Incorporation of incompatible trace elements into molybdenite: Layered PbS precipitates within molybdenite

YIPING YANG\textsuperscript{1,2,3}, HONGPING HE\textsuperscript{1,2,3}, WEI TAN\textsuperscript{1,2,*,||}, QI TAO\textsuperscript{1,2,†}, JUNMING YAO\textsuperscript{1,2,‡}, HAIYANG XIAN\textsuperscript{1,2,‡}, SHANGYING LI\textsuperscript{1,2,‡}, JIAXIN XI\textsuperscript{1,2,3}, JIANXI ZHU\textsuperscript{1,2,3}, and HUIFANG XU\textsuperscript{1,2,§}

\textsuperscript{1}CAS Key Laboratory of Mineralogy and Metallogeny/Guangdong Provincial Key Laboratory of Mineral Physics and Materials, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
\textsuperscript{2}CAS Center for Excellence in Deep Earth Science, Guangzhou, 510640, China
\textsuperscript{3}University of Chinese Academy of Sciences, Beijing 100049, China
\textsuperscript{‡}Department of Geoscience, University of Wisconsin-Madison, 1215 West Dayton Street, Madison, Wisconsin 53706, U.S.A
\textsuperscript{§}Xinjiang Research Center for Mineral Resources, Xinjiang Institute of Ecology and Geography, Chinese Academy of Sciences, Urumqi 830011, China

Abstract

Trace elements in molybdenite can provide important information regarding the composition of ore-forming fluid and the evolution and genesis of ore deposits. However, the occurrence states and behavior of relatively incompatible trace elements (e.g., Pb and Os) in natural molybdenite remain ambiguous. Here, we report an abnormally high enrichment of Pb and layered PbS precipitate within molybdenite grains from the Huanglongpu carbonatite-hosted Mo-Pb deposit in the Qinling orogenic belt of Northern China. High-resolution transmission electron microscopy (HRTEM) and related nanobeam techniques were applied to characterize the occurrence states of Pb within molybdenite at the atomic scale. The results show that up to several weight percent of Pb can be incorporated into the molybdenite structure during initial crystallization, which can lead to the formation of screw dislocations and 3R/disordered stacking of S-Mo-S sandwich layers. Observations using a scanning transmission electron microscope also reveal that Pb diffuses from the host molybdenite into the layered PbS precipitates under prolonged electron beam irradiation. Pb-bearing molybdenite tends to transform into a Pb-poor ordered 2\text{Hf} polytype upon Pb exsolution during cooling. Pb preferentially exsolves along the (001) plane of molybdenite and is stored in structural defects (e.g., dislocation loops) and grain boundaries, resulting in nano-scale Pb heterogeneities in molybdenite. Further coarsening of the exsolved Pb results in the formation of layered PbS precipitates along the (001) plane of molybdenite. This study provides an example of the consequences of the incorporation and exsolution of incompatible trace elements in molybdenite and demonstrates that careful mineralogical examination is required to interpret geochemical data obtained by in situ analysis techniques.

Keywords: Molybdenite, layered PbS, polytype, incompatible trace elements; Applications of Fluid, Mineral, and Melt Inclusions

Introduction

Molybdenite (MoS\textsubscript{2}) is a layered-structure sulfide mineral with two hexagonally coordinated S layers and one sandwiched Mo layer. The sandwich-like [S-Mo-S] layers that stack along the c-axis are weakly bonded by van der Waals forces. Molybdenite hosts important economic resources of Mo and Re (Fleischer 1959; Frondel and Wickman 1970; Terada et al. 1971; Plotinskaya et al. 2018). \textsuperscript{187}Re-\textsuperscript{187}Os systematics in molybdenite are also widely applied to date geological events (Stein et al. 2001, 2003), and trace element (e.g., Pb, Bi, Re, and W) characteristics provide important insight into the multi-stage mineralization history of related deposits (Ciobanu et al. 2013; Barra et al. 2017).

Highly compatible trace elements (e.g., Re and W) are preferentially incorporated into the molybdenite structure due to their same valence and similar ionic radii (e.g., Re\textsuperscript{4+}, 0.63 Å; W\textsuperscript{4+}, 0.66 Å) as Mo\textsuperscript{4+} (0.65 Å), and are commonly considered to be relatively immobile (Stein et al. 2003). In contrast, relatively incompatible trace elements (e.g., Pb, Bi, Te, and Au) commonly occur as independent mineral phases in molybdenite (Petruk 1965; Ciobanu et al. 2013; Pašava et al. 2016; Plotinskaya et al. 2018), have relatively higher mobilities (Stein et al. 2003), and tend to form atomic clusters within structural defects and millimeter-to-nanometer-sized exsolution/inclusion phases (Stein et al. 2003; Pašava et al. 2016).

An understanding of the mobility of relatively incompatible trace elements in molybdenite is critical to accurately interpreting the trace element data and retrieved isotopic ages. Previous studies have demonstrated the effectiveness of using transmission electron microscopy (TEM) to observe the behavior (e.g., occupancy and migration) of Au and Re in synthetic MoS\textsubscript{2} under electron beam irradiation (Lin et al. 2014a, 2014b). However, the occurrence states and mobility of relatively incompatible trace elements in