Telescoped boiling and cooling mechanisms triggered hydrothermal stibnite precipitation: Insights from the world’s largest antimony deposit in Xikuangshan China

Hao-Cheng Yu¹, Kun-Feng Qiu¹*, Adam C. Simon², Da Wang¹, Ryan Mathur³, Ruo-Qi Wan¹, Xiang-Yong Jiang¹, Jun Deng¹

¹ State Key Laboratory of Geological Processes and Mineral Resources, School of Earth Sciences and Resources, China University of Geosciences, Beijing 100083, China
² Department of Earth & Environmental Sciences, University of Michigan, Ann Arbor, MI 48109, USA
³ Department of Geology, Juniata College, Huntingdon, PA 16652, USA

*Corresponding author

Dr. Kun-Feng Qiu
KunfengQiu@qq.com; ORCID: 0000-0002-3185-9446
Professor, China University of Geosciences, Beijing
No. 29 Xueyuan Road, Haidian District, Beijing, 100083, P.R. China
Abstract

Society annually consumes 250% more Sb relative to the year 1960 and a sustainable supply of antimony depends critically on understanding the precipitation mechanism of stibnite (Sb$_2$S$_3$) that is the globally predominant source of this important technology metal. Previous solubility studies revealed that antimony is transported in mesothermal hydrothermal fluids mainly as thioantimonite (H$_2$Sb$_2$S$_4$, HSb$_2$S$_4^-$, Sb$_2$S$_4^{2-}$) and hydroxothioantimonite (Sb$_2$S$_2$(OH)$_2$). Thioantimonite can transform to hydroxothioantimonite as the decline of H$_2$S concentration. However, whether this transition occurs in hydrothermal systems and its role in stibnite precipitation are unknown.

In this work, bulk Sb isotope measurements for stibnite from the world’s largest Sb deposit in Xikuangshan China were conducted to address ore fluid evolution and stibnite precipitation mechanisms. The abundance of the stable antimony isotopes $^{121}$Sb and $^{123}$Sb were measured in stibnite from the Xikuangshan orebodies and reported as $\delta^{123}$Sb. The $\delta^{123}$Sb values show a trend of decreasing first and then increasing from proximal to distal parts of orebodies. This reveals that $^{123}$Sb had been preferentially partitioned from the ore fluid into stibnite first, then $^{123}$Sb remained preferentially dissolved in the ore fluid. These data indicate that the dominant Sb-complex transforms to Sb$_2$S$_2$(OH)$_2$ from H$_2$Sb$_2$S$_4$ with consuming of H$_2$S. Speciation diagram considerations indicate that stibnite precipitation from the ore fluid was controlled by two telescoped processes: 1) boiling of the ore fluid induced a decrease in H$_2$S that reduced the solubility of H$_2$Sb$_2$S$_4$, and 2) subsequent cooling that induced a decrease in the solubility of Sb$_2$S$_2$(OH)$_2$. This study highlights that understanding the controls of Sb isotope fractionation is critical to constrain fluid evolution and stibnite precipitation mechanisms in Sb-rich mineral systems. In particular, the stable Sb
complex in the hydrothermal ore fluid may change during fluid evolution and affect the isotope fractionation mechanism.

Keyword: Sb isotope; stibnite precipitation; boiling; cooling; Xikuangshan Sb deposit

1. Introduction

Antimony is a critical mineral commodity essentially for a wide variety of products including flame retardants and alloys for batteries, plain bearings, and solders (Schulz et al., 2018). This metal is found in more than 100 minerals in a variety of deposits. The most common antimony ore mineral is stibnite (Sb₂S₃) occurring as fault-controlled or strata-bound orebodies (Hofstra et al., 2013; Xie, 2018; Fu et al., 2020d). Simple stibnite-bearing quartz ± carbonate veins account for most of the current and recent mine production.

Antimony resources are unevenly distributed globally (Fig. 1). The majority of identified Sb resources are located in China who leads global production (Schulz et al., 2018; Yu et al., 2022). Society annually consumes 250% more Sb relative to the year 1960, while the antimony production continued to decline (Schulz et al., 2018). A sustainable supply of antimony depends critically on understanding the ore fluid evolution and stibnite precipitation mechanisms in hydrothermal Sb deposits.

Antimony displays a wide range of oxidation states (Sb³⁺ to Sb⁵⁺), most of which are present in trivalent and pentavalent forms in crustal fluids (Zotov et al., 2003; Fu et al., 2020d). Under surface oxidizing conditions, Sb⁵⁺ may be predominant, and Sb-bearing hydrothermal fluids mainly contain Sb³⁺ (Fu et al., 2020d). In hydrothermal fluids, Sb is transported mainly as thioantimonite (H₂Sb₂S₄, H₂Sb₂S₄, Sb₂S₄²⁻), hydroxothioantimonite
(Sb₂S₄)⁰, hydroxide complexes (Sb(OH)₂⁺, Sb(OH)₃⁰, and Sb(OH)₄⁻), chloride complexes, and carbonate or bicarbonate species (Krupp, 1988; Hagemann and Luders, 2003; Zotov et al., 2003; Wilson et al., 2007; Fu et al., 2020d). Given that (1) hydroxide complexes are formed in sulfur-free system, (2) chloride complexes are unimportant in antimony speciation except in extremely acid, chloride-rich solutions, and (3) carbonate or bicarbonate species are unimportant in antimony transport, thioantimonite and hydroxothioantimonite are thus likely to be dominant in ore fluids (Krupp, 1988; Williams-Jones and Norman, 1997). In mesothermal ore fluids, solubility experimental studies revealed the distribution of antimony species as a function of pH. Hydroxothioantimonite controls antimony transport at acidic pH, and thioantimonite is dominant at intermediate to alkaline pH (Krupp, 1988). In addition, the solubility experimental studies indicated that H₂Sb₂S₄ can transform to Sb₂S₄(OH)₂ with the consuming of H₂S (Krupp, 1988; Zotov et al., 2003). Previous research showed that different processes can decrease the solubility of corresponding Sb complexes in aqueous hydrogen sulfide solutions, e.g., consuming of H₂S can induce the stibnite precipitation from thioantimonite, while decreasing temperature can decrease the solubility of both thioantimonite and hydroxothioantimonite (Krupp, 1988; Zotov et al., 2003). Both pH change and cooling have been shown to be the causes of stibnite deposition in geothermal power stations in New Zealand (Wilson et al., 2007). Numerous fluid inclusion studies have been carried out on hydrothermal Sb-rich deposits and proposed various models proposed for the major geological processes, including fluid cooling, fluid boiling, fluid mixing, and fluid-rock interaction (Hagemann and Luders, 2003; Su et al., 2009; Muntean et al., 2011; Hu and Peng, 2018; Xie, 2018; Deng et al., 2020b; Fu et al., 2020c; Qiu et al., 2020; Voisey et al., 2020; Wu et al., 2021; Yu et al., 2021). These
studies inferred these geological processes decrease the solubility of Sb complexes and
control stibnite precipitation. It's clear that the concentration of H₂S will change with the
precipitation of stibnite, likely inducing the transition of dominant Sb complexes. However,
none of these studies focus on the transition of dominant Sb complexes as fluid evolution
and explore its role in stibnite precipitation.

