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Micro-textures and in situ sulfur isotopic analysis of spheroidal and zonal sulfides in the giant Jinding Zn–Pb deposit, Yunnan, China: Implications for biogenic processes

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ABSTRACT

The Jinding deposit in Yunnan, southwest China, is the largest sandstone- and conglomerate-hosted Zn–Pb deposit in the world. In this paper, we report various micro-textures of spheroidal and zonal sulfides, such as pellet-shaped and colloform aggregates of pyrite and sphalerite, from the deposit and interpret them to be possibly related to micro-colonies of sulfate reducing bacteria, probably supporting an in situ BSR hypothesis. Micro-scale sulfur isotope analysis in different parts of the spheroidal and zonal sulfide aggregates, using secondary ion mass spectrometry (SIMS), revealed $\delta^{34}S$ (VCDT) values as low as −48.4‰ for sulfides formed in the early-main stage disseminated ores in the western part of the deposit, possibly suggesting maximum sulfur isotopic fractionation through BSR. Relatively elevated $\delta^{34}S$ (VCDT) values (−7.7‰ to −34.8‰, mainly from −10‰ to −20‰) for the late-stage, cavity-filling ores in the eastern part of the deposit, are interpreted to be possibly related to elevated temperatures close to the hydrothermal conduit and elevated $\delta^{34}S$ values of the remaining sulfates resulting from the preceding BSR processes. The apparent discrepancy between the low temperatures required for BSR and the high temperatures indicated by fluid inclusions (>120 °C) may be reconciled through invoking episodic influx of ore-forming hydrothermal fluids into a shallow, relatively cool environment. It is proposed that the host rocks of the Jinding deposit have not been buried to great depths (⩽1 km), which, combined with the availability of hydrocarbons in the Jinding dome (a paleo-oil and gas reservoir), provides an ideal environment for BSR. Episodic influx of metal-carrying hydrothermal fluids temporarily and locally suppressed BSR and promoted thermo-chemical sulfate reduction (TSR), resulting in deposit- and micro-scale variations of $\delta^{34}S$.

1. Introduction

The Jinding Zn–Pb deposit in Yunnan, southwestern China, is the largest sandstone- and conglomerate-hosted Zn–Pb deposit in the world, with a reserve of 220 Mt of ore grading 6.1% Zn and 1.3% Pb (Third Geological Team, 1984). The deposit has been investigated by numerous previous studies, including geologic characteristics and setting (Shi et al., 1983; Third Geological Team, 1984, 1990; Bai et al., 1985; Gao, 1989; Yin et al., 1990; Qin and Zhu, 1991; Ye et al., 1992; Kyle and Li, 2002; Gao et al., 2005; Chi et al., 2007, 2012; Wang et al., 2009), sulfur and lead isotopes (Zhao, 1989; Zhang, 1991; Zhou and Zhou, 1992; Tang et al., 2014), noble gas isotopes (Hu et al., 1998; Xue et al., 2003, 2007a,b), fluid inclusions (Wen et al., 1995; Xue et al., 2002, 2007a; Chi et al., 2005), organic geochemistry (Hu, 1989; Zhang and Chang, 2003; Xue et al., 2007b, 2009), geochronology (Xue et al., 2003; Gao et al., 2012), trace element geochemistry (Ye et al., 2011; Tang et al., 2011), fluid flow dynamics (Qin and Zhu, 1991; Kyle and Li, 2002; Xue et al., 2006; Chi et al., 2005, 2006, 2007, 2012), and comparison with SEDEX and MVT deposits (Wang et al., 1992; Kyle and Li, 2002; Xue et al., 2007a). However, many questions remain unanswered regarding the mineralization environments and processes. An epigenetic origin (e.g., Kyle and Li, 2002; Xue et al., 2007a) has been generally favored over a syngenetic origin (e.g., Zhao, 1989; Wang et al., 1992), because orebodies occur in sandstones of the Lower Cretaceous Jinxing Formation as well as sandstones and conglomerates of the Palaeocene Yunlong Formation, which are separated by a hiatus and a thrust fault (Qin and Zhu, 1991; Kyle and Li, 2002; Xue et al., 2007a). However, the age of mineralization remains poorly

