Rates and mechanisms of uranyl oxyhydroxide mineral dissolution

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ABSTRACT

Uranyl oxyhydroxide minerals are important weathering products in uranium-contaminated surface and subsurface environments that regulate dissolved uranium concentrations. However, dissolution rates for this class of minerals and associated dissolution mechanisms have not been previously reported for circumneutral pH conditions, particularly for the case of flow through porous media. In this work, the dissolution rates of K- and Na-compreignacite ($\text{K}_2(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot 8\text{H}_2\text{O}$ and $\text{Na}_2(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot 8\text{H}_2\text{O}$ respectively) were measured using flow-through columns reacted with two simulated background porewater (BPW) solutions of low and high dissolved total carbonate content (ca. 0.2 and 2.8 mmol L⁻¹). Column materials were characterized before and after reaction with electron microscopy, bulk chemistry, and EXAFS to identify structural and chemical changes during dissolution and to obtain insight into molecular-scale processes. The reactive transport code CrunchFlow was used to calculate overall dissolution rates while accounting for fluid transport and changes in mineral volume and reactive surface area and results were compared to steady-state dissolution rate calculations. In low carbonate BPW systems, interlayer K and Na were initially leached from both minerals, and in Na-compreignacite, K and minor divalent cations from the input solution were incorporated into the mineral structure. Results of characterization analyses suggested that after reaction both K- and

Na-compreignacite resembled a disordered K-compreignacite with altered surfaces. A 10-fold increase in dissolved carbonate concentration and corresponding increase in pH (from 6.65 to 8.40) resulted in a net removal of 58-87% of total uranium mass from the columns, compared to <1% net loss in low carbonate BPW systems. Steady-state release of dissolved uranium was not observed with high carbonate solutions and post-reaction characterizations indicated a lack of development of leached or altered surfaces. Dissolution rates (normalized to specific surface area) were about 2.5-3 orders-of-magnitude faster in high versus low carbonate BPW systems, with Na-compreignacite dissolving more rapidly than K-compreignacite under both BPW conditions, possibly due to greater ion exchange ($1.57 \cdot 10^{-10}$ vs. $1.28 \cdot 10^{-13} \text{ mol m}^{-2} \text{ s}^{-1}$ [log R = -9.81 and -12.89] and $5.79 \cdot 10^{-10}$ vs. $3.71 \cdot 10^{-13} \text{ mol m}^{-2} \text{ s}^{-1}$ [log R = -9.24 and -12.43] for K- and Na-compreignacite respectively). Experimental and spectroscopic results suggest that the dissolution rate is controlled by bond breaking of a uranyl group and detachment from polyhedral layers of the mineral structure. With higher dissolved carbonate concentrations, this rate-determining step is accelerated by the formation of Ca-uranyl carbonate complexes (dominant species under these conditions), which resulted in an increase of the dissolution rates. Optimization of both dissolution rate and mineral volume fraction in the reactive transport model to account for uranium mass removal during dissolution more accurately reproduced effluent data in high carbonate systems, and resulted in faster overall rates compared with a steady-state dissolution assumption. This study highlights the importance of coupling reaction and transport processes during the quantification of mineral dissolution rates to accurately predict the fate of contaminants such as uranium in porous geomedial media.

Keywords

Uranyl oxyhydroxides, compreignacite, dissolution rate, reactive transport, EXAFS

1. INTRODUCTION

Uranyl oxyhydroxide minerals are commonly formed in natural environments from the weathering of U(IV) oxide solids under oxidizing conditions (Hazen et al., 2009), corrosion of spent nuclear fuel in a geological repository (Finch et al., 1999), or potential precipitation from liquid uranium (U) waste released directly into the subsurface (Zachara et al., 2007). In the absence of dissolved phosphate or silicate, U(VI) has been observed to form a variety of

crystalline and amorphous oxyhydroxide mineral phases in oxic subsurface environments (Hunter and Bertsch, 1998; Morris et al., 1996) and in synthetic acidic-to-circumneutral wastewaters (Kanematsu et al., 2014). The first oxidized alteration phase from the weathering of synthetic or natural $\text{UO}_2(\text{s})$ is typically a simple oxyhydroxide, either schoepite $((\text{UO}_2)_8\text{O}_2(\text{OH})_{12} \cdot 12\text{H}_2\text{O})$ or metaschoepite $((\text{UO}_2)_4\text{O}(\text{OH})_6 \cdot 5\text{H}_2\text{O})$ (Finch and Ewing, 1992). Under most natural conditions, however, schoepite is metastable with a strong tendency to undergo structural transformation to more stable secondary phases, such as becquerelite $(\text{Ca}(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot 8\text{H}_2\text{O})$ or compreignacite $(\text{K}_2(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot 7\text{H}_2\text{O})$ after incorporation of Ca and K, respectively (Sandino and Grambow, 1994; Wronkiewicz et al., 1996). A Na analogue of compreignacite $(\text{Na}_2(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot 7(\text{H}_2\text{O}))$ was tentatively identified among the alteration phases observed on spent fuel in contact with groundwater for six years (Finch et al., 1999), and is an important alteration phase due to the ubiquitous presence of dissolved Na in groundwaters (Gorman-Lewis et al., 2008a). The thermodynamic solubility and dissolution rates of common uranyl oxyhydroxides play a key role in controlling uranium release and mobility in environmental scenarios (Finch and Murakami, 1999). Due to the high solubility and reactivity of K-, Na- and Ca-uranyl oxyhydroxides compared with uranyl silicate and phosphate phases, their importance in determining U concentrations in saturated and unsaturated soils and sediments may have been overlooked in prior studies.

As reviewed by Gorman-Lewis et al. (2008a), the solubility of K- and Na- compreignacite has been rarely studied compared to the oxyhydroxide phases schoepite, metaschoepite, and becquerelite (e.g., Giammar and Hering (2004), Sandino and Grambow (1994)). To our knowledge, there have been only two studies investigating the thermodynamic solubility of the K and Na end-members, both conducted as batch experiments. Sandino and Grambow (1994) calculated the solubility product of synthetic compreignacite in 1 M KCl ($\log K_{sp} = 39.16 \pm 0.31$) and observed no mineral phase alteration despite evidence of reduction in crystallinity based on X-ray diffraction (XRD) powder data and scanning electron microscope (SEM) micrographs. Gorman-Lewis et al. (2008b) carried out solubility measurements on different uranyl oxide hydrate phases, including K- and Na-compreignacite, using solutions with pH between 4.0 to 5.3. In their study, K-compreignacite solubility experiments reached steady-state conditions in 3 to 4 days from undersaturated solutions and in 7 to 14 days from supersaturated solutions, while Na-compreignacite required between 2 and 20 days. Although the crystallinity of both minerals was

reduced substantially by the end of the experiments, no phases other than K- and Na-compreignacite were observed. For both minerals, dissolution was non-stoichiometric and excess K and Na was measured in solution. These minerals, along with becquerelite, share topologically identical α -U₃O₈ sheets and have identical anion distribution (Burns, 1998; Burns and Li, 2002), favoring cation leaching or exchange. Gorman-Lewis et al. (2008b) concluded that when steady-state between the outer leached layer and the inner bulk material is achieved, the outer leached layer also reached steady-state with the aqueous solution. The calculated solubility products of end-member K- and Na-compreignacite differed by approximately 3.5 orders of magnitude ($\log K_{sp} = 35.8$ and 39.4 for K- and Na-compreignacite, respectively), showing the large dependence of mineral solubility on interlayer cation identity.