Several studies have underpinned the crucial importance of metal isotope tracing as a
prerequisite to constrain the evolution of large-scale ore-forming systems (Mathur et al.,
2005; Toutain et al., 2008; Kelley et al., 2009; Qiu et al., 2017; Gao et al., 2018; Mathur et
al., 2018; Ohmoto, 2018; Zhu et al., 2018; Li et al., 2019; Wang et al., 2020a; Yu et al.,
2020). The application of the Sb isotope system as a process tracer for ore deposits is in its
infancy (Rouxel et al., 2003; Zhai et al., 2021). Although the dominant Sb species involved
and their associated isotope fractionations are poorly understood, initial studies explored the
range of Sb isotope compositions for natural samples (Rouxel et al., 2003; Wen et al., 2018;
Kaufmann et al., 2021), fractionation mechanisms (Lobo et al., 2012; Resongles et al., 2015;
Wen et al., 2018), and mineralization processes (Zhai et al., 2021). Reduction processes
from Sb⁵⁺ to Sb³⁺ exert a strong fractionation of 0.9 ‰ (Rouxel et al., 2003). Lighter Sb
isotopes preferentially partition into the Sb³⁺ phase, whereas heavier Sb isotopes remain in
the Sb⁵⁺ phase (Rouxel et al., 2003). Additionally, Sb isotope fractionation can be caused by
evaporation and precipitation of Sb during Sb-containing waste combustion and Sb ore
smelting (Tanimizu et al., 2011). Zhai et al. (2021) proposed that separation of stibnite from
an Sb-bearing fluid related to reaction kinetics as a cause for Sb isotope fractionation. These
studies demonstrate that the Sb isotope have the potential to be used as a process tracer for
the fluid evolution of large Sb ore systems.
The Xikuangshan deposit in Hunan Province, China, is the world’s largest Sb deposit, which has supplied more than half of all globally mined Sb (Yang et al., 2006; Deng and Wang, 2016; Hu et al., 2017; Goldfarb et al., 2019; Fu et al., 2020a; Luo et al., 2020). It provides a natural case to better understand the ore fluid evolution and stibnite precipitation mechanisms in hydrothermal Sb deposits. In this study, we report $\delta^{123}$Sb isotope values for stibnite from the proximal steeply-dipping orebodies. This new dataset can be compared with existing $\delta^{123}$Sb isotope values from the distal shallowly-dipping orebodies to address ore fluid evolution and stibnite precipitation mechanisms.

2. Geology of the Xikuangshan Sb deposit

The Xiangzhong province of China hosts the world’s largest Sb reserves in the world, with over 171 known antimony mineral deposits and 2.7 Mt Sb reserves (Deng et al., 2017; Hu and Peng, 2018; Wang et al., 2020b; Fu et al., 2022; Yan et al., 2022). Estimates of historic mining activity indicate that approximately 1 Mt of Sb have been produced from the Xikuangshan Sb deposit beginning in the 16th century and pre-mining reserves are 2.5 Mt at an average Sb grade of 4.0 wt. % (Fu et al., 2020c). The Sb resource of the deposit is mined by four mines, referred to as Laokuangshan and Tongjiayuan mines in the North Ore Block and Wuhua and Feishuiyan mines in the South Ore Block (Fig. 2A). The mining area is dominated by Middle Devonian to Lower Carboniferous carbonate rocks and minor shale, which is locally interbedded with siltstone and argillite and formed a NE-striking anticline. An Early Cretaceous (127.8 Ma; biotite K-Ar) lamprophyre dike aligned in the NE direction was emplaced into the strata in the eastern part of the mine (Wu and Hu, 2000). It exhibits a calc-alkaline affinity, with geochemical signatures implying it was derived from enriched
lithospheric mantle (Xie et al., 2001; Hu and Peng, 2018). A series of broadly parallel NE-striking normal faults crosscut the mine and were cut by later NW-striking strike-slip faults (Fig. 2A).

