Silicon control of strontium and cesium partitioning in hydroxide-weathered sediments

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Received 9 July 2007; accepted in revised form 22 January 2008; available online 12 February 2008

Abstract

Cation partitioning and speciation in an aqueous soil suspension may depend on the coupling of reaction time, sorbate amount and mineral weathering reactions. These factors were varied in sediment suspension experiments to identify geochemical processes that affect migration of Sr$^{2+}$ and Cs$^+$ introduced to the subsurface by caustic high level radioactive waste (HLRW). Three glacio-fluvial and lacustrine sediments from the Hanford Site (WA, USA) were subjected to hyperalkaline (pH > 13), Na–Al–NO$_3$–OH solution conditions within a gradient field of (i) sorptive concentration ($10^{-5}–10^{-3}$ m) and (ii) reaction time (0–365 d). Strontium uptake ($q_{Sr}$) exceeded that of cesium at nearly all reaction times. Sorbent affinity for both Cs$^+$ and Sr$^{2+}$ increased with clay plus silt content at early times, but a prolonged slow uptake process was observed over the course of sediment weathering that erased the texture effect for Sr$^{2+}$; all sediments showed similar mass normalized uptake after several months of reaction time. Strontium became progressively recalcitrant to desorption after 92 d, with accumulation and aging of neoformed aluminosilicates. Formation of Cs$^+$ and Sr$^{2+}$-containing cancrinite and sodalite was observed after 183 d by SEM and synchrotron μ-XRF and μ-XRD. EXAFS data for $q_{Sr}$ $\approx$ 40 mmol kg$^{-1}$ showed incorporation of Sr$^{2+}$ into both feldspathoid and SrCO$_3$(s) coordination environments after one year. Adsorption was predominant at early times and low sorbate amount, whereas precipitation, controlled largely by sediment Si release, became increasingly important at longer times and higher sorbate amount. Kinetics of contaminant desorption at pH 8 from one year-weathered sediments showed significant dependence on background cation (Ca$^{2+}$ versus K$^+$) composition. Results of this study indicate that co-precipitation and ion exchange in neoformed aluminosilicates may be an important mechanism controlling Sr$^{2+}$ and Cs$^+$ mobility in siliceous sediments impacted by hyperalkaline HLRW.

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1. INTRODUCTION

Sorption of metal ions at the soil particle-aqueous solution interface is characterized by a continuum from surface complexation to precipitation. Whereas adsorption tends to predominate at short times and low sorbate concentrations, longer contact times and higher concentrations may favor the formation of surface precipitates (Chorover and Brusseau, 2008). When such precipitates form as a result of interactions between exogenous metals and soluble products of sediment weathering (e.g., Al, Fe or Si), incongruent dissolution of native minerals may control the mechanism of metal uptake to the solid phase (Scheidegger et al., 1996; Chorover et al., 2003; Voegelin et al., 2005). In addition, increased sorbate-sorbent contact time may produce sorbate species that exhibit slower release kinetics because...
of recrystallization or ripening processes (Ainsworth et al., 1994; Scheckel et al., 2000). Hence, prolonged contact of metal or radionuclide contaminants with actively weathering sorbents can result in a time evolution contaminant speciation and mobility.

The release of caustic high level radioactive waste (HLRW) into soils and sediments represents a scenario where mineral weathering reactions may impact the trajectory of contaminant sorption processes. Mineral transformation thus can influence strongly the environmental geochemistry of radionuclides (Ildefonse et al., 1990; Riley and Zachara, 1992; Brady and Kozak, 1995). Approximately 100 million gallons of HLRW were generated in the US during the Cold War as a result of the reprocessing of irradiated uranium fuel and plutonium extraction for nuclear weapons production. This HLRW has been stored in massive underground tanks at U.S. Department of Energy (DOE) facilities including the Hanford Site in Washington, the Idaho National Engineering Laboratory and the Savannah River Site in South Carolina, where it also has been introduced by accidental release into the subsurface environment. Similar sites comprising underground storage of HLRW exist worldwide and many have documented accidental release of radionuclide-containing fluids. At the Hanford Site, 67 of 177 underground tanks are suspected to have leaked over 3800 m$^3$ of HLRW into the vadose and saturated zones (DOE, 1995; Ahearne, 1997). Most of the tank-waste leachate is characterized by high ionic strength (Na$^+$–NO$_3^-$, –NO$_2^-$), high pH and Al(OH)$_3^-$ concentration, and concentrations of radionuclides ($^{99}$Tc, $^{137}$Cs, $^{90}$Sr, $^{129}$I, $^{238}$U) that vary with location. The bulk of the radioactivity released was $^{137}$Cs and $^{90}$Sr, amounting to more than 1 million curies, with mass concentrations up to milligrams per kilogram of solution (Behrens et al., 1998; Serne et al., 2000b). These radionuclides are dissolved in hyperalkaline solutions that react with underlying sediments to create an extreme subsurface geochemical environment that is also one of the most contaminated in the world (NRC, 2006; Zachara et al., 2007). Adsorption of cationic contaminants is expected to be mediated by high surface area constituents in the sediments, particularly phyllosilicate minerals (clays and mica) (Sposito et al., 1999).

From the perspective of ionic potential and geochemical reactivity, Cs$^+$ and Sr$^{2+}$ are analogues of K$^+$ and Ca$^{2+}$, respectively. Like K$^+$, Cs$^+$ has low hydration energy. This facilitates its inner-sphere coordination at charged siloxane sites on layer silicate surfaces and results in a particularly high affinity for frayed edge sites of micaceous minerals (Cornell, 1993; Kim et al., 1996; Sutton and Sposito, 2001; Bostick et al., 2002; Steefel et al., 2003). Similar in ionic potential to Ca$^{2+}$, the Sr$^{2+}$ cation has higher hydration energy than Cs$^+$ and it typically forms outer-sphere surface complexes at negatively charged sites on clay minerals and oxides (Jeong et al., 1996; Sahai et al., 2000). Strontium mobility is also influenced by co-precipitation in CaCO$_3$(s) or discrete SrCO$_3$(s) precipitates (Parkman et al., 1998; Sahai et al., 2000; McKinley et al., 2007).

The extreme weathering environment associated with HLRW introduces additional factors that may affect Cs$^+$ and Sr$^{2+}$ mobility. Several experimental studies have shown that reaction of Al-bearing caustic waste simulants with silicate minerals results in Si dissolution and subsequent co-precipitation with waste-derived Al to form feldspathoid solids, including cancrinite and sodalite, with near unit Si/Al molar ratio (Bickmore et al., 2001; Chorover et al., 2003; Qafoku et al., 2003b; Choi et al., 2005b; Mashal et al., 2005a). Feldspathoid formation is also observed when aqueous Si is present as a reactant in caustic aluminate solutions (Zheng et al., 1997; Deng et al., 2006). A principal finding of the prior research on weathering of Hanford sediments under HLRW conditions is that the identity and character of reaction products are dependent on the chemical composition of waste solution simulants and also on the time scale of reaction (Qafoku et al., 2003a,b; Mashal et al., 2004; Ainsworth et al., 2005; Mashal et al., 2005a). These weathering processes likely alter the geochemical mobility of Cs$^+$ and Sr$^{2+}$, since both ions can be incorporated into exchange sites in zeolites or feldspathoids (Perona et al., 1995; Mon et al., 2005). Silicates depleted during hyperalkaline reaction with Hanford sediments include the layer silicates biotite, smectite and kaolinite (Qafoku et al., 2003b; Ainsworth et al., 2005; Mashal et al., 2005a), which are also potential sorbents for Cs$^+$ and Sr$^{2+}$. Whereas new sorbent phases are known to form at the expense of native minerals, the net effect of mineral transformation on contaminant fate is unknown.

We hypothesized that under these conditions, the fate of Cs$^+$ and Sr$^{2+}$ includes adsorption to mineral surfaces in the native sediments as well as incorporation into neofomed precipitates. We postulated that sorptive fate depends on (i) the identity of the contaminant (Cs$^+$ versus Sr$^{2+}$), since this influences its reactivity toward native and neofomed solids, and (ii) progress along the weathering reaction path. The objectives of the study, therefore, were (i) to examine the uptake and lability of Cs$^+$ and Sr$^{2+}$ in STWL-impacted Hanford sediments as a function of reaction time and mineral transformation, (ii) to assess the microscale distribution and speciation of these contaminants in the reacted media (including dissolved, colloidal and sediment bound forms) and (iii) to measure the kinetics of contaminant desorption from weathered sediments in circumneutral background pore water simulators. We employed a multi-faceted approach that combined measurements of reaction rate and extent with micro- and molecular-scale investigations of mineral transformation and contaminant speciation. The complement of methods helped to elucidate a transition from adsorption to co-precipitation of the cationic contaminants that occurs as the sediments traverse a two-dimensional field of sorbate amount and reaction time.