Other environmental parameters that influence uranyl mineral stability include pH and dissolved carbonate concentration. In solution, uranyl reacts with dissolved carbonate and Ca, forming stable neutral or anionic carbonate, Ca-carbonate, and hydroxo-carbonate aqueous complexes (Grenthe et al., 1992; Guillaumont et al., 2003). These complexes become important above pH 4 and increase mineral solubility (Gorman-Lewis et al., 2008a), creating mobile species that promote U(VI) migration in natural waters. Dissolution rates have not been reported for any uranyl oxyhydroxide minerals, and differences in rates at different pH and carbonate concentrations have not been investigated. Dissolution rate studies of other uranyl mineral families included three uranyl silicates (Ilton et al., 2006; Pérez et al., 2000; Pérez et al., 1996) and two uranyl phosphates (Gudavalli et al., 2013). In these studies, higher concentration of dissolved carbonate and pH enhanced apparent mineral solubility or dissolution rate by 1 to 3 orders of magnitude, with the mechanism for U(VI) detachment attributed to the formation of aqueous complexes of uranyl-carbonate and Ca-uranyl-carbonate species. Thus, in some prior studies, dissolution rate laws were written as a function of bicarbonate concentration in order to capture the dependence of the dissolution rate on the proposed mechanism (Pérez et al., 2000).

Most prior dissolution studies of uranyl minerals were carried out as batch experiments, although some studies employed continuously stirred tank flow-through reactors (Pérez et al., 2000) or single-pass flow-through batch reactors (Gudavalli et al., 2013). An advantage of dynamic over static experimental systems is the removal of reaction products that may influence reaction rate or solubility of mineral phases (Handley-Sidhu et al., 2009). In flow-through tank or

batch reactors, the ratio of solution volume to reactant solid is usually high in order to maintain dilute conditions and allow solutions to access solid surfaces. Packed-column flow-through experiments offer a different type of dynamic system that better simulates hydrologic conditions representative of saturated subsurface environments. This experimental approach, however, has the potential disadvantages of preferential flow paths, transport-limited rather than surface-limited reactions, and non-uniform contact of the reactant solution with surfaces (Steefel and Maher, 2009; Zhu, 2009). Column experiments have been used to study the release of U from contaminated soils and sediments under different environmental conditions (Eagling et al., 2013; Liu et al., 2008; Qafoku et al., 2005). However, no studies have reported dissolution rates of uranyl oxyhydroxide minerals under thermodynamically undersaturated and/or dynamic conditions of flow within porous media to simulate subsurface conditions.

Developing a molecular-scale understanding of dissolution, desorption, and mineral transformation processes in simplified systems is crucial for improving predictions of uranium transport and fate in complex subsurface environments over time. The overall aim of this study was to determine the dissolution rates and mechanisms of two uranyl oxyhydroxide end-members (K- and Na-compreignacite) in a simulated porewater flow regime with different total dissolved carbonate concentrations and pH. Experimental solutions were chosen with relevance to a site of uranium contamination, the Department of Energy's Hanford site (WA, USA), but the solution composition is also typical of freshwater aquifer systems. Solution and solid phases were analyzed and characterized by chemical, microscopic, and spectroscopic techniques before and after reaction to help establish dissolution mechanisms. To accurately account for the coupled effects of reaction and transport on dissolution rate, solution effluent data from experimental columns was used to parameterize a multicomponent reactive transport model that was then used to determine optimized overall reaction rates and investigate the importance of changes in mineral mass with time. This approach enables comparison of uranyl mineral dissolution rates measured in static or batch-flow experiments with those in flow conditions relevant to U mobilization in a porous medium.

2. MATERIAL AND METHODS

2.1 Synthesis of uranyl oxyhydroxide minerals

Uranyl minerals were synthesized following a method adapted from Gorman-Lewis et al.(2008b). In a 23 mL Teflon-lined Parr bomb containing 5 mL of ultrapure water (18.2 MΩ·cm, EASYpure UV, Barnstead Thermolyne), 0.21 g of uranyl nitrate hexahydrated ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; Spectrum Chemicals, USA) were reacted with 0.03 g of K_2CO_3 or 0.09 g of NaHCO_3 to synthesize K-compreignacite and Na-compreignacite, respectively. The pH of the mixtures was adjusted to ~5 with 10-20 μL of 15.7 M HNO_3 . The Parr bomb was uniformly heated at 100-105 °C in a furnace for 24 h. The dark yellow precipitates that formed were rinsed with hot(just below boiling) ultrapure water, vacuum filtered (0.45 μm Metrice Membrane filters), and finally air dried. The syntheses were repeated several times until a total of 0.6-0.8 g of each mineral was attained. Reaction yields with respect to initial uranyl nitrate mass were 87.8% on average for both minerals. The air dried precipitates were homogenized and characterized (details in section 2.3) prior to preparation of flow-through columns.

2.2 Dissolution flow-through column experiments

Three sets of experiments were carried out in this work using a flow-through reactor design in which uranyl mineral species were mixed with quartz and packed into columns: i) dissolution of the two uranyl oxyhydroxide minerals with a representative background porewater solutions (BPW) of low dissolved carbonate (ca. 0.2 mmol L^{-1}), ii) dissolution of the two minerals under the same BPW conditions but with higher total dissolved carbonate (ca. 2.8 mmol L^{-1}), and iii) control columns with low and high carbonate BPW (with and without dissolved U(VI)), and without U minerals, to measure background concentrations and characterize uranyl sorption onto quartz during transport through the column. The three sets were prepared in the same manner as described below, and full experiment characteristics are summarized in Tables 1 and 2.

Synthesized uranyl minerals were mixed with cleaned quartz grains (200-400 μm size) as background filler to obtain a homogenous distribution within columns. Approximately 3.8 g of cleaned quartz (Unimin, Inc.; see S1 in SI for cleaning procedure) were combined with 0.06-0.40 g of K-compreignacite or Na-compreignacite. Mixtures were divided in two portions for duplicate, simultaneous column dissolution experiments, with a small fraction (0.05-0.10 g) used

for total acid digestion of solids and elemental analysis by inductively coupled plasma mass spectrometry (ICP-MS, section 2.3) to determine total U mass in each column. K- or Na-compreignacite-quartz mixtures (1.87 ± 0.07 g) were gently dry-packed into 1.0053cm^3 volume polypropylene Rezorlan tubes (0.8 cm ID x 2 cm length; Sigma Aldrich) and capped with polyethylene frits (20 μm pore size). Disposable syringe filters (0.2 μm pore size, nylon; Whatman) were placed before and after the packed column material to avoid particle loss out of the column. The exact mass introduced in each column was accurately recorded.

A total of eight columns with either K-compreignacite or Na-compreignacite were reacted at room temperature and ambient atmospheric CO_2 with continuous upward flow of a synthetic BPW solution containing either low or high total dissolved carbonate (Table 1) using a peristaltic pump and 2-stop PharMed BPT tubing (orange-blue, 0.25 mm ID; Cole-Parmer). The low carbonate BPW solution was representative of NO_3 -free Hanford porewater of pH 7.1-7.2 (Thompson et al., 2010). Carbonate salts were substituted for chloride salts to produce the high carbonate BPW solution (pH 8.0-8.2). Influent solution pH to the columns drifted slightly (0.15-0.45 pH units) from pH measured in reservoir bottles (especially in the unbuffered systems) likely due to leaching of trace amounts of mineral oil or blend material present in new PharMed BPT tubing (www.masterflex.nl, (Malczewski and Inman Jr., 2007)). Table 1 reports the solution pH reaching the columns after passing through the tubing. Replicates at low or high carbonate concentration were run simultaneously for the durations and flow rates shown in Table 2. Effluent solution samples were collected using a fraction collector (CF-2, Spectrum Laboratories, Inc.) every 8 min (~ 1 PV) for the first 160 min, every 40 min (~ 5 PV) from 160 to 600 min, and every 160 min (~ 20 PV) for the rest of the run. Effluent samples were: i) diluted with 2% HNO_3 for elemental analysis (U, Na, Ca, K and Mg) by ICP-MS, ii) diluted with ultrapure water for anion determination by IC, and iii) measured undiluted for total dissolved carbon by TC analysis (details in section 2.3). The pH was measured in 6-10 individual effluent samples per column experiment. Two types of control columns (in duplicate) were prepared in the same manner as described above with cleaned quartz but no uranyl minerals (Table 2), and leached with low and high carbonate BPW input solutions (Table 1): i) containing no dissolved U(VI) and ii) containing $\sim 4 \mu\text{mol L}^{-1}$ dissolved U(VI) (prepared from uranyl acetate salt; Spectrum Chemicals, USA). After reaction, columns were disassembled, and the contents

homogenized and air dried before storage. Solids were characterized before and after reaction by methods described in section 2.3.