Much of the Sb resource in the Xikuangshan deposit is hosted in the footwall of the NE-striking fault F75. It hosts three types of orebodies: (1) steeply-dipping orebodies along the footwall of the major deep-seated fault F75, (2) shallowly-dipping orebodies within the strata controlled by a NE-striking anticline, and (3) transitional zones between the steeply-dipping and shallowly-dipping orebodies (Fig. 2B). All of the three types of orebodies show a southward plunge, leading to a relatively deeper mining depth in the South Ore Block of the Xikuangshan deposit. The ore-bearing zones are commonly hosted within the Devonian silicified limestone (Fig. 3). Hydrothermal alteration of the three types of orebodies is similar in appearance and mineral assemblages. It is characterized by quartz alteration and carbonate alteration (Figs. 3A, 3C, 4A), as well as local fluorite alteration. Ores in the Xikuangshan deposit are divided into quartz-stibnite and calcite-quartz-stibnite vein-style mineralization and disseminated minor barite-quartz-stibnite and fluorite-quartz-stibnite veinlet-style mineralization around the vein-style mineralization (Fig. 4). In general, the shallowly-dipping orebodies are dominated by the quartz-stibnite ores (Fig. 4C), while the steeply-dipping orebodies are dominated by the calcite-quartz-stibnite ores (Fig. 4D).

Optical microscopic investigation revealed that stibnite is the dominant sulfide mineral, with quartz, calcite, fluorite, and barite as gangue minerals (Fig. 5). Stibnite crystals from the shallowly-dipping and steeply-dipping orebodies are identical in mineralogy assemblages. Their size varies largely, ranging from tens of microns to several centimeters. Most of them are anhedral, growing along the margin of the quartz and calcite (Fig. 5A-C). Euhedral
needle-shaped crystals in limestone wall rock and calcite grains are also visible (Figs. 4B, 5D). Detrital zircons separated from the altered host rocks from the Xikuangshan deposit yielded (U-Th)/He ages ranging from 156 to 117 Ma, constraining the antimony event to late Mesozoic (Fu et al., 2020a). Microthermometry data for fluid inclusions hosted in stibnite from both types of orebodies reveal similar ore fluid conditions. The homogenization temperatures of stibnite from the shallowly-dipping orebodies range from 105 to 305 °C (averaging at 194 °C), with an average salinity of 6.0 wt.% NaCl equiv. For fluid inclusions within stibnite in the steeply-dipping orebodies, their homogenization temperatures range from 163 to 218 °C (averaging at 192 °C) with an average salinity of 8.1 wt.% NaCl equiv. (Lin, 2014; Hu and Peng, 2018; Zhang, 2018). Integrated He-Ar-C-O-Sr isotopic data indicate that the ore fluids are modified air-saturated meteoric water (Fu et al., 2022). The concentrations of Sb in different types of rocks in the region and S isotope show that most of the Sb was derived from the Neoproterozoic basement rocks (Fu et al., 2022; Long et al., 2022).

3. Sampling strategy and methods

Zhai et al. (2021) measured Sb isotope abundances in stibnite sampled from the shallowly-dipping orebodies and the transitional zones between the steeply-dipping and shallowly-dipping orebodies. To further understand the ore fluid evolution and stibnite precipitation mechanisms in the Xikuangshan deposit, the steeply-dipping orebodies are sampled in this study. Twenty-six samples spanning all the main steeply-dipping orebodies at different levels in the Feishuiyan mine at the Xikuangshan deposit were collected (Fig. 10).
Optical microscopic investigation of all samples indicated that no sulfide inclusions were present in the analyzed stibnite (Fig. 5).

Stibnite separation was done by using standard methods of concentration including crushing, heavy liquids, and magnetic separation at Beijing Precambrian Inc., Beijing, China. The purity of all stibnite concentrates was assessed microscopically prior to isotopic analysis to ensure they were monomineralic and not oxidized. Stibnite aliquot purities were commonly \( \geq 99\% \) and never \( < 95\% \). Antimony isotope compositions of the 26 samples were measured on a Thermo Scientific Neptune Plus MC-ICP-MS in low resolution mode, wet plasma using Ni cones at Pennsylvania State University. The full analytical procedures are provided in Zhai et al. (2021). Alfa Star verified acids were used and total blanks of these acids are certified at less than 0.01 ppb Sb. Approximately 30-50 mg of stibnite was dissolved for 18 hours in 15 ml teflon beakers containing 2 ml of aquaregia. Complete dissolution of materials was visually confirmed. Samples were diluted with 2 % nitric acid with 100 ppb NIST 3161 Sn internal standard. Mass bias was corrected using \( ^{124}\text{Sn}/^{116}\text{Sn} \) and samples were bracketed with NIST 3102a standard. One block of 35 ratios with on peak blank subtraction with an integration time of 12s was conducted as part of the measurement protocol. The mass of \( ^{123}\text{Sb} \) was set in the standard between 5-6 volts (solutions at 100 ppb), all measurements reported are within 20% matching of this voltage. The variation of the bracketing the standard throughout the run is considered the largest source of error and it varied 0.018 ‰ (2SD). The majority of the samples were duplicated and fall within the reported error (Table 1). At this moment no stibnite standards are reported as a means of QA/QC, thus a High Purity ICPMS standard which have been now measured over 15 times
was used. The internal stibnite standard yields $\delta^{123}\text{Sb}$ values of 0.336 ‰ and 0.338 ‰, which are consistent with the standard analyses of 0.31 ± 0.02 ‰ in Zhai et al. (2021).

4. Results and previous data

The Sb isotope compositions of stibnite from this study and from the study of Zhai et al. (2021) are shown in Fig. 6A and listed in Table 1. Previous 39 Sb isotope measurements from Xikuangshan Zhai et al. (2021) were conducted either using the same analysis procedures at Pennsylvania State University as these new data (1/39 analyses) or at Rutgers University (39/39 analyses) and Washington State University (1/39 analyses), where cross-checking of standards and identical samples allows direct comparison of isotope ratios of samples.

