

# Cadmium and sulfur isotopic compositions of the Tianbaoshan Zn–Pb–Cd deposit, Sichuan Province, China



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## ABSTRACT

Although Zn–Pb deposits are one of the most important Cd reservoirs in the earth, few studies have focused on the Cd isotopic fractionation in Zn–Pb hydrothermal systems. This study investigates the causes and consequences of cadmium and sulfur isotope fractionation in a large hydrothermal system at the Tianbaoshan Zn–Pb–Cd deposit from the Sichuan–Yunnan–Guizhou (SYG) metallogenic province, SW China. Moderate variations in Cd and S isotope compositions have been measured in sphalerite cover a distance of about 78 m. Sphalerite has  $\delta^{114/110}\text{Cd}$  values ranging from 0.01 to 0.57‰, and sulfides (sphalerite, galena and chalcopyrite) have  $\delta^{34}\text{S}_{\text{CDT}}$  values ranging from 0.2 to 5.0‰. Although  $\delta^{34}\text{S}_{\text{CDT}}$  and  $\delta^{114/110}\text{Cd}$  values in sphalerites have no regular spatial variations, the  $\delta^{34}\text{S}_{\text{CDT}}$  values in galena and calculated ore-forming fluid temperatures decreased from 2.1 to 0.2‰ and from about 290 to 130 °C, respectively, from the bottom to the top of the deposit. Heavy Cd isotopes are enriched in early precipitated sphalerite in contrast to previous studies. We suggest that Cd isotopic compositions in ore-forming fluids are heterogeneous, which result in heavy Cd isotope enrichment in early precipitated sphalerite. In comparison with other Zn–Pb deposits in the SYG area, the Tianbaoshan deposit has moderate Cd contents and small isotope fractionation, suggesting differences in origin to other Zn–Pb deposits in the SYG province.

In the Tianbaoshan deposit, the calculated  $\delta^{34}\text{S}_{\Sigma\text{S-fluids}}$  value is 4.2‰, which is not only higher than the mantle-derived magmatic sulfur ( $0 \pm 3\text{‰}$ ), but also quite lower than those of Ediacaran marine sulfates (about 30 to 35‰). Thus, we suggest that reduced sulfur of ore-forming fluids in the deposit was mainly derived from the leaching of the basement, which contains large amount of volcanic or intrusive rocks. Based upon a combination of Cd and S isotopic systems, the Tianbaoshan deposit has different geochemical characteristics from typical Zn–Pb deposits (e.g., the Huize deposit) in SYG area, indicating the unique origin of this deposit.

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## 1. Introduction

Although it is important to determine the ore-forming fluid pathways and the environment, and to quantify of sulfide crystallization, these factors are often poorly known. The extent and causes of isotope fractionation of transition metals (e.g., Zn and Cd) have shown potential for ore exploration (Kelley et al., 2009; Gagnevin et al., 2012; Zhou et al., 2014; Zhu et al., 2015). Studies of Cd isotopes in hydrothermal systems suggest the incorporation of light isotopes in sphalerite in deeper parts of the hydrothermal environments, with Raleigh isotope fractionation accounting for the evolution from light to heavy Cd isotopic composition (Schmitt et al., 2009; Zhu et al., 2013). In published studies, the Cd isotope databases are limited in terms of their sample coverage, mass balance and their ability to quantify relative fractionations.