For all columns, the fluid or pore volume (PV), calculated from the total column volume minus the volume of the solids (quartz and U-minerals), was between 0.2985 and 0.3451 mL (Table 2). Column porosity values, estimated from pore volume divided by total column volume, were between 0.29 and 0.34. Volumetric flow rate (Q) of the solution was calculated from the weighed effluent volumes (0.035 to 0.038 mL min⁻¹ in uranyl mineral columns, and 0.027 to 0.044 mL min⁻¹ in control columns; Table 2). A 40-min pulse of a conservative tracer solution (BPW solution containing 0.5-1 mmol L⁻¹ Br) was introduced at the beginning and end of each dissolution experiment to determine column transport properties. Effluent solution samples were collected every 8 min (~1 PV) and Br concentration was determined by ICP-MS (details in section 2.3). Representative fits to Br breakthrough curves are shown in the SI (Fig. S1). The linear fluid velocity (v , cm min⁻¹) and longitudinal dispersion coefficient (D_L , cm² min⁻¹) values (Table 2) were obtained by fitting the Br breakthrough curves to an advection-dispersion finite-length pulse source model (Runkel, 1996). Dispersivity (α_L , cm) was calculated as $\alpha_L = D_L/v$ (Table 2). Transport properties from Br tracer fits showed differences of less than 5% between the beginning and the end of each experiment.

2.3 Analytical and spectroscopic techniques

2.3.1 Solid phase characterization

Synthesized uranyl minerals were characterized by the methods described below. Column mixtures before and after reaction with BPW solutions were characterized by SEM imaging, specific surface area measurements, and acid digestion and total element analyses.

X-ray diffraction (XRD). Samples were mounted on zero-background Si holders and scanned from 4 to 80 degrees 2 θ (0.01 steps) using a Philips X'Pert MPD diffractometer and an ultra-fast X'Celerator detector (Ni-filtered Co K- α source, $\lambda = 1.78$ Å, 50 kV, 40 mA). XRD patterns were analyzed with X'Pert HighScore Plus software using its internal library reference spectra (ICDD Powder Diffraction File (1998)). The detection limit of the analysis is ~ 2-3% wt.

Vibrational Spectroscopy (Raman and Fourier Transform Infrared). An ExamineR 785 (DeltaNu, Laramie, WY) Raman module equipped with a 785 nm, 120 mW laser excitation source, a CCD detector (0.5 cm^{-1} resolution) and an Olympus BX51 microscope (50x objective, 0.75 numerical aperture) was used to collect the Raman spectra on single crystals (30 s integration time), and to confirm uranyl bonds and hydration of the minerals. No corrections were performed on the measured spectra. FT-IR reflectance spectra (25 per sample) were acquired on a Bruker, Alpha-P infrared reflectance spectrometer. Solid samples were directly loaded in the diamond window. Spectra were averaged for each sample using the OPUS/Mentor Operating software.

SEM and thermogravimetric analyses (TGA). Air-dried particles of the minerals were imaged using a FEI Quanta 200 environmental scanning electron microscope (ESEM) with a tungsten filament. Images were obtained at high vacuum ($< 10^{-4}$ Torr), 20 kV voltage and 90-100 μA emission current. The water content of the uranyl minerals was determined by TGA by heating ~20 mg of air-dried mineral powder from room temperature to 600°C at $10^\circ\text{C min}^{-1}$ in an Ar purge (2000 mL min^{-1}) using a Seiko model TGA/DTA 320. Number of water molecules (hydration and structural water) was calculated from the weight loss at the temperature range 20- 400°C .

Particle size and surface area. Particle size distribution of an aliquot of dried mineral suspended in ultrapure water was measured at a wavelength of 633 nm and 45° angle for 2 min using Dynamic Laser Scattering (DLS, Brookhaven Instruments BI-9000AT). Specific surface area (SSA) was determined on dried samples by the N_2 -BET method (Brunauer–Emmett–Teller (BET)) using a surface area analyzer (Tri-Star 3000, Micrometrics).

Elemental analysis of solids. Microwave acid digestion (40 min, 160°C , 18 bar; Anton Paar Multiwave 3000) was carried out in duplicate by adding 9 mL HCl and 3 mL HNO_3 to 0.04-0.06 g of air-dried samples. The digests were subsequently diluted with ultrapure water to a final 1-5% HNO_3 v/v concentration for ICP-MS analysis.

2.3.2 Solution chemical analysis

Dissolved U, Na, Ca, K, Mg and Br concentrations from effluent solutions and acid digests were measured using inductively couple plasma-mass spectrometry (ICP-MS, Agilent 7500ce Cetac - ASX-510 Autosampler). Samples and standards were analyzed in 2% HNO_3 matrix and

the latter were freshly prepared from 1000 $\mu\text{g mL}^{-1}$ ICP standard solutions obtained from GFS Chemicals, Inorganic Ventures and Fluka Chemicals. Blank and check standard solutions were analyzed every 10-12 samples to account for any signal drift. Method detection limits were 10 pg L^{-1} for U and 10-25 $\mu\text{g L}^{-1}$ for Na, K, Ca, Mg and Br; the repeatability of the analyses, as relative standard deviation (RSD), was always $\leq 2\%$ for all elements.

The concentration of anions (Cl^- , SO_4^{2-}) in the effluent solutions was determined by ion chromatography (IC) using a Dionex ICS-2000 chromatography system (AS18 chromatographic column) with suppressed conductivity detection. Total dissolved carbon (TC) concentration was analyzed from undiluted effluent solutions using a Shimadzu TOC-Vcsh Total Organic Carbon Analyzer coupled with an ASI 5000A autosampler. IC and TOC systems were daily calibrated with standard solutions freshly prepared from 1000 $\mu\text{g mL}^{-1}$ seven anion IC aqueous standard (Dionex) and potassium hydrogen phthalate ($\text{C}_6\text{H}_4(\text{COOK})(\text{COOH})$) stock solution, respectively. Standard checks and blanks were run every 10-15 samples to account for signal drift. The limit of detection was 10-25 $\mu\text{g L}^{-1}$ for both anions and 50 $\mu\text{g L}^{-1}$ for dissolved TC. Both analytical techniques present a RSD of $< 3\%$ on their measurements.

2.3.3 X-ray absorption spectroscopy (XAS)

Uranium L_{III}-edge Extended X-ray absorption fine structure (EXAFS) spectra of unreacted minerals and reacted column mixtures were collected on beamlines 4-1 and 11-2 at the Stanford Synchrotron Radiation Lightsource (SSRL) under dedicated conditions (current 500 mA). Air-dried K-compreignacite and Na-compreignacite (synthesized minerals) were diluted with sucrose (1:4 ratio) to achieve a maximum log absorbance (I_0/I_t) around 1 in transmission mode. For data collection in fluorescence mode, reacted column mixtures (containing quartz and synthesized uranyl minerals) were ground manually and diluted with sucrose to ~ 2000 ppm U; reacted control columns (containing only quartz with sorbed U) were ground but not diluted. Samples were loaded in aluminum holders, sealed with Kapton tape and held in a liquid nitrogen cryostat to maintain low vacuum and temperature (~ 77 K). Samples were measured using a Si(220) monochromator crystal with the second crystal detuned 20-30% at 17,600 eV to reject harmonic reflections. Beam size on the sample was 1 x 4-7 mm and XAS data was collected with either a 30- or 100-element solid-state Ge fluorescence detector. Energy was calibrated using a Y foil standard with the first inflection on the absorption edge set to 17,038 eV.

