U(VI) and Sr(II) batch sorption and diffusion kinetics into mesoporous silica (MCM-41)

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1 **ABSTRACT**

2 Important reactive phenomena that affect the transport and fate of radioactive material
3 such as uranium (U) and strontium (Sr) in the environment occur at the mineral-water interface,
4 particularly in mesoporous materials which are ubiquitous in surface and near-surface
5 environments, and typically dominate the reactive surface area of geologic media. Ion sorption
6 and physical bonding forces (including electrostatic forces) can be significantly modified within
7 these confined pore spaces, leading to preferential enrichment of trace elements in mesopores.
8 Pore space confinement may also lead to kinetic restraints on thermodynamically favorable
9 sorption/desorption, precipitation/dissolution, and redox reactions, due to slow migration of
10 metals out of mesopores, chemical gradients within the pore space, or steric constraints for
11 inward migration of larger molecules. Using a combination of benchtop sorption experiments,
12 TEM, and synchrotron-based x-ray absorption spectroscopy, U(VI) and Sr(II) uptake on
13 mesoporous silica (MCM-41) with a 4.67 nm pore diameter was measured in batch conditions at
14 pH 4.0 and 9.8 as a function of time and metal speciation. Uptake of U was determined for U-
15 hydrolysis, U-CO_3 , and $\text{U-CO}_3\text{-Ca}$ aqueous species. This suite of techniques enabled
16 determination of the rate of metal sorption and precipitation in the pore spaces, and identification
17 of the reaction products. Our results indicate that Sr and U (at less than 10 μM total U) rapidly
18 diffuse into MCM-41. U at higher concentration than 10 μM also rapidly diffuses in, but the
19 higher pore volume U concentration eventually leads to polymerization and precipitation of
20 nano-U-bearing phases. The steady state U sorption maximum after 48 hours of exposure to
21 MCM-41 prior to precipitation was dependent on the size and charge of the dominant U species
22 in solution, where the trend is: $\text{UO}_2(\text{OH})_3^- > \text{UO}_2^{+2} > \text{UO}_2(\text{CO}_3)_3^{-4} \approx \text{CaUO}_2(\text{CO}_3)_3^{-2}$. Precipitation of
23 a U-bearing phase within the silica pore spaces occurred only after a threshold time point and

indicated that U uptake was both thermodynamically and kinetically controlled. Initial diffusion and adsorption were controlled by aqueous speciation and precipitation was controlled by the buildup of sorption species that subsequently created a bottleneck effect near pore openings. Acidic solutions were more efficient at extracting U than carbonate solutions once the U has diffused into the mesopore region, and this may explain frequent observations of this behavior in extractions of natural sediments. A nitric acid wash was not completely effective at desorbing U and Sr from the mesoporous silica, where there was 5% (initial pH 4.0) and 20% (pH 9.8) remaining even after 500 hours of exposure to the nitric acid wash. The results show that U and Sr diffusion and sorption into mesopores results in a recalcitrant pool of ions that are sequestered in deep internal pore spaces, and this may have significant impacts on attempts to clean up contaminated soils and sediments.

Keywords: sorption, mesoporous silica, uranium, strontium, TEM, EXAFS

1. INTRODUCTION

The fate and transport of metals and contaminants in the environment are affected by a range of phenomena occurring at the mineral-water interface, including sorption and diffusion reactions.(Brown Jr. and Parks, 2001) Specific reactions that can limit transport include sequestration of metals into immobile flow domains, particularly within porous mineral coatings, and have been shown to play an important role in sequestering heavy metals and radionuclides (Davis et al., 2004; Liu et al., 2013; Penn et al., 2001; Singer et al., 2013; Stubbs et al., 2009; Zhang et al., 2011). Typical mineral coating phases usually contain complex mineral and organic components and their composition and morphology are dependent on local biogeochemical conditions (Coston et al., 1995; Penn et al., 2001). One typical and important property of such materials is a high degree of porosity, which allows for spatial domains with limited flow potential (Haggerty and Gorelick, 1995). These domains can exist as intra-aggregate and intragranular spaces, over a wide range of spatial scales (Brusseau and Rao, 1990). In particular, pore spaces in the nanometer and sub-micron size domain may account for a large volume of reactive pore space due to their high specific surface areas, despite accounting for only a small fraction of the total pore volume.(Wood et al., 1990) With respect to contaminant transport, these regimes contribute to the immobile fraction of total porosity, and solute transport may be dominated by diffusion between extragranular and intragranular pore space, driven by concentration gradients (Hay et al., 2011; Liu et al., 2013; Sammartino et al., 2003). In contaminated aquifers, it is not known whether porous surface coatings or underlying grain surfaces play the dominant reactive role in retarding contaminant transport. These issues are extremely important to resolving long-term transport predictions at DOE sites such as Hanford, Savannah River, and Rifle, where equilibrium and kinetic models are being evaluated

(Greskowiak et al., 2011; Yabusaki et al., 2008). Recent work at one of these sites using pore-scale simulations revealed the importance of coupled mass transport and reactions in both intragranular and inter-granular domains, which caused both spatial and temporal dependence of U(VI) surface complexation rates in the sediment (Liu et al., 2013). Further, these pore-scale simulations also revealed that the rate of coupled diffusion and molecular surface complexation reaction in the intragranular porous domains was slower than either individual process alone. A critical component of building predictive models of contaminant transport is therefore determining the specific controls on metal sorption and diffusion in porous material.

Porous materials are broadly classified according to IUPAC nomenclature as microporous (< 2 nm), mesoporous (2-50 nm), and macroporous (> 50 nm) (Rouquerol et al., 1994). Synthetic porous materials are ideal models for studying naturally occurring porous earth materials because they can be tailored to have simplified pore geometry, a well constrained pore size distribution, and reproducible surface properties (Kresge et al., 1992; Selvam et al., 2001). These materials have a broad range of applications, including catalysis, selective molecular separation, and chemical sensors. Mesoporous materials represent a pore size regime which can account for a significant fraction of the reactive surface area of porous earth materials and secondary mineral coatings (Sammartino et al., 2003). Silica is an important constituent in these settings, both as quartz and amorphous silica gels, playing an important role in surface environments by attenuating contaminant transport by sorption and precipitation reactions (Chen and Hayes, 1999; Ford et al., 2001). These materials are also relevant to metal transport phenomena in the weathering and degradation of glass and other amorphous materials used in nuclear waste forms (Greaves et al., 1989). Mesoporous silica is therefore a useful and relevant model for these materials, while allowing for a high degree of control over the physical and

chemical properties of the sorbent. Members of the mesoporous silica family of materials, designated MCM-41, have a hexagonal structure with a unidimensional pore structure of uniform channels that can be synthesized to have a highly specific pore size. Pore size is controlled by the intercalation of layered silicates with surfactant species that are calcined off by heating the solid phase, where the final product retains, in part, the layered nature of the precursor material (Kresge et al., 1992).

