

Formation of Misfit Layered PbS Within Molybdenite

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The concentration and distribution of trace elements in minerals can well depict ore-forming fluid composition, evolution, and genesis information of ore deposits. A fundamental question remains, however, as to how the distribution and mobility of incompatible elements in minerals evolve under varying geological environments [1]. Here, we present an unusual Pb enrichment and precipitate of layered PbS within molybdenite from a carbonatite-hosted Mo-Pb ore in Huanglongpu deposit, the Qinling orogenic belt, Northern China. Natural cleaved flakes of the molybdenite samples were embedded in epoxy resin and dried at 100°C for 3 hours. Then the solidified block was cut into slices in thickness of ~50 nm using an ultramicrotome with a diamond knife. The obtained slices were transferred onto holey carbon-coated Cu/Ni grids for TEM observation. Cutting was performed so as to get sections perpendicular to (001) plates as close as possible. High-resolution transmission electron microscopy (HRTEM) and the related nanobeam techniques were used to determine the crystal structure and the distribution of trace elements within molybdenite at an atomic scale.

The STEM-EDS results reveal that Pb is heterogeneously distributed in molybdenite, showing oscillatory zoning and overgrowths in some cases (Figure 1a). The presence and enrichment of Pb in molybdenite led to the disordered stacking sequences of molybdenite sheets (Figure 1b-d). The Pb-free region in TEM image displays a smooth surface (Figure 1b-top) and corresponds to sharp and bright diffraction spots in the NBED pattern, suggesting a well-crystallized crystal of molybdenite with a $2H_1$ -polytype (Figure 1c). However, the crystal surface of the Pb-rich region shows non-periodic features/contrast (Figure 1b-bottom) and its NBED pattern shows streaks in $00l$ and $h0l$ diffractions (Figure 1d). ABF/HAADF-STEM images of the Pb-rich zone show the occurrence of layered PbS within the host molybdenite (Figure 2a-b), which is most possibly formed by the exsolved Pb from the molybdenite under a decrease of temperature (Figure 2c-d). Our TEM observations suggest that such unique structure that NaCl-type PbS layers are hosted by “sandwich”-type MoS_2 layers was formed via the following procedure: at the initial crystallization stage with higher temperature and pressure, a large amount of Pb atoms were incorporated into molybdenite lattice via the isomorphous substitution of Pb for Mo, and thus, the resultant phase is unstable; with a decrease of temperature and pressure during upwelling of formerly formed molybdenite, layered PbS (NaCl-type) formed through the exsolution of Pb from Pb-rich molybdenite.

This study demonstrates that high-resolution TEM is a powerful technique to determine the distribution of trace elements at nanoscale and to identify nano-mineral structure in geological systems. The migration and storage of incompatible Pb in molybdenite may have some implications to understand the occurrence states and behaviors of Os in molybdenite, which play a significant role in molybdenite Re-Os geochronometer. Also, our finding about the formation and stability of a new natural van der Waals crystal is of importance in material science, which could be a model for the synthesis of MoS_2/PbS heterostructure materials.