## 2. MATERIALS AND METHODS

### 2.1. Sample collection

Sediments similar in character to those beneath the leaking underground tanks at the DOE Hanford Site were collected from uncontaminated areas within the Hanford Formation (glacio-fluvial sediments) and Upper Ringold Formation (fluvial–lacustrine deposits). Hanford Coarse (HC) sediments, consisting of medium- to coarse-grained...
sand and gravel, and Hanford Fine (HF) sediments, consisting of thinly bedded, silty, fine-to-coarse-grained sand, were collected from the 218-E-12B Burial Ground excavation site. Ringold Silt (RS) sediments, composed of fine sand interbedded with silt, were obtained from White Bluffs across the Columbia River from the Hanford Site. Sediments were air dried, sieved to obtain the <2 mm fraction, and used without further modification. Mineral composition of the bulk sediment, silt and clay size fractions was determined at Pacific Northwest National Laboratory (PNNL) on a Scintag XRD unit with a Pelletier thermostatically cooled detector and CuK\(\alpha\) radiation (Serne et al., 2002a). Total elemental analysis was performed by both X-ray fluorescence and lithium metaborate fusion followed by ICP-OES or ICP-MS. “External” and “total” specific surface areas were determined operationally on the basis of \(N_2\) BET and ethylene glycol monooethyl ether (EGME) adsorption, respectively (Carter et al., 1986). Sediment calcite contents were measured by coulometric titration (Serne et al., 2002a).

2.2. Sediment–synthetic tank waste reaction

Acid washed Nalgene \textsuperscript{TM} polypropylene copolymer (PPCO) vessels were used instead of glassware at all stages of the experiment to prevent Si contamination. Stock solutions were prepared using ultrapure (MiliQ) water and reagent grade NaNO\(_3\), NaOH, CsCl, SrCl\(_2\)-6H\(_2\)O (J.T. Baker) and NaAlO\(_2\)-xH\(_2\)O powder (EM Science) as obtained from the manufacturer. Sediments were reacted with a synthetic tank-waste leachate (STWL) that was prepared on a mass basis (all solution concentrations are given in units of molality [m], mol kg\(^{-1}\)). The STWL was prepared from a CO\(_2\)-free solution composed of 0.05 m NaAlO\(_2\), 2.0 m Na\(^+\), 1.0 m NO\(_3^-\) and 1.0 m OH\(^-\) (pH \~ 13.7). Aqueous NaNO\(_3\) and NaOH were mixed with NaAlO\(_2\)-xH\(_2\)O powder, stirred magnetically for 20 min, then vacuum filtered through a 0.45 \(\mu\)m Pall-Gelman hydrophilic polypropylene filter. Both CsCl and SrCl\(_2\)-6H\(_2\)O were added to the STWL stock solution as co-contaminants to give three initial aqueous phase Cs\(^+\) and Sr\(^{2+}\) concentrations, where both cations were present in each STWL solution at 10\(^{-5}\), 10\(^{-4}\) or 10\(^{-3}\) m. The solutions were then stirred for approximately 5 min and used immediately. Sediment–STWL reactions were conducted in batch systems using 50 mL polypropylene copolymer (PPCO) centrifuge tubes containing 0.8 g of air dry sediment in 40.0 g of STWL solution, yielding a solid-to-solution mass ratio of 1:50. All reactions were carried out in triplicate. Two types of sediment-free controls were used to confirm the absence of precipitates under those conditions: (i) STWL solution only and (ii) Al-free STWL solution. All reaction vessels were kept in a dark, temperature-controlled room at 298 ± 2 \(K\) on an end-over-end mixer rotating at 1 rpm. Vessels were sampled at time intervals of 1, 7, 29, 92, 183 and 374 d. At the termination of each designated reaction period, suspensions were allowed to settle and a subsample of colloidal suspension (particles <2 \(\mu\)m) was obtained in accordance with Stoke’s Law (assuming a particle density of 2.65 g cm\(^{-3}\)). These samples also contained dissolved material and are hereafter referred to as the “colloidal plus dissolved fraction”. Suspensions were then centrifuged for 20 min at 25,260 relative centrifugal force (RCF) and supernatant solutions were filtered through 0.2 \(\mu\)m Gelman Acrodisc “GH Polypro” filters to collect the dissolved fraction. All solutions were acidified to pH \~ 2 with trace metal grade HNO\(_3\) and preserved at 4 \(^\circ\)C. Control samples were analyzed for dissolved inorganic carbon (DIC) at the beginning of the experiment and after 12 months (Shimadzu TOC-VCSH wet combustion high sensitivity carbon analyzer) to determine CO\(_2\) transfer from the headspace and possibly from the ambient air into reaction vessels and solutions. The centrifuged pellets were re-suspended in 95% ethanol (adjusted to pH 10.0 ± 0.1) to remove entrained STWL solution. Two additional ethanol washes were conducted without pH adjustment.

The following procedure was then completed for all sampling times except that a second set of samples also reacted for one year was reserved for desorption kinetics studies. Two of the three replicate pellets were reacted with 0.1 m Mg(NO\(_3\))\(_2\) (adjusted to pH 7.00 ± 0.05) for one hour to extract Mg\(^{2+}\)-exchangeable Cs\(^+\) and Sr\(^{2+}\). Solutions from Mg(NO\(_3\))\(_2\) extraction were centrifuged for 20 min at 25,260 RCF, filtered (0.2 \(\mu\)m), acidified, and solutions stored in PPCO bottles at 4 \(^\circ\)C. Pellets were then washed three times with ethanol (no pH adjustment) prior to extracting “poorly crystalline” precipitates using 0.2 M acid ammonium oxalate (AAO) (4 h at pH 3 on a reciprocal shaker in the dark).

2.3. Desorption kinetics measurements

To measure the rate of Cs\(^+\) and Sr\(^{2+}\) release from weathered sediments in solutions representative of background pore waters present in uncontaminated regions of the site (i.e., to model interaction of weathered sediments with solutions characteristic of those occurring after removal of the HLRW source), ethanol-washed 374 d reacted solids were re-suspended in 40.0 g of either 10 mM KCl or 5 mM CaCl\(_2\) solution at pH 8.0, in triplicate. These solutions provide a direct comparison between K\(^+\) and Ca\(^{2+}\) effects on Cs\(^+\) and Sr\(^{2+}\) desorption since they comprise equal (10 mmol L\(^{-1}\)) concentrations of cation charge. Desorption kinetics and Al/Si dissolution were measured using a batch technique that involved repeated reaction of weathered sediments with these solutions. For each time step corresponding to 1, 6, 24, 48, 72, 96, 120, 144, 168 and 240 h of desorption reaction, suspensions were centrifuged at 25,260 RCF the supernatant solutions were removed, entrained solution masses were measured, fresh CaCl\(_2\) or KCl solutions were added, and the desorption reactions were continued. The mass of entrained solution was used to correct contaminant release kinetics for aqueous phase Cs\(^+\) and Sr\(^{2+}\) deriving from the preceding step.

2.4. Solution analysis

An Accumet solid-state pH electrode with a Si free glass bulb was calibrated by Gran titration at the experimental ionic strength to measure directly the molal hydroxide con-
Concentration in reacted STWL solutions. Dissolved Cs$^{+}$ and K$^{-}$ were measured by atomic emission (AE) spectrometry using a flame AE spectrophotometer (Instrumentation Laboratory Video 22). Dissolved Al, Si, Fe and Sr were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES, Thermo Jarrell Ash Model 61E). Samples below the ICP-AES detection limit for Sr$^{2+}$ (19 μg L$^{-1}$) were reanalyzed by graphite furnace atomic absorption (GFAA) spectrometry on a Perkin-Elmer Zeeman 5100PC GFAA (Sr$^{2+}$ detection limit 2.1 μg kg$^{-1}$).

Solution chemistry data were modeled using GMIN, an equilibrium geochemistry program that employs free energy minimization and Pitzer equations to assess aqueous phase speciation and solution phase saturation state with respect to potential precipitation of solid phases (Felmy, 1995). Calculations indicated that, prior to contact with sediment, all STWL solutions were initially undersaturated with respect to potential precipitates. The one exception was the highest initial Sr concentration case, which was slightly supersaturated with respect to SrCO$_3$(s)(log $\Omega$ = 0.58).

Aqueous speciation calculations indicated that dissolved strontium and cesium were present as Cs$^{+}$ and Sr$^{2+}$, respectively. 5% of the added NO$_3$ was present as Al(OH)$_4$(aq) complexes and all added Al was present as Al(OH)$_3$(aq).

2.5. Solid phase analysis

Time-dependent changes in mineral composition and contaminant speciation were assessed for reacted and AAO-extracted sediments using bulk and microfocused X-ray diffraction (XRD), X-ray fluorescence (XRF), electron microscopy (TEM and SEM), and infrared, NMR and EXAFS spectroscopies in order to provide complementary information on the samples.