Predicting metal uptake behavior in mesoporous material is complicated by the uncertainty currently existing about the nature of sorption phenomena inside small pore volumes (less than approximately 10 nm), where nearly molecular-scale physical restraints can limit solute transport and change the behavior of water near the surface electrical double layer (Floquet et al., 2004; Morishige and Kawano, 1999; Senapati and Chandra, 2001). Further, the pore surface structure of both natural and synthetic mesoporous materials is unknown (Kresge et al., 1992), limiting knowledge of the nature of reactive surface sites. Although recent work has aimed at elucidating the nature of the electrical double layer in small pore spaces (Wang et al., 2002; Yang et al., 2002), a general understanding of solute diffusion into mesoporous materials remains uncertain. One approach to resolving these questions is to compare the sorption behavior and diffusion kinetics of aqueous metals with unique solute properties, such as hexavalent uranium (U) and strontium (Sr). Both metals are considered “high inventory” contaminants within the US Department of Energy sites because of their environmental mobility and persistence (Zachara et al., 2007). Under acidic and oxidizing conditions, U exists in the form of the uranyl moiety $[\text{UO}_2^{2+}]$ and uranyl hydrolysis products, and readily forms aqueous complexes with carbonate (CO_3) and calcium (Ca) including $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ at circumneutral and alkaline pH and $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ and $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ at alkaline pH values (Davis et al.,

2004). All of these U species have significantly different solute properties and sorption behavior compared to aqueous Sr, which generally forms only hydrolysis products (Baes and Mesmer, 1976). Although the interactions between Sr and U with quartz and silica have been explored, (Chen and Hayes, 1999; Fox et al., 2006; Kohler et al., 1996; Sahai et al., 2000; Štamberg et al., 2003; Sylwester et al., 2000) it is unclear how their sorption behavior in macroporous systems will translate to mesoporous regimes. Therefore, in addition to being important contaminants in a variety of surface settings, U and Sr offer an interesting comparison for metal uptake into mesoporous material.

In the current study, we have used MCM-41 synthesized with a pore space of 4.7 nm to study the sorption and diffusion kinetics of aqueous U and Sr into mesoporous silica. Using a combination of benchtop sorption experiments, transmission electron microscopy (TEM), and synchrotron-based x-ray absorption spectroscopy (XAS), we have measured U and Sr uptake on MCM-41 as a function of time and solution composition (pH, $[\text{CO}_3]_{\text{T}}$, $[\text{Ca}]$) under batch conditions. The suite of techniques used here enabled the determination of the rate of metal sorption and precipitation in the pore spaces, the binding strength of the sorption products, and identification of the reaction products.

2. MATERIALS AND METHODS

2.1 Mesoporous silica (MCM-41) synthesis and preparation

MCM-41 was prepared according to Kresge et al. (1992) (Kresge et al., 1992) at the Environmental Molecular Sciences Laboratory (Pacific Northwest National Laboratory). The mesoporous silica was wet-sieved below 63 μm using distilled, deionized H_2O (DDI- H_2O), and then dried at 50° C for three days prior to gas adsorption analysis. A Micromeritics TriStar II

(Micromeritics Instrument Corporation) was used to characterize the surface area and porosity properties of the MCM-41; following sieving, the N₂-BET surface area was $603.4 \pm 0.8 \text{ m}^2/\text{g}$ and the BJH average pore volume and pore size were $0.737 \pm 0.003 \text{ cm}^3/\text{g}$ and $4.67 \pm 0.01 \text{ nm}$, respectively.

2.2 Batch sorption/desorption

Uptake of U and Sr by mesoporous silica was determined as a function of time and solution composition. For a given solution composition, 0.1 g of silica powder was added to a 15 mL Falcon tube with 10 mL of an electrolyte solution of 1 mM NaNO₃, with an N₂ gas headspace. The pH of the suspension was adjusted with aliquots of either 1 N HNO₃ or 1 N NaOH to reach pH 4.0 or pH 9.8. These pH values were chosen for three reasons (1) to ensure that U(VI) speciation was dominated by only one or two aqueous species, particularly at higher pH, while working with a high enough U concentration to yield successful EXAFS spectroscopy experiments, (2) ensure that calcite precipitation did not occur and (3) that the aqueous Si concentration was minimized to prevent significant complexation with U(VI). After adjusting pH, the MCM-41-electrolyte suspensions were placed on shaking table for five days, after which time the aqueous Si concentration had reached a steady-state (Figure 1), and it was determined that the solution was in equilibrium with the mesoporous silica powder (Figure 2). Previous work has shown that the solubility of MCM-41 is comparable to amorphous silica (Guthrie and Reardon, 2008), and the equilibrium Si concentrations under the current experimental conditions were 1.97 mM and 3.30 mM at pH 4.0 and 9.8, respectively.