Three to twelve scans were collected for each sample and averaged using SIXpack (Webb, 2005). The ATHENA and ARTEMIS software package (Ravel and Newville, 2005) was used for background subtraction, normalization, and EXAFS fits. Background was subtracted by a linear fit through the pre-edge region and a spline fit through the EXAFS region ($k = 0 \text{ \AA}^{-1}$ was set to 17,185 eV) using Autoback in ATHENA, and spectra were normalized to the post-edge step height. Non-linear least-squares shell-by-shell EXAFS fits (k^3 -weighing, k range = 2 to 13.5-14.5 $\text{\AA}^{-1}$, R -range = 1.1-7 $\text{\AA}$) were carried out using ARTEMIS on the unreacted minerals to verify the local bonding environment of U(VI) compared to published crystal structure analysis. The crystallographic interatomic distances reported in Burns (1998) for K-compreignacite were used as the initial model for calculation of K- and Na-compreignacite theoretical EXAFS spectra for shell-by-shell fits (no structure determination was found for Na-compreignacite). Groups of backscattering atoms at similar interatomic distances were determined by trial-and-error fitting based on this ideal crystal structure. The amplitude reduction factor (S_0^2) was set to 1 and energy shift (ΔE_0) was linked as a single parameter for all shells. For uranyl bonded to 2 axial oxygen atoms (U-O_{ax}), coordination number (N) was fixed at 2 for single scattering (SS) and 4 for multiple scattering (MS), distance (R) was constrained to double the SS distance, and Debye-Waller factors (σ^2) were allowed to vary. For all other shells, N was fixed on the weighted average of all U environments in the crystal structure for a given shell, and σ^2 and R varied.

The EXAFS spectra of reacted columns were analyzed by both least-squares linear combinations of uranyl reference compound spectra and shell-by-shell fits with theoretical standards to identify changes in the U(VI) bonding environment. Reference compounds included uranyl oxyhydroxides (K-compreignacite, Na-compreignacite, becquerelite, schoepite), uranyl nitrate, and uranyl sorbed on quartz (reference spectra from this work and Kanematsu et al. (2014)). Component weights of the reference spectra were constrained between 0 and 1 in linear combination fits but not forced to sum to unity. Components with a fraction of less than 10% in the fit were removed as they did not significantly improve fit statistics. Spectra were fit as described above for shell-by-shell analysis (k -weight = 3; k -range = 2 to 13.0-14.0 $\text{\AA}^{-1}$; R -range = 1.1-7 $\text{\AA}$) except that σ^2 was fixed to the value or average value obtained in fits to reference spectra for a given backscattering atom, and R and N were allowed to vary.

2.4 Dissolution rates and reactive transport modeling

Reactive transport (RT) calculations of column experiments were carried out using the code CrunchFlow (Steefel et al., 2015). This RT code considers all solid-aqueous phase reactions to be kinetic, and uses rate laws and coefficients included in the database in addition to thermodynamic solubility constants. Thermodynamic constants were obtained from available databases and the literature. Table S3 in SI gives the principal chemical equilibria and surface adsorption reactions considered in this study. To our knowledge, there are no published dissolution rates or constants for uranyl oxyhydroxide minerals. Therefore, CrunchFlow was used in conjunction with the present experimental data set to calculate rates for uranyl mineral dissolution and release of U under flow conditions.

CrunchFlow operates by running multiple parallel reaction pathways affecting the same solid phase and using a specified type of mineral dissolution or precipitation rate law (Steefel et al., 2015). In this work, the transition state theory (TST) rate law was selected for RT simulations to include the thermodynamic mineral solubility of the overall dissolution reaction and the mineral surface area (Steefel et al., 2015). The general rate law formulation (linear or nonlinear) for TST-type precipitation or dissolution reactions (R_m , mol m⁻³ porous medium s⁻¹) takes into account the reactive surface area of a mineral m (A_m , m² mineral m⁻³ porous media), a rate constant (k_m , mol m⁻² s⁻¹), a product term for reaction catalysis or inhibition (Πa^n), and a term for thermodynamic affinity, which includes the ion activity product for the mineral-water reaction (Q_m), and the corresponding thermodynamic equilibrium constant (K_{eq}) (positive for precipitation, negative for dissolution):

$$\begin{aligned} R_m &= A_m k_m \Pi a^n \left[\left(\frac{Q_m}{K_{eq}} \right)^\eta - 1 \right]^m \quad \text{when } \log(Q_m/K_{eq}) > 0 \\ R_m &= -A_m k_m \Pi a^n \left[\left(\frac{Q_m}{K_{eq}} \right)^\eta - 1 \right]^m \quad \text{when } \log(Q_m/K_{eq}) < 0 \end{aligned} \quad (1).$$

The catalysis or inhibition term (Πa^n) is the product of all far from equilibrium effects by various species in solution on the reaction (such as pH), with n as the reaction order, and m and η are experimentally or theoretical determined exponential dependences (see details in Steefel et al. (2015)). In this study, no dependence on the concentration of solution species was used (i.e., variables in the term Πa^n were not included). Since column experimental conditions were

undersaturated with respect to uranyl mineral solubility (see section 4.1), the contribution of the thermodynamic affinity term is insignificant; hence, the TST rate law (Eq. 1) is a function of only A_m and k_m . Under these conditions, the rate constant (k_m) becomes equivalent to a surface area normalized rate, R_s in $\text{mol m}^{-2} \text{s}^{-1}$ (Eq. 2) applied to a congruent, overall mineral dissolution reaction:

$$R_s = k_m = -\frac{R_m}{A_m} \quad (2).$$

In our RT simulations, measurements of specific surface area (A_s , $\text{m}^2 \text{g}^{-1}$) by the N_2 -BET method (N_2 -BET SSA in Table 3) and the measured mass of uranyl mineral loaded into the column (Table 2) were used to calculate the initial A_m following Eq.3:

$$A_m = \frac{A_s \cdot \phi_m \cdot \text{MW}_m}{V_m} \quad (3)$$

where ϕ_m is the volume fraction (m^3 mineral m^{-3} total volume), MW_m is the molecular weight (g mol^{-1}), and V_m is the molar volume ($\text{m}^3 \text{mol}^{-1}$) of the mineral phase m . Since changes in A_s of a specific dissolving mineral in a porous medium over the course of an experiment are unknown, changes in particle size (and thus reactive surface area, A_m) with dissolution were examined through changes in the mineral volume fraction (ϕ_m) and total porosity, ϕ (Eq. 4):

$$\phi = 1 - \sum_{m=1}^{N_m} \phi_m \quad (4).$$

Initial column porosity and ϕ_m of uranyl minerals and quartz were calculated from the initial mineral mass and volume packed in the column (Table 2). The code was set to update column porosity at each time step as a result of mineral mass dissolved and transferred from the solid phase to the aqueous phase. The linear fluid velocity (or pore velocity, v) obtained from fitting Br tracer breakthrough curves (Table 2, Fig. S1 in SI) was set as a constant in the RT model, but the update of porosity (ϕ) was allowed to change the volumetric flux (or Darcy flux), q ($\text{m}^3 \text{m}^{-2} \text{medium s}^{-1}$), according to Eq. 5 (Lichtner, 1997):

$$q = \phi \cdot v \quad (5).$$

These flow and mineral parameters are considered in the mass conservation equation for the transport of solute species in a multicomponent porous medium used by CrunchFlow, which describes the evolution of total concentration of the solute i , Ψ_i , as a function of time following the governing differential equation (Lichtner, 1997; Steefel et al., 2015):

$$\frac{\partial(\phi\Psi_i)}{\partial t} = \nabla(\phi D^* \nabla\Psi_i) - \nabla(q\Psi_i) - \sum_{m=1}^{N_m} v_{im} R_m \quad (6)$$

where the first two divergence operators (∇) involving porosity, ϕ , the dispersion-diffusion coefficient, D^* , and volumetric flux, q , are terms related to the transport through the porous medium, and the last reaction term includes the number of moles of i in each mineral m (v_{im}) and the TST mineral dissolution/precipitation rate, R_m .