2.5.1. Microfocused XRD and XRF analyses

Synchrotron-based microfocused XRF and XRD data were collected at the Advanced Light Source (ALS, Lawrence Berkeley National Laboratory, Berkeley, CA) on beamline 10.3.2. Reacted and AAO-extracted samples aged for 374 d at Sr$^{2+}$/Cs$^{+}$ initial solution concentrations of 10$^{-3}$ m were dried and spread on Kapton tape at room temperature. Data were collected using monochromatic X-rays at 17 keV and a spot size of 5 x 5, 7 x 7 or 16 x 7 μm. For fluorescence measurements, energy was calibrated with Fe metal by setting the first inflection on the absorption edge to 7110.75 eV. A Canberra 7-element Ge detector with XIA electronics (DXP2X Model T) was used for fluorescence mapping. For microfocused XRD, Laue patterns were collected in transmission mode using a CCD detector. The 2θ scale was calibrated with α-Al$_2$O$_3$(corundum) with the CCD detector placed at a standardized distance from the sample (150 mm). For XRD data processing, the program FIT2D (Hammersley et al., 1996) was used to convert Laue patterns to diffractograms of 2θ versus peak intensity using a calibrated wavelength of 0.7295 Å (17 keV). Because samples are usually coarsely crystalline on the microscale and the sampled diffraction volume is small, Laue patterns from micro-XRD often have spotty and discontinuous rings. This arises from diffraction of a finite number of single crystals inside the diffracting volume and fewer individual crystals satisfying the Bragg condition compared to bulk powder XRD. Thus, micro-diffractograms (after conversion from Laue patterns) often contain anomalous peak intensities and missing hkl reflections compared reference bulk powder diffractograms (Manseau et al., 2002). Laboratory and synchrotron X-ray diffractograms were analyzed to determine mineral identities using the JADE program (MDI Products) with the ICDD database by matching at least two to three of the major reflections and allowing for variation in peak intensities in the micro-diffractograms.

2.5.2. Synchrotron X-ray absorption spectroscopy (XAS) data collection and analysis

Strontium K-edge fluorescence EXAFS (extended X-ray absorption fine structure) spectra for Hanford sediments reacted for 369 d (Cs$^{+}$tot = Sr$^{2+}$tot = 10$^{-2}$ m) before and after Mg(NO$_3$)$_2$ + AAO extraction were collected at Stanford Synchrotron Radiation Laboratory Source (SSRL) on beamline 11–2 (3 GeV, ∼100 mA) (data were not collected after only the Mg(NO$_3$)$_2$ extraction step). Samples were held at 4 K during data collection with a Si(220) monochromator crystal and either a 13- or 30-element Ge solid-state detector. Energy was calibrated by setting the mid-point of the main absorption edge of reference SrCO$_3$(s) to 16,105 eV. Bulk powdered samples were packed evenly in Teflon holders and sealed with Kapton tape. Successive scans were averaged, background-subtracted, and normalized to edge-step height. EXAFS spectra were fit qualitatively using linear combinations of reference spectra to identify major Sr components; however, reference compounds did not adequately fit the neoformed Sr-bearing phases. Spectra were fit quantitatively using the shell-by-shell method over a k-range of 2 to 11.5–13 Å$^{-1}$ (depending on data quality) with theoretical reference functions calculated by the program FEFF (Rehr et al., 1992; Rehr, 1993) using atomic clusters from reference Sr compounds calculated with the program ATOMS (Ravel, 2001). Distance (R) and backscatterer number (N) were varied; Debye–Waller factors ($\sigma^2$) were fixed on values determined from reference compound fits (O’Day et al., 2000) to reduce the total number of adjustable parameters. Amplitude reduction factor ($S_0^2$) was fixed (=1); photoelectron threshold energy difference (AE$_0$) was fit as a single parameter for all shells. Based on empirical fits to reference compounds in previous studies, estimated errors in the EXAFS fit are R ± 0.02 Å; N ± 25% (O’Day et al., 2000; Sahai et al., 2001).

2.5.3. Magic angle spinning nuclear magnetic resonance spectroscopy

$^{29}$Si MAS experiments were preformed on a Varian/Chemagnetics Infinity-500 spectrometer with an 11.7 T magnet (1H resonance frequency of 500 MHz). $^{27}$Al MAS experiments utilized a medium bore 21.1 T magnet and Varian Inova console (1H resonance frequency of 900 MHz). At 11.7 T, a 3.2 mm HX double-resonance MAS probe was used at a frequency of 234.653 MHz for $^{29}$Si measurements, while at 21.1 T a homebuilt probe with
a Varian 3.2 mm MAS stator assembly was used. The $^{27}$Al resonance frequency was 243.653 MHz at 21.1 T. Single-pulse $^{27}$Al-free induction decays (FID) were acquired after a radio frequency pulse of 0.6 μs (corresponding to an approximate tip angle of $\pi/20$). The spinning rate was approximately 20 kHz, and for each sample 4800 transients were acquired using a recycle delay of 1 s. The FIDs were processed with Fourier transformation following the application of an exponential weighting equivalent to 50 Hz of Lorentzian line broadening. The $^{27}$Al shifts (in ppm) were referenced to the octahedral $^{27}$Al resonance from a 1 M aqueous sample of AlCl$_3$. For the $^{29}$Si MAS experiments, a total of 1200 transients were acquired from each sample with MAS rates of 15 kHz and recycle delays of 60 s. Time-domain data were processed with Fourier transformation following the application of an exponential weighting equivalent to 300 Hz of Lorentzian line broadening. The $^{29}$Si shifts (in ppm) were referenced to the $^{29}$Si resonance from neat tetramethylsilane (TMS) through a secondary reference of tetrakis(trimethylsilyl)silane (which displays resonances at $-9.6$ and $-135.2$ ppm with respect to TMS).

2.5.4. Additional solid phase characterizations

For scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDS), freeze-dried sediments were mounted and gold sputtered (Technics, Inc.) for 1–2 min to minimize charging under the electron beam. All samples were examined with a Phillips XL 20 SEM with a secondary electron detector and KeVex EDS between 17 and 22.5 kV. Selected, uncoated sediment samples were analyzed by FEI XL 30 EFSEM with EDS at 30 kV with a probe diameter 0.4 nm. Reacted and AAO-treated sediments were also analyzed on a Nicolet Magna 560 FTIR spectrometer across the frequency range 4000–400 cm$^{-1}$ (optical resolution of 4 cm$^{-1}$) to obtain diffuse reflectance infrared Fourier transform (DRIFT) spectra. Samples were prepared by gently grinding 9 mg of freeze-dried sediment with 441 mg of ground analytical grade KBr crystals.

3. RESULTS

3.1. Sediment composition

Hanford Coarse (HC) sediment derives its name from the field condition that includes a large gravel fraction (430 g kg$^{-1}$) (Serne et al., 2002a). This gravel was removed during sieving to obtain the <2 mm size fraction prior to the laboratory studies. This made the texture more like Hanford Fine (HF), which originally contained only 2 g kg$^{-1}$ gravel, and only smaller differences between the sediments remained following sieving (Table 1). After sieving, HC had more sand than did HF, whereas HF had more silt plus clay (Table 1), so the names “Hanford Coarse” and “Hanford Fine” were retained. Despite this textural difference, measurements using dinitrogen BET (for “external” surface area) and EGME (for “total” surface area, including expansible clay interlayers) indicate that both SSA indices decrease in the order RS > HC > HF (Table 1).
However, RS and HF both have higher ratios of “total” to “external” surface area (ca. 3.6) than does HC (ca. 3.0), consistent with their higher content of fine (silt plus clay) particles.

The dominant minerals in all sediments are quartz, K-feldspar (microcline and orthoclase), plagioclase (albite, anorthite), biotite/illite, pyroxene and chlorite/smectic/vermiculite. Quartz, K-feldspar and plagioclase dominate the XRD patterns, possibly obscuring identification of other minerals including calcite, whose highest intensity peak is close to that of feldspar. HC and HF contain more quartz and plagioclase than RS (Table 1), consistent with their larger particle size distributions. Between HC and HF, XRD indicate that HF contains more quartz and slightly more feldspar and plagioclase, whereas HC contains more biotite and pyroxene. Semi-quantitative XRD analysis of the clay fraction indicates that the most abundant clay minerals are smectite, illite and chlorite, with smaller amounts of kaolinite. Sediments are similar in clay mineral composition, with the exception that RS sediments has a relatively high quantity of illite and no detectable kaolinite. Bulk chemical composition of the sediments indicates the presence of native strontium (Table 1). An 8 M HNO₃ extraction of the sediments solubilized 0.02, 0.05 and 0.04 g kg⁻¹ of Sr²⁺ from HC, HF and RS, respectively, which is about 5–25% of the total Sr²⁺ reported in Table 1. Cesium was not detected in the XRF of unreacted sediments, but trace levels were measured following lithium metaborate fusion. Further details regarding physical–chemical and mineralogical characterization of these same uncontaminated Hanford and Ringold sediments are reported elsewhere (Rotenberg, 2002; Serne et al., 2002a).

3.2. Sediment dissolution and secondary phase precipitation

Following reaction with STWL, we measured close agreement between element concentrations in the <2 μm and the <0.2 μm suspension fractions (with the exception of Fe, which was slightly elevated in the <2 μm fraction). Hence, a stable colloidal pool of aluminosilicate particles >200 nm—that could have contributed to colloid-mediated contaminant mobilization in pure STWL fluids at the field scale—was not detected, and the dissolved fraction is predominant. Evidently, colloid-sized, neoformed precipitates (discussed below) were bound to the surfaces of the centrifuged sediment grains or flocculated at the high ionic strength of the STWL solution. Because the colloid fraction was insignificant, further results and discussion are limited to data on the dissolved fraction.