After reaching equilibrium with the electrolyte solution, the solution composition was set as follows for the U sorption experiments; pH 4.0 or 9.8, 1 or 10 μM U(VI) (introduced as uranyl

nitrate), $[\text{CO}_3]_{\text{T}} = 0$ or 0.4 mM (introduced as NaHCO_3), and $[\text{Ca}] = 0$ or 0.05 mM (introduced as CaCl_2). For the Sr sorption experiments, pH was set at either 4.0 or 9.8 , with 1 or 10 μM Sr(II) (introduced as $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$). After changing the solution composition, the background Si concentration did not change significantly over the course of the sorption experiments (Figure 1). Solubility and aqueous speciation calculations were performed with Visual MINTEQ, version 5.52 (Allison et al., 1991) using a U(VI) thermodynamic database, (Grenthe et al., 1992) with supplementary thermodynamic data for U(VI)- CO_3 aqueous complexes (Guillaumont et al., 2003) and U(VI)- CO_3 -Ca aqueous complexes (Dong and Brooks, 2006). A summary of the dominant U(VI) solution species for each experimental condition is given in Table 1. The saturation index value for all relevant phases (schoepite, rutherfordine, liebigite, and calcite) were all < 0 under all sets of conditions. All solutions were prepared using N_2 -purged distilled-deionized H_2O (DDI- H_2O) with a dissolved $\text{O}_2 < 0.01$ ppm, and all experiments were performed in a Coy Laboratories, Inc. anoxic chamber (2% $\text{H}_2/98\%$ N_2 , < 0.1 ppm O_2), primarily to exclude dissolved CO_2 gas. Previous experiments conducted under similar conditions have shown that dissolved carbonate does not degas from the sealed Falcon centrifuge tubes during the sorption/desorption experiments performed in the anaerobic chamber (Singer et al., 2009). The H_2 concentration in the anaerobic chamber is not high enough to induce U(VI) reduction, and only U(VI) was observed by x-ray absorption spectroscopy (discussed below). The solutions were not buffered in order to avoid any interference between an organic buffer and U and Sr adsorption. Over the course of the U sorption experiments, the pH decreased from 4.0 to $3.9 (\pm 0.05)$ and from 9.8 to $9.6 (\pm 0.05)$, for all solution compositions. For the Sr experiments, no change in pH was observed over the course of the experiments.

At the conclusion of the sorption experiment, the suspensions were centrifuged (Eppendorf 5810R) for 30 minutes at 12k rpm, and the solution decanted off prior to performing two separate desorption experiments using replicate sorption samples. Although indirect, selective extractions are a well-established method for assessing resistance to desorption. The two extraction solutions were a bicarbonate wash and an acid wash. The bicarbonate extraction used here has been shown to effectively release labile, adsorbed U (Kohler et al., 2004). The bicarbonate wash was prepared from NaHCO_3 (0.0144 M) and Na_2CO_3 (0.0028 M); the solution pH was 9.45 and alkalinity of 20 meq/L. The acid wash was 0.1 N HNO_3 , prepared from N_2 -purged concentrated HNO_3 diluted with N_2 -purged DDI- H_2O . For both extractions, 10 mL of washing solution was added to the silica paste.

Suspensions from the sorption experiments were sampled at time points ranging from 10 minutes to 336 hours (two weeks) of exposure, and suspensions from the desorption samples were sampled at time points ranging from 24 hours to 336 hours (two weeks). For all samples, 0.5 mL aliquots were extracted and centrifuged for 10 minutes at 12k rpm and passed through a 20 nm filter and then acidified. Previous experiments conducted under similar conditions have shown that U(VI) sorption onto the filters is negligible (Singer et al., 2009). Aqueous U, Sr, Si, and Ca concentrations were determined using a Perkin Elmer SCIEX Elan DRC II Inductively Coupled Plasma Mass Spectrometer (ICP-MS). The ICP-MS methodological detection limits for Sr, Si, Ca, and U are 0.05 ppm, 4 ppm, 1 ppm, and 0.006 ppm, respectively, and the average uncertainty (two standard deviations) for the current experiments for Sr, Si, Ca, and U are ± 2 ppm, ± 100 ppm, ± 7 ppm, and ± 2 ppm.

2.3 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) images were collected at the National Center for Electron Microscopy, Lawrence Berkeley Lab, on an FEI Tecnai F20 for high-resolution STEM images, and a Philips CM200 for EDS spectra. At the conclusion of the U(VI) sorption experiment (i.e. after 336 hours of exposure time) and after centrifugation, the reacted mesoporous silica samples were dried at room temperature for two days. The powder was then mixed with methanol and placed in an ultrasonic bath for 20 minutes to re-suspend the particles. A drop of the suspension was deposited on a carbon film-coated copper grid for preparing a TEM sample.

2.4 U L_{III}-edge EXAFS spectroscopy

Uranium L_{III}-edge EXAFS spectra were measured at room temperature on the Molecular Environmental Science Beamline 11-2 (Bargar et al., 2002) at the Stanford Synchrotron Radiation Lightsource (SSRL) using a cryogenically cooled Si (220), $\phi = 90^\circ$, double-crystal monochromator. Samples were prepared by the same method as the batch uptake experiments, and examined after 336 hours of reaction time. After centrifugation, the U(VI)-bearing mesoporous silica samples were mounted as wet pastes in aluminum sample holders and sealed with Kapton tape in an O₂-free environment. The sample holder was mounted in a cryostat and data was collected under vacuum conditions (10^{-8} Torr); the samples were not cooled to avoid potential freezing effects in the mesoporous silica sorption samples. Fluorescence-yield data were collected using a high-throughput 30-element solid-state germanium detector. The x-ray energy was calibrated using an yttrium foil; the first inflection point in the Y K-edge was set to 17038 eV. EXAFS spectra were extracted from the averaged data files by pre-edge subtraction followed by spline fitting using SixPack (Webb, 2005). Background-subtracted k^3 -weighted

EXAFS data were analyzed using the SixPack interface to IFEFFIT (Newville, 2001). Phase-shift and backscattering amplitude functions for quantitative EXAFS fitting were generated using FEFF 7.0 (Ankudinov and Rehr, 1997) from the crystal structure of soddyite (Demartin et al., 1992).

3. RESULTS

3.1 Uranium sorption

Uranium sorption at pH 4 was independent of solution composition when the initial aqueous U concentration was 1 μM and 10 μM (Figure 3A and C). This is not surprising as the initial U speciation under these conditions are essentially the same and independent of the U concentration and solution composition, with U speciation dominated by the UO_2^{+2} species (Table 1). However, the total sorption loading and diffusion kinetics are strongly dependent on the initial U concentration. When the starting U concentration was 1 μM , slow uptake occurred initially until reaching approximate steady state conditions within 24 hours. The maximum sorption loading was 0.1 nmoles/ m^2 , which corresponds to 78 % of the initial U removed from solution. The U sorption behavior was quite different at a starting concentration of 10 μM ; approximately 20 % of the U was quickly removed from solution within an hour of exposure to the MCM-41, followed by a slow increase in the sorption loading. However, after approximately 168 hours of exposure, the U sorption loading increased until approximately 78 % of the initial U in solution was removed, corresponding to a sorption loading of 1.3 nmoles/ m^2 . The step function-like increase over time suggests that a U-bearing precipitate may have formed following adsorption, and identification of such a phase will be discussed below. Further, the total amount of U removed from solution did not reach 100%. It is unlikely that U precipitation was limited

by available pore space, given the internal pore volume of MCM-41, suggesting that internal precipitation was limited by access to deeper pore spaces, discussed below.

