

Mechanism of Oxidative Dissolution and Sequestration of Stibnite on Pyrite

The dissolution and transformation of stibnite (Sb_2S_3) on mineral surfaces are fundamental steps that control the fate of antimony (Sb) in the environment. X-ray absorption spectra show that the heterogeneous electron transfers from Sb_2S_3 to pyrite (FeS_2) facilitate the generation of hydroxyl and superoxide radicals to oxidize Sb(III). Furthermore, oxidation and sequestration of Sb(III) on a FeS_2 surface coupled $\text{Fe}^{2+}/\text{Fe}^{3+}$ cycling and inhibited FeS_2 dissolution. The insights gained from this study extend our understanding of the transformation and transport of Sb_2S_3 at environmental mineral-water interfaces.

S b_2S_3 is the most important and ubiquitous antimony ore; its exposure to weathering is considered as the dominant source of Sb in aqueous solutions. Environmental factors, such as light irradiation and mineral surfaces, play an important role in controlling the transformation and mobilization of Sb_2S_3 . FeS_2 is the most common natural mineral associated with Sb_2S_3 , regulating diverse environmental processes such as reduction-oxidation and sequestration to control the geochemical cycling of Sb. Understanding the reactions at the Sb_2S_3 - FeS_2 -water interfaces at a molecular level is hence of paramount importance to elucidate the weathering and environmental fate of mineral tailings.

The dissolution and transformation of Sb_2S_3 arise from reactive oxygen species (ROS) that are generated with electron transfer. That condition is exactly what Chuan-Yong Jing (Chinese Academy of Sciences, China) and his team implemented to investigate the oxidative dissolution and sequestration of Sb_2S_3 on FeS_2 . Collaborating with Ting-Shan Chan (NSRRC), Jing's team recorded Sb K-edge X-ray-absorption near-edge structure (XANES) spectra at **TLS 01C1** at cryogenic temperature (77 K) in an ultrahigh vacuum condition, which could prevent damage to the sample from X-ray-induced Sb(III) oxidation on FeS_2 . Collectively, Fe K-edge and S K-edge XANES spectra were recorded at **TLS 16A1**.

