite and replacing pyrite, and associated with sphalerite coexisting with pyrite; (b) chalcopyrite coexisting with fluorite or

present as inclusions in fluorite; (c) quartz vein containing wolframite; (d) molybdenite located along the contact zone between a quartz vein and fluorite; (e) columbite coexisting with wolframite, fluorite, zircon, and biotite; (f) K-feldspar containing apatite and zircon inclusions, and a pyrite vein distributed along the contact zone between the feldspar and the surrounding matrix, with the latter also containing sphalerite; (g) sulfide replacing K-feldspar; (h) pyrite containing galena inclusions and coexisting with sphalerite. Abbreviations are as follows: Wf = wolframite, Col = columbite, Zrn = zircon, Bt = biotite, Fl = fluorite, Qtz = quartz, Kfs = potash feldspar, Mo = molybdenite, Sp = sphalerite, Py = pyrite, Gn = galena, Ap = apatite, Ccp = chalcopyrite.

Fig. 5. Representative hand specimens from the Huangshaping deposit. (a) Magnetite cross-cut garnet skarn; (b) scheelite coexisting with fluorite within garnet skarn; (c) molybdenite disseminated within tremolite skarn cross-cut by a calcite vein; (d) molybdenite with a quartz vein located in fractures within the granite porphyry; (e) contact zone between tremolite skarn and marble; (f) vein-type sulfide ore body cross-cut the wall rock limestone; (g) galena coexisting with pyrite in a fluorite and calcite gangue; (h) sphalerite coexisting with pyrrhotite in a fluorite gangue; (i) vein-hosted sphalerite cross-cutting pyrrhotite. Abbreviations are as in Fig. 4 with Grt = garnet, Mt = magnetite, Sch = scheelite, Cal = calcite, Mb = marble, Tr = tremolite, Po = pyrrhotite.

Fig. 6. (a) Magnetite vein cross-cutting early garnet skarn (plane-polarized light); (b) radial polycrystalline textured tremolite skarn (cross-polarized light); (c–d) disseminated scheelite and fluorite coexisting within garnet skarn with later chalcopyrite and molybdenite filling fractures

viewed under cross-polarized light (c) and reflected light (d); (e) quartz vein containing pyrite and molybdenite cross-cutting scheelite (reflected light); (f) galena and sphalerite replacing pyrrhotite, and galena replacing sphalerite (reflected light). Abbreviations are as in Figs 4 and 5.

Fig. 7. Paragenetic sequence for minerals within the Huangshaping deposit.

Fig. 8. Sulfur isotopic compositions of samples from the Huangshaping deposit; (a)-(b) sulfide ores for different levels; (c) pyrites disseminated in Shidengzi Formation limestone and granitoids. Data for the 273 m level are from [Xi et al., 2009](#), some of the data for the -56 m level are from [Zhu et al., 2012](#), and the remaining data are from this study.

Fig. 9. Rb/Sr vs. Rb diagram for samples from the Huangshaping deposit (some data from this study and others from our unpublished data).

Fig. 10. Sr isotopic composition of samples from the Huangshaping deposit, with initial Sr isotopic compositions calculated based on the 155 Ma age of mineralization determined by [Yao et al., 2007](#).

Fig. 11. Pb isotopic composition of samples from the Huangshaping deposit plotted with the evolution curve of [Zartman and Doe, 1981](#) and the two-stage model of [Stacey and Kramer, 1975](#). U = upper crust; O = orogen; L = lower crust; (a) $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$; (b) $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$; (c) $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ for pyrite within granitoids and the hosting granitoids;

1 903 (d) Pb isotopic composition of samples from mineral deposits in southern Hunan Province; data
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3 904 for the Baoshan deposit are from [Xie et al., 2015](#) and for the Hehuaping deposit are from [Yao et al.,](#)
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6 905 [2014](#). Shaded field indicates typical Cathaysia basement lead from [Zhang et al., 2002b](#) and [Min et](#)
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Fig. 1.

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Table 1.