Uranium sorption at pH 9.8 with an initial U concentration of 1 μM appeared to be independent of solution composition (Figure 3B) similar to the pH 4 experiments; U sorption initially increased for approximately 24 hours until reaching equilibrium with a maximum U sorption loading of 0.16 nmoles/ m^2 , or 96% of the U removed from solution. However, in contrast to the pH 4 conditions, U(VI) speciation at pH 9.8 is strongly dependent on the presence of carbonate and calcium for both 1 and 10 μM U(VI) (Table 1). It was expected that speciation changes would affect diffusion, as observed for the 10 μM U(VI) experiments described below. The lack of speciation-dependent U sorption and diffusion at 1 μM suggests that aqueous speciation change kinetics are faster than the rate of diffusion and uranyl and uranyl-hydrolysis diffuse faster into the pore spaces due to of steric constraints discussed below. Therefore, the uptake rates at 1 μM U at pH 9.8 did not depend on chemical conditions, because dissociation of the complexes is faster than diffusion. However, diffusion did depend on chemical conditions at 10 μM U, suggesting that the rate of polymerization (occurring between 20-168 hr) did depend on the chemical conditions and only occurred at 10 μM U.

When the initial U concentration was 10 μM at pH 9.8 (Figure 3D), the overall reaction trend was comparable to the 10 μM at pH 4 experiment, however the kinetics of U uptake prior to 168 hours was dependent on U speciation. The rate and amount of speciation-dependent U(VI) diffusion was as follows: no CO_3 and Ca > CO_3 -bearing ~ Ca- CO_3 -bearing systems. As with the pH 4.0 system, after approximately 200 hours of reaction time with the MCM-41, U uptake rapidly increased until the maximum sorption loading was independent of the solution composition (1.6 nmoles/ m^2 , or 99 % U removed from solution). In general, the steady state U

sorption maximum after 48 hours of exposure to MCM-41 prior to precipitation was dependent on the size and charge of the dominant U species in solution, where the trend is: $\text{UO}_2(\text{OH})_3^- > \text{UO}_2^{+2} > \text{UO}_2(\text{CO}_3)_3^{-4} \approx \text{CaUO}_2(\text{CO}_3)_3^{-2}$ (Figure 4). This suggests U sorption and diffusion into the pore spaces was thermodynamically controlled by aqueous speciation prior to polymerization and the precipitation events.

Comparison of U sorption on bulk silica (including quartz, amorphous silica, and silica gels) and mesoporous silica is challenging because of differences in reported sorption parameters and uncertainties in the sorption site densities of the various silica phases. Assuming a charged site density of 4.6 sites nm^{-2} (Sahai and Sverjensky, 1997), the maximum sorption loading in the current study is 0.0007 U nm^{-2} . Sorption loadings for silica gel range from 0.0002 to 0.058 U nm^{-2} (Pathak and Choppin, 2007; Reich et al., 1998; Sylwester et al., 2000), 0.002 U nm^{-2} for quartz (Huber and Lützenkirchen, 2009), and 0.003 to 0.2 U nm^{-2} for mesoporous silica (Michard et al., 1996; Štamberg et al., 2003; Vidya et al., 2001; Wang et al., 2013). It is not surprising that the sorption loadings in the current study are lower than reported values, given the higher surface area, lower U concentration, and higher mass of silica per volume solution used.

3.2 Strontium sorption

Strontium uptake by MCM-41 was measured as a function of pH and the initial Sr concentration (Figure 3E and F). At pH 4.0, Sr uptake increased for approximately 10 hours until reaching approximate steady state conditions, with a maximum sorption loading for 10 μM of 0.36 nmoles/ m^2 and for 1 μM of 0.11 nmoles/ m^2 , corresponding to 22 % and 63 % of the initial Sr removed from solution, respectively. At pH 9.8, the sorption plateau was reached quicker, within one hour of exposure with a higher sorption loading than at pH 4.0; the

maximum sorption loadings and percent Sr removed from solution for 10 μM and 1 μM were 0.41 nmoles/ m^2 (75 %) and 0.16 nmoles/ m^2 (95 %), respectively. The higher sorption loadings at pH 9.8 are consistent with the favorable electrostatic interaction between Sr^{2+} and the negatively charged silica surface. The difference between the percent sorption of 1 μM and 10 μM may be the result of sorption sites in the pore space that are not all energetically equivalent. At lower concentrations, Sr reacts with strong(er) sites; at higher concentration, there Sr reacts with weak(er) sites after the strong(er) sites are fully coordinated. Finally, in contrast to U uptake, no rapid increase in Sr removal was observed over time, and there was no TEM evidence for any precipitates forming in these experiments (discussed below).

Similar to U, comparison of Sr sorption on bulk silica phases is difficult due to differences in reported sorption parameters and uncertainties in the sorption site densities of the various silica phases. To the author's knowledge, there is no reported data for Sr sorption onto mesoporous silica. Assuming again a charged site density of 4.6 sites nm^{-2} (Sahai and Sverjensky, 1997), the maximum sorption loading in the current study is 0.0002 Sr nm^{-2} . Reported sorption loadings for silica gel are 0.008 Sr nm^{-2} (Sahai et al., 2000), 0.008 Sr nm^{-2} for amorphous silica (Carroll et al., 2008), and 0.011 Sr nm^{-2} for quartz (Bellenger and Staunton, 2008). Similar to the U sorption trends, it is not surprising that the sorption loadings in the current study are lower than reported values, given the higher surface area, lower Sr concentration, and higher mass of silica per volume solution used.