Concentrations of dissolved hydroxide were relatively constant measuring ca. 0.7 m in all systems with no clear time-dependent decreases. Close agreement in [OH⁻] between sediment–STWL systems and sediment-free controls (with and without Al) indicates that OH⁻ was present in excess, and reaction with sediments did not significantly diminish its concentration over the one-year reaction period. Although CO₂ was excluded from the solutions during preparation, some diffusion into the reaction vessels may have occurred during the experiment and inorganic carbon may have also dissolved from carbonates that were present at mass concentrations ranging from 1% to 3% in the sediments (Table 1). The highest concentration of dissolved inorganic carbon (DIC) measured in solution at the onset of reaction was 0.5 mmol kg⁻¹, whereas after 12 months the highest value measured was 1.3 mmol kg⁻¹. As mentioned in Section 2.4, GMIN calculations indicated that initial solutions containing 0.5 mmol kg⁻¹ were slightly oversaturated (logΩ = 0.58) with respect to SrCO₃(s) when all Sr²⁺ was present in solution at its highest concentration (10⁻³ m). However, no precipitation was observed in the corresponding sediment-free controls for the duration of the experiment. Following initial mixing of STWL with sediment all solutions were undersaturated with respect to SrCO₃(s) because of sorptive uptake. Systems containing lower initial Sr²⁺ concentrations were always undersaturated with respect to SrCO₃(s).

Soluble Si and Al exhibited similar trends for HC, HF and RS sediments at all initial Cs⁺ and Sr²⁺ concentrations. In most cases, the concentration of soluble Si and Al reached a maximum at 29 d (92 d for soluble Si in HF sediment) and decreased subsequently over the remaining reaction period (Figs. 1 and 2, left side). Coincident with the decline of Si and Al in the aqueous phase is an increase in the acid ammonium oxalate (AAO) extractable Si and Al in the solid phase (Figs. 1 and 2, right side). The largest conversions of dissolved to AAO-extractable Si and Al occurred for RS followed by HC and then HF. The mass ratio of AAO-extractable Al or Si generated in the HF/HC/RS sediments was, on average, 1.2/4/3.3. That is, relative to HF, more than twice as much conversion occurred in HC and three times as much in RS. These transformation trends follow differences in SSA. After 374 d, the amount of dissolved Si in all systems had decreased to a concentration equal to or less than that in solution after only 1 d.

Removal of soluble Al and Si from solution was concurrent, consistent with co-precipitation into an AAO-extractable secondary phase that is relatively insoluble in STWL. The amount of dissolved plus AAO-extractable Al in the sediment–STWL systems never exceeded the amount of dissolved Al in the sediment-free controls, which indicates that net Al dissolution was negligible and Si release from the sediments limits co-precipitation of aluminosilicate neophases. Molar Si/Al ratios of AAO-extractable material remained relatively constant after 90 d and ranged from 0.7 to 0.9 after one year of reaction. Iron partitioning followed trends similar to that shown for Si, but dissolved Fe reached a maximum earlier in the reaction (ca. 2 mmol kg⁻¹ released at 7 d), and the AAO-extractable Fe mass peaked at 183 d of reaction (130, 70 and 90 mmol kg⁻¹ for HC, HF and RS, respectively), and then decreased by about 20–30% thereafter (not shown). GMIN speciation calculations indicated that, at the time of maximum dissolved Si, solutions were oversaturated with respect to hydroxy-sodalite dihydrate, Na₈(AlSiO₄)₆(OH)₂·2H₂O(s) and goethite, α-FeOOH.

Mineral weathering and precipitate formation on surfaces of all sediments were evident by scanning electron microscopy (SEM) after 183 d. Clusters of round, interpenetrating discs with sharp edges extending in three dimensions were observed on particles of 1–2 μm in size (data
Bulk XRD analysis of reacted sediments did not provide clear evidence of neoformed crystalline solid phases before 374 d because of peak overlap with sediment minerals. Neoformed precipitates were detected by bulk XRD at 374 d in HC and RS at $10^{-5}$ and $10^{-3}$ mol kg$^{-1}$ Cs/Sr, whereas none were detected in HF. Diffractogram peaks were identified as sodium aluminum nitrate silicate hydrate (feldspathoid cancrinite, Na$_8$(AlSiO$_4$)$_6$(NO$_3$)$_2$(H$_2$O), d-spacing 3.24 Å) and sodium aluminum nitrate silicate (feldspathoid sodalite, Na$_8$(AlSiO$_4$)$_6$(NO$_3$)$_2$, d-spacing 3.66 Å).

Fig. 1. (a–c) Aqueous Si in STWL and (d–f) Si extracted by AAO from 1 to 374 d. Top to bottom: initial solution concentrations of $10^{-5}$, $10^{-4}$ and $10^{-3}$ mol kg$^{-1}$ Cs/Sr.

not shown).
induced alteration in relative abundances of silicate species. The quartz phase appears to decrease with reaction time, whereas solid phase precipitation introduces new resonances in the spectral region from $-75$ to $-105$ ppm (consistent with feldspathoid neoformation). $^{27}$Al spectra, acquired at 21.1 T for the highest possible resolution through reduction of the quadrupolar-induced line broadening, are expanded to show only the region that contains resonances from four-coordinate aluminum species, since these change markedly as a function of time and treatment (Fig. 3b–d). Loss of octahedral Al signal (ca. 0 ppm) is also detectable (not shown), but a large background from trace amounts of alumina contained in the zirconia rotors used in these experiments prohibits accurate quantification.

Spectral deconvolution indicates an increase in resonance intensity attributable to feldspathoid phases at ca. 62 ppm (Crosson et al., 2006) with increased sediment weathering time. An overall loss in spectral intensity of the peak at ca. 58 ppm indicates dissolution of a measurable amount of the native tetrahedral Al in the HF sample.
Similar changes in spectral intensity are noted in the weathered RS sample, which shows an additional resonance from unreacted material at greater than 70 ppm. While this latter peak has not yet been identified, it does not change significantly in intensity during the weathering process. As with HF, feldspathoid peak intensity (ca. 62 ppm) for RS increases as a function of weathering time. A resonance at ca. 58 ppm that also gains intensity (approximately doubling in area) has been previously assigned to formation of a putative high-aluminum chabazite (zeolite) phase (Crosson et al., 2006) in STWL-kaolinite systems. Additional spectral intensity is also gained between 65 and 70 ppm, consistent with resonances previously identified as arising from an unknown, possibly amorphous, neophase in weathered kaolinite systems. Calculations based on a two-peak deconvolution of the spectra reveal that the high frequency and low frequency peaks both increase in intensity by approximately 200%. The degree of neophase formation is slightly retarded in the HF sample weathered with lower concentrations of Cs⁺ and Sr²⁺ co-contaminants; the growth of feldspathoid resonances (at 62 ppm) is only half as great as in the sample weathered under higher co-contaminant concentrations.

Diffuse reflectance infrared Fourier transform (DRIFT) data of STWL-reacted HC, HF, and RS samples show distinct changes in vibrational absorption features with longer aging time but little effect from different initial Cs⁺ and Sr²⁺ concentrations. With increasing reaction time (bottom to top in Fig. 4, 10⁻³ m Cs⁺/Sr²⁺), the most intense Si–O–Si(Al) stretching band in HC sediments increased in intensity and shifted to lower frequencies from ca. 1030 to 1000 cm⁻¹, the latter observation indicating accumulation of neoformed aluminosilicate weathering products with molar Si/Al ratios ≤1 (Milkey, 1960; Ming and Mumpton, 1989). New absorption bands at 1380 and 1420 cm⁻¹ begin to appear as early as 93 d in HC and RS (prior to XRD-detectable precipitates), and are intense in all sediments by 374 d. These bands, in addition to a broad shoulder at 1480 cm⁻¹, are indicative of nitrate-containing secondary solids; inorganic nitrate has strong asymmetric stretching bands in the region of 1300–1550 cm⁻¹ (Nyquist et al., 1997; Socrates, 2001). Nitrate-cancrinite (identified by XRD after 374 d reaction) has sharp IR bands at 1380, 1420 and 1440 cm⁻¹ (Buhl and Lons, 1996; Buhl et al., 2000) and nitrate-sodalite is characterized by a sharp band at 1380 cm⁻¹ (Buhl and Lons, 1996). Absorption bands observed in the DRIFT spectra of reacted HC, HF and RS sediments are, therefore, consistent with neoformed nitrate-sodalite and -cancrinite. Bands at 729 and 661 cm⁻¹, associated with nitrate (N–O) in-plane bending (Nyquist et al., 1997; Socrates, 2001), also appeared with increasing reaction time (Fig. 4).
Elemental analysis by EDS showed Si and Al at similar abundances, followed by O and Na. Other elements present in smaller quantities included K, Ca, Mg, and Fe. The presence of Cs and Sr was detected in spheroidal particles including some with relatively high concentrations of Cs (Fig. 5). A notable difference between unreacted and reacted sediments was an increase in Na in the reacted sediment particles.

