

## Stabilities of metal-thioarsenite complexes: Testing some theoretical predictions

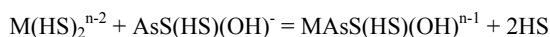
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Clarke and Helz (2000) discovered that dithioarsenite binds  $\text{Cu}^I$  extremely strongly, making an uncharged, 1:1 complex likely to be mobile in subsurface fluids. Such binding of metals by thiometalloids can explain sulfosalts in hydrothermal ores and cotransport of harmful elements near hazardous waste sites. With quantum theory, Tossell (2000a,b) showed why  $\text{CuAsS}(\text{SH})(\text{OH})^0$  has high stability and predicted which other metals might bind similarly. Solubilities of Ag, Hg and Pb sulfides in the presence of As sulfide phases are examined here to test some of these predictions. Dissolution of an  $\text{Ag}_2\text{S} + \text{Ag}_3\text{AsS}_3$  mixture produces  $\Sigma\text{Ag}$  concentrations exceeding those from  $\text{Ag}_2\text{S}$  alone. With no UV-Vis spectral evidence of polysulfide ions, excess  $\Sigma\text{Ag}$  is attributed to:



Similar experiments with  $\text{HgS} + \text{S} + \text{As}_2\text{S}_3$  reveal no excess  $\Sigma\text{Hg}$  compared to experiments with  $\text{HgS} + \text{S}$ . Thus at thioarsenite concentrations up to  $\text{As}_2\text{S}_3$  saturation, thioarsenite ligands cannot compete successfully for Hg against  $\text{HS}^-$  ligands at  $[\text{HS}] \geq 10^{-4}$  M. Likewise Pb thioarsenite complexes are not seen. In their trend, these results agree with expectations from theory:



If theory continues to be upheld,  $\text{Au}^+$  will be shown to bind less strongly than  $\text{Cu}^+$  or  $\text{Ag}^+$  with  $\text{AsS}(\text{HS})(\text{OH})^-$ , but  $\text{TI}^+$ , a rare element in nature except in sulfosalts, will be shown to bind much more strongly than metals tested so far.

$\text{M}^{n+}$	Theoretical $\Delta H_R$	Measured $\log K_{25C}$
$\text{Cu}^+$	-26 kJ/mol	+2.64
$\text{Ag}^+$	-19 kJ/mol	-0.37
$\text{Hg}^{2+}$	+1040 kJ/mol	No complex observed
$\text{Pb}^{2+}$	+306 kJ/mol	No complex observed

### References

- Clarke M.B. and Helz G.R. (2000) *Environ. Sci. Technol.* **34**, 1477-1482.  
Tossell J.A. (2000a) *Environ. Sci. Technol.* **34**, 1483-1488.  
Tossell J.A. (2000b) *Geochem. Trans.* Article 3.

## Dissolution rate of the lead phosphate mineral pyromorphite

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Traditional remediation methods for lead contaminated soil involve expensive excavation and offsite disposal. However, the formation of insoluble lead phosphate minerals provides a potential *in situ* remediation strategy. To understand immobilization mechanisms of lead and phosphate in soils and the rates of remobilization from contaminated soils, we have used synthetic chloropyromorphite (CPY,  $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ ) to assess the dissolution rates. The material was synthesized by mixing 0.15 M  $\text{H}_3\text{PO}_4$  and 0.25 M  $\text{PbCl}_2$  and purging with  $\text{N}_2$  at room temperature. The solution was adjusted to pH 7 and aged for 1 month before freeze-drying. Dissolution rates of CPY were investigated in flow-through reactors and batch reactors. Experiments used synthetic chloropyromorphite under different pH, hydraulic residence time, solid concentrations, and solution saturation conditions. Effluent concentrations over time were measured by inductively coupled plasma atomic emission spectrometry (ICP) and inductively coupled plasma mass spectrometry (ICP-MS). The solid characteristics following reaction were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR).

The equilibrium concentrations in batch reactors and steady-state effluent concentrations of lead in flow-through reactors increased with decreasing pH. The steady-state concentrations were close to the equilibrium concentration at each pH. Only slight changes of steady-state concentration occurred with different residence time and solid concentration, which indicates that equilibrium had already been approached. Net precipitation of lead occurred under supersaturated conditions with respect to CPY.

SEM images show that nanoparticles attached to the ripened hexagonal CPY dissolved preferentially at low pH. FTIR data also show that a more soluble amorphous lead phosphate solid was present initially and dissolved preferentially with decreasing pH and increasing reaction time. However, XRD does not show significant changes in crystalline solid phases reacted at different pH conditions. The nanoparticles, which are possibly growing CPY or a  $\text{Pb}(\text{OH})_{2(s)}$  impurity, might affect the net dissolution rate because of their different dissolution rates.