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constrained. It is generally agreed that basinal fluids were involved in mineralization, but some geochemical evidence such as Pb isotopes of sulfides and noble gas isotopes of fluid inclusions suggest participation of ore-forming fluids from a mantle source (e.g., Yin et al., 1990; Xue et al., 2003). It is still unclear how mantle fluids may have moved into the basin and to the sites of mineralization, and how much they contributed to the metal and sulfur budgets. Hydrocarbons recorded as oil and gas inclusions and solid bitumen were inferred to have acted as reductants to produce H_2S from sulfates (e.g., Hu, 1989; Zhang and Chang, 2003; Xue et al., 2007b, 2009), but the actual sulfate reduction processes remain unclear.

Previous sulfur isotope studies of bulk sulfides from Jinding have yielded $\delta^{34}S$ values from −1.7‰ to −30.4‰ (VCDT) (Bai et al., 1985; Zhang, 1991; Ye et al., 1992; Zhou and Zhou, 1992; Xue et al., 2007a), which have been interpreted to indicate both bacterial sulfate reduction (BSR) and thermo-chemical sulfate reduction (TSR). A recent secondary ion mass spectrometry (SIMS) analysis of sulfides from the deposit recognized a systematic difference in $\delta^{34}S$ between stage-1 mineralization (−42.1‰ to −10.2‰ VCDT) and stage-2 (−8.3‰ to 7.7‰ VCDT), suggesting a BSR-dominated sulfur source in the early stage followed by a TSR-dominated source in the later stage (Tang et al., 2014). Although most previous studies agree that the ^{34}S-depleted reduced sulfur required to form the Jinding deposit was derived from BSR (Gao, 1989; Zhao, 1989; Qin and Zhu, 1991; Kyle and Li, 2002; Chi et al., 2006; Xue et al., 2006, 2007a; Tang et al., 2014), these studies have not considered whether the BSR process took place at the site of mineralization, or in a distal area whereby the produced reduced sulfur was transported to the site of mineralization. One of the biggest challenges for the in situ BSR model is that fairly high temperatures (>120 °C) have been inferred for the ore-forming fluids from fluid inclusion studies (Wen et al., 1995; Chi et al., 2005; Xue et al., 2007a), which would have been too high for bacteria to survive (Stetter et al., 1990; Machel, 2001; Kashefi and Lovley, 2003). In order to determine whether or not in situ BSR actually took place in the formation of the Jinding deposit, it is important to investigate sulfide textural evidence, in addition to depleted $\delta^{34}S$ signatures, that supports the presence of bacteria during mineralization. This paper documents the petrographic characteristics of various micro-textures of spheroidal and zonal sulfides in Jinding ores, and sulfur isotope compositions and their variation within these sulfides using SIMS analysis. Many studies have demonstrated that sulfur isotopes can be highly variable at micrometer scale, and that the SIMS method can be used to reveal the detailed isotopic heterogeneity (e.g., McKibben and Eldridge, 1995; Riciputi et al., 1998; Bawden et al., 2003; Southam and Saunders, 2005; Ingham et al., 2014).

2. Geology of the Jinding Zn–Pb deposit

The Jinding Zn–Pb deposit is located in the northern part of the Lanping-Simao basin (Fig. 1), which is a narrow (50–150 km wide and >400 km long), NNW-trending basin filled with Late Triassic to Neogene sediments up to more than 10 km thick. The basin is developed on the old Tethys basement of Proterozoic–Paleozoic metamorphic rocks, and is filled with mainly continental siliciclastic rocks (with evaporite intervals) except for some Triassic limestones. The strata of the basin have been folded and faulted but not regionally metamorphosed, and were locally intruded by alkaline magmatic bodies (Third Geological Team, 1990).