3.3 Desorption Experiments; Bicarbonate extraction of U

A bicarbonate extraction was used to estimate the amount of adsorbed U at the conclusion of the uptake experiment (Figure 5). Exposing the sorption samples to the bicarbonate solution resulted in an initial release of U into solution, ranging from 23 to 32 %

released (pH 4 samples) and 10 to 12 % (pH 9.8 samples) after 24 hours. However, continued exposure to the bicarbonate solution resulted in a loss of U from solution. This behavior could be due to the release of adsorbed U on the exterior surfaces of the mesoporous silica which subsequently diffuses into the pore spaces, leading to further possible precipitation. The greater amount of U released initially from the pH 4 samples is likely due to the formation of more weakly bound U(VI) sorption complexes under acidic conditions compared to more alkaline solutions (Michard et al., 1996; Singer et al., 2009). The exterior surface area of the mesoporous silica accounts for approximately 0.1 % of the total mass normalized surface area, based on the average particle size (~50 to 100 μm) and previously determined density of mesoporous silica of 0.3 g/cc (Chiola, 1971). Therefore, the initial amount of extracted U could not be due to desorption from external surface area only. It is possible that some of the U-bearing precipitates that formed near the pore mouth openings (discussed below) may have been dissolved by the bicarbonate solution, allowing for further diffusion into the pore spaces by eliminating a bottlenecking effect at the opening of the pore channels.

At the conclusion of the sorption experiments, it was unclear what fraction of the sequestered U was precipitated and how much remained adsorbed. As indicated by the TEM images discussed below, the precipitates filled up some but not all of the pore spaces. Further, although the sorption capacity of the MCM-41 exceeded the amount of U initially present during the sorption experiments, some U remained in solution even after 336 hours of exposure. One possible explanation for this behavior is that the U-bearing precipitates form primarily near the pore channel opening creating a bottlenecking effect, discussed in more detail below, which prevents further U diffusion into the mesopores. This would explain the behavior of the sorption samples after exposure to the bicarbonate extraction; the bicarbonate solution dissolved some of

the precipitates near the pore channel openings allowing some desorbed U to continue diffusing into the MCM-41. It is also possible that the sorbed U inside the mesopores is non-labile. This is consistent with previous work that has shown that nonlabile U bound to mesoporous mineral surfaces does not readily desorb compared to the equivalent non-porous substrate (Jung et al., 2012). This is also consistent with observed non-labile pools of sorbed U(VI) in natural sediments (Liu et al., 2013; Stoliker et al., 2013).

3.4 Desorption Experiments; Acid extraction of U and Sr

The amount and rate of U and Sr released using a 0.1 N HNO₃ acid extraction was dependent on the initial solution pH during the uptake experiments (Figure 6). Approximately 60% of the release of U and Sr from the pH 4.0 samples occurred rapidly, within one hour of exposure to nitric acid. This was followed by a slower release of U and Sr, with approximately 95 % released after 336 hours of exposure. The trends of the desorption curves suggests that complete extraction of U and Sr would have occurred at longer exposure time. For the pH 9.8 sorption samples, approximately 75 % of Sr and U were rapidly extracted within one hour, followed by a slower release compared to the pH 4 samples. However, the trend of the desorption curve also suggests that complete desorption would have been reached with longer exposure time. The Sr desorption behavior was very similar to that of U, despite the fact that there was no evidence for Sr precipitation over the course of the sorption experiment. This suggests that for both U and Sr, there is a pool of adsorbed metals that is immobilized within the mesoporous silica that is highly recalcitrant. These results are consistent with Michard et al (Michard et al., 1996). who noted that carbonate solutions were not as effective in extracting uranyl that had diffused into mesoporous silica gels compared to acidic solutions.

3.5 Identification of U-bearing reaction products

The rapid increase in the U sorption loadings after 168 hours of reaction time of 10 μ M U with mesoporous silica suggests that a U-bearing precipitate may have formed. TEM images of reacted samples confirm that a precipitate is present (Figure 7). Images of washed, unreacted MCM-41 show the typical porous structure of the material in which the pore spaces are not filled. The same is true for images of MCM-41 reacted with 10 μ M Sr; this is consistent with the sorption data which showed that there was no rapid increase in the Sr sorption loading over time. In contrast, images of MCM-41 reacted with 10 μ M U at pH 4.0 and 9.8 show that some of the pore spaces have been filled in with a precipitate. Although EDS spectroscopy could not detect the presence of U in these phases, the precipitate is a high contrast phase relatively to the silica substrate and therefore contains a higher Z-number element.

Based on the TEM analysis, we cannot rule out the presence of a U-bearing silicate or calcium carbonate phase in the 10 μ M U experiments; further characterization of the reaction product was performed by U L_{III}-edge EXAFS spectroscopy. The EXAFS spectra and Fourier transform plots of the sorption samples indicates that the dominant U-bearing phase is dependent on the initial solution pH (Figure 8), but independent of the presence of CO₃ and Ca at both pH values. This observation is consistent with the sorption loading trends which indicated that although the initial sorption of 10 μ M U was dependent on solution composition, the same final sorption loading was reached over time. The pH 4.0 sample spectra were fit with an axial oxygen shell at an average distance of 1.81 Å, and a split equatorial oxygen shell, resulting in U-O_{eq} distances of 2.22 Å (U-O_{eq1}) and 2.47 ± 0.01 Å (U-O_{eq2}) (Table 1). These two U-O_{eq} distances are consistent with the asymmetry of the local structural environment of disordered

uranyl-bearing precipitates such as schoepite (Allen et al., 1996). The pH 9.8 sample spectra were fit with an axial oxygen shell at an average of 1.89 Å, and a split equatorial oxygen shell, resulting in U-O_{eq} distances of 2.30 Å (U-O_{eq1}) and 2.50 Å (U-O_{eq2}) (Table 1). This coordination environment is consistent with that of an alkali metal uranate such as clarkeite (Na₂U₂O₇), in which the uranyl group becomes elongated and the equatorial bonds contract (Allen et al., 1996; Catalano and Brown Jr, 2004). This coordination environment is consistent with aqueous U(VI) under alkaline conditions, and Clark et al. (Clark et al., 1999) have shown that this lengthening and weakening of the U=O bond may be partially explained by the strong σ -donating ability of the equatorial OH⁻ ligands. However, OH⁻ ligands are also strong π -donors which might facilitate rapid oxo ligand exchange. Under acidic and near-neutral aqueous solution conditions, the uranyl ion typically shows little to no chemical exchange in the presence of σ -donor ligands such as H₂O, Cl⁻, NO₃⁻, and CO₃²⁻. However, with OH⁻ ligands capable of π -donation, rapid exchange may occur which can result in the weakening and lengthening of the U=O bond, and resulting uranate structure (Clark et al., 1999). Ultimately, at pH 9.8, the high alkalinity in the MCM-41 pore space combined with an increasing U concentration over time results in the precipitation of a uranate-like phase, whereas at pH 4.0, a schoepite-like phase precipitated. Precipitation of schoepite and clarkeite liberates protons as the initial uranyl complex undergoes hydrolysis; for every mole of U(VI) precipitated, 2 moles of H⁺ (schoepite) and 3 moles H⁺ (clarkeite) are released (Gorman-Lewis et al., 2008). The observed pH decrease at the end of the sorption experiments is consistent with these reactions. Further, both the pH 4.0 and 9.8 samples were fit with a U-U pair correlation of approximately 2 U atoms at 3.9 Å. Adding a U-U pair correlation to the shell-by-shell fit resulted in a lower reduced χ^2 value (by a factor of 1.5) and matched features within the EXAFS spectra that could not be reproduced by other elements

