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

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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 (Sb2S3) 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 (H2Sb2S4, HSb2S4–, Sb2S42–) and hydroxothioantimonite [Sb2S2(OH)2]. Thioantimonite can transform to hydroxothioantimonite with a decline of H2S 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 123Sb and 125Sb were measured in stibnite from the Xikuangshan orebodies and reported as δ123Sb. The δ123Sb values show a trend of decreasing first and then increasing from proximal to distal parts of orebodies. This reveals that 123Sb had been preferentially partitioned from the ore fluid into stibnite first, then 123Sb remained preferentially dissolved in the ore fluid. These data indicate that the dominant Sb-complex transforms to Sb2S2(OH)2 from H2Sb2S4 with consumption of H2S. 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 H2S that reduced the solubility of H2Sb2S4, and (2) subsequent cooling that induced a decrease in the solubility of Sb2S2(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

Introduction
Antimony is a critical mineral commodity essential for a wide variety of products including flame retardants and alloys for batteries, bearings, and solders (Schulz et al. 2018). This metal is found in more than 100 minerals in various deposits. The most common antimony ore mineral is stibnite (Sb2S3) that is found 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, which leads global production (Schulz et al. 2018; Yu et al. 2022). Society annually consumes 250% more Sb relative to the year 1960, while antimony production continues 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). 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

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