The $\delta^{123}\text{Sb}$ values for samples from the steeply-dipping orebodies in the Feishuiyan mine range from +0.483 to +0.988 ‰ and decrease systematically from deep (proximal) to shallow (distal) levels in the system. Stibnite from the -604 m, -468 m, -192 m, -142 m, and -106 m levels of the steeply-dipping orebody yielded averaged $\delta^{123}\text{Sb}$ values of +0.958 ‰ ± 0.086 ‰ (n=2), +0.767 ‰ ± 0.043 ‰ (n=6), +0.590 ‰ ± 0.091 ‰ (n=7), +0.559 ‰ ± 0.071 ‰ (n=6), and +0.534 ‰ ± 0.079 ‰ (n=5) (2σ), respectively (Fig. 6B; Table 1). Zhai et al. (2021) measured Sb isotope abundances in stibnite sampled from the shallowly-dipping orebodies in the Feishuiyan mine in the South Ore Block. The $\delta^{123}\text{Sb}$ values of stibnite sampled from the shallowly-dipping orebody range from +0.21 ‰ to +0.86 ‰, but show a systematical increase from proximal to distal ores in the system (Fig. 6B; Table 1). The shallowly-dipping orebodies and the transitional zones between the steeply-dipping and shallowly-dipping orebodies in the North Ore Block were also measured by Zhai et al.
(2021). Those authors reported the $\delta^{123}$Sb values ranging from 0.30 ‰ to 0.62 ‰ at the transitional zones. Similar to the South Ore Block, stibnite from the shallowly-dipping orebodies in the North Ore Block show an increase from proximal to distal ores in the system, ranging from -0.27 ‰ to +0.70 ‰ (Fig. 6B; Table 1)

5. Antimony isotopic fractionation model

Some geological processes that may lead to the variation in $\delta^{123}$Sb values of stibnite reported here and from Zhai et al. (2021) in the Xikuangshan deposit include 1) mixing of hydrothermal fluid with an external-derived fluid (e.g., meteoric water; Neyedley et al., 2017; Qiu et al., 2017) and 2) isotope fractionation during hydrothermal processes (e.g., redox change, ore precipitation; Moynier et al., 2017; Teng, 2017; Deng et al., 2020a; Wang et al., 2020a; Qiu et al., 2021). Given the extremely low Sb concentration in meteoric water, the effect of external-derived fluid mixing on the Sb isotopic composition in the ore system can be easily excluded. Likewise, unaltered host rocks show low Sb concentration (Fu et al., 2020b), implying that the fluid-rock interaction cannot modify the Sb isotopic composition of the system. Considering that the reduced sulfur complexes (thioantimonite and hydroxothioantimonite) are dominant agents for transporting Sb in the hydrothermal fluids in Xikuangshan, it follows that S and Sb could originate from the same source (Long et al., 2022). As evidenced by the relatively homogeneous $\delta^{34}$S of stibnite (average of 8.0 ± 0.5 ‰, 2σ; Fu et al., 2020c; Long et al., 2022 and references therein), fluid mixing may not be the cause of variation in $\delta^{123}$Sb values. The most reasonable explanation for the observed variation in $\delta^{123}$Sb values of stibnite are isotope fractionation during hydrothermal processes.
A few studies explored possible causes of Sb isotopic fractionation in natural and experimental settings by assessing the effects of redox reactions (Rouxel et al., 2003; Kendall et al., 2017; Moynier et al., 2017) and kinetic Rayleigh fractionation (Watkins et al., 2017; Wang et al., 2020a; Zhai et al., 2021). Rouxel et al. (2003) reported the significant Sb isotopic fractionation of up to 0.9 ‰ in aqueous solutions during reduction of Sb$^{5+}$ to Sb$^{3+}$ in two duplicate experiments. The effect of reduction on the observed variation of $\delta^{123}$Sb values in stibnite samples can be eliminated, considering that Sb$^{3+}$ is the predominant ion species in Sb-bearing hydrothermal fluids and Sb$^{5+}$ mostly exist in surficial environments (Zotov et al., 2003; Fu et al., 2020d). We propose that the systematic variability of $\delta^{123}$Sb values in stibnite in the Xikuangshan orebodies are best explained by Rayleigh fractionation during the precipitation of stibnite from hydrothermal fluids. Rayleigh fractionation has been demonstrated to be a potential factor that can lead to metal isotope fractionation of, for example, copper (e.g., Gregory and Mathur, 2017), iron (e.g., Wang et al., 2018; Zhu et al., 2018; Zhang et al., 2021), molybdenum (e.g., Hannah et al., 2007; Li et al., 2019), zinc (e.g., Mondillo et al., 2018), cadmium (e.g., Wen et al., 2016; Zhu et al., 2017), and lead (e.g., Gao et al., 2018) during the precipitation of sulfide minerals from hydrothermal fluids in types of mineral systems. The Rayleigh fractionation model for Sb is illustrated in Fig. 6B as determined by using the equations

$$\delta^{123}\text{Sb}_{\text{F}} = (\delta^{123}\text{Sb}^{123}_{\text{F}} + 10^3) \times F - 10^3 \quad (1)$$

$$\delta^{123}\text{Sb}_{\text{S}} = (\delta^{123}\text{Sb}^{123}_{\text{F}} + 10^3) \times \alpha - 10^3 \quad (2)$$

where F = ore-forming fluid, S = stibnite, $\delta^{123}\text{Sb}^{123}_{\text{F}}$ = initial Sb isotopic compositions, F = the fraction of reactant remaining, $\alpha$ = fractionation factor. We use subscript 1 ($F_1$, $S_1$, $\alpha_1$)
for the steeply-dipping orebody and transitional zone and subscript 2 (F₂, S₂, α₂) for the shallowly-dipping orebody in the fractionation equations.

