Modelling the initial stages of the greigite Fe₃S₄(001) surface oxidation by water

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The spinel-structured greigite (Fe_3S_4), the sulfide counterpart of magnetite (Fe_3O_4), is a mineral with long environmental persistence that can be found in aquatic environments and soils, where it can be oxidized, thereby producing extremely acid solutions of sulfur-rich wastewaters, so-called acid mine drainage (AMD) or acid rock drainage (ARD).

Here we report a computational study of the partial replacement of sulfur (forming H_2S) by oxygen (from H_2O) in the Fe_3S_4(001) surface, derived from density functional theory calculations with on-site Coulomb approach and long-range dispersion corrections (DFT+U−D2) [1]. We have proposed three pathways for the oxidation of the surface as a function of H_2O coverage and pH. Different pathways give different intermediates, some of which are followed by a solid-state diffusion of the O atom. Low levels of H_2O coverage, and especially basic conditions, seem to be essential, leading to the most favorable energetic landscape for the oxidation of the Fe_3S_4(001) surface. We have derived the thermodynamic and kinetic profile for each mechanism and plotted the concentration of H_2S and protons in aqueous solution and thermodynamic equilibrium with the stoichiometric and partially oxidized Fe_3S_4(001) surface as a function of the temperature. Changes in the calculated vibrational frequencies of the adsorbed intermediates are used as a means to characterize their transformation. We have also applied thermodynamic arguments to examine the pH conditions and the H_2S concentration, in aqueous solution and temperatures at which these species are in equilibrium with the stoichiometric and oxidized Fe_3S_4(001) surface, which is relevant to the geochemical formation of AMD.

[1] Santos-Carballal, Roldan, de Leeuw (2016), *The Journal of Physical Chemistry C* 120, 8616–8629.