Sample No.	Study object	Sample location	$\delta^{34}\text{S}_{\text{CDT}}\text{‰}$	$^{206}\text{Pb}/^{204}\text{Pb}$	2σ	$^{207}\text{Pb}/^{204}\text{Pb}$	2σ	$^{208}\text{Pb}/^{204}\text{Pb}$	2σ
Sulfide ores									
11HSP86	pyrrhotite	-96 m	4.4	18.616	0.003	15.804	0.003	39.208	0.007
11HSP90	pyrrhotite	-96 m	4.4						
11HSP86	sphalerite	-96 m	4.7						
11HSP90	sphalerite	-96 m	5.3	18.596	0.002	15.769	0.002	39.094	0.005
11HSP88	pyrrhotite	-96 m	5.4						
12HSP18	sphalerite	-96 m	5.8						
11HSP100	sphalerite	-96 m	5.9						
11HSP99	pyrrhotite	-96 m	6.0	18.542	0.002	15.711	0.002	38.902	0.005
11HSP98	sphalerite	-96 m	6.2	18.566	0.002	15.738	0.002	38.992	0.005
11HSP98	pyrrhotite	-96 m	6.3						
11HSP97	pyrrhotite	-96 m	6.4						
11HSP99	sphalerite	-96 m	6.5						
11HSP96	pyrrhotite	-96 m	6.6						
12HSP22	sphalerite	-96 m		18.596	0.003	15.773	0.003	39.106	0.008
12HSP32-1	galena	-56 m	9.7	18.545	0.002	15.722	0.002	38.937	0.005
12HSP32-2	galena	-56 m	13.4	18.525	0.002	15.688	0.002	38.828	0.004
12HSP33	galena	-56 m	13.7	18.572	0.002	15.746	0.001	39.019	0.004
12HSP29	galena	-56 m	13.9	18.560	0.002	15.732	0.002	38.968	0.006
11HSP124	galena	20 m	8.3	18.526	0.002	15.686	0.002	38.821	0.004
11HSP135	galena	20 m	9.2	18.560	0.002	15.729	0.002	38.965	0.004
11HSP124	pyrrhotite	20 m	9.2	18.652	0.002	15.845	0.002	39.345	0.004
11HSP115	galena	20 m	9.3						

11HSP115	pyrite	20 m	10.3	18.613	0.001	15.797	0.001	39.184	0.004
11HSP127	galena	20 m	10.9						
11HSP137	galena	20 m	10.9						
11HSP52	sphalerite	20 m	11.0						
11HSP137	pyrite	20 m	12.2						
11HSP127	pyrrhotite	20 m	12.8						
11HSP125	pyrrhotite	20 m	13.0						
11HSP123	galena	20 m	13.3						
11HSP114	pyrrhotite	20 m	13.4						
11HSP116	pyrite	20 m	13.7	18.566	0.002	15.737	0.002	38.991	0.004
11HSP118	galena	20 m	13.8						
11HSP123	pyrrhotite	20 m	15.1						
12HSP13	pyrite	20 m	15.3	18.544	0.003	15.719	0.002	38.928	0.005
12HSP13	sphalerite	20 m	15.3						
11HSP59	sphalerite	20 m	16.3						
Pyrite in Shidengzi Formation limestone									
1212HSP02	pyrite	Shidengzi Fm.	-22.6						
1212HSP01	pyrite	Shidengzi Fm.	-21.2	18.395	0.002	15.608	0.002	38.356	0.004
1212HSP08	pyrite	Shidengzi Fm.	-11.1	18.484	0.001	15.645	0.001	38.188	0.003
1212HSP09	pyrite	Shidengzi Fm.	-9.3	18.415	0.002	15.631	0.001	38.193	0.004
1212HSP07	pyrite	Shidengzi Fm.	-7.7	18.460	0.001	15.642	0.001	38.233	0.004
1212HSP12	pyrite	Shidengzi Fm.	-2.5	18.370	0.002	15.607	0.002	38.122	0.005
Pyrite in granitoids									
11HSP60	pyrite	felsite	3.9						
1212HSP27	pyrite	felsite	5.5	18.567	0.001	15.740	0.001	38.972	0.003
11HSP-131	pyrite	felsite	11.3						

1212HSP17	pyrite	quartz porphyry	4.3	18.547	0.001	15.695	0.001	38.989	0.003
11HSP-94	pyrite	quartz porphyry	4.7						
1212HSP14	pyrite	quartz porphyry	9.8	18.525	0.001	15.712	0.001	38.887	0.003
1212HSP36	pyrite	quartz porphyry	10.0						
1212HSP30	pyrite	quartz porphyry	10.5	18.547	0.001	15.712	0.001	38.904	0.001
11HSP-47	pyrite	quartz porphyry	11.2						
11HSP-159	pyrite	granite porphyry	0.2						
11HSP-160	pyrite	granite porphyry	15.1						
11HSP-107	pyrite	granite porphyry	16.5						

Table 2.

