Experimental Determination of Contaminant Metal Mobility as a Function of Temperature, Time and Solution Chemistry

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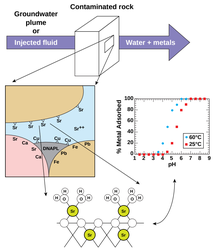
Introduction

➡ This work is motivated by the lack of fundamental data needed to assess long-term hazards from metal pollution and the need for technologies to remediate subsurface metal pollution.

➡ Geochemical factors that may contribute to Sr mobility in natural waters are the solubilities of phases such as strontianite ($SrCO_3$) and formation of aqueous and surface complexes.

➡ Why Strontium?
Strontium is more mobile than other hazardous radioactive elements.

➡ Our objective is to determine the processes controlling Sr mobility by combining macroscopic experiments, molecular analysis of solids, and geochemical modeling.



On all solids, Sr sorption

➡ increases at pH > 7, with minimal sorption at pH < 7

➡ is independent of temperature from 25 to 80°C

➡ scales with initial Sr concentration

➡ is faster than strontianite precipitation from solution

Experimental Methods

Strontium Batch Sorption Experiments

Temperature: 25, 50, 80°C

Solution: $[Sr]_i$ 10^{-7} to 10^{-3}M
pH 4 to 10
0.1 N NaCl/$NaNO_3$

pCO_2: $10^{-3.45}$ and 0 atm

Solids: Goethite
Kaolinite
Silica Gel

Time: 48 hours

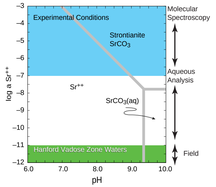
Molecular Spectroscopy — X-ray Absorption Fine Structure (XAFS)

Batch Sorption Experiments:
$[Sr]_i$ 10^{-3}M
25°C
pH 8 to 9

Time: 48 hours and 2 months

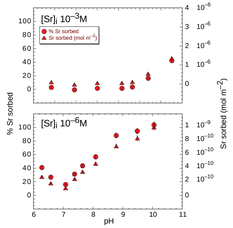
Spectra Collection:
SSRL on beam line 4-3
Si(220) monochromator crystal
unfocused beam
13-element Ge array detector
10, 70, and 298 K
~40 scans per sample
EXAFSPAK and FEFF

Strontium Solubility 25°C, 0.1M NaCl, pCO_2 = $10^{-3.45}$ atm

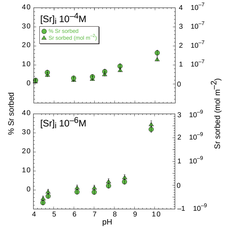


Results: Batch Sorption Experiments

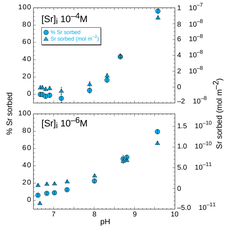
Goethite
pCO_2 = $10^{-3.45}$ atm,
0.1 N NaCl, 25°C



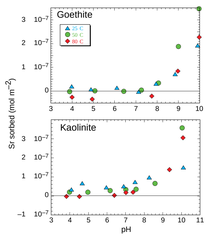
Kaolinite
pCO_2 = $10^{-3.45}$ atm,
0.1 N $NaNO_3$, 25°C



Silica Gel
pCO_2 = $10^{-3.45}$ atm,
0.1 N NaCl, 25°C



No Temperature Dependence
$[Sr]_i$ 10^{-4}M, pCO_2 = $10^{-3.45}$ atm,
0.1 N $NaNO_3$



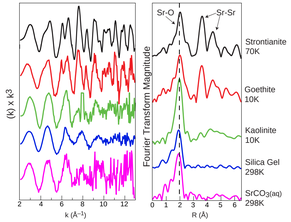
Results: Molecular Spectroscopy

Strontium Structure at Solid-Water Interface

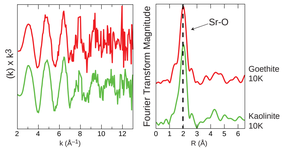
➡ Kaolinite and Silica Gel
In both the 48 hour and 2 month experiments, outersphere Sr surface complexes form at the kaolinite- and silica gel-water interfaces even in solutions supersaturated with respect to strontianite.

➡ Goethite
In the 48 hour experiments supersaturated with respect to strontianite, "$SrCO_3$" multi-nuclear complexes form at the goethite-water interface. As the sample ages, outersphere Sr surface complexes are observed. This implies competition between Sr and Fe for carbonate sorbed at the goethite-water interface.
Outersphere Sr surface complexes are observed at the goethite-water interface in CO_2-free solutions.

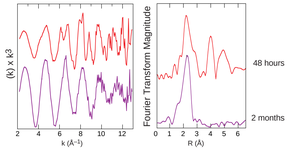
Strontium Sorption
pCO_2 = $10^{-3.45}$ atm, $[Sr]_i$ 10^{-3} M, 25°C



Strontium Sorption
CO_2 free, $[Sr]_i$ 10^{-3} M, 25°C



Comparison of Sr on Goethite after 48 hours and 2 months reaction



Summary and Future Work

➡ Strontium is a very mobile element in groundwaters, because it does not sorb strongly to mineral surfaces. It forms hydrated outersphere surface complexes in alkaline waters. The multi-nuclear "$SrCO_3$" complexes that form on goethite are not stable, and transition to outersphere complexes within a couple months reaction.

➡ Our experiments show similar sorption behavior over a range of initial Sr concentrations. However, experiments with radioactive Sr isotopes are needed to investigate Sr sorption at concentration ranges found at DOE sites.

➡ During the third year of our project, will focus on modeling the sorption data and conducting flow-through experiments to determine the rate of Sr sorption at the goethite-solution interface, as well as study the transition from "$SrCO_3$" surface precipitation to outersphere Sr surface complexation.