An investigation on the extreme silver enrichment at tennantite surfaces in alkaline solutions: An XPS-based study

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Extreme silver enrichment at the surface of the complex sulfide, tennantite ($Cu_{10}Zn_2As_4S_{13}$), occurs in alkaline solutions, involving the development of a silver-rich sulfide species. The tennantite has a low bulk silver content of 0.3 At %, and a surface enrichment of silver is 36 times that of the bulk. The techniques of X-ray Photoelectron Spectroscopy (XPS) and Reflection Extended X-ray Absorption Fine Structure (REFLEXAFS) show the new phase to be a silver sulfide species compositionally similar to cupriferous proustite ($(Cu, Ag)_3AsS_3$). Solution experiments and XPS depth profiling show the surface is most depleted in copper and zinc, and enriched in silver compared to the bulk tennantite. Dissolution of the tennantite cannot explain the diffusion and enrichment of silver from the bulk. Diffusion and enrichment have been driven by the leaching of copper which produces a metal-depleted surface, and the relative incompatibility of silver in the tennantite lattice. To account for the extreme enrichment at the surface, silver diffusion must have occurred from a depth of up to 9 nm, probably diffusing via structural weaknesses and vacancies in the tennantite lattice.

Monte Carlo simulation of surface energetic heterogeneity of goethite

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Goethite is of abundant importance in many geochemical processes and industrial applications, where its surfaces play key roles. Molecular probe method has been proved as a powerful tool to characterize solid surface and interface property. In order to study surface energetic heterogeneity of goethite and underlying adsorption mechanisms theoretically, argon adsorption on a well-defined (010) face is simulated using Monte Carlo techniques. Grand Canonical Monte Carlo is performed to obtain Ar adsorption isotherm at 77.4 K, and Canonical Monte Carlo to determine both adsorbate-adsorbent interaction energy distribution and adsorption density distribution along z-axis. During running simulation, atom-atom interaction is approximated with the Lennard-Jones 12-6 potential. The adsorption potential minimum map above (010) is shown in Fig. 1. Fig. 2 illustrates distributions of energy and density at a representative submonolayer coverage, 0.82.

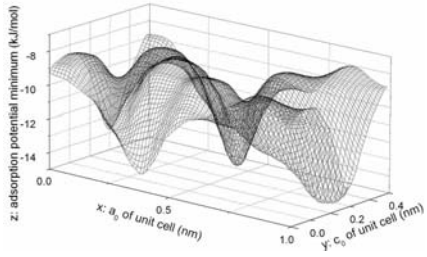
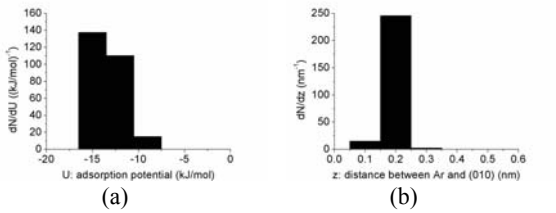


Fig. 1: Goethite adsorption potential minima above (010).



(a) (b)

Fig. 2: (a) Energy distribution and (b) adsorption density profile, at coverage 0.82.

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