3.3. Metal cation uptake during sediment weathering

Cesium and Sr$^{2+}$ exhibited distinctly different uptake patterns as a function of reaction time (Fig. 6). The Cs$^+$ and Sr$^{2+}$ data are plotted on common scales for each initial contaminant concentration to facilitate comparison. The term sorption is defined here to include all adsorption and co-precipitation processes resulting in removal from aqueous solution to the solid phase (Sposito, 2004). Maximum values on the Y axes (0.5, 5, and 50 mmol kg$^{-1}$) are those that would be measured for complete sorptive removal from solution. Thus, while Sr$^{2+}$ uptake consistently approaches 80–90% at all loadings after one-year reaction time (Fig. 6d–f), Cs$^+$ uptake is lower, ranging from 20–40% at low Cs$^+$ concentrations in solution (Fig. 6a) to 10–20% at higher solution concentrations (Fig. 6b and c). Although limited in extent, Cs$^+$ uptake was rapid initially, with little or no further accumulation with time. Strontium uptake was also rapid initially, with 40–80% sorption occurring within the first 7 d. However, in this case and particularly at the higher solution concentrations of $10^{-3}$ and $10^{-4}$ m, rapid sorption was followed by prolonged uptake that occurred over several months, with maximum values being reached only after one-year reaction time. Furthermore, the fraction of total uptake that results from prolonged sorption increases with Sr$^{2+}$ concentration (i.e., going from Fig. 6d–f).

The distribution of sorbed Cs$^+$ and Sr$^{2+}$ among (i) exchangeable, (ii) poorly crystalline and (iii) residual pools is defined operationally as follows: (i) desorption in 0.1 m Mg(NO$_3$)$_2$, (ii) desorption in 0.2 m AAO, and (iii) solid phase retention. The distribution of total sorbed Cs$^+$ and Sr$^{2+}$ at all initial concentrations is shown as a function of...
reaction time in Figs. 7 and 8. Whereas Fig. 6 shows that Sr$^{2+}$ uptake significantly exceeds that of Cs$^+$, the extraction data show that sorbed Cs$^+$ is relatively resistant to ion exchange with Mg$^{2+}$, and that a substantial residual Cs$^+$ pool persists following AAO dissolution of poorly crystalline solids (Fig. 7). Conversely, a large fraction of sorbed Sr$^{2+}$ is readily desorbed in Mg(NO$_3$)$_2$ solution at early reaction times, but becomes increasingly recalcitrant to desorption with increased reaction time (Fig. 8). Consistent across all of the experiments is a transient residual Sr$^{2+}$ pool at 7 d that disappears by 29 d in favor of a large AAO-extractable pool. This is followed by a subsequent increase in size of the residual pool. The total mass of Sr$^{2+}$-extracted never exceeded the amount added in the STWL solution. This indicates that Sr$^{2+}$ native to the unreacted sediments (dominantly in feldspars) did not contribute detectably to these measurements of lability.

3.4. Microscale strontium incorporation

Given the apparent influence of mineral transformation on Sr$^{2+}$ uptake, further studies were conducted to resolve Sr$^{2+}$ partitioning and speciation in the weathered sediments. In order to minimize peak interference from the bulk sediment minerals, synchrotron microfocused ($\mu$)-XRF and -XRD were used to examine dispersed particles. Sample regions were mapped for Sr$^{2+}$ and Fe fluorescence to identify areas of the sample with high Sr$^{2+}$. Cesium fluorescence could not be resolved. Fig. 9 shows $\mu$-XRF maps and $\mu$-XRD patterns of sediments reacted for 374 d at the highest contaminant concentrations ($10^{-3}$ m). The Sr$^{2+}$-containing areas identified in each sample are around 100 $\mu$m. Given that SEM shows individual particle sizes on the order of 1–5 $\mu$m, these areas are most likely particle aggregates. However, the area sampled by the beam is still considerably smaller ($7 \times 7$ or $7 \times 16$ $\mu$m) than the imaged high Sr$^{2+}$ areas. The $\mu$-diffractograms indicated the presence of mostly sodalite and cancrinite in addition to detrital quartz and feldspar. Microfocused XRF and XRD data collected on 374 d reacted samples after AAO extraction indicate the persistence of Sr$^{2+}$ associated with cancrinite and sodalite (Fig. 9). Diffractograms were more complex for these samples, however, with peaks indicating the presence of quartz, plagioclase/K-feldspar and clays in addition to sodalite and cancrinite within the particle aggregates. In the AAO-extracted samples, some particles with high Sr$^{2+}$ may be detrital feldspar minerals with native Sr$^{2+}$, as was measured in the bulk analyses of unreacted sediments.

3.5. Strontium coordination environment

Analysis of bulk Sr EXAFS spectra for HC, HF, and RS sediments after 369 d of reaction provides information on the average structural coordination of sequestered Sr$^{2+}$. In HC and HF sediments, EXAFS indicates the presence of a fraction of Sr$^{2+}$ associated with SrCO$_3$(s) (Fig. 10 and Table 2, shaded areas), which was below detection by XRD. The RS spectra showed no evidence for SrCO$_3$(s). Because of the strong backscattering characteristic of the SrCO$_3$(s) structure, its presence tends to dominate the bulk EXAFS spectrum even when it is not a major component. After the Mg-exchange and AAO extraction step, all
SrCO₃(s) was removed from sample spectra and remaining Sr²⁺ is associated with neoformed aluminosilicate phases (native Sr²⁺ in the sediments is too low for detection in bulk XAS compared with Sr²⁺ incorporated during reaction for one year). Quantitative fits of AAO-extracted samples give an interatomic Sr–Al/Si distance for HC, HF, and RS between 3.61 and 3.63 Å, which is consistent with Sr²⁺ substitution in the Na(2) site of nitrate cancrinite (Fechtelkord et al., 2001) (Table 2). Shorter Sr–Al/Si distances between 3.28 and 3.35 Å associated with either the Na(1) site of cancrinite (Fechtelkord et al., 2001) or with sodalite (Hasan and Grundy, 1983; Buhl and Lons, 1996) are absent, possibly because of cancellation from backscattering Al/Si atoms at different distances. The RS AAO-extracted spectrum was fit with an additional Sr–Al/Si distance at 4.06 Å that may be associated with a zeolite phase, such as a heulandite-type structure (O’Day et al., 2000). The AAO-extracted spectra also contain backscattering features at distances greater than ~4 Å that are not associated with framework Al/Si atoms. These features can be fit with Sr²⁺ atoms at interatomic distances that are consistent with the presence of heavy atoms in adjacent cation sites in feldspathoid or zeolite cages. Although these sites may be occupied by Na or Ca atoms, backscattering in EXAFS spectra biases toward heavy atoms. The spectra were best fit in most cases assuming Sr²⁺ rather than Cs⁺, Na⁺, or Ca²⁺, although this fit result is not necessarily unique.

In the unextracted HC and HF spectra, backscattering from SrCO₃(s) dominates the EXAFS and masks the neoformed phases, but does not exactly match the spectra.

---

**Table 2**

<table>
<thead>
<tr>
<th>Reaction time (d)</th>
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<th>AAO Extractable</th>
<th>Residual</th>
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</tr>
<tr>
<td>374</td>
<td>374</td>
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</tr>
</tbody>
</table>

**Fig. 7.** Cesium partitioning determined by sequential extractions of HC, HF and RS sediments following reaction with STWL from 1 to 374 d. Initial Cs/Sr solution concentrations of (top to bottom) 10⁻⁵, 10⁻⁴ and 10⁻³ mol kg⁻¹. Left to right: HC, HF and RS.
Trial-and-error linear combinations and shell-by-shell fitting indicated the presence of neoformed phases in addition to SrCO$_3$(s); however, the HC and HF spectra could not be fit with a combination of only SrCO$_3$(s) and the AAO-extracted spectrum. Best shell-by-shell fits give two interatomic Sr–Al/Si distances at 3.76–3.79 Å and 4.04–4.08 Å, suggesting the presence of zeolite-type phases. It is likely that Sr–Al/Si backscattering at shorter distances characteristic of feldspathoid-type phases are masked or canceled out. The RS unextracted spectrum (which lacks carbonate), can be fit with three Sr–Al/Si distances and shows evidence for cation–cation backscattering at long interatomic distances (Fig. 10 and Table 2). The lack of similarity in fitted interatomic distances between reacted and AAO-extracted samples suggest the formation of multiple neophases, probably a mixture of zeolites and feldspathoids, of differing crystallinity. The interatomic distances derived from RS fits suggest that zeolite-type phases such as chabazite may be sequestering a greater fraction of Sr$^{2+}$ than in the HC and HF spectra, which is consistent with the $\text{}^{27}$Al NMR data reported above.

3.6. Contaminant desorption from weathered sediments

The use of three different initial co-contaminant concentrations during a 12-month uptake period permitted the measurement of subsequent Cs$^+$ and Sr$^{2+}$ desorption kinetics as a function of initial sorbed contaminant concentra-
Fig. 9. Microfocused XRF maps and XRD patterns of Sr-rich particles observed in (a) HC, (b) HF and (c) RS after 374 d reaction (top of each) and the same samples are subjected to AAO extraction (bottom of each). Samples reacted at $10^{-3}$ m Cs/Sr. Electron diffraction patterns are shown in inset to XRF image.
ion composition (Table 3). As indicated by comparison of the left and right sides of Figs. 10 and 11, Cs + desorption is generally greater in KCl relative CaCl 2 solution, whereas the inverse trend is observed for Sr 2+ release. This effect is characterized quantitatively by the rate coefficient ratios \( k_{\text{KCl}} / k_{\text{CaCl}_2} \) in columns 5 and 8 of Table 3. In both electrolyte solutions, initial Cs + desorption rate constant \( k_{\text{Cs}^+} \) values were significantly lower at the lowest sorbed concentrations for all three sediments. No such trend was observed for Sr 2+.

