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

## HAO-CHENG YU<sup>1</sup>, KUN-FENG QIU<sup>1,\*,</sup>§, ADAM C. SIMON<sup>2,†</sup>, DA WANG<sup>1,‡</sup>, RYAN MATHUR<sup>3</sup>, RUO-QI WAN<sup>1</sup>, XIANG-YONG JIANG<sup>1</sup>, AND JUN DENG<sup>1,4</sup>

 <sup>1</sup>State Key Laboratory of Geological Processes and Mineral Resources, School of Earth Sciences and Resources, China University of Geosciences, Beijing 100083, China
<sup>2</sup>Department of Earth & Environmental Sciences, University of Michigan, Ann Arbor, Michigan 48109, U.S.A.
<sup>3</sup>Department of Geology, Juniata College, Huntingdon, Pennsylvania 16652, U.S.A.
<sup>4</sup>Geological Research Institute of Shandong Gold Group Co., Ltd., Jinan 250013, 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  $(Sb_2S_3)$  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 the aqueous species thioantimonite  $(H_2Sb_2S_4, HSb_2S_4^-, Sb_2S_4^-)$  and hydroxothioantimonite  $[Sb_2S_2(OH)_2]$ . Thioantimonite can transform to hydroxothioantimonite with a decline of H<sub>2</sub>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 <sup>121</sup>Sb and <sup>123</sup>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 <sup>123</sup>Sb had been preferentially partitioned from the ore fluid into stibnite first, then <sup>123</sup>Sb remained preferentially dissolved in the ore fluid. These data indicate that the dominant Sb-complex transforms to Sb<sub>2</sub>S<sub>2</sub>(OH)<sub>2</sub> from H<sub>2</sub>Sb<sub>2</sub>S<sub>4</sub> with consumption of H<sub>2</sub>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  $H_2S$  that reduced the solubility of  $H_2Sb_2S_4$ , and (2) subsequent cooling that induced a decrease in the solubility of  $Sb_2S_2(OH)_2$ . 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; Isotopes, Minerals, and Petrology: Honoring John Valley