Therefore, surface area normalized rates (R_s) of K- and Na-compreignacite in low and high carbonate BPW flow-through conditions were calculated by numerical optimization using a Model-Independent Parameter Estimation and Uncertainty Analysis (PEST) (Doherty, 2015) implemented in CrunchFlow to fit the experimental total U concentration in the effluent solution ($[U]_{\text{tot}}$, mol L⁻¹, as Ψ_i in Eq. 6) over time. Two approaches were followed: i) optimization of the rate constant, k_m , using a fixed uranyl mineral volume fraction (ϕ_m) calculated from initial mineral mass (method RT-TST); and ii) optimization of k_m and ϕ_m simultaneously, with the maximum ϕ_m set to that calculated from initial mineral masses (method RT-TST-VF). Note that the initial ϕ_m of uranyl mineral was 2.8-4.4% of total column volume for low carbonate BPW experiments and less than 1% of column volume in high carbonate BPW experiments (Table 2). For both RT calculations, the physical properties of the columns and their transport characteristics (Table 2) were obtained from fitting Br tracer breakthrough curves as described in section 2.2. Mineral volume fractions (from masses), specific surface areas, and BPW solution compositions were used in the simulations (Table 1, 2 and 3), with control columns used to check validity of flow parameters. To assess sorption of dissolved uranyl on quartz, control columns reacted with low carbonate BPW containing dissolved U(VI) were used to estimate U(VI) surface complexation equilibrium constants (details in S5, Table S4 and Fig. S6 in SI). These constants were subsequently applied in the RT simulations of uranyl mineral dissolution.

Other authors studying mineral dissolution in flow conditions calculated dissolution rates when the system reached steady-state dissolution conditions, i.e. $d[U]/dt = 0$, with the assumption that the solution is sufficiently undersaturated with respect to thermodynamic mineral solubility. In that case, the overall rate can be derived from a mass balance as presented in Ulrich et al. (2008). The equation takes the form:

$$R_n = \frac{Q \cdot [U]}{V \cdot A_s \cdot [\text{solid}]} \quad (7)$$

where R_n is the dissolution rate at steady-state ($\text{mol m}^{-2}\text{s}^{-1}$), Q is the volumetric flow rate (mL s^{-1}), $[U]$ is steady-state effluent concentration (mol L^{-1}), V is the fluid volume within the column (mL), A_s is the specific surface area ($\text{m}^2 \text{g}^{-1}$) and $[\text{solid}]$ is the mass concentration of U in the column ($\text{g solid L}^{-1} \text{fluid}$). Similar rate equations were used for flow reactor experiments in Pérez et al. (2000) and Gudavalli et al. (2013), but without considering the mass in the reactor or the decrease of particle size and solid concentration as the mineral dissolved. Here, Eq. 7 was used to calculate K- and Na-compreignacite dissolution rates for each duplicated mineral column using U effluent concentration once an apparent steady-state was reached. In this steady-state dissolution approach (method SSD), the specific surface area and mass concentration of U were not updated with dissolution. Calculated R_n rates were averaged for each mineral and each BPW condition (between 6 and 14 data points). These calculations allow comparison of steady-state and RT methods for calculating overall dissolution rates as R_s (surface area normalized rate).

3. RESULTS

3.1 Flow-through column experiments

3.1.1 Control columns

Quartz columns with no uranyl solid were reacted with low and high carbonate BPW without (Control1) and with $U(VI)$ in solution (Control2) (Fig.1). In the low carbonate systems, influent U was retarded for the first ~200 PV and reached input concentration after ~800 PV. An estimated average of $1.55 \cdot 10^{-7} \text{ U mol g}^{-1} \text{ quartz}$ was retained in the columns after reaction based on U mass introduced in the column and integrated effluent concentrations. In contrast, the high carbonate systems showed no U retardation and U effluent reached input concentrations within the first 20 PV (150 min). Effluent pH in low carbonate systems slightly decreased from pH 6.95-

7.00 in input solutions to an average of pH 6.93, and the total dissolved carbon (TC) concentrations were within error of the input solutions ($0.34 \pm 0.04 \text{ mmol L}^{-1}\text{TC}$). In the high carbonate experiments both values stabilized to the input solution (ca. pH 7.80 and $2.2 \text{ mmol L}^{-1}\text{TC}$) by 200 PV. For both controls, effluent concentrations of non-uranyl components, i.e., cation and anion concentrations, were not detectably altered from input solution concentrations (data shown in SI, Fig. S2).

3.1.2 Low carbonate BPW experiments

Effluent concentrations of U, cations, anions, total carbon and pH relative to input solution concentrations for K- and Na-compreignacite with low carbonate BPW columns are shown in Fig. 2. In the first 200 PV, a pronounced U release was observed for both minerals, with a higher pulse released in the case of K-compreignacite (maximum of $50 \mu\text{mol L}^{-1}\text{U}$ at 60 PV), and by 800 PV an apparent steady-state was reached ($\sim 3 \mu\text{mol L}^{-1}\text{U}$). Over the entire experiment, total U removed from the columns was only 0.5% of the initial U mass (Table 2). Similar to U, K from K-compreignacite and Na from Na-compreignacite were initially flushed from the columns and reached a steady effluent concentration after ~ 200 PV. In Na-compreignacite columns, K from the input solution was strongly retained within the column as evidenced by the failure to reach steady-state after 1400 PV. In K-compreignacite columns, K-effluent reached influent concentrations after ~ 200 PV, but then slightly decreased at 800 PV. However, there was no apparent uptake of Na from the input solution in the K-compreignacite columns. For both minerals, Mg and Ca reached steady-state within the first 25 and 100 PV, respectively, without a significant retardation in the column. Anions (Cl^{-} and SO_4^{2-}) were also not retarded in the columns. The effluent pH of all columns stabilized after 500 PV to input solution pH of 6.65. Effluent TC concentrations of K-compreignacite columns presented some scatter between duplicates and with higher concentration than input solutions until ca. 800 PV. Na-compreignacite duplicated columns resulted in more consistent TC concentrations that stabilized to influent concentration (0.21 mmol L^{-1}) after 100 PV.

3.1.3 High carbonate BPW experiments

Increasing total carbonate concentration in the BPW greatly enhanced the dissolution of K- and Na-compreignacite (Fig. 3) compared to the low carbonate systems. The concentration of

dissolved U reached a maximum of $\sim 500 \mu\text{mol L}^{-1}$ and the total amount of U released from the column corresponded to $\sim 60\%$ of the initial U mass present for three of the four replicate columns (Table 2). At the end of the experiments after 1400 PV, effluent U concentrations still did not attain steady-state for either mineral. Similar to the low carbonate systems, the initial U release was associated with a high release of K in the first 200 PV, which decreased steadily throughout the experiment and only reached input solution (steady-state) concentrations in the last 200 PV. Higher Na concentrations in the input solution showed more variability in the effluent data and masked the evolution of Na release in Na-compreignacite columns, yet a slight decreasing concentration trend over time can be observed. Potassium (K) present in the influent was not retained significantly in these columns in contrast to the low carbonate columns, although it showed a slower increase (ca. 150 PV) towards the input solution concentration than the divalent cations (Ca and Mg) and anions (Cl^- , SO_4^{2-}) which did not undergo a significant retention and reached input solution concentrations in the first few PV. For both minerals, the effluent TC started slightly higher than input solution concentration but reached influent values after 100 PV, followed, only in the Na-compreignacite columns, by a small increase over time. From the first few PV, effluent pH for both minerals was about one pH unit lower than the influent solution and increased gradually over time. Na-compreignacite column effluent had higher pH than K-compreignacite systems and approached the influent pH of 8.40 after 1100 PV.