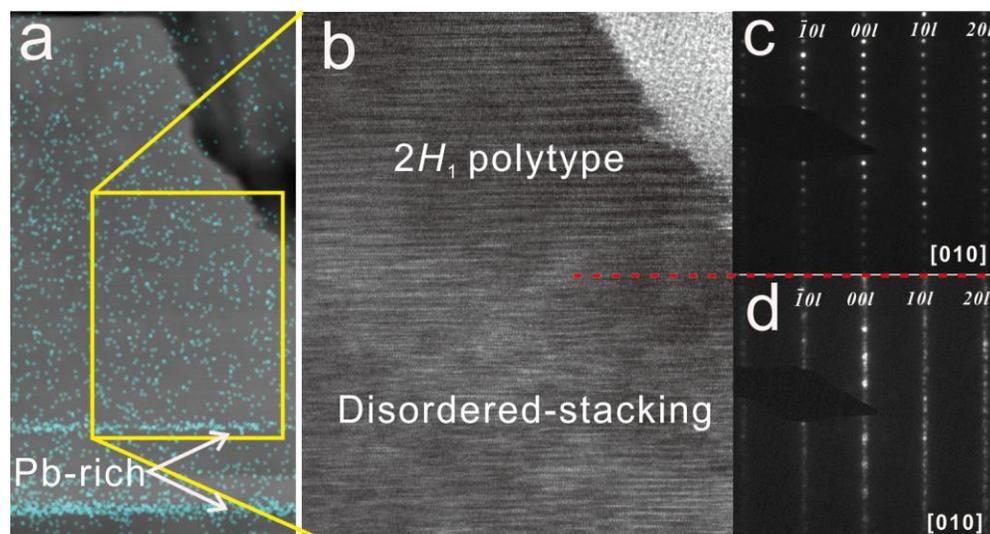


Figure 1. STEM-EDS mapping (a), enlarged HRTEM image (b), and the corresponding nano-beam electron diffraction (NBED) patterns (c-d) of Pb-rich molybdenite.

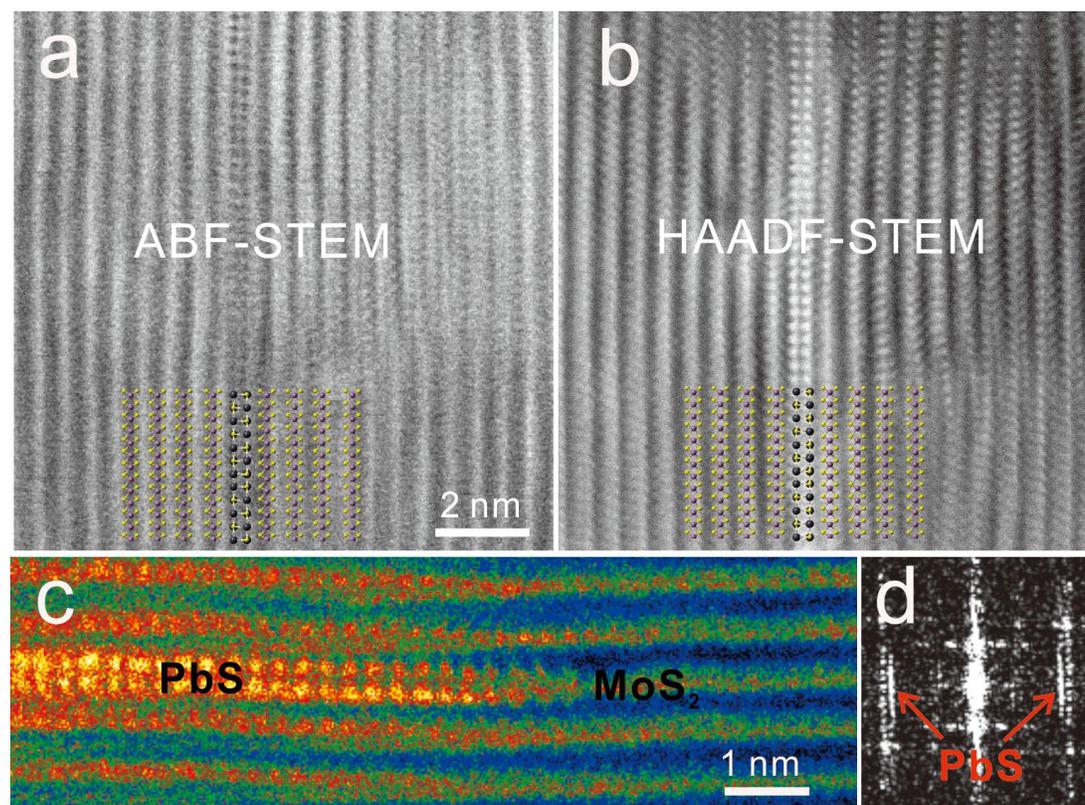


Figure 2. ABF-STEM image (a) and HAADF-STEM images (b-c) and the FFT pattern (d) show layered PbS of two atomic thick within the host molybdenite.

References

- [1] T. Hiraga, I. Anderson, D.L. Kohlstedt, *Nature*. **427** (2004) p. 699-703.