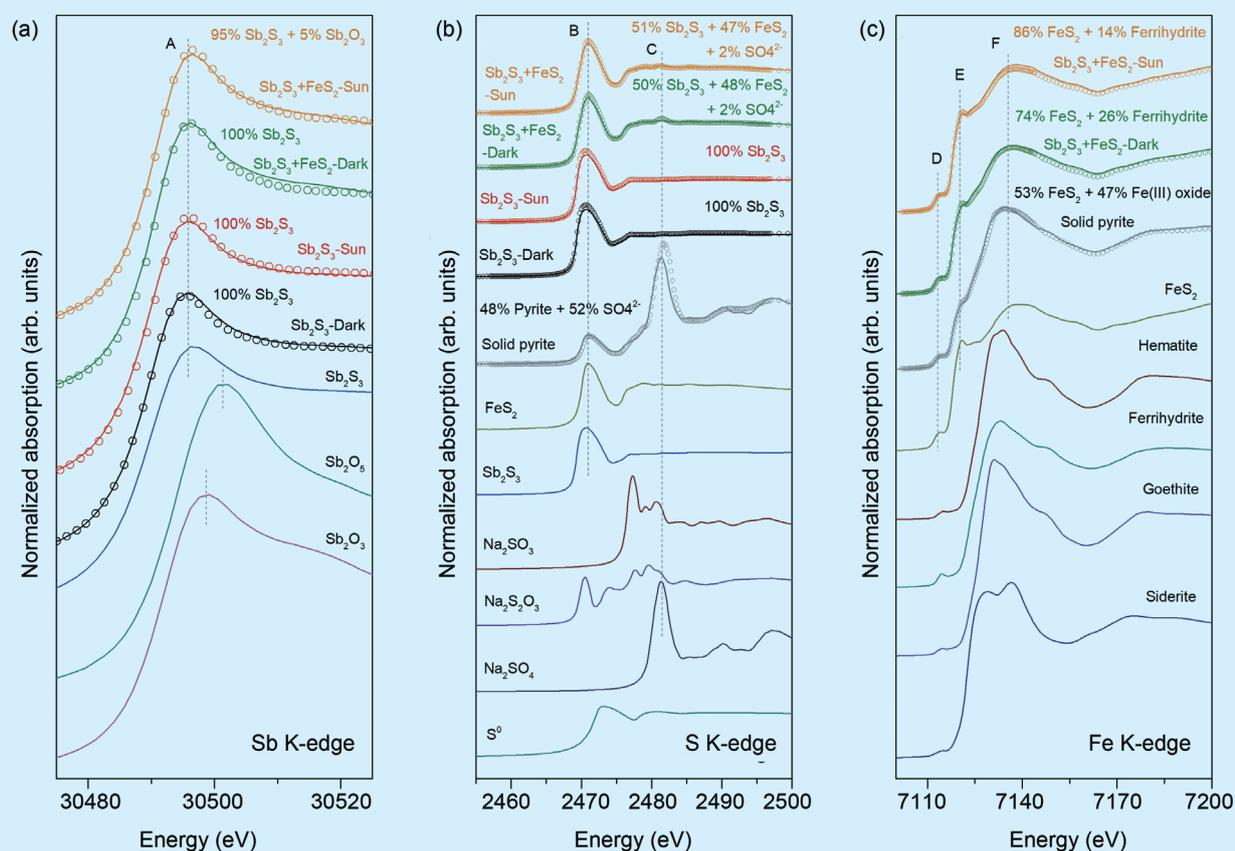


Fig. 1: XANES spectra of (a) Sb K-edge, (b) S K-edge, and (c) Fe K-edge of solid minerals after reaction. Linear-combination fitting is shown as lines. [Reproduced from Ref. 1]

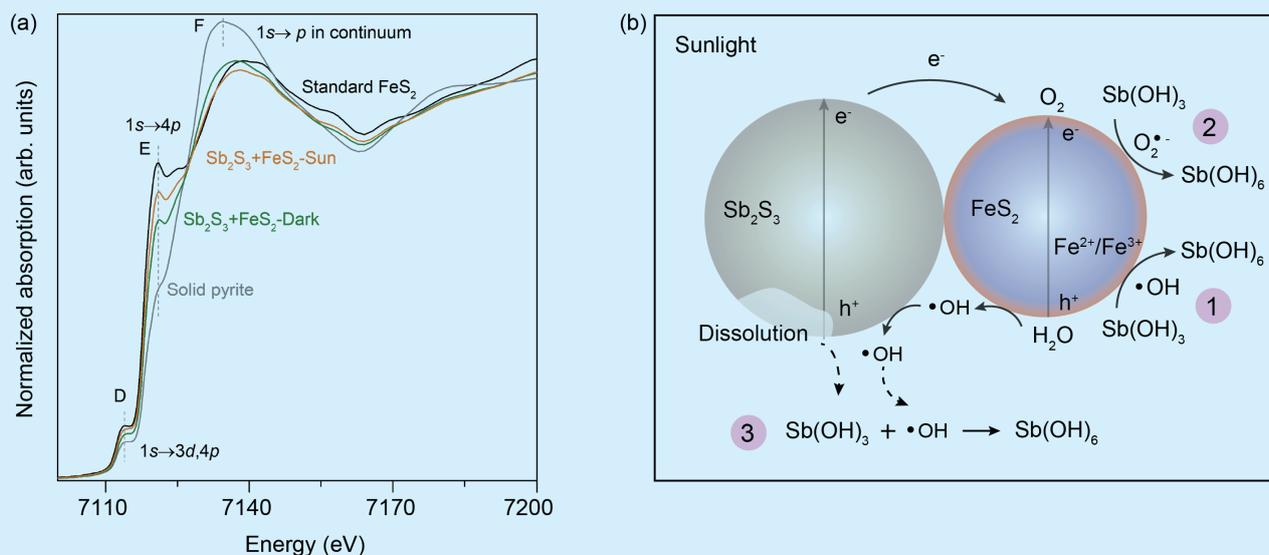


Fig. 2: (a) Fe K-edge XANES spectra for samples in a mixed Sb_2S_3 and FeS_2 system. (b) Reaction mechanisms of Sb_2S_3 oxidative dissolution and sequestration on FeS_2 . (1) Sb(III) oxidation by $\bullet\text{OH}$ radicals that were generated with $\text{Fe}^{2+}/\text{Fe}^{3+}$ cycling; (2) Sb(III) oxidation by $\text{O}_2^{\bullet-}$ radicals on FeS_2 surface under light. (3) Sb(III) oxidation by $\bullet\text{OH}$ radicals in solution. The solid arrow presents reactions on the surface; the dashed arrow shows the dissolution. [Reproduced from Ref. 1]