An Sb isotope fractionation model for the steeply-dipping and shallowly-dipping orebodies is constructed by integrating the new data reported here and data in Zhai et al. (2021) (Fig. 6). For the shallowly-dipping orebodies, an initial δ¹²³Sb value (δ¹²³Sbf₂=�) of -0.16 ‰ ± 0.03 ‰ for stibnite is used based on the average δ¹²⁵Sb value of stibnite from the most proximal samples of the shallowly-dipping orebodies. A final δ¹²³Sbs₂=0 value of 0.85 ‰ ± 0.01 ‰ for stibnite is used to model the most distal samples of the shallowly-dipping orebodies. The fractionation factor α₂ is calculated as 0.99978 ± 0.00001. The initial δ¹²³Sb value of the ore fluid (δ¹²³Sbf₂=�) that precipitated the shallowly-dipping orebodies is thus calculated as 0.060 ‰ ± 0.011 ‰. Given that the hypogene ore-forming fluid ascended along the major fault F75 and stibnite precipitated first from that fluid within the steeply-dipping orebody and subsequently in the shallowly-dipping stratigraphically controlled orebodies, we use a final δ¹²³Sb value of 0.060 ‰ ± 0.011 ‰ for the ore fluid (δ¹²³Sbfİ₁=0.34) in the steeply-dipping orebodies. As the average δ¹²³Sb values from the deepest and shallowest ore samples are 0.958 ‰ and 0.490 ‰, the initial and final δ¹²³Sb values (δ¹²³Sbs₁=� and δ¹²³Sbs₁=0) of stibnite in the steeply-dipping orebodies are calculated to be 0.960 ‰ ± 0.029 ‰ and 0.493 ‰ ± 0.002 ‰. The fractionation factor α₁ and the initial δ¹²³Sb value of the ore fluid (δ¹²³Sbfİ₁=�) are calculated to be 1.00043 ± 0.00003 and 0.530 ‰ ± 0.016 ‰, respectively (Fig. 6B).

6. Fluid evolution and precipitation mechanisms of ores
Rayleigh fractionation modeling of Sb isotopic compositions from the steeply- and shallowly-dipping orebodies in the Xikuangshan deposit reveals opposite trends in $\delta^{123}\text{Sb}$ values during stibnite precipitation (Fig. 6B). This result is consistent with a difference in the dominant Sb-complex dissolved in the ore fluid in different parts of the system. In hydrothermal fluids, Sb$^{3+}$ may be transported mainly as thioantimonite ($\text{H}_2\text{Sb}_2\text{S}_4$, $\text{HSb}_2\text{S}_4^-$, $\text{Sb}_2\text{S}_4^{2-}$), hydroxothioantimonite ($\text{Sb}_2\text{S}_2(\text{OH})_2$), hydroxide ($\text{Sb(OH)}_3$, $\text{Sb(OH)}_4^-$), and chloride ($\text{SbCl}_3$, $\text{SbCl}_4^-$, and $\text{SbCl}_5^{2-}$) complexes (Krupp, 1988; Williams-Jones and Norman, 1997; Hagemann and Luders, 2003). Previous studies of the Xikuangshan deposit reported that Sb mineralization precipitated from a hydrothermal fluid with a salinity of 0.2-14.8 wt.% NaCl equiv., and a slightly acidic to neutral pH (~5.5-6.5) over the temperature range 105-305 °C (Lin, 2014; Hu and Peng, 2018; Zhang, 2018). For a hydrothermal fluid at those conditions, thermodynamic calculations indicate that the dominant Sb complexes in the fluid are $\text{H}_2\text{Sb}_2\text{S}_4$ and $\text{Sb}_2\text{S}_2(\text{OH})_2$ (Fig. 6C). Although their associated isotope fractionations are poorly understood, heavier isotope ($^{123}\text{Sb}$) is preferentially partitioned into the site with the highest bond energy, which is demonstrated for many systems (Penniston-Dorland et al., 2017). Bond energies of Sb-H (56.4 kcal/mol), Sb-S (90.5 kcal/mol), and Sb-O (102.8 kcal/mol) increase in turn (Luo, 2005), indicating that $^{123}\text{Sb}$ is preferentially complexed as Sb-O, then Sb-S, and finally Sb-H during precipitation of stibnite ($\text{Sb}_2\text{S}_3$) from the hydrothermal fluid. The Rayleigh fractionation model results reported here (Fig. 6B) indicate that $^{123}\text{Sb}$ is preferentially partitioned into stibnite, indicating the dominant Sb complex is $\text{H}_2\text{Sb}_2\text{S}_4$ in the fluid responsible for mineralization in the steeply-dipping orebody, whereas $^{121}\text{Sb}$ is preferentially partitioned into stibnite in the shallowly-dipping
orebody indicating the dominant Sb complex is Sb$_2$S$_4$(OH)$_2$ in the fluid responsible for mineralization in the shallowly-dipping orebody.

Precipitation of stibnite from an H$_2$Sb$_2$S$_4$-bearing fluid in the steeply-dipping orebody would follow a decrease in activity of H$_2$S ($a$H$_2$S) in the fluid, as shown by the following equation from Krupp (1988):

$$H_2Sb_2S_4 = Sb_2S_3 + H_2S \quad (3)$$

Boiling and wall rock sulfidation are major mechanisms to decrease the $a$H$_2$S. The modally-minor amount of pyrite and arsenopyrite in the host rock at Xikuangshan rule out the possibility of wall rock sulfidation. Thus, the most likely mechanism of ore precipitation in the steeply-dipping orebodies was fluid boiling, which could have occurred by dramatic pressure fluctuations through both localized fracture dilation and fluid ascent along the major fault (Fig. 7; Voisey et al., 2020). Notably, as $a$H$_2$S decreases, Sb$_2$S$_4$(OH)$_2$ becomes the dominant stable Sb complex in the fluid (path from point 1 through 2 in Fig. 6C), wherein $^{121}$Sb is preferentially partitioned into stibnite as it crystallizes from the fluid.