Rock type	Quartz porphyry			Felsite			Granite porphyry		
Sample	1212HSP36	1212HSP30	1212HSP14	1212HSP27	11hsp103	11hsp60	1212hsp22	1212hsp25	12702-05
$^{206}\text{Pb}/^{204}\text{Pb}$	18.256	18.270	18.149	18.457	18.911	18.789	19.444	19.287	18.849
2 σ	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
$^{207}\text{Pb}/^{204}\text{Pb}$	15.640	15.651	15.627	15.692	15.731	15.734	15.759	15.752	15.726
2 σ	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
$^{208}\text{Pb}/^{204}\text{Pb}$	38.522	38.561	38.410	38.796	39.271	39.167	39.340	39.259	39.182
2 σ	0.002	0.002	0.002	0.001	0.003	0.004	0.002	0.002	0.002
U (ppm)	13.0	14.4	14.9	8.62	9.53	9.91	26.6	29.0	28.4
Th (ppm)	38.1	41.7	40.0	35.0	31.5	32.6	42.2	37.0	29.7
Pb (ppm)	122	120	54.9	2150	56.0	37.7	63.6	56.8	84.2
T (Ma)	155	155	155	155	155	155	155	155	155
$(^{206}\text{Pb}/^{204}\text{Pb})_i$	18.094	18.087	17.737	18.451	18.646	18.381	18.789	18.489	18.325
$(^{207}\text{Pb}/^{204}\text{Pb})_i$	15.632	15.642	15.607	15.692	15.718	15.714	15.727	15.712	15.701
$(^{208}\text{Pb}/^{204}\text{Pb})_i$	38.367	38.387	38.048	38.788	38.985	38.729	39.000	38.927	39.003

Note: Initial Pb isotopic compositions were calculated by a single-stage evolution model following [Zhang et al., 2002a](#). T = age of mineralization within the deposit

determined by [Yao et al., 2007](#).

Table 3.

Sample No.	Study object	Rb ($\mu\text{g/g}$)	Sr ($\mu\text{g/g}$)	$^{87}\text{Sr}/^{86}\text{Sr}$	2 σ	$(^{87}\text{Sr}/^{86}\text{Sr})_i^*$
Carbonate						
11HSP87	Shidengzi Fm. limestone	8.7	127	0.707923	9	0.707484
11BS97-2	Shidengzi Fm. limestone	23.9	505	0.708000	9	0.707698
11BS95-1	Shidengzi Fm. limestone	0.4	515	0.707780	8	0.707775
11HSP08	Shidengzi Fm. limestone	1.8	440	0.707876	11	0.707850
11HSP61	Shidengzi Fm. limestone	3.5	420	0.708009	5	0.707956
11BS83	Zimenqiao Fm. dolomite	0.1	46.2	0.708042	12	0.708034
11BS85	Zimenqiao Fm. dolomite	0.2	70.6	0.707821	12	0.707807
Gangue calcite						
11HSP36	gangue calcite	2.2	131.0	0.708996	9	0.708888
11HSP82	gangue calcite	0.9	30.5	0.708971	13	0.708774
11HSP110	gangue calcite	3.9	143.6	0.709451	7	0.709278
Sulfide ores						
11HSP25Pb	galena	1.4	1.1	0.715318	9	0.707662
11HSP31Pb	galena	0.3	1.3	0.710362	12	0.708745
12HSP13Zn	sphalerite	2.3	3.3	0.713960	9	0.709557
11HSP52Zn	sphalerite	5.7	0.7	0.759097	5	0.708493
11HSP86Fe	pyrrhotite	10.1	2.0	0.742089	10	0.709429
11HSP127Fe	pyrrhotite	0.7	1.9	0.712073	17	0.709846
Granitoids						
11HSP-46	quartz porphyry	254	74.8	0.731305	5	0.709654
11HSP-12	quartz porphyry	330	75.8	0.738708	4	0.710950
11HSP-69	quartz porphyry	642	91.9	0.755674	9	0.711133
11HSP-103	felsite	506	74.8	0.756653	4	0.713522
11HSP-131	felsite	638	62.5	0.781189	7	0.716105
11HSP-132	felsite	532	50.8	0.785041	5	0.718271

*Initial Sr isotopic compositions ($(^{87}\text{Sr}/^{86}\text{Sr})_i$) were calculated using the 155 Ma age of

mineralization within the deposit determined by Yao et al., 2007.