3.2 Mineral phase transformations

3.2.1 Structure and properties of synthesized K- and Na-compreignacite

For the unreacted minerals, TGA analysis indicated 6.60 and 7.29% mass loss from K- and Na-compreignacite, respectively (Table 3), which corresponds to 7.5-8 water molecules. This is higher than the estimated structural water ($n = 7$) (Burns, 1998; Burns et al., 2004), but still within 1% permissible error of the TGA measurement. A ratio of 2.13 ± 0.05 U:K and 3.78 ± 0.05 U:Na were determined by elemental analysis for K- and Na-compreignacite, respectively, compared with the expected stoichiometric ratio of 3 for the pure phase (Table 3). N_2 -BET surface area was higher for K-compreignacite ($9.64 \pm 0.52 \text{ m}^2 \text{ g}^{-1}$) than for Na-compreignacite ($3.53 \pm 1.80 \text{ m}^2 \text{ g}^{-1}$). X-ray diffractograms of K- and Na-compreignacite matched the primary reflections of reference minerals well (Fig. 4 A1-A2), but lower peak intensity and line broadening were observed in the samples. In both K- and Na-compreignacite FTIR spectra,

bands around 920 cm^{-1} and at $2900\text{--}3600\text{ cm}^{-1}$ were observed (Fig. 4 B) that correspond, respectively, to the stretching vibrations of uranyl-oxygen bonds and to hydroxyl groups from surface adsorbed water, structurally incorporated water or OH. The K-compreignacite spectrum also had a sharp peak at 1630 cm^{-1} corresponding to structurally incorporated water. In the Na-compreignacite spectrum, this band was broad and less intense, probably due only to surface adsorbed water. Both Raman spectra (Fig. 4 C) presented a very intense, sharp peak at $\sim 830\text{ cm}^{-1}$, which corresponds to the symmetric stretching of the uranyl U-O bonds. The peaks at ~ 325 and $\sim 250\text{ cm}^{-1}$ can be assigned to the U-O ligand vibration, and to the uranyl bending and lattice vibrations, respectively. Particle size analysis (Fig. 4 D1-D2) showed a similar distribution for both minerals, with a main population at $80\text{--}300\text{ nm}$ and a second group at $975\text{--}2700\text{ nm}$ for K-compreignacite and $425\text{--}1300\text{ nm}$ for Na-compreignacite. The smaller size fraction was more abundant in K-compreignacite than Na-compreignacite. SEM images of both minerals (Fig. 5 B-C) showed $50\text{--}200\text{ }\mu\text{m}$ agglomerations of particles smaller than $10\text{ }\mu\text{m}$ with flakey and needle-shape morphology. Similar particle shapes were observed by Sandino and Grambow (1994) for K-compreignacite.

The EXAFS spectrum of unreacted K-compreignacite was fit shell-by-shell starting with the crystal structure refinement reported in the literature (Table 4, Fig. 6 A). Equatorial oxygens were grouped in three shells (U-O_{eq}) and the longest XRD distance at $2.85\text{ }\text{\AA}$ was excluded as it did not contribute significantly to the fit. The first U-U shells were grouped in two interatomic distances, with the shortest one converging to a distance shorter than reported by XRD ($\sim 3.70\text{ }\text{\AA}$ vs. $3.82\text{ }\text{\AA}$ from structure refinement). For the unreacted Na-compreignacite EXAFS spectrum (Table 4, Fig. 6 B), U-O_{eq} distances were distributed in 3 shells with similar distances to K-compreignacite, whereas the first U-U shells were grouped in fitting at $3.89\text{ }\text{\AA}$, resembling the EXAFS fit to the becquerelite structure (Table 4, Fig. 6 C). In the becquerelite structure, the five equatorial oxygen shells are grouped in just two distances at 2.26 and $2.47\text{ }\text{\AA}$, instead of three distances as seen in the K- and Na-compreignacite fits. Control columns reacted with low carbonate BPW containing aqueous uranyl provided a reference spectrum of dissolved U(VI) sorbed on quartz (Fig. 6 D) (the amount of U sorption on quartz was too low in high carbonate BPW columns to collect EXAFS spectra). The optimum shell-by-shell fit (Table 4) was obtained by grouping U-O_{eq} shells at distances similar to those reported in the literature for sorbed aqueous uranyl on silica ($R = 2.28$ and $2.48\text{ }\text{\AA}$) (Batuk et al., 2011; Sylwester et al., 2000) and

varying N with σ^2 fixed on average values determined from fits to crystalline reference compounds. This EXAFS model informed the stoichiometry chosen for the two uranyl surface complexation reactions and estimation of their sorption constants in RT simulations (section S5 and Table S4 in SI).

3.2.2 Column materials before and after dissolution reactions

Electron microscopy images of the quartz control columns (Fig. 5 A1-A3) showed clean particles before and after reaction with low and high carbonate BPW solutions. When quartz was mixed with K- and Na-compreignacite, quartz particles were completely covered by the uranyl minerals (Fig. 5 B1 and C1). After reaction with low carbonate BPW, loose uranyl mineral grains were less abundant, but quartz grains were still covered with particles (Fig. 5 B2 and C2). After reaction with high carbonate BPW, SEM images showed a much lower density of uranyl mineral particles on the quartz grains. K-compreignacite particles on quartz (Fig. 5 B3) had a flaky morphology similar to the unreacted mineral, whereas Na-compreignacite particles (Fig. 5 C3) showed a more spherical shape after reaction.

Specific surface area (SSA) was measured on the quartz-uranyl mineral mixtures before and after reaction (Table 3). Quartz controls did not show significant variations after reaction, with SSA values averaging $0.125 \pm 0.008 \text{ m}^2 \text{ g}^{-1}$. When the quartz was mixed with K- and Na-compreignacite, the mixture's SSA increased slightly from quartz-only to 0.196 and $0.291 \text{ m}^2 \text{ g}^{-1}$, respectively. After reaction with low carbonate BPW, the SSA of K-compreignacite column mixtures increased to $0.351 \text{ m}^2 \text{ g}^{-1}$, while Na-compreignacite remained similar to unreacted values. After reaction with high carbonate BPW, measured SSA was similar to that of quartz-only control columns (0.122 and $0.104 \text{ m}^2 \text{ g}^{-1}$ for K- and Na-compreignacite, respectively).

Acid digestion and total element analysis of K-compreignacite and quartz mixtures before and after reaction with low carbonate BPW showed a decrease in K concentration after reaction (from 125 to $29 \mu\text{mol g}^{-1}$), resulting in a U:K ratio of 2.64 compared with 2.03 before reaction (Table 3). In high carbonate BPW experiments, U concentration decreased from 252 to $76 \mu\text{mol g}^{-1}$ and K concentration was decreased even further to $6.6 \mu\text{mol g}^{-1}$. For Na-compreignacite columns, the Na concentration decreased from 51 to $18 \mu\text{mol g}^{-1}$ in low carbonate BPW columns, although U concentration did not vary within measurement error (ca.

200 $\mu\text{mol g}^{-1}$; Table 3). Noticeably, the K concentration increased about 65 $\mu\text{mol g}^{-1}$ compared to unreacted column concentrations. In the high carbonate BPW columns, U concentration decreased markedly to 3.8 $\mu\text{mol g}^{-1}$, while K decreased to a comparable concentration to quartz control columns and Na was below detection (Table 3). For both minerals and column mixtures, the concentrations of Mg and Ca were below detection, with the exception of Na-compreignacite columns reacted with low carbonate BPW, which showed a measurable increase in Mg and Ca compared to unreacted columns (Table 3).