4. DISCUSSION

Within a two-dimensional field defined by (i) the quantity of sorbate and (ii) reaction time, uptake of Sr 2+ and Cs + from STWL to Hanford sediments involves a transition from adsorption to incorporation within neoformed aluminosilicates. The transition to co-precipitation is more significant for Sr 2+ than for Cs +, but both ions are incorporated into neophases. Distinguishing uptake mechanisms is facilitated by the use of three sediment types, three co-contaminant concentrations, and a time series of macroscopic and spectroscopic measurements along the reaction path. The data suggest that adsorption is favored by low (<10^{-4} m) contaminant concentrations and short (<30 d) reaction times, whereas at longer times and higher concentrations mineral transformation exerts a dominant control.

Evidence for adsorption to native particle surfaces at short times and low sorbate concentrations includes rapid Sr 2+ and Cs + uptake prior to the onset of aluminosilicate precipitation at 29 d (Fig. 6). A positive relation between adsorbed ion mass \( q \) and clay plus silt content or CEC was also observed at times <29 d and at contaminant concentrations \( \leq 10^{-4} \) m, indicating that phyllosilicates likely play an important role in contaminant uptake under these conditions. The Sr 2+ sorbed during this time was largely exchangeable. The fact that Sr 2+ became increasingly resistant to extraction after 29 d (Fig. 8) indicates that it was either occluded by—or incorporated into—the neoformed precipitates.

At longer times and higher sorbate concentrations, sorption—desorption of Sr 2+ and (to a lesser extent) Cs + is coupled to the precipitation of Si that is triggered by hydroxide attack on sediment minerals. After 29 d (92 d for soluble Si in HF sediments, which showed the lowest overall dissolution—precipitation), a decrease in dissolved Si and Al concentrations was coincident with a large increase in AAO-extractable Si and Al (Figs. 1 and 2) signaling the formation of secondary aluminosilicate solids. Slower dissolution of HF relative to HC sediments may be due to lower SSA and higher quartz relative to biotite and pyroxene contents of the former. In hyperalkaline systems, quartz dissolution rates have been shown to be significantly decreased (as much as 85%) when Al(OH) 4 is present at concentrations below gibbsite solubility (Bickmore et al., 2006). The contribution of biotite and pyroxene to Si release in HC is suggested by the fact that Fe release to solution and incorporation into AAO-extractable form was also highest for this sediment relative to HF and RS (not shown).

Spectroscopic evidence of nitrate-bearing cancrinite and sodalite solids (e.g., Figs. 3–5 and 9, 10) is consistent with prior studies of STWL-type solutions reacted with Hanford sediments (Qafoku et al., 2003b; Mashal et al., 2005a), specimen clays (Chorover et al., 2003; Choi et al., 2005b) and quartz sand (Bickmore et al., 2001). The neoformation of aluminosilicate precipitates has also been observed in proximity to documented hyperalkaline tank leaks at the Hanford Site (Zachara et al., 2004). Cancrinite, sodalite and related feldspathoid phases are known to form under highly alkaline conditions and in the presence of soluble Si, Al and nitrate (Buhl and Lons, 1996; Barnes et al., 1999; Buhl et al., 2000; Mashal et al., 2005b). Their crystal structures are microporous, containing channels and cages with a large number of extraframework sites that can sorb cations, anions and/or water (Grundy and Hassan, 1982; Hassan and Grundy, 1991; Meier and Olson, 1992; Zheng et al., 1997; Barnes et al., 1999). Sorption to these neoformed aluminosilicates affected Sr 2+ and (to a lesser extent) Cs + partitioning behavior and release, which in turn likely impact contaminant mobility in subsurface sediments of the Hanford Site.
4.1. Cesium partitioning dynamics

The observation of rapid and reproducible Cs⁺ uptake (10–40%) in all experiments, despite the much higher (2 m) background Na⁺ concentration (Fig. 6), indicates a limited density of sorption sites selective for Cs⁺. These include frayed edge sites (FES) and interlayers of 2:1 layer type mica, illite and vermiculite (Sawhney, 1970; Cornell, 1993; Steefel et al., 2003; McKinley et al., 2004). According to Fig. 6a, the amount of Cs⁺ sorbed from low initial concentrations, and hence the availability of high affinity sites, increased in the order HC < HF < RS. The fact that clay plus silt content and CEC increase in the same order (Table 1) suggests that the well-known Cs selectivity of phyllosilicate type mica, illite and vermiculite (Sawhney, 1970; Cornell, 1993; Steefel et al., 2003; McKinley et al., 2004).

<table>
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<th>Sample</th>
<th>Sr EXAFS*</th>
<th>SrCO₃(s): XRDb</th>
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<tr>
<td></td>
<td>Z</td>
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<tr>
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<tr>
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* Z is the backscatterer atom; N is the number of backscattering atoms at distance (R); σ² (Debye–Waller term) is the absorber-backscatterer mean-square relative displacement (fixed on values estimated from fits to reference compounds); ΔE₀ is the energy shift in the least-squares fit; χ² is a reduced least-squares goodness-of-fit parameter (= (F-factor)/(no. of points – no. of variables)); scale factor (S₀) fixed on values estimated from fits to reference compounds.

b Crystallographic distances for SrCO₃(s) from X-ray diffraction studies: R₁—interatomic distances from Pannhorst and Lohn (1970); R₂—interatomic distances from Devillers (1971).

c Parameter varied in least-squares fit/parameter proportionally linked in least-squares fit to preceding value in table based on crystal structure stoichiometry.

d Sample after extraction with acid ammonium oxalate (AAO).
sorbents at low Cs$^+$ sorbate concentrations (Jeong et al., 1996; Wauters et al., 1996; Sutton and Sposito, 2002) is applicable even under the extremely high ionic strength and pH conditions imposed. The non-labile (residual) pool of sorbed Cs$^+$ also increases in the order HC > HF > RS (see top three graphs in Fig. 7 $[Cs^+]_0 = 10^{-5}$ m). A high fraction of sorbed Cs$^+$ was not extractable under the experimental conditions employed, even after just 24 h of reaction time. Semi-quantitative analysis by XRD indicates that the fine earth (<2 mm) fraction of Hanford sediments...
Table 3
First-order desorption rate coefficients for biphasic cesium and strontium desorption in 10 mM KCl and 5 mM CaCl₂ solutions (pH 8) as a function of sorbed mass following 12 months of weathering in STWL

<table>
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<th>Sediment</th>
<th>$q_{Cs,0} \pm sd$ (mmol kg$^{-1}$)</th>
<th>$k^1_{Cs,KCl} \pm sd$ (s$^{-1}$)</th>
<th>$k^1_{Cs,CaCl_2} \pm sd$ (s$^{-1}$)</th>
<th>$k^1_{Cs,CaCl_2} k^1_{Cs,KCl}$</th>
<th>$k^2_{Cs,KCl} \pm sd$ (s$^{-1}$)</th>
<th>$k^2_{Cs,CaCl_2} \pm sd$ (s$^{-1}$)</th>
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<td><strong>Cesium desorption kinetics</strong></td>
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<tr>
<td>HF</td>
<td>8.7 (±0.99)</td>
<td>1.8 (±0.29) E–06</td>
<td>0.7 (±0.11) E–06</td>
<td>0.37</td>
<td>3.2 (±0.64) E–08</td>
<td>5.7 (±0.77) E–08</td>
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<td>1.2 (±0.23)</td>
<td>1.59 (±0.033) E–06</td>
<td>0.7 (±0.12) E–06</td>
<td>0.46</td>
<td>5.2 (±0.85) E–08</td>
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<td>0.295 (±0.007)</td>
<td>0.72 (±0.070) E–06</td>
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<td>0.22</td>
<td>18 (±2.8) E–08</td>
<td>11 (±1.1) E–08</td>
<td>0.57</td>
</tr>
<tr>
<td>RS</td>
<td>1.5 (±0.11)</td>
<td>2.01 (±0.019) E–06</td>
<td>1.2 (±0.19) E–06</td>
<td>0.61</td>
<td>7 (±1.3) E–08</td>
<td>10 (±3.2) E–08</td>
<td>1.4</td>
</tr>
<tr>
<td>RS</td>
<td>0.335 (±0.0081)</td>
<td>1.2 (±0.18) E–06</td>
<td>&lt;0.01 E–6</td>
<td>&lt;0.01</td>
<td>3.7 (±0.67) E–08</td>
<td>&lt;1E–8</td>
<td>&lt;0.27</td>
</tr>
<tr>
<td><strong>Strontium desorption kinetics</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HF</td>
<td>43.0 (±0.15)</td>
<td>3.6 (±0.7) E–06</td>
<td>9 (±2.9) E–06</td>
<td>2.5</td>
<td>11.4 (±0.5) E–07</td>
<td>22 (±1.0) E–07</td>
<td>1.9</td>
</tr>
<tr>
<td>HF</td>
<td>4.47 (±0.029)</td>
<td>4 (±2.1) E–06</td>
<td>15 (±9.9) E–06</td>
<td>3.4</td>
<td>1.9 (±0.16) E–07</td>
<td>2.3 (±0.32) E–07</td>
<td>1.2</td>
</tr>
<tr>
<td>HF</td>
<td>0.469 (±0.0013)</td>
<td>4 (±1.4) E–06</td>
<td>20 (±10) E–06</td>
<td>5.4</td>
<td>2.0 (±0.16) E–07</td>
<td>2.1 (±0.43) E–07</td>
<td>1.1</td>
</tr>
<tr>
<td>HC</td>
<td>34 (±4.5)</td>
<td>0.7 (±0.18) E–06</td>
<td>8 (±1.3) E–06</td>
<td>11</td>
<td>0.74 (±0.074) E–07</td>
<td>4.6 (±0.57) E–07</td>
<td>6.3</td>
</tr>
<tr>
<td>HC</td>
<td>4.16 (±0.093)</td>
<td>0.5 (±0.22) E–06</td>
<td>12 (±4.6) E–06</td>
<td>25</td>
<td>0.56 (±0.033) E–07</td>
<td>6.3 (±0.83) E–07</td>
<td>11</td>
</tr>
<tr>
<td>HC</td>
<td>0.462 (±0.0077)</td>
<td>0.5 (±0.23) E–06</td>
<td>13 (±3.3) E–06</td>
<td>27</td>
<td>0.65 (±0.073) E–07</td>
<td>4.4 (±0.78) E–07</td>
<td>6.8</td>
</tr>
<tr>
<td>RS</td>
<td>39 (±2.74)</td>
<td>4 (±2.2) E–06</td>
<td>9 (±5.7) E–06</td>
<td>2.1</td>
<td>1.3 (±0.142) E–07</td>
<td>2.8 (±0.28) E–07</td>
<td>2.2</td>
</tr>
<tr>
<td>RS</td>
<td>4.67 (±0.021)</td>
<td>0.6 (±0.22) E–06</td>
<td>8 (±3.7) E–06</td>
<td>13</td>
<td>0.29 (±0.028) E–07</td>
<td>1.7 (±0.27) E–07</td>
<td>5.9</td>
</tr>
<tr>
<td>RS</td>
<td>0.480 (±0.0013)</td>
<td>0.6 (±0.25) E–06</td>
<td>9 (±3.1) E–06</td>
<td>15</td>
<td>0.25 (±0.032) E–07</td>
<td>1.3 (±0.30) E–07</td>
<td>5.1</td>
</tr>
</tbody>
</table>