present within the system. This interatomic distance is common in U(VI)-bearing phases (Catalano and Brown Jr, 2004), however the low coordination number indicates that a nanoparticle-like phase precipitated.

Both the pH 4.0 and 9.8 spectra were also fit with approximately 2 silicon atoms at 3.8 Å. Like the U shell, adding a U-Si pair correlation to the shell-by-shell fit resulted in a lower reduced χ^2 value (by a factor of 2) and matched features within the EXAFS spectra that could not be reproduced by other elements present within the system, including carbon; the precipitate lacked the characteristic uranium-carbon pair correlation observed in a carbonate-bearing U phase (Allen et al., 1996; Catalano and Brown Jr, 2004). This U-Si distance indicates the presence of a U-bearing phase in close association with the silica surface, and not a U-bearing sorption complex or U-bearing silicate precipitate. It is unlikely that the dominant U-bearing phase is a U-silicate; the U-Si pair correlation would be expected at a distance of 3.1 Å (Catalano and Brown Jr, 2004). U-bearing sorption complexes would have a U-Si pair correlation at approximately 3.08 Å for a bidentate complex and 3.8 Å for a monodentate complex (Sylwester et al., 2000). Given the high sorption loading and evidence of precipitation, it is unlikely that the dominant U-bearing phase is a monodentate complex. Previous work has shown that U(VI) adsorption on SiO₂ can form as monodentate sorption complexes (Reich et al., 1998), or proceed from monodentate to bidentate inner sphere sorption complexes (Ilton et al., 2012). It is possible that U(VI) first attached to the MCM-41 pores surfaces as a monodentate surface complex, and that polymerization and precipitation occurred before losing equatorial waters to form a bidentate complex. Therefore, the observed U-Si pair correlation in the current work could represent residual bonding coordination information from the initial U(VI) sorption

complex, and retained during formation of the U-bearing nanoprecipitates which are in close association with the pore wall of the mesoporous silica.

It is also possible that there is a mixture of both U adsorption complexes and U-bearing precipitates present in the samples analyzed. Preliminary attempts at linear-combination fitting of the EXAFS spectra using reference spectra for adsorbed U complexes and simulated spectra for U-bearing nanoprecipitates were unsuccessful at fitting the sample data. However, this approach is hindered by a lack of reference spectra for likely nanoprecipitates phases and uncertainty regarding the nature of possible U-bearing adsorption complexes, including mono- and/or poly-nuclear species. The U sorption loadings prior to the precipitation event were too low for EXAFS spectroscopic analysis of adsorption complexes; future work aims to determine the nature of both U and Sr adsorption complexes within the mesopore channels of MCM-41 prior to and during precipitation, and using small angle X-ray scattering (SAXS) to probe the nature of nanophases in contact with a confined pore space (e.g. Stack et al., 2014) (Stack et al., 2014).

4. DISCUSSION AND CONCLUSIONS

4.1 Ion sorption and desorption in confined pore spaces

In the absence of the U precipitation events, most of the U and Sr removed from solution occurred within 24 hours of exposure, which is consistent with previous work on metal sorption rates into mesoporous materials; for example, Ni diffuses completely within mesoporous alumina within 5 minutes (Baca et al., 2008; van de Water et al., 2005). Although the surface chemistry of alumina differs from silica, MCM-41 has long channels absent in other mesoporous materials.

Slower diffusion deeper into the channel system may explain the slow but steady uptake of 1 μM U and both the 1 and 10 μM Sr. Further, under experimental conditions in which no precipitation was observed (i.e. 1 μM U and 1 and 10 μM Sr), the nitric acid wash was not completely effective at desorbing U and Sr from the mesoporous silica, where there was 5% (initial pH 4.0) and 20% (pH 9.8) remaining even after 500 hours of exposure to the nitric acid wash. Higher nitric acid concentrations and/or longer exposure time may have released the remaining U and Sr sorbed more deeply within the mesopore channels.

The observation that carbonate solutions were not as effective in extracting uranyl that diffuses into mesoporous regions compared to acidic solutions is likely relevant to natural sediments systems as well. Bond et al. (2008) (Bond et al., 2008) observed that acidic solutions extracted a much higher percentage of uranyl than carbonate solutions from slightly contaminated subsurface sediments from the Hanford 300 area that are characterized by mesoscale porosity (Hay et al., 2011). Similarly, uncontaminated aquifer sediments located near two different uranium mill tailings sites exhibited higher extraction efficiencies of background uranyl in acidic extractions than in carbonate solutions (Davis et al., 2004; Hyun et al., 2009; Kohler et al., 2004), and it seems likely that the mesoporous mineral regime is responsible for the stronger bonding of uranyl in these sediments. Whether precipitation of uranyl phases occurs in these systems is unknown at present because of current limitations in spectroscopy in the low nanomolar range for uranium.