3.2.3 Structural changes after reaction from EXAFS spectroscopy

Uranium-L_{III} EXAFS spectra of K-compreignacite columns reacted with low and high carbonate BPW (Table 5) were best fit by a linear combination (LC) of spectra of unreacted K-compreignacite (78-88%) and sorbed U(VI) on quartz (20-14%). For Na-compreignacite reacted with the low carbonate BPW, the spectrum was fit with a combination of unreacted K-compreignacite (58%), rather than unreacted Na-compreignacite, and a significant contribution from the sorbed U(VI) on quartz spectrum (33%), although the fit had a higher R-factor than the K-compreignacite LC fit (0.18 vs. 0.07). The spectrum of Na-compreignacite reacted with high carbonate BPW was not fit well by LC of any reference spectra, and a single component fit with K-compreignacite was a poor match (R-factor = 0.25).

Shell-by-shell fits of K-compreignacite reacted with low and high carbonate BPW were initially based on the EXAFS fit of the unreacted K-compreignacite spectrum (Table 4). For both spectra, the best fits showed no changes in U-O_{ax} interatomic distances for the SS and MS paths compared to unreacted K-compreignacite, but σ^2 decreased for the MS path (Table 5; Fig. 6 shows total fit results; deconvolutions of all backscattering paths are shown in Fig. S3 and S4 in SI). The fits improved significantly when another U-O_{eq} shell was included at a longer distance, i.e., 2.81 and 2.88 Å for high and low carbonate BPW samples, respectively. This shell contributes to the FT peak between 2 and 2.8 Å (Fig. 6). The additional U-O_{eq} shell increased the total equatorial oxygens from fitting to N = 6.1-6.9 (σ^2 fixed). Backscattering amplitude from U-U shells was greatly reduced compared with the unreacted spectrum, with U-U at 3.91-3.92 Å the only detectable shell at distances beyond the equatorial oxygen atoms (Table 5).

For reacted Na-compreignacite spectra, shell-by-shell fits were based on unreacted K- and Na-compreignacite models (Fig. 6, Table 5). As observed in the reacted K-compreignacite spectra, the fit of the low carbonate BPW Na-compreignacite spectrum was improved significantly when a longer distance at 2.85 Å was added for the U-O_{eq} shells. In high carbonate BPW experiments, fits to the spectrum showed changes in the U-O_{ax} shell compared with unreacted compreignacite, with distance increasing to 1.84 Å. To obtain a better fit, the average σ^2 values of U-O_{eq} shells in the sorbed U(VI) model fit were used. However, the high carbonate BPW spectrum model included only three U-O_{eq} shells, with two predominant shorter distances at 2.22 and 2.39 Å, plus a longer distance shell at 2.90 Å (Table 5). This distribution is similar to the unreacted Na-compreignacite fit model, although the longest U-O_{eq} distance is longer than obtained in the spectrum fit of unreacted Na-compreignacite (Table 4). Backscattering from U-U shells was greatly reduced and only one U-U shell was significant in the fit (N=1.0-2.4 at 3.88-3.89 Å) of reacted compared to unreacted Na-compreignacite.

3.3 Reactive transport simulation of dissolution

The simulation of mineral dissolution using CrunchFlow under low carbonate BPW conditions considering only thermodynamic equilibrium (achieved by using high rate constants) resulted in U effluent concentrations reaching a steady-state within the first 10 PV (5 h) of the experiment that were about one order-of-magnitude higher than experimental observations. Concentrations of U set by equilibrium solubility of oxyhydroxide minerals schoepite and becquerelite were tested in the model with low carbonate BPW, and also resulted in one to two orders-of-magnitude higher dissolved U concentrations than observed (data not shown; solubility constants given in Table S3 in SI). In the high carbonate BPW systems, simulated dissolution under equilibrium conditions was rapid and mass decreased such that all U-mineral was dissolved by the end of the experiment, instead of the observed gradual dissolution over time. These initial tests verified that kinetically-controlled dissolution was a valid assumption for the simulations and the RT-TST rate law was included in the model (Fig. 7 and Fig. S7 in SI).

For low carbonate BPW systems, effluent U concentrations were simulated well with the kinetic RT-TST approach once apparent steady-state was reached (750-890 PV; 80-100 h in Fig. 7 A1-B1). Based on the simulations, uranyl sorption on quartz (Fig. S6 in SI) was important for retaining U in the column only during initial reaction (80-100 h). Model simulations of effluent

pH and TC were constant from the first PVs and matched experimental concentrations at steady-state, with the exception of TC concentrations in Na-compreignacite columns, which were slightly overestimated by the model (Fig. 7 A2-B2 and A3-B3). Cation and anion concentrations were simulated well, excluding the initial release of K and Na from K- and Na-compreignacite columns and the K uptake from input solution by both minerals (Fig.S7 in SI). Optimized dissolution rates (R_s and R_n) at apparent steady-state using the three calculation methods (SSD, RT-TST and RT-TST-VF) are compared in Table 6. The SSD calculations produced faster dissolution rates than RT-TST optimized values, particularly for K-compreignacite ($\Delta \log R = 0.84$ higher, or almost 7 times faster). Simultaneous optimization of mineral volume fraction (ϕ_m) and dissolution rate constant (RT-TST-VF method) resulted in no significant changes for either R_s or ϕ_m in the low carbonate experiments (Table 6).

In the high carbonate BPW systems, the RT-TST model without ϕ_m optimization captured the high initial U release followed by a slow decrease over time, but overestimated the U concentrations after the first 200 PV (25 h) (results not shown). However, effluent U, pH, and TC were well matched for most of the experiment when the RT-TST-VF optimization model was applied (Fig. 7). Although effluent pH was underestimated in the first part of the experiment, the simulations exhibited an increase over time that satisfactorily matched the pH evolution in both mineral systems (Fig. 7 A2-B2). The TC simulated curves closely matched experimental data for K-compreignacite after initial flush out (20 h), but simulations slightly underestimated data for Na-compreignacite systems (Fig. 7 A3-B3). Effluent cation and anion concentrations were also simulated well by the models, including decreasing K and Na effluent in K- and Na-compreignacite systems, respectively (Fig.S7 in SI). The decrease in ϕ_m for K- and Na-compreignacite determined in the RT-TST-VF optimization (Table 6) compares well with the U mass column loss calculated from total integrated U effluent (Table 2). For K-compreignacite, average ϕ_m decreased from 0.99% to 0.58% of total volume, and average U mass lost from the column was ~60% of the initial mass. For Na-compreignacite, ϕ_m decreased from 0.51% to 0.46% (mass loss of 87%) for replicate C, and from 0.50% to 0.31% (mass loss of 58%) for replicate D (Table 2).

The three calculation methods showed that the difference between K- and Na-compreignacite dissolution rates were within an order-of-magnitude in either low or high

carbonate solutions. However, dissolution rates in the high carbonate BPW systems were higher than in low carbonate systems by 2 to 3 orders-of-magnitude for both minerals, regardless of the calculation method.

4. DISCUSSION

4.1 Dissolution rates

For both minerals and both BPW systems, the dissolution of the uranyl oxyhydroxide minerals was kinetically controlled. Comparison of RT-TST optimized rates shows that dissolution was 2.9-3.6 times faster for Na-compreignacite than for K-compreignacite in either BPW solution (Table 6, Fig.S8 in SI). Although mineral mass and surface area were higher in K-compreignacite experiments compared to Na-compreignacite (Tables 2 and 3), normalization of the overall dissolution rate to the specific surface area and mass among all experiments showed this consistent result. A thermodynamic solubility study showed that substituting Na for K in the compreignacite structure increased the mineral solubility by approximately 3.5 orders-of-magnitude (Gorman-Lewis et al., 2008b). In the dissolution experiments of this study, solutions were at least 3 to 4 orders-of-magnitude undersaturated with respect to K- and Na-compreignacite over the course of the experiment, and thus the contribution of the affinity term in the TST rate law was negligible (Eq. 1). Therefore, the dissolution mechanism must have a key role in the rate difference between the two compreignacite compositions.