Precipitation of stibnite from the ore fluid can be described by the reaction:

$$Sb_2S_4(OH)_2 + H_2S = Sb_2S_3 + 2H_2O \quad (4)$$

which indicates that decreasing the $a$H$_2$S does not decrease the concentration of Sb in the fluid but rather shifts the fluid-stable Sb complex to Sb$_2$S$_4$(OH)$_2$. Therefore, the most plausible precipitation mechanism for the shallowly-dipping orebodies is a decrease in temperature (path from point 2 through 3 in Fig. 6C). Cooling of the hypogene ore fluid can occur by bringing deeply sourced fluids into colder wall rock or mixing with meteoric waters. Published fluid inclusion data and H-O isotope data of quartz veins coeval with stibnite indicate that meteoric and pore fluids was present in the host rocks for the
shallowing dipping orebodies prior to infiltration of the Sb-bearing ore fluid (Hu and Peng, 2018). This means that the fluid mixing with meteoric and pore fluids would have resulted in cooling of the ore fluid and precipitation of stibnite in the shallowly-dipping orebodies with the range of δ^{123}Sb values reported here (Figs. 6C, 7).

7. Implications

Transition of the dominant Sb complex from thioantimonite (H_2Sb_2S_4) to hydroxothioantimonite (Sb_2S_3(OH)_2) in hydrothermal fluids occurs with consuming of H_2S. The initial dominant Sb complex maybe H_2Sb_2S_4 in hydrothermal fluids. In this stage, boiling of the ore fluid inducing a decrease in H_2S that reduced the solubility of H_2Sb_2S_4 is the main precipitation mechanism. Meanwhile, ^{123}Sb is preferentially complexed as Sb-S, showing a systematical decrease in δ^{123}Sb values. As consuming of H_2S, Sb_2S_3(OH)_2 becomes the dominant stable Sb complex in the fluid, wherein ^{121}Sb is preferentially partitioned into stibnite as it crystallizes from the fluid. Precipitation of stibnite from the ore fluid is triggered by fluid cooling. Our work shows that stable metal complex in the hydrothermal ore fluid may change induced by fluid evolution and affect the isotope fractionation and metal precipitation mechanisms.

Acknowledgements

This research was financially supported by the National Natural Science Foundation of China (42072087, 42130801), the Beijing Nova Program (Z201100006820097), and the 111 Project of the Ministry of Science and Technology (BP0719021). Adam C. Simon acknowledges support from NSF EAR #1924192. We thank the anonymous reviewers and
Associate Editor William Peck for their constructive reviews, which helped improve the quality of this paper.

References


America Bulletin.


Fu, S.L., Lan, Q., and Yan, J. (2020c) Trace element chemistry of hydrothermal quartz and its genetic significance: A case study from the Xikuangshan and Woxi giant Sb deposits in southern China. Ore Geology Reviews, 126, 103732.


deposits, Western Australia: conventional and infrared microthermometric constraints. Mineralium Deposita, 38(8), 936–952.


Fluid and metal sources of the Wenquan porphyry molybdenum deposit, Western Qinling, NW China. Ore Geology Reviews, 86, 459–473.


for an uncertainty estimation of the standard atomic weight of antimony.

Geochemical Journal, 45(1), 27–32.


**Figure captions**
Fig. 1. Map showing the global distribution of representative antimony deposits. Modified after Deng et al. (2019) and Zhang et al. (2020).

Fig. 2. (A) Geological map of the world’s largest Sb deposit in Xikuangshan (modified from Fu et al., 2020b). (B) Cross section map of No. 41 exploration line (A-B) showing two types of orebodies (modified from Zhai et al., 2021; Long et al., 2022)

Fig. 3. Underground exposures showing the Sb orebody hosted in the silicified limestone. Antimony occurs chiefly as the stibnite from the quartz-stibnite vein (A, B) and calcite-quartz-stibnite vein (C, D).

Fig. 4. Silicified limestone (A), euhedral stibnite in limestone (B), stibnite-quartz vein ore (C) and stibnite-calcite-quartz vein ore (D).

Fig. 5. Mineral assemblages of the Sb ores. Anhedral stibnite along the margin of the quartz and calcite (A-C) and euhedral needle-shaped crystals in calcite grains (D). Cal = calcite, Stb = stibnite, Qz = quartz.

Fig. 6 (A) Schematic cross-section showing sample locations from this work and Zhai et al. (2021). Note that the orebodies of the Xikuangshan deposit show a southward plunge, inducing a relatively deeper mining depth in the southern part of the deposit. As a result, the elevations of the samples represent positions projected on the cross-section rather than the real elevations. (B) The Sb isotopic Rayleigh distillation model of the steeply-dipping and shallowly-dipping orebodies of the Xikuangshan Sb deposit. The grey dots are from Zhai et al. (2021). The initial $\delta^{123}\text{Sb}$ values of the hydrothermal fluid is defined to 0.530 ‰. The fractionation factors ($\alpha_1$ for steeply-dipping orebodies and $\alpha_2$ for shallowly-dipping orebodies) between stibnite and solution are 1.00043 and 0.99978. The $\delta^{123}\text{Sb}$ values of stibnite change abruptly at the transitional zone. F means the fraction of reactant remaining.
(C) Speciation diagram of aqueous Sb species in hydrothermal fluids with superimposed Sb fluid solubility contours. Bold lines indicate boundaries between aqueous Sb species. Circled numbers indicate hypothetical points for illustrating fluid property changes. Superimposed Sb fluid solubility contours of aqueous Sb species in hydrothermal fluids are from Hagemann and Luders (2003).

Fig. 7. A schematic cartoon showing telescoped stibnite precipitation mechanisms steeply-dipping and shallowly-dipping orebodies.