$^a$ Values for $k^1$ are calculated from initial 0 to 6 h desorption data, whereas $k^2$ values are calculated from 6 to 240 h desorption data, as a function of initial sorbed mass ($q_0$) following sediment weathering for 12 months.
contains ca. 20–60 g kg\(^{-1}\) biotite, whereas the isolated clay (<2 μm) fractions contain ca. 15, 15 and 35 g kg\(^{-1}\) illite for HC, HF and RS, respectively (Serne et al., 2002a). Thus, the higher clay and illite content of RS relative to HC and HF explains the higher Cs\(^{+}\) uptake (Fig. 6a) and strong retention (Fig. 7, top) on this sediment at low initial Cs\(^{+}\) concentration. Likewise, Zachara et al. (2002) observed high Cs\(^{+}\) selectivity in ion exchange experiments conducted on Hanford sediments at high ionic strength, but at circumneutral pH.

The influence of mineral transformation by OH\(^{-}\) attack is most apparent at high initial Cs\(^{+}\) concentration (10\(^{-5}\) m) after 29 d. Under these conditions, the amount of Cs\(^{+}\) sorbed increased in the order HF < HC < RS (Fig. 6c), which does not trend directly with clay plus silt content or CEC, but rather with SSA and the rate of Si dissolution and precipitation (Fig. 1f). Furthermore, despite much higher sorbate concentration, the Cs\(^{+}\) sorbed to HC and HF was also partitioned into more recalcitrant forms (Fig. 7, bottom), suggesting that another mechanism for Cs\(^{+}\) sorption is operative at this higher sorbate concentration. Based on a kinetic model, Cs\(^{+}\) diffusion into illite interlayers has been calculated to proceed at less than 1 nm year\(^{-1}\); at shorter time intervals Cs\(^{+}\) is mainly confined to FES (Comans et al., 1991). Thus, the residual pool (Fig. 7) could comprise Cs\(^{+}\) sorbed to high affinity FES sites and/or that incorporated into non-extractable neoformed solids.

Zachara et al. (2002) used multi-site sorption modeling to calculate that FES make up 0.03–0.08% of the Hanford sediment CEC. Although it is likely that FES densities were underestimated, Cremers and coworkers reported K\(^{+}\) desorption data; the fractional release of Cs\(^{+}\) is much lower than the FES (Cremers et al., 1988). Thus, the residual pool (Fig. 7) could comprise Cs\(^{+}\) sorbed to high affinity FES sites and/or that incorporated into non-extractable neoformed solids.

The competitive effect of K\(^{+}\) is exemplified by the greater fractional Cs\(^{+}\) desorption from one-year reacted sediments when K\(^{+}\) (Fig. 11c and d) rather than Ca\(^{2+}\) (Fig. 11a and b) is present in solution at pH 8. The influence of high affinity (e.g., FES) sites is also apparent from the desorption data; the fractional release of Cs\(^{+}\) is much lower at lower sorbate concentrations. The ratios of first order rate coefficients (\(k_{0}^{\text{KCl}}/k_{0}^{\text{CaCl}}\)) for both phases of desorption—approach zero at the lowest initial Cs\(^{+}\) concentrations (Table 3). This further illustrates the importance of site selectivity for trace levels of Cs\(^{+}\) at the Hanford Site, where Ca\(^{2+}\) is the predominant cation in background pore waters (Dong et al., 2005). Greater release at higher sorbate concentrations, particularly in the presence of K\(^{+}\), indicates that the augmentation of sorption associated with aluminosilicate precipitation can be diminished after removal of the caustic source, at a rate that depends on the identity of cations in solution.
4.2. Strontium partitioning dynamics

Sorption of Sr\(^{2+}\) exhibited partitioning that was strongly dependent on reaction time and sorbate amount. At low initial Sr\(^{2+}\) concentrations, most (55–80\%) of the Sr\(^{2+}\) uptake occurred within the first 7 d of reaction, and during this time the sorbed amount increased with sediment clay plus silt content (RS > HF > HC, Fig. 6d). With increasing initial Sr\(^{2+}\) concentration (Fig. 6d–f), the fraction removed within the first 7 d was reduced, while the portion removed between 29 and 374 d (i.e., beginning immediately after the onset of Si precipitation) was increased significantly. At the highest Sr\(^{2+}\) concentration, the amount of Sr\(^{2+}\) sorbed trended with clay plus silt content only for the first two sampling periods (1 and 7 d), and thereafter it increased in the order HF < HC < RS, which follows the SSA (Table 1) and Si dissolution and precipitation (Fig. 1) trends.

The gradual increase in Sr\(^{2+}\) uptake over time in the sediment–STWL systems after 29 d was apparently due to sediment Si dissolution that promoted aluminosilicate co-precipitation because the mass of AAO-extractable Si and Al increased over the same reaction time (Figs. 1 and 2). In most cases, the additional Sr\(^{2+}\) uptake is largely complete by 180 d (Fig. 6) although incongruent silicate weathering continues to 374 d (Figs. 1 and 2). A plot of sorbed Sr\(^{2+}\) (q\(_{Sr}\)) versus precipitated Si and Al clearly shows that most of the “longer-term” Sr\(^{2+}\) uptake occurs during precipitation of the first few hundred millimoles per kilogram (Si or Al basis) of aluminosilicate material (Fig. 13a and b). Furthermore, AAO-extractable Si or Al and total Sr\(^{2+}\) sorption continued to increase with reaction time but, unlike bulk Al and Si, the extractable fraction of sorbed Sr\(^{2+}\) decreased after 29 d (Fig. 8). This time-dependent increase in “recalcitrance” of sorbed Sr\(^{2+}\) indicates that the aluminosilicates that formed early in the process (which are also those that sorbed the Sr\(^{2+}\) during their formation) are becoming relatively more resistant to dissolution compared to the total pool of neoformed precipitates. Micro-XRF and -XRD results further support this assertion by showing that Sr\(^{2+}\) is spatially correlated with precipitated nitrate–sodalite and nitrate–cancrinite phases that, after 374 d, are also resistant to decomposition in AAO (Fig. 9). This observation—that Sr\(^{2+}\)-containing feldspathoids are relatively recalcitrant to dissolution—could be because (i) the longer Ostwald ripening time of Sr\(^{2+}\)-containing phases diminishes their solubility relative to the bulk precipitates and/or (ii) incorporation of Sr\(^{2+}\) into the precipitates stabilizes them against AAO attack. In any case, after 374 d, between 70\% and 96\% of the total sorbed Sr\(^{2+}\) was in the residual fraction for all systems, compared to 45–70\% for sorbed Cs\(^+\) (Figs. 7 and 8). Even when the total amount of sorbed Sr\(^{2+}\) had approached a maximum, the amount partitioned into the residual fraction continued to increase with time, which suggests that long-term contact between hyperalkaline HLRW and Hanford sediments may promote the immobilization of contaminant \(^{90}\)Sr\(^{2+}\) in situ.