The Jinding area is characterized by a dome structure (the Jinding dome) located adjacent to a NNE-trending, high-angle regional fault (the Pijiang fault) that controlled Paleocene to Miocene sedimentation (Fig. 1). The strata comprising the Jinding dome include the Upper Triassic Sanhedong (T_3s), Waluba (T_3w) and Maichuqing (T_3m) formations, the Middle Jurassic Huakaizuo Formation (J_2h), the Lower Cretaceous Jinxing (K_1j) and Nanxin (K_1n) formations, the Middle Cretaceous Hutoushi Formation (K_2h), the Paleocene Yunlong Formation (E_1y) and the Eocene Guolang Formation (E_2g) (Fig. 1). The T_3s is made of marine limestone and dolomitic limestone, which is locally rich in bitumen, while the T_3w consists of mudstone and siltstone, and the T_3m is composed of dark gray shale, siltstone and fine-grained sandstone, locally with coal seams. The T_3s is unconformably overlain by the J_2h, which consists of purple colored siltstone and mudstone. The K_1j unconformably overlies the J_2h, and is composed of gray sandstone with local conglomerate. The K_1j is conformably overlain by the K_1n consisting of purple sandstone, conglomerate, siltstone and silty mudstone, which is in turn overlain by the K_2h composed of gray to purple quartz arenite and arkosic arenite. The E_1y unconformably overlying the K_2h is divided into two members: the lower member (E_1y^a) consists of purple siltstone, silty fine sandstone, and fine sandstone, while the upper member (E_1y^b) is composed of gray and reddish fine sandstone and gravelly sandstone in the west and conglomerate near the Pijiang Fault in the east (Fig. 1). The E_2g above the E_1y is composed of purple sandstone, siltstone and gypsum. The strata in the deposit area are divided into a lower, autochthonous, normal sequence, and an upper, allochthonous, overturned sequence (a nappe), separated by a thrust fault (F2, Fig. 1). The autochthonous sequence consists of J_2h, K_1j, K_1n, K_2h and E_1y (younging upward), whereas the allochthonous sequence comprises K_1j, J_2h, T_3s, T_3w and T_3m (reversed). Both the autochthonous and allochthonous sequences, together with the thrust fault, have been affected by the Jinding dome (Fig. 1). The sequence of geologic events, partly overlapping each other, has been interpreted as follows: (1) Mesozoic to Eocene sedimentation, (2) Paleocene to Eocene thrusting, (3) Eocene to Oligocene doming, and (4) Oligocene to Miocene Zn–Pb mineralization (Kyle and Li, 2002; Xue et al., 2006, 2007a).

The Jinding deposit consists of more than 100 orebodies distributed around the Jinding dome, and is divided into seven segments: the Beichang segment on the northern side of the Jinding dome, Fengzishan and Xipo in the west, Baicaoping and Nanchang in the south, Jiayashan in the east, and Paomaping to the northeast (Fig. 1). The orebodies are mainly hosted in the Lower Cretaceous Jinxing (K_1j) and the upper member of Paleocene Yunlong (E_1y^b) formations. Sand injection structures and hydraulic fractures crosscutting the strata are locally developed and mineralized, especially in the Jiayashan and Paomaping segments (Gao et al., 2005; Chi et al., 2005, 2007, 2012). The Zn–Pb mineralization is mainly of disseminated style, and the ores can be broadly divided into two types according to the predominant host rocks, i.e., the sandstone-hosted (Fig. 2a and b) and conglomerate-hosted (Fig. 2c and d). The first type is the dominant one in the deposit, and is characterized by fine-grained sulfides (sphalerite, galena, pyrite and marcasite) disseminated in sandstones of K_1j and E_1y^b (Fig. 2b). The second type is mainly distributed in the eastern part of the deposit, with mineralization occurring in fractures and cavities in the conglomerate and dissemination in the matrix and fragments of the E_1y^b (Fig. 2d). The Zn/Pb ratios decrease from 7.8 in the east, through 4.9 in the central north, to 0.3 in the west (Xue et al., 2007a), with an average of 4.7. Common gangue minerals include calcite, barite, celestite, gypsum, anhydrite and quartz.

The mineralization has been divided into three stages, i.e., (1) quartz + pyrite + sphalerite + galena stage, (2) pyrite + sphalerite + galena + celestite stage, and (3) galena + sphalerite + pyrite + calcite + celestite + gypsum stage (Xue et al., 2007a). The stages 1 and 2 (broadly corresponding to stage 1 in Tang et al., 2014) are generally characterized by fine-grained textures and disseminated structures, whereas those of stage 3 (broadly corresponding to