Figure 1 displays XANES spectra at the Sb K-edge, Fe K-edge and S K-edge taken from solid minerals after reaction for 4 h under simulated sunlight irradiation and dark conditions. The Sb_2S_3 standard exhibited a signal at 30490 eV (feature A in **Fig. 1(a)**); Sb_2O_3 and Sb_2O_5 standards showed distinct signals at 30493 and 30495 eV, respectively. The Sb_2S_3 species was unchanged after dissolution, as evident from linear-combination-fitting (LCF) results of 100% Sb_2S_3 , consistent with S K-edge XANES spectra (**Fig. 1(b)**). Minor 5% Sb_2O_3 was observed in a mixed Sb_2S_3 and FeS_2 system under sunlight irradiation (**Fig. 1(a)**), indicating the adsorption of dissolved Sb species. The normalized S K-edge XANES spectrum of solid pyrite shows two obvious signals at 2469 (feature B) and 2481 eV (feature C in **Fig. 1(b)**), corresponding to 48% FeS_2 and 52% SO_4^{2-} species. From the LCF results of S K-edge XANES spectra for samples in a mixed Sb_2S_3 and FeS_2 system, ratio 50% Sb_2S_3 and 48% FeS_2 was derived.

The normalized Fe K-edge XANES spectrum of solid pyrite exhibited three signals at 7114 eV (feature D), 7121 eV (feature E), and 7136 eV (feature F in **Fig. 1(c)**). Feature D is assigned to the transition from a 1s core state to a hybrid state of 3d and 4p ($1s \rightarrow 3d, 4p$); feature E corresponds to a transition from 1s to 4p state ($1s \rightarrow 4p$), and feature F is interpreted as a multiple scattering resonance of Fe p-like states in the continuum. Notably, for samples in a mixed Sb_2S_3 and FeS_2 system, the heights of features D and E increased, but decreased for feature F (**Fig. 2(a)**), indicating the occupation of electrons in p states in the continuum. The accumulation of electrons on the Fe species resulted in Fe(III) reduction. The ratio of Fe(III) oxide, which was best fitted as ferrihydrite in the XANES spectra, decreased

from 47% to 26% in darkness, and further to 14% under sunlight (**Fig. 1(c)**). Correspondingly, a FeS_2 ratio increased from 53% to 74% in darkness and to 86% under light was observed. The heterogeneous electron transfers from Sb_2S_3 to FeS_2 hence promoted Sb(III) oxidation and Fe(III) reduction on the surfaces.

In summary, Jing used XAS measurements to reveal heterogeneous electron transfers between Sb_2S_3 and FeS_2 interfaces. The electron transfers from Sb_2S_3 to FeS_2 separated photo-generated hole (h^+) and electron (e^-) pairs, facilitating the generation of hydroxyl radicals ($\bullet\text{OH}$) on Sb_2S_3 and FeS_2 , and superoxide radicals ($\text{O}_2^{\bullet-}$) on FeS_2 , contributing to the oxidative dissolution of Sb_2S_3 (**Fig. 2(b)**). The knowledge of the reactions and mechanisms gained from this work is crucial for an understanding of the environmental fate of sulfide minerals and the generation of acid mine drainages. (Reported by Ting-Shan Chan)

This report features the work of Chuan-Yong Jing and his collaborators published in Environ. Pollut. 262, 114309 (2020).

TLS 01C1 SWLS – EXAFS TLS 16A1 BM – Tender X-ray Absorption, Diffraction

- XANES
- Environmental Science, Chemistry

Reference

1. L. Yan, T. S. Chan, C.-Y. Jing, Environ. Pollut. **262**, 114309 (2020).