EXAFS data pertain to the highest initial concentration of Sr\(^{2+}\) (10^{-3}\ m) so that contributions of native Sr\(^{2+}\) can be neglected. Structural results from analyses of bulk Sr
EXAFS spectra are consistent with incorporation of Sr$^{2+}$ into the cation sites of sodalite and/or cancrinite, although spectral results also suggest the presence of zeolite-type phases. Bulk Sr EXAFS analyses indicated the presence of SrCO$_3$(s) in addition to neoformed aluminosilicates in HC and HF sediments reacted for 374 d. SrCO$_3$(s), whose formation was found by GMIN calculations to be favored thermodynamically (solution oversaturation at early reaction time) only at this highest loading case, was not detected in the EXAFS spectra after Mg(NO$_3$)$_2$ plus AAO extractions. The backscattering features associated with the neoformed phases are weak compared to scattering in SrCO$_3$(s), probably because of overlap of backscattering paths from Sr$^{2+}$ bonded in multiple sites and from structural disorder (O’Day et al., 2000). Thus, fractional estimates of Sr-bearing phases are not reliable from the EXAFS spectra. Sequential extraction results indicated that a total 1.2 and 12 mmol kg$^{-1}$ Sr$^{2+}$ were removed by extractions for one-year reacted HC and HF sediments (Sr$^{2+}$ = 10$^{-3}$ m), respectively. This places an upper limit on the amount of Sr$^{2+}$ associated with SrCO$_3$(s) at one year of ca. 5% (for HC) and ca. 30% (for HF) of the total sorbed Sr$^{2+}$, assuming all extracted Sr$^{2+}$ was associated with SrCO$_3$(s). After one year of reaction, sequential extraction of RS sediment indicates that ~25% of sorbed Sr$^{2+}$ is removed after Mg(NO$_3$)$_2$ plus AAO steps, with most removed in the exchangeable Mg(NO$_3$)$_2$ step (Fig. 8). The RS Sr EXAFS indicates no SrCO$_3$(s) in unextracted or extracted spectra. This suggests that the 25% of sorbed Sr$^{2+}$ in the RS sediments is associated with an exchangeable fraction that is not carbonate. If this fraction of Sr$^{2+}$ was present as a hydrated surface complex (i.e., outer-sphere), it would not be detected by EXAFS. However, the RS Sr EXAFS also suggested association of Sr$^{2+}$ with a zeolite-type phases (possibly chabazite or heulandite), which is supported by $^{27}$Al NMR results (Section 3.2). Thus, some of the exchangeable Sr$^{2+}$ in RS sediments, and perhaps also in HF sediments, may be associated with zeolite-type phases that are more readily exchangeable than feldspathoid-type phases, in addition to a surface-adsorbed fraction.

These differences in bonding environment of Sr$^{2+}$ in the three weathered Hanford sediments provide a framework useful to evaluating the potential for Sr$^{2+}$ remobilization subsequent to removal of the caustic HLRW source. Based on the EXAFS and extraction data we conclude that the fraction of sorbed Sr$^{2+}$ in SrCO$_3$(s) decreases in the order HF > HC > RS. Since this trend is consistent with that of Si precipitation rate, it suggests that under the experimental conditions, partitioning of Sr$^{2+}$ between carbonate and aluminosilicate phases depends on the rate at which the Sr$^{2+}$-sequestering silicates are formed. That is, sorption of Sr$^{2+}$ in the neoformed silicates is favored by rapid silicate weathering, whereas carbonate formation is favored by slower weathering rates.

After one year of weathering in STWL, the HF sediment, which contained the largest fraction of carbonate-bound Sr$^{2+}$ at $10^{-3}$ m initial concentration, also exhibited the highest Sr$^{2+}$ desorption rate under all measured conditions (Fig. 12 and Table 3). Hence, the SrCO$_3$(s) pool is expected to be more susceptible to rapid remobilization in background pore waters following removal of the HLRW source. In direct contrast to the case for Cs$^{+}$, greater Sr$^{2+}$ desorption/dissolution was observed in the presence of Ca$^{2+}$ relative to K$^+$ (Fig. 12 and Table 3), which can be attributed to the higher affinity of Ca$^{2+}$ relative to K$^+$ for Sr$^{2+}$ exchange sites in both neoformed aluminosilicates and on native sediment particle surfaces. In particular, phyllosilicates native to the Hanford sediments could potentially have re-adsorbed Sr$^{2+}$ following its release from feldspathoid, zeolite or carbonate-phases, but competitive ion exchange with Ca$^{2+}$ greatly diminishes this effect (McKinley et al., 2007).

Evidently, some Sr$^{2+}$ is desorbing from feldspathoid and/or zeolite sites during these dissolution experiments because the mass removed from all sediments in the presence of Ca$^{2+}$ exceeds that attributable to SrCO$_3$(s) or exchangeable forms. A plot of $q_{sr}$ against Si (Fig. 13c) and Al (Fig. 13d) dissolved during the desorption experiments indicates that a relatively small amount of net Si and Al dissolution has co-occurred with the Sr$^{2+}$ release (in comparison to the precipitated amounts, shown in Fig. 13a and b). The extensive Al dissolution in the RS case suggests the presence of an Al-rich precipitate that is not apparently part of an aluminosilicate structure. In any case, these data suggest that more effective desorption of Sr$^{2+}$ from the weathered sediments in the presence of Ca$^{2+}$ relative to K$^+$ involves a Sr$^{2+}$ → Ca$^{2+}$ exchange reaction in the neophas; their complete dissolution is not required to liberate a fraction of the aluminosilicate-sequestered Sr$^{2+}$. A recent study by McKinley et al. (2007) modeled desorption of Sr$^{2+}$ from caustic HLRW-impacted Hanford sediments as including ion exchange on native (phyllosilicate) mineral surfaces and carbonate dissolution–precipitation reactions. The present work suggests that sorption–desorption reactions associated with neoformed aluminosilicates should also be considered in the context of predicting Sr$^{2+}$ mobility and fate under the unique conditions imposed by caustic waste.

These observations on Sr$^{2+}$ uptake exhibit both similarities and differences with our prior studies of specimen clay systems subjected to weathering in STWL (Chorover et al., 2003; Choi et al., 2005a,b). In contrast to the slow sorptive uptake observed for all sediments (Fig. 6), in model clay systems (kaolinite, montmorillonite, vermiculite and illite) we observed little time-dependency in uptake (removal appeared complete after 24 h) except for kaolinite at the highest ($10^{-3}$ m) Sr$^{2+}$ concentration. This can be attributed to the much higher suspension density of reactive surface sites for cation adsorption in phyllosilicate clay suspensions relative to the heterogeneous Hanford sediments, since both were present at the same solid/solution ratio. For kaolinite reacted with STWL at the highest Sr$^{2+}$ concentration, EXAFS data revealed the formation of transient SrCO$_3$(s) precipitates whose contribution to the spectra diminished over time as Sr$^{2+}$ was transferred into the more slowly forming, and apparently more stable, feldspathoids (Choi et al., 2006). Those results are consistent with the present study in that they emphasize the importance of mineral dissolution rate—particularly Si release and reprecipitation—in controlling the coordination environment of sorbed Sr$^{2+}$.

REFERENCES


mineral precipitation rates (kaolinite and montmorillonite) also showed a progressive accumulation of Sr²⁺ into recalcitrant (AAO-extractable and residual) pools, similar to the trends observed here for the Hanford sediments.

**5. CONCLUSIONS**

Strontium and cesium partitioning in aqueous suspensions of Hanford sediments impacted by hyperalkaline STWL were affected by sorbate amount and reaction time because of the rate and trajectory of silicate weathering reactions. At short reaction time (<29 d) and low sorptive concentration (<10⁻⁴ M), uptake of both cations followed trends in clay plus silt content. However, at longer time and higher concentration, contaminant partitioning was coupled to sediment weathering reactions and, therefore, controlled largely by Si dissolution–precipitation processes that resulted in incorporation of Sr²⁺ and Cs⁺ in neo-formed feldspathoid and/or zeolite phases.

However, dissolution kinetics studies suggest that remobilization of the sequestered contaminants may occur without extensive dissolution of the aluminosilicate framework, depending on the concentration and type (e.g., K⁺ and Ca₂⁺) of cations in the soil solution. An improved understanding of contaminant remobilization in circumneutral pH solutions (characteristic of background pore waters) after removal of the caustic waste source is essential for predicting the long-term fate and transport of ¹³⁷Cs⁻ and ⁹⁰Sr²⁺ in the subsurface.

**ACKNOWLEDGMENTS**

Gratitude is expressed to Dr. Andrew Felmy who assisted with GMIN speciation calculations, and to Liane Benning and three anonymous reviewers whose comments led to significant improvement to an earlier version of this manuscript. This research was supported by the Office of Science (BER), U.S. Department of Energy, Grants No. DE-FG07-02ER63504 and DE-FG02-06ER64190. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. The Stanford Synchrotron Radiation Laboratory is a national user facility operated by Stanford University on behalf of the U.S. Department of Energy, Office of Basic Energy Sciences. The high-field component of the NMR research reported here was performed at the Environmental Molecular Sciences Laboratory (a national scientific user facility sponsored by the U.S. DOE Office of Biological and Environmental Research) located at the Pacific Northwest National Laboratory, operated by Battelle for the DOE. The NMR spectrometer used within the Penn State NMR Laboratory was purchased by Battelle for the DOE. The NMR spectrometer used within the Penn State NMR Laboratory was purchased with support from PSU and the National Science Foundation through Grant CHE-9601572.

**REFERENCES**


*Associate editor:* Liane G. Benning