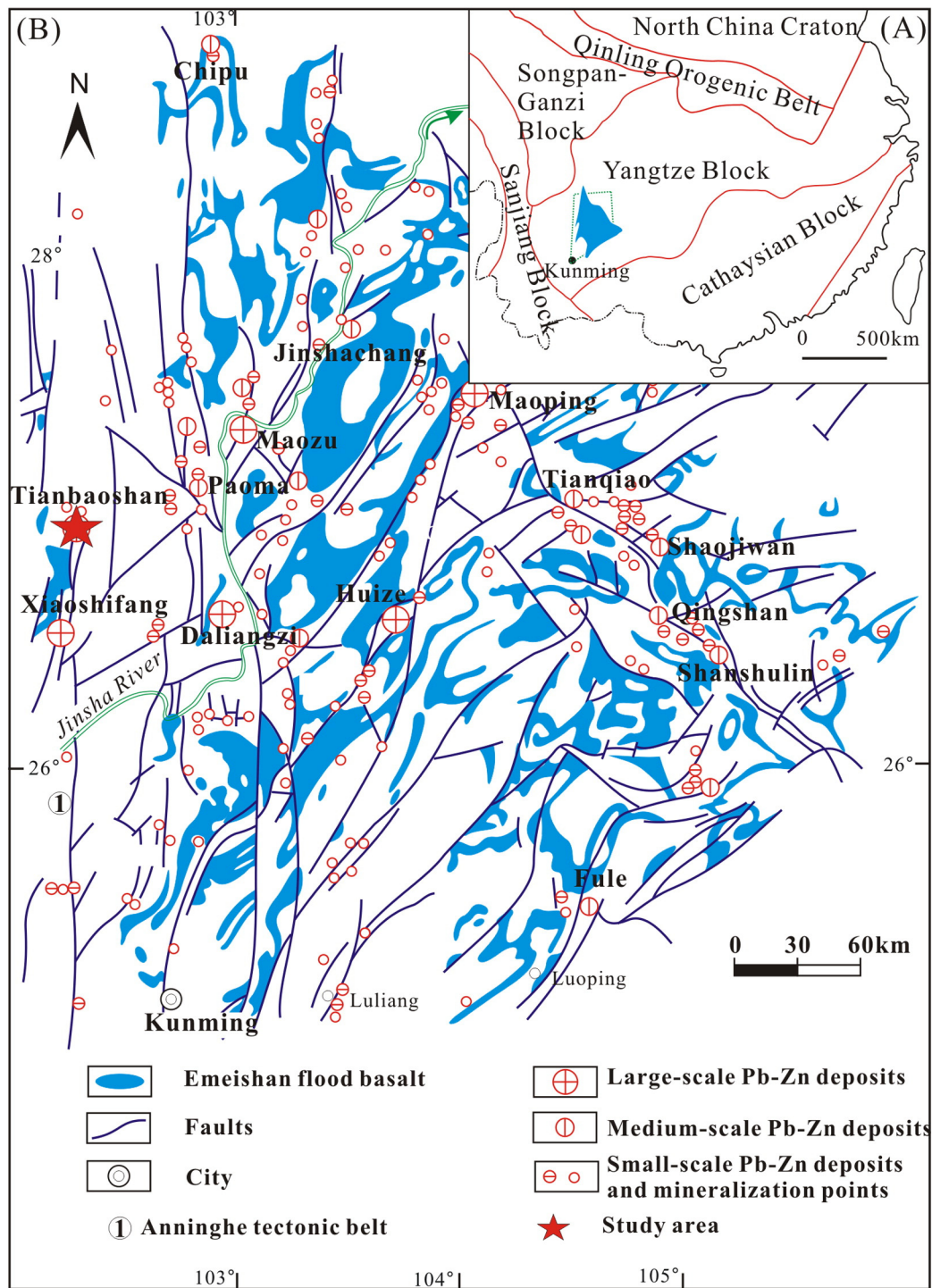
In the western Yangtze Block, SW China, more than 400 Zn–Pb deposits with about 200 Mt. of Zn–Pb ores are located in the Sichuan–Yunnan–Guizhou (SYG) metallogenic province, which contains

deposits known for super-enrichment of trace elements, such as the Huize Ge-rich Zn–Pb deposit (Fu, 2004; Han et al., 2012; Ye et al., 2011; Wu, 2013; Zhu, 2014), the Fule Cd-rich Zn–Pb deposit (Si, 2005; Zhu et al., 2013; Zhu, 2014) and the Tianbaoshan Cd-rich Zn–Pb deposit (Fu, 2004; Zhu, 2014). These deposits are hosted in Ediacaran to Permian carbonate rocks and structurally controlled by thrust fault-fold, and are spatially associated with the Emeishan flood basalts (~260 Ma). Previous studies focused on the geology and origin of these deposits (e.g., Xie, 1963; Huang et al., 2003, 2004; Li, 2003; Li et al., 2007; Zhang et al., 2015), and proposed many models to determine the enrichment of Zn and Pb in this region. More detailed information on the arguments concerning the enrichment mechanisms have been described in Huang et al. (2003), Zhu et al. (2013) and Zhang et al. (2015).

This study examines the Tianbaoshan Zn–Pb–Cd deposit, located in the SYG metallogenic province (Fig. 1), to elucidate temporal variations of Cd isotopes within a large hydrothermal system. These data are coupled with new data on S isotopes, whose behavior in the Tianbaoshan Zn–Pb deposit is already well established (e.g., Wang et al., 2000; Zhou et al., 2013). By taking samples of sphalerites from

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**Fig. 1.** (A) Tectonic sketch; (B) regional geological map of the Sichuan–Yunnan–Guizhou Zn–Pb metallogenic province, SW China. Modified from Liu and Lin (1999).

the deposit, we are able to examine the processes of Cd isotopic fractionation and to gain insights into the behavior of Cd isotopes during the formation of the Zn–Pb deposits. The Cd isotopic compositions in sphalerite of different stages were measured to understand temporal Cd isotopic variations during hydrothermal fluid precipitation.

## 2. Geological setting and sampling

The Tianbaoshan Zn–Pb–Cd deposit, including the Tianbao and Xinshan ore blocks, is located in the northwestern part of the SYG

metallogenic province at the northwestern margin of the Yangtze Craton. The Yangtze Craton is composed of ~2.9 to ~3.3 Ga crystalline basement complexes (mainly consisting of metamorphic series), Meso- to Neo-Proterozoic folded basements (mainly magmatic rocks) and Paleozoic to Mesozoic cover sequences (mainly carbonate rocks) (Liu and Lin, 1999; Fu, 2004). Wang et al. (2000) and Zhou et al. (2013) have described the regional geological background and the geological characteristics of this deposit in detail. The deposit is hosted in Ediacaran carbonate rocks and structurally controlled by the NS-trending Anninghe tectonic belt and its branch structures (Figs. 1

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