

# **Anaerobic dissolution of arsenopyrite a potential underestimated arsenic pollution source**

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Arsenic mineral dissolution in natural waters is a topic of strong interests because As in drinking water is a primary source of bio-intake. Of the As-bearing earth materials concerned, arsenopyrite (FeAsS) has received most attention due to the mineral's wide occurrence. To date, extensive studies have been carried out to explore the oxidative dissolution of arsenopyrite to address the concerns of As liberation in aerobic environment. For anaerobic processes such as those associated with groundwater, however, little attention is paid to assess the extent and mechanisms of arsenopyrite dissolution. In present study, we examine the behavior of arsenopyrite in O<sub>2</sub>-free solutions under controlled pH and temperatures to determine the dissolution stoichiometry and rates of elemental release. We ran parallel experiments with loellingite (FeAs<sub>2</sub>) and pyrite (FeS<sub>2</sub>) in hope to reveal mechanistic insight of the dissolution reaction. The two-week experiments showed that the arsenic concentrations reached as high as ~150 and ~350 ppb for arsenopyrite and loellingite at the experimental conditions (25 °C, solid to water ratio 0.3g/100ml), greatly surpassing the guideline value 10 ppb set by the World Health Organization. Furthermore, although the release of As and S from arsenopyrite is mostly stoichiometric at all pHs, the cation/anion ratio (Fe/[As+S]) decreased from near-stoichiometry with falling acidity in solutions. This pattern remains intact for loellingite but becomes more bimodal for pyrite as Fe release at acidic conditions becomes more prominent.

Surface complexation theory is applied to explain these observations. Firstly, at low pH of ~2, H<sup>+</sup> eroded mineral surface through stabilizing As and S sites by complexation reactions to promote Fe release. For pyrite, the precipitation of S<sup>0</sup> via disproportionation reaction of S<sub>2</sub><sup>2-</sup> led to a non-stoichiometric dissolution. Secondly, at higher pH (~5.5 and ~8.8), OH<sup>-</sup> enhanced the release of As and S ions by combining with surface Fe sites. The surface complexation mechanism appears to be consistent with the kinetic parameters derived from dissolution rates using the Eyring equation. Compared with that at pH ~5.5,  $\delta G^\ddagger$  (298 K) of arsenopyrite was lower at pH ~2 and ~8.8, indicating the enhancement of dissolution through surface complexation of H<sup>+</sup> and OH<sup>-</sup>.