4.2 Precipitation in confined pore spaces

The precipitation of a U-bearing phase within the silica pore spaces occurred only after a threshold time point and indicates that U uptake is both thermodynamically and kinetically

controlled; where initial diffusion and adsorption is controlled by aqueous speciation and precipitation is controlled by the buildup of sorption species creating a bottleneck effect near pore openings. The thermodynamic driving force for precipitation within the pore spaces is likely dominated by heterogeneous nucleation. The formation of a highly hydrated U-bearing phase could explain why precipitation occurred at all. The free energy barrier for the nucleation of a new phase from a supersaturated solution is described as:

$$\Delta g \propto \alpha^3 / \sigma^2$$

Where α is the solid/solution interfacial energy and σ is the saturation index (De Yoreo and Vekilov, 2003). A highly hydrated phase would likely have a lower interfacial energy (α) and a higher solubility than a non-hydrated phase. It is therefore possible that precipitation of such a phase would be possible even if the solution is undersaturated with respect to other crystalline U-bearing phases like rutherfordine and clarkeite. Although precipitation could also be moderated by a pore size controlled solubility (PCS) effect which predicts that small pores can hold higher supersaturated solutions compared to bulk solutions (Emmanuel and Ague, 2009), the PCS effect goes in the opposite direction to what we observe, i.e., that pores enhance and moderate nucleation. The PCS effect does not consider heterogeneous nucleation, but only homogeneous nucleation from solution. Therefore, an alternative explanation for precipitation within MCM-41 is heterogeneous nucleation, especially if the surface is negatively charged and the ions in solution can adsorb strongly (i.e. the first step for heterogeneous nucleation). Under these conditions, the energetic barrier to heterogeneous nucleation would be lower than that for homogeneous nucleation and the presence of the surface cannot be ignored in a restricted pore space. However, because interfacial energy values are generally not known, we cannot quantify the relative importance of these two mechanisms.

One possible mechanism to explain the time dependency of U precipitation is selective nucleation at corners of pore spaces; recent work on the geometrical constraints on heterogeneous nucleation in confined pore spaces suggests that pore-mediated nucleation happens first by nucleation within a pore followed by nucleation from the filled pore into the pore solution (Hedges and Whitlam, 2013; Page and Sear, 2006). Although the TEM images do not show evidence for U-bearing precipitates forming outside of the pore spaces on the external MCM-41 surfaces, it is possible that this nucleation pathway has instead proceeded deeper into the pore channels. As U diffuses into the pore channels, sorption along the pore walls would lead to polymerization and prevent U from diffusing more deeply into the channels. As the concentration gradient near the channel openings increases, polymerization at these corner sites would lead to a precipitation front that moves deeper into the channels along the pore walls through the polymerized surface adsorbed species. This highlights the role of confined pore spaces, and how U uptake can be effected by a given pore diameter; using MCM-41 with a pore diameter of 30 Å and similar U sorption loadings, solution composition, and time scales for uptake, Štamberg et al. (2003) did not observe precipitation with and without carbonate in solution (Štamberg et al., 2003). Further, Wang et al. (2013) used SBA-15, a mesoporous material similar to MCM-41, with a pore diameter of 6.09 Å did not observe U precipitation and observed higher amounts of U desorption (Wang et al., 2013) under similar solution condition, compared to the current work.

4.3 Synergistic effects in confined pore spaces

As our results indicate, rates of desorption from small pores are not only scale dependent, but may be concentration dependent due to polymerization and precipitation. A similar

synergistic effect was noted by Liu et al. (2013), who found that the coupled process of diffusion with molecular U(VI) surface reaction in the intragranular domains was slower than either diffusion or molecular surface reaction alone, indicating that neither the diffusion nor the molecular reaction rate-limited the overall U(VI) sorption and desorption (Liu et al., 2013). Liu et al. conclude that in the intragranular domains, all individual processes regardless faster or slower will contribute to the overall rate-limiting step if they are coupled, and the rate of coupled processes can be significantly slower than the rates of individual processes. Ultimately, we have shown that U and Sr diffusion and sorption into mesopores results in a recalcitrant pool of ions that are sequestered in deep internal pore spaces, highlighting the need future work aimed at elucidating the relationship between coupled geochemical processes occurring in confined pore spaces.

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Tables

Table 1. U(VI) speciation at the initial addition of U(VI) to the pH adjusted mesoporous silica suspension, for U(VI) species greater than 1% abundance. Speciation was calculated for solutions in equilibrium with amorphous silica; this $[\text{Si}]_{\text{eq}}$ was confirmed prior to addition of U(VI).

Solution Composition	pH 4.0		pH 9.8	
	U(VI) species	% Abundance	U(VI) species	% Abundance
1 uM U, no CO_3 / no Ca	UO_2^{+2}	79	$\text{UO}_2(\text{OH})_3^-$	98
	$\text{UO}_2\text{H}_3\text{SiO}_4^+$	17	$\text{UO}_2(\text{OH})_2$	2
	UO_2OH^+	4		
1 uM U, 0.4 mM CO_3 / no Ca	UO_2^{+2}	79	$\text{UO}_2(\text{CO}_3)_3^{-4}$	75
	$\text{UO}_2\text{H}_3\text{SiO}_4^+$	17	$\text{UO}_2(\text{OH})_3^-$	22
	UO_2OH^+	4	$\text{UO}_2(\text{CO}_3)_2^{-2}$	3
1 uM U, 0.4 CO_3 / 0.05 mM Ca	UO_2^{+2}	79	$\text{CaUO}_2(\text{CO}_3)_3^{-2}$	74
	$\text{UO}_2\text{H}_3\text{SiO}_4^+$	17	$\text{UO}_2(\text{CO}_3)_3^{-4}$	14
	UO_2OH^+	4	$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$	8
			$\text{UO}_2(\text{OH})_3^-$	4
10 uM U, no CO_3 / no Ca	UO_2^{+2}	80	$\text{UO}_2(\text{OH})_3^-$	97
	$\text{UO}_2\text{H}_3\text{SiO}_4^+$	16	$(\text{UO}_2)_3(\text{OH})_7^-$	2
	UO_2OH^+	4	$\text{UO}_2(\text{OH})_2$	1
10 uM U, 0.4 mM CO_3 / no Ca	UO_2^{+2}	80	$\text{UO}_2(\text{CO}_3)_3^{-4}$	78
	$\text{UO}_2\text{H}_3\text{SiO}_4^+$	16	$\text{UO}_2(\text{OH})_3^-$	20
	UO_2OH^+	4	$\text{UO}_2(\text{CO}_3)_2^{-2}$	2
10 uM U, 0.4 CO_3 / 0.05 mM Ca	UO_2^{+2}	80	$\text{CaUO}_2(\text{CO}_3)_3^{-2}$	64
	$\text{UO}_2\text{H}_3\text{SiO}_4^+$	16	$\text{UO}_2(\text{CO}_3)_3^{-4}$	24
	UO_2OH^+	4	$\text{UO}_2(\text{OH})_3^-$	7
			$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$	4