Table caption

Table 1 The \(\delta^{123}\text{Sb}\) values of the steeply-dipping and shallowly-dipping orebodies of the Xikuangshan Sb deposit.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample No.</th>
<th>Mineral assemblage</th>
<th>Elevation (m)</th>
<th>Weight (g)</th>
<th>Batch</th>
<th>(\delta^{123}\text{Sb}) (abs)</th>
<th>(2\sigma) (repeat)</th>
<th>(2\sigma) (abs)</th>
</tr>
</thead>
</table>
| South Ore Block
<p>| Steeply-dipping orebodies |
| 1   | XKS22       | Stb-Cal-Qz       | -604          | 0.06       | 1     | 0.927           | 0.03            | 0.930            | 0.03            |
| 2   | XKS23       | Stb-Cal-Qz       | -604          | 0.06       | 1     | 0.988           | 0.03            | 0.956            | 0.03            |
| 3   | XKS19       | Stb-Qz-Cal       | -468          | 0.2        | 1     | 0.798           | 0.03            | 0.816            | 0.03            |
| 4   | XKS20       | Cal-Qz-Stb       | -468          | 1.0        | 1     | 0.766           | 0.03            | 0.753            | 0.03            |
| 5   | XKS21       | Qz-Cal-Stb       | -468          | 0.04       | 1     | 0.737           | 0.03            | -                | -                |
| 6   | XKS24       | Stb-Cal-Qz       | -468          | 0.1        | 1     | 0.753           | 0.03            | 0.743            | 0.03            |
| 7   | XKS25       | Qz-Cal-Stb       | -468          | 0.33       | 1     | 0.766           | 0.03            | -                | -                |
| 8   | XKS26       | Cal-Stb          | -468          | 0.35       | 2     | 0.782           | 0.03            | -                | -                |
| 9   | XKS12       | Stb-Qz-Cal       | -192          | 0.5        | 2     | 0.659           | 0.03            | 0.666            | 0.03            |
| 10  | XKS13       | Stb-Cal-Qz       | -192          | 1.0        | 2     | 0.578           | 0.03            | 0.603            | 0.03            |
| 11  | XKS14       | Stb-Cal-Qz       | -192          | 0.5        | 2     | 0.591           | 0.03            | 0.579            | 0.03            |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>XKS15</td>
<td>Stb-Cal-Qz</td>
<td>-192 m</td>
<td>1.0 g</td>
<td>2</td>
<td>0.565</td>
<td>0.03</td>
<td>0.552</td>
</tr>
<tr>
<td>XKS16</td>
<td>Stb-Cal-Qz</td>
<td>-192 m</td>
<td>1.0 g</td>
<td>2</td>
<td>0.523</td>
<td>0.03</td>
<td>0.483</td>
</tr>
<tr>
<td>XKS17</td>
<td>Stb-Qz-Cal</td>
<td>-192 m</td>
<td>0.25 g</td>
<td>1</td>
<td>0.637</td>
<td>0.03</td>
<td>0.663</td>
</tr>
<tr>
<td>XKS18</td>
<td>Qz-Cal-Stb</td>
<td>-192 m</td>
<td>0.03 g</td>
<td>1</td>
<td>0.577</td>
<td>0.03</td>
<td>0.574</td>
</tr>
<tr>
<td>XKS06</td>
<td>Qz-Cal-Stb</td>
<td>-142 m</td>
<td>1.0 g</td>
<td>2</td>
<td>0.610</td>
<td>0.03</td>
<td>0.582</td>
</tr>
<tr>
<td>XKS07</td>
<td>Cal-Qz-Stb</td>
<td>-142 m</td>
<td>1.2 g</td>
<td>2</td>
<td>0.583</td>
<td>0.03</td>
<td>0.578</td>
</tr>
<tr>
<td>XKS08</td>
<td>Cal-Qz-Stb</td>
<td>-142 m</td>
<td>0.8 g</td>
<td>1</td>
<td>0.535</td>
<td>0.03</td>
<td>0.528</td>
</tr>
<tr>
<td>XKS09</td>
<td>Stb-Qz</td>
<td>-142 m</td>
<td>0.7 g</td>
<td>1</td>
<td>0.572</td>
<td>0.03</td>
<td>0.570</td>
</tr>
<tr>
<td>XKS10</td>
<td>Stb-Qz</td>
<td>-142 m</td>
<td>0.8 g</td>
<td>1</td>
<td>0.514</td>
<td>0.03</td>
<td>0.554</td>
</tr>
<tr>
<td>XKS11</td>
<td>Stb-Qz</td>
<td>-142 m</td>
<td>0.2 g</td>
<td>1</td>
<td>0.541</td>
<td>0.03</td>
<td>0.496</td>
</tr>
<tr>
<td>XKS01</td>
<td>Qz-Cal-Stb</td>
<td>-106 m</td>
<td>0.8 g</td>
<td>2</td>
<td>0.589</td>
<td>0.03</td>
<td>0.601</td>
</tr>
<tr>
<td>XKS02</td>
<td>Cal-Qz-Stb</td>
<td>-106 m</td>
<td>1.0 g</td>
<td>2</td>
<td>0.536</td>
<td>0.03</td>
<td>0.503</td>
</tr>
<tr>
<td>XKS03</td>
<td>Cal-Qz-Stb</td>
<td>-106 m</td>
<td>1.0 g</td>
<td>2</td>
<td>0.514</td>
<td>0.03</td>
<td>0.474</td>
</tr>
<tr>
<td>XKS04</td>
<td>Stb-Cal-Qz</td>
<td>-106 m</td>
<td>1.0 g</td>
<td>2</td>
<td>0.547</td>
<td>0.03</td>
<td>0.534</td>
</tr>
<tr>
<td>XKS05</td>
<td>Cal-Qz-Stb</td>
<td>-106 m</td>
<td>1.0 g</td>
<td>2</td>
<td>0.483</td>
<td>0.03</td>
<td>0.470</td>
</tr>
</tbody>
</table>

