

Incorporation of a Pertechnetate analog – Perrhenate – by Sodalite in Competition with other Anions

JOHNBULL DICKSON¹, JAMES HARSH¹ AND ERIC PIERCE²

¹Washington State University, Pullman, WA, USA,
(j.dickson@wsu.edu)

²Oak Ridge National Laboratory, Oak Ridge, TN, USA

Spent nuclear fuel/waste is dubbed “one of the most hazardous substances ever created by humans” and the U.S. is credited with 104 nuclear power plants that have already generated 70,000 metric tons of radioactive waste. Currently these spent nuclear fuel/wastes are being stored in swimming-pool-like tanks, and steel/concrete tanks at reactor sites in 33 U.S. States due to lack of permanent repository (C&EN, 2012). Radionuclide contamination at nuclear sites and power plants are a worldwide hazardous waste problem. Technetium-99 (⁹⁹Tc), a long-lived radionuclide at select DOE waste sites, presents a major concern due to its long half-life (211,000 y) and high mobility in oxidized subsurface environments. ⁹⁹Tc contamination has been found in the sediments beneath the Washington State Hanford Site Tank Farms after leakage of caustic, Al-rich, and high ionic strength high-level waste (HLW) solutions. Due to these releases, ⁹⁹Tc inventory (5.31x10³ Ci) is predicted to leach into the ground water table at concentrations in excess of the MCL of 53 µg L⁻¹. Interestingly, nearly 50 years after the release of the contaminant into the environment, most of the ⁹⁹Tc persists in the deep subsurface sediment. We hypothesize that the formation of feldspathoid-type minerals within native Hanford sediment is sequestering ⁹⁹Tc. Previous studies demonstrated ⁹⁰Sr and ¹³⁷Cs incorporation into feldspathoid minerals, such as sodalite, that formed as a result of contact between Hanford primary silicate minerals and HLW solutions [1, 2]. To elucidate the role of competing anions on TcO₄⁻ incorporation, we used ReO₄⁻ as an analog to synthesize various anionic sodalites. The pure and mixed anion-bearing sodalites were characterized by XRD, XRF, electron microprobe, and wet digestion. ReO₄⁻ concentrations in the resulting sodalite samples ranged from 13 mmol kg⁻¹ in the mixed-anionic sodalites to 760 mmol kg⁻¹ in the pure ReO₄⁻ sodalite. Prolonged aging appeared to increase crystallinity; however, enclathration of ReO₄⁻ into the sodalite framework with time was inconsistent. Using the 211 x-ray diffraction peak of sodalite, the unit cell parameter linearly increased with increasing anionic radius. These data imply that ⁹⁹Tc found in Hanford tank waste stream loaded with smaller competing anions (NO₃⁻, NO₂⁻, Cl⁻, SO₄²⁻, etc.) is unlikely to be sequestered into sodalite. As sodalite group mineral can deform to host guest anions of varying ionic sizes, detailed information on the structural refinements for these various mixed anion-bearing sodalites will shed light on the tilting/deformation of sodalite framework structure. Our future work will be directed at elucidating these structural changes and conditions under which Tc incorporation might be favored.

[1] Chorover, *et al.* 2008, GCA 72, 2024-2047. [2] Deng Y., *et al.* 2006, Applied Geochemistry, 21, 1392-1409.

Formation and transformation of nanocrystalline iron carbonate precursors

K. DIDERIKSEN¹, C. FRANDSEN², N. BOVET¹, A.F. WALLACE³, T. ARBOUR⁴, J. DEYOREO⁵, S.L.S. STIPP¹ AND J. F. BANFIELD⁴

¹Nano-Science Center, Dept. of Chemistry, University of Copenhagen, Denmark (knud@nano.ku.dk)

²Dept. of Physics, Technical University of Denmark

³Earth Sciences Division, Lawrence Berkeley National Laboratory, USA

⁴Dept. of Earth & Planetary Science, University Of California, Berkeley, USA

⁵Molecular Foundry, Lawrence Berkeley National Laboratory, USA

Fe(II)-carbonates, such as siderite, form in environments where O₂ is scarce, e.g. during marine sediment diagenesis, corrosion and possibly CO₂ sequestration but little is known about its formation pathways. Precipitates from carbonate solutions containing 0.1 M Fe(II) with varying pH produced broad peaks in X-ray diffraction and contained Fe and CO₃ when probed with X-ray photoelectron spectroscopy.

In pair distribution function (PDF) analysis, peaks are limited to interatomic distances below 1.5 nm. The peaks are well defined compared to those for amorphous calcium carbonate and differ in position from those for known iron carbonates and hydroxides, indicating that a previously unidentified nanocrystalline iron carbonate had formed. Also, Mössbauer spectra differ from that expected for known iron carbonates and suggest a less symmetric structure. Replica exchange molecular dynamics simulations of Fe-carbonate clusters yield PDF peak positions that agree well with those from experiments. PDF measurements of samples aging in solution coupled with refinement with the software PDFgui show that the material transforms to siderite within hours and that the transformation rate depends on pH (Fig. 1).

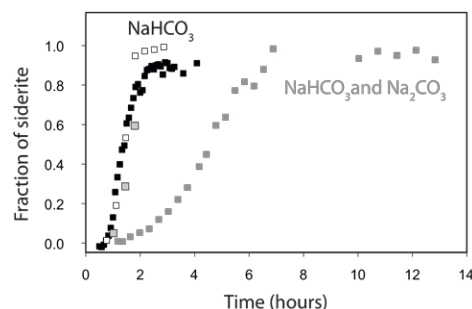


Figure 1: Fraction of siderite as a function of time from PDF