# Predicting arsenic behavior in high-iron subsurface environments

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Arsenic sorption depends on biotically and abiotically driven pH and redox processes, and can be controlled in low-sulfur subsurface environments by the activity of Fe. Reaction-path modeling of redoximorphic sediments suggests that phosphate can play an important role by competing with arsenic for sorption sites on Fe surfaces and by potential precipitation of Fe phosphate phases. Modeling of an As-contaminated system at oxic conditions with very low sulfate [log($SO_4^{2-}$) = -7], high Fe [(log($Fe^{2+}$) = -3], and low phosphate [log($HPO_4^{2-}$) = -5.5] predicts that ferrihydrite is the metastable Fe phase. At the modeled pH range (4-10), $H_xPO_4^{x-3}$ will compete with $H_xAsO_4^{x-3}$ for sorption sites on ferrihydrite. As conditions become suboxic (pe < -1) at pH > ~7, a green rust phase, modeled here as ($GRICO_3$) $[Fe^{(II)}{}_4Fe^{(III)}{}_2(OH)_{12}]^{2+}[CO_3{\cdot}3H_2O]^{2-}$ is predicted and overlaps with the stability fields of dissolved $As^{(V)}$ and $As^{(III)}$. If present, $GRICO_3$ provides a substrate for sorption in suboxic sediments, and may also intercalate $H_xPO_4^{x-3}$ and $H_xAsO_4^{x-3}$. At pH < ~7, $GRICO_3$ is not stable and Fe is present as $Fe^{2+}_{(aq).}$ At modeled conditions of high Fe and high phosphate [log($HPO_4^{2-}$) = -3.5], phosphate will compete more strongly with arsenate for sorption sites on ferrihydrite at pe > 1. As conditions become suboxic (pe < -1) and pH = ~7, the GR phase may not form, as vivianite [$Fe_3(PO_4)_2$. $8H_2O$] is the predicted stable Fe phase and the GR stability field is shifted to higher pH (> ~7.5).

Model predictions were compared to sediment data from field investigations at North Haiwee Reservoir (Olancha, CA, USA). An $Fe^{(II,III)}$ phase similar to $GRICO_3$ was identified by X-ray absorption spectroscopy. The GR-like phase formed at depths above and overlapping a release to pore waters of As, P, and Fe, determined by *in situ* gel probe sampling. Field investigations indicate that phosphate can be released to porewaters at concentrations greater than contaminant arsenic (10-25µM versus 2-5µM) and may inhibit re-adsorption of As. As conditions become more reducing (pe < -2), it is predicted that the number of sorption sites will decrease by reductive dissolution of the host Fe phase (GR) and phosphate will out compete $As^{(III)}$, releasing As to porewater.

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# Sulfur and Oxygen isotopes: Evidence of $H_2S$ spring sources, Southern Mexico

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Anomalously high $H_2S$ concentrations up to 240 ppm exhale from springs on the surface and in caves in Tabasco-Chiapas states, Mexico. The proposed sources are basinal fluids [1] and gas from an active volcano [2]. Further regional sampling of spring water seeks to elucidate the extent of the $H_2S$ generation and its relation to the subsurface evaporites [4]. Although $\delta D$-$\delta^{18}O$ analysis suggests that meteoric water is the main water-source of the $H_2S$-springs, the water composition ranges from 1400 to 6600 mg/l TDS (brackish water); [$Cl^-$] = 250 to 2000 ppm; and [$SO_4^{2-}$] = 250 to 4000 ppm. This composition may be reached by interaction of groundwater with Late Jurassic salt and Lower Cretaceous anhydrite through lateral faults and anticline axis fractures. $H_2S$ degassing from the spring water suggests the presence of an open system. The similarities of the $\delta^{34}S$ and $\delta^{18}O$ between the spring soluble sulfate, the brine-related oil sulfate, and the subsurface anhydrite propose a common origin. These isotopes do not show any evidence of a volcanic $H_2S$ input to the springs. A relatively constant fractionation from 28 to 45‰ $\delta^{34}S$-VCDT between the aqueous sulfides and sulfates of the $H_2S$ springs points to an equilibrium sulfate reduction fractionation process. These values are inside the sulfate-sulfide fractionation range reported for microbial [4] sulfate reduction suggesting this mechanism can be producing the $H_2S$. The driving force for reduction, (temperature, pH, or the presence of organic matter) is not yet defined. The near neutral pH of the water (6.4 to 7.5) and a temperature at most three degrees Celsius above atmospheric temperature, points to the latter. The lack of change in the sulfate suggests there is an infinite reservoir of this compound. The produced $H_2S$ re-oxidizes to $H_2SO_4$, reacting with the limestone host rock in caves to produce gypsum/selenite with the same isotopic signature as the precursor $H_2S$. Further data is being collected to clarify the $H_2S$ source.

[1] Hose *et al.* (2000) *Chemical Geology* **169**, 399-423. [2] Spilde *et al.* (2004) *GSA Abs.* **36**, 5, 106-11. [3] Meneses-Rocha (2001) *AAPG Mem.* **75**, 183-216. [4] Johnston (2007) *GCA* **71**, 3929–3947.