Shallowly-dipping orebodies

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>19xkss-47</td>
<td>74 m</td>
<td>0.22 %</td>
<td></td>
</tr>
<tr>
<td>19xkss-48</td>
<td>74 m</td>
<td>0.21 %</td>
<td></td>
</tr>
<tr>
<td>19xkss-40</td>
<td>2 m</td>
<td>0.6 %</td>
<td></td>
</tr>
<tr>
<td>19xkss-42</td>
<td>2 m</td>
<td>0.27 %</td>
<td></td>
</tr>
<tr>
<td>19xkss-39</td>
<td>-34 m</td>
<td>0.41 %</td>
<td></td>
</tr>
<tr>
<td>19xkss-37</td>
<td>-34 m</td>
<td>0.5 %</td>
<td></td>
</tr>
<tr>
<td>19xkss-32</td>
<td>-70 m</td>
<td>0.57 %</td>
<td></td>
</tr>
<tr>
<td>19xkss-31</td>
<td>-70 m</td>
<td>0.53 %</td>
<td></td>
</tr>
<tr>
<td>19xkss-25</td>
<td>-106 m</td>
<td>0.45 %</td>
<td></td>
</tr>
<tr>
<td>19xkss-29</td>
<td>-106 m</td>
<td>0.54 %</td>
<td></td>
</tr>
<tr>
<td>19xkss-18</td>
<td>-192 m</td>
<td>0.63 %</td>
<td></td>
</tr>
<tr>
<td>19xkss-15</td>
<td>-192 m</td>
<td>0.75 %</td>
<td></td>
</tr>
<tr>
<td>19xkss-5</td>
<td>-242 m</td>
<td>0.83 %</td>
<td></td>
</tr>
<tr>
<td>19xkss-2</td>
<td>-242 m</td>
<td>0.86 %</td>
<td></td>
</tr>
</tbody>
</table>

North Ore Block

Transitional zones between the steeply-dipping and shallowly-dipping orebodies

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>19xks-45-1</td>
<td>510 m</td>
<td>0.30 %</td>
</tr>
<tr>
<td></td>
<td>19xks-45-2</td>
<td>510 m</td>
</tr>
<tr>
<td>---</td>
<td>------------</td>
<td>-------</td>
</tr>
<tr>
<td>29</td>
<td>19xks-45-3</td>
<td>510 m</td>
</tr>
<tr>
<td>30</td>
<td>19xks-45-4</td>
<td>510 m</td>
</tr>
<tr>
<td>31</td>
<td>19xks-45-5</td>
<td>510 m</td>
</tr>
<tr>
<td>32</td>
<td>19xks-45-6</td>
<td>510 m</td>
</tr>
<tr>
<td>33</td>
<td>19xks-45-7</td>
<td>510 m</td>
</tr>
</tbody>
</table>

**Shallowly-dipping orebodies**

<table>
<thead>
<tr>
<th></th>
<th>19xks-33-1</th>
<th>480 m</th>
<th>-0.27 ‰</th>
</tr>
</thead>
<tbody>
<tr>
<td>48</td>
<td>19xks-43</td>
<td>480 m</td>
<td>-0.05 ‰</td>
</tr>
<tr>
<td>49</td>
<td>19xks-23</td>
<td>450 m</td>
<td>0.01 ‰</td>
</tr>
<tr>
<td>50</td>
<td>19xks-24</td>
<td>450 m</td>
<td>-0.11 ‰</td>
</tr>
<tr>
<td>51</td>
<td>19xks-58-1</td>
<td>440 m</td>
<td>-0.11 ‰</td>
</tr>
<tr>
<td>52</td>
<td>19xks-58-2</td>
<td>440 m</td>
<td>-0.16 ‰</td>
</tr>
<tr>
<td>53</td>
<td>19xks-58-3</td>
<td>440 m</td>
<td>-0.11 ‰</td>
</tr>
<tr>
<td>54</td>
<td>19xks-58-4</td>
<td>430 m</td>
<td>-0.07 ‰</td>
</tr>
<tr>
<td>55</td>
<td>19xks-58-5</td>
<td>430 m</td>
<td>-0.09 ‰</td>
</tr>
<tr>
<td>56</td>
<td>19xks-58-6</td>
<td>430 m</td>
<td>-0.08 ‰</td>
</tr>
<tr>
<td>57</td>
<td>19xks-61-1</td>
<td>430 m</td>
<td>0.31 ‰</td>
</tr>
<tr>
<td>58</td>
<td>19xks-61-2</td>
<td>430 m</td>
<td>0.43 ‰</td>
</tr>
<tr>
<td>59</td>
<td>19xks-61-3</td>
<td>430 m</td>
<td>0.40 ‰</td>
</tr>
<tr>
<td>60</td>
<td>19xks-61-4</td>
<td>430 m</td>
<td>0.14 ‰</td>
</tr>
<tr>
<td>61</td>
<td>19xks-61-5</td>
<td>430 m</td>
<td>0.42 ‰</td>
</tr>
<tr>
<td>62</td>
<td>19xks-61-6</td>
<td>430 m</td>
<td>0.31 ‰</td>
</tr>
<tr>
<td>63</td>
<td>19xks-54</td>
<td>420 m</td>
<td>0.70 ‰</td>
</tr>
<tr>
<td>64</td>
<td>19xks-52-1</td>
<td>420 m</td>
<td>0.18 ‰</td>
</tr>
</tbody>
</table>

The weight is complete amount of the stibnite powder. Samples of transitional zones and shallowly-dipping orebodies are from Zhai et al. (2021).
Euhedral stibnite in limestone

Stibnite-calcite-quartz vein
Data from this work
Data from Zhai et al. (2021)

Transition: Steeply-dipping ores → Shallowly-dipping ores

Hydrothermal fluid

\[
\begin{align*}
\Delta \text{Sb} &= 0.99978 \\
\end{align*}
\]

\[
\begin{align*}
\text{Sb}_2 \text{(OH)}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_2 \text{Sb}_2 \text{S}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{PH}=5.5, \text{P}=L-V \text{ saturation} \\
\end{align*}
\]
Boiling

\[ \text{H}_2\text{Sb}_2\text{S}_4 \rightarrow \text{Sb}_2\text{S}_3 \]

Shallowly-dipping orebody

Meteoric water

Pore fluid

Main fault

Dre fluids

Steeply-dipping orebody