Table 2. Shell-by-shell Fit Results of the U L_{III}-edge EXAFS Spectra of mesoporous silica exposed to U(VI) at pH 4.0 and 9.8.

solution composition	scattering path	pH 4.0					pH 9.8				
		N ^a	R (Å) ^b	σ ² (Å ²) ^c	ΔE ^{0 d}	χ _v ^{2 e}	N	R (Å)	σ ² (Å ²)	ΔE ⁰	χ _v ²
0 mM CO ₃	U-O _{ax}	2 ^f	1.82(1)	0.008(1)	11(1)	41.1	2	1.89(1)	0.005(1)	9(1)	32.5
0 mM Ca	U-O _{eq1}	3.2(2)	2.30(2)	0.002(1)			4.9(4)	2.23(1)	0.008(2)		
	U-O _{eq2}	3.5(3)	2.52(2)	0.007(2)			2.6(2)	2.46(2)	0.006(2)		
	U-Si	3(1)	3.82(4)	0.017(1)			2(1)	3.9(1)	0.005(1)		
	U-U	2(1)	4.21(2)	0.007(2)			2(1)	4.2(1)	0.009(1)		
0.4 mM CO ₃	U-O _{ax}	2	1.81(1)	0.008(1)	12(1)	38.6	2	1.89(1)	0.007(1)	10(1)	43.2
0 mM Ca	U-O _{eq1}	3.3(3)	2.31(2)	0.004(1)			4.6(3)	2.23(1)	0.008(2)		
	U-O _{eq2}	3.9(1)	2.50(2)	0.008(2)			2.7(3)	2.47(2)	0.007(2)		
	U-Si	3(1)	3.81(3)	0.015(2)			2(1)	3.9(2)	0.004(1)		
	U-U	2(1)	4.20(4)	0.009(2)			2(1)	4.2(1)	0.008(1)		
0.4 mM CO ₃	U-O _{ax}	2	1.81(1)	0.007(1)	11(1)	38.1	2	1.89(1)	0.005(1)	9(1)	35.6
0.05 mM Ca	U-O _{eq1}	3.4(2)	2.29(1)	0.004(1)			4.3(3)	2.22(1)	0.005(1)		
	U-O _{eq2}	3.6(3)	2.49(1)	0.007(2)			2.6(2)	2.48(2)	0.004(1)		
	U-Si	4(2)	3.82(4)	0.019(1)			2(1)	3.9(1)	0.005(1)		
	U-U	2(1)	4.19(2)	0.009(1)			2(1)	4.2(1)	0.008(2)		

Note: The estimated standard deviations are listed in parentheses, representing the errors in the last digit; values without reported errors were fixed during fitting.

a. Coordination number

b. Interatomic distance

c. Debye-Waller factor

d. Difference in threshold Fermi level between data and theory

e. Reduced χ², a goodness-of-fit parameter (Newville, 2001)

f. coordination number of the axial uranyl oxygen atoms was set at 2

Figures

Figure 1. The aqueous Si concentration at pH 4.0 (bottom) and 9.8 (top) while washing mesoporous silica for 5 days in 1 mM NaNO₃ (at left), and then after adding U or Sr (at right), and CO₃ and Ca for the U experiments at pH 4.0 (filled symbols) and pH 9.8 (open symbols). Error bars represent two standard deviations for data points collected in triplicate.

Figure 2. The Aqueous Si concentration after washing the mesoporous silica for 5 days in 1 mM NaNO₃ at pH 4.0 (open blue circle) and 9.8 (open green circle); the MCM-41 solubility curve was calculated based on experimental thermodynamic data (Guthrie and Reardon, 2008). Error bars represent two standard deviations for data points collected in triplicate.

Figure 3. Cumulative U and Sr sorption on mesoporous silica as a function of time and solution composition: (A) 1 μM U at pH 4.0, (B) 1 μM U at pH 9.8, (C) 10 μM U at pH 4.0, (D) 10 μM U at pH 9.8, (E) Sr at pH 4.0, and (F) Sr at pH 9.8. The percent U and Sr removed from solution is noted on each plot at the maximum sorption loading. Error bars represent two standard deviations for data points collected in triplicate.

Figure 4. The Sr and U sorption loadings after 48 hours (see Figure 3) after having reached steady state but before U precipitation events. The noted U species represent the dominant U-bearing solution species (Table 1) at the initial exposure of MCM-41 for pH 4 (UO₂⁺²) and pH 10 without CO₃ or Ca (UO₂(OH)₃⁻), pH 10 with CO₃ and no Ca (UO₂(CO₃)₃⁻⁴) and pH 10 with CO₃ and with Ca (CaUO₂(CO₃)₃⁻²). The effective radius for the U species was set at 1.8 Å, as it was assumed that the species would diffuse into the pore spaces orthogonal to the uranyl axis to minimize steric interactions.

Figure 5. Amount of U in solution (μM) after exposure to the bicarbonate extraction solution for samples with a starting with an initial U concentration of $10 \mu\text{M}$ and pH of 4.0 (left) and 9.8 (right). The initial amount of U released from the sample after 24 hours ranged from 23 to 32% (pH 4 samples) and 10 to 12 % (pH 9.8 samples), with a subsequent loss of U from solution.

Figure 6. Percent desorption of U and Sr after the sorption samples were exposed to 1 N HNO₃, for sorption samples at an initial pH of 4.0 (left) and 9.8 (right).

Figure 7. TEM images of (A) washed, unreacted mesoporous silica (insert: cross section of a particle exhibiting the regular channel array structure), and mesoporous silica reacted with (B) 10 μM Sr, (C) 10 μM U at pH 4.0 with no CO_3 and no Ca present, and (D) 10 μM U at pH 9.8 with no CO_3 and no Ca present.

Figure 8. U L_{III}-edge EXAFS spectra (A) and Fourier transform plots (B) of the U sorption samples as a function of solution composition (pH 4.0; red lines, and pH 9.8; blue lines); fits are shown as the black dashed lines.

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Graphical abstract