In the low carbonate BPW systems, SSD rates of both minerals were higher but within an order-of-magnitude of RT optimized values (Table 6). This is expected as the optimization in the RT models was applied to effluent concentrations after initial high U flush-out, presumably of mineral particles < 200 nm in size (Fig. 4 D1-D2), and apparent steady-state was reached. Under these conditions, there was relatively little change in U mass in the column, and thus porosity, because of the overall slow dissolution rate. This interpretation is supported by the lack of improvement of the fit to effluent data with ϕ_m optimization (RT-TST-VF). In the high carbonate BPW systems, a clear steady-state was not reached over the course of the experiment. Thus, the SSD method was only applied to effluent data during the final 60-80 h when the dissolved U concentrations were low. This resulted in lower dissolution rates than calculated by the RT-TST optimization (Table 6), which considered data from ca. 4-5 h. A flush-out in the first few pore

volumes of smaller mineral particles (Fig.4 D1-D2) and possible colloidal U(VI) through the 0.2 μm filter could have reduced the total mineral mass available for dissolution. An over-estimation of mass would cause the SSD rate (Eq.7) to be higher than that determined in the RT-TST models, where ϕ_m , porosity, and chemical composition are updated at each time step. The simultaneous optimization of k_m and ϕ_m using the RT-TST-VF approach confirmed that the amount of the dissolving mineral (and consequently the particle size and reactive surface area) was significantly reduced over the course of the experiment in the high carbonate systems and must be considered in the derivation of an overall dissolution rate.

Comparison of dissolution rates between low and high carbonate BPW solutions shows that a 10-fold increase of dissolved total carbonate concentration and corresponding increase in pH (from 6.65 to 8.4) resulted in about 2.5-3 orders-of-magnitude faster rate (Table 6, Fig.S8 in SI). This increase agrees with previous observations for the dissolution of other silicate and phosphate uranyl minerals. The dissolution rate of uranophane ($\text{Ca}(\text{H}_3\text{O})_2(\text{UO}_2)_2(\text{SiO}_4)_2 \cdot 3\text{H}_2\text{O}$) in flow experiments increased from $2.98 \cdot 10^{-11}$ to $5.89 \cdot 10^{-11} \text{ mol m}^{-2} \text{ s}^{-1}$ from pH 8 to 9 and one order-of-magnitude higher dissolved bicarbonate concentration (Pérez et al., 2000). For soddyite ($(\text{UO}_2)_2\text{SiO}_4 \cdot 2\text{H}_2\text{O}$), a uranyl silicate without interlayer cations, rates were on the order of $10^{-14} \text{ mol m}^{-2} \text{ s}^{-1}$ with a very slight increase in the dissolution rate even with 10 times higher carbonate concentration (Pérez et al., 1996). In a study of Ca-autunite ($\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$) dissolution in batch flow-through experiments, overall uranium dissolution rates on the order of $10^{-11} \text{ mol m}^{-2} \text{ s}^{-1}$ at pH 7-8 were reported, and increased by 2 to 3 orders-of-magnitude at pH 10-11 and 6 fold higher carbonate concentration (Gudavalli et al., 2013). The Na-endmember mineral ($\text{Na}(\text{UO}_2)(\text{PO}_4) \cdot 3\text{H}_2\text{O}$) was more stable than Ca-autunite (between 4 and 21 times lower dissolution rate) and the rate increased by about one order-of-magnitude with higher pH and carbonate. The overall dissolution rates calculated here for K- and Na-compreignacite in low carbonate BPW solutions are lower by about 2 orders-of-magnitude than those reported by Gudavalli et al (2013) for Ca-autunite at pH 7, but rates are similar or higher for K- and Na-compreignacite in high carbonate BPW solution experiments at pH 8.4. These contrasting rates may be a consequence of intrinsic surface and structural differences between uranyl phosphate and oxyhydroxide minerals, as well as differences between measurements in batch flow versus porous media.

4.2 Mechanisms of dissolution in low carbonate systems

Both K- and Na-compreignacite minerals incorporated K into the structure during dissolution experiments with low carbonate BPW based on column effluent K concentration and bulk chemical analyses (control columns with quartz had no retardation of input solution species). Between 800-1400 PV (90-100 h) during steady-state U release in the K-compreignacite column, effluent solution K decreased relative to influent concentration. By the end of the experiment, the total K concentration determined by acid digestion of the reacted column material had decreased relative to total U, resulting in a ratio closer to the ideal 3:1 U:K in stoichiometric compreignacite than in the unreacted mineral (~2:1; Table 3). For Na-compreignacite, effluent K concentration was still significantly below input concentration by the end of the experiment and acid digestions of reacted column material showed a significant increase in K, from below detection to almost four times the Na concentration, and a decrease in Na concentration. The U:cation ratio (considering Na and K content together) was 2.72, which is within error of the K-compreignacite reacted samples (Table 3). Uniquely among the reacted samples, analysis of Na-compreignacite showed a significant Ca concentration and a small amount of Mg after reaction, indicating that other exchangeable cations were also incorporated into the interlayer of the mineral structure for charge balance. Other studies have reported the formation of uranyl neoprecipitates on the mineral surface, as observed during the dissolution of becquerelite single crystals in batch, closed systems with ultrapure water (pH 7) for 24 h (Schindler et al., 2006; Schindler et al., 2011). In the flow-through porous media of our experiments, solutions were undersaturated with respect to uranyl phases, and thus cation exchange appears to be the mechanism of surface alteration of the original compreignacite minerals.

Uranyl oxyhydroxide minerals consist of U(VI)-OH polyhedral sheets that incorporate a variety of cations and water molecules into the interlayer and are held together by hydrogen bonds (Burns, 1998; Burns and Hill, 2000) (Fig. 8). These low atomic number interlayer species are weak photoelectron scatterers when present at distances $> \sim 3 \text{ \AA}$, and thus do not contribute detectable scattering amplitude to the EXAFS spectra. Nonetheless, changes in the concentration, type, and charge of interlayer cations can influence interatomic distances between U(VI) and oxygen atoms in the polyhedral sheets, particularly for cations with a large ionic

radius or higher charge (Allen et al., 1997; Kanematsu et al., 2014). Unreacted K-compreignacite was stoichiometrically deficient in K compared to U (Table 3), which suggests that H^+ (H_3O^+) accounts for charge balance. Analysis of EXAFS spectra by shell-by-shell fitting indicated more disorder in U-U distances from adjacent uranyl polyhedral in unreacted K-compreignacite compared with Na-compreignacite, which had an excess U:Nastoichiometric ratio (> 3), although U-O_{ax} and U-O_{eq} shells and distances were similar in both compounds (Table 4). In unreacted Na-compreignacite, U-U interatomic distances determined from EXAFS were more similar to U shells in becquerelite ($Ca(UO_2)_6O_4(OH)_6 \cdot 8H_2O$) than in K-compreignacite (Table 4). After reaction for both compounds, U-O_{eq} bonding was more disordered (more oxygen shells needed to fit the spectrum) and more distorted (greater range of bond distances), and long-range order was diminished as shown by the lack of U-U scattering from adjacent polyhedra at long distances (Table 5). Semi-quantitative spectral fitting by linear combinations of reference compounds suggests that sorbed uranyl may contribute to the EXAFS after reaction (~14-20% for K-compreignacite; ~33% but with poor fit results for Na-compreignacite), although the local U-O bonding environment is similar for sorbed U(VI) and unreacted K- or Na-compreignacite (Table 4) and thus difficult to distinguish. Although steady-state dissolution rates differed by 2-3 times between K- and Na-compreignacite (Table 6), the total fraction of U dissolved over the course of all low BPW experiments was less than 1%. The chemical and structural results show that during flow-through reactive dissolution, K is preferentially taken up from solution in both compounds, with Na exchanged from Na-compreignacite and K and minor divalent cations (Ca, Mg) incorporated into the Na-compreignacite interlayer. As such, both compounds resemble a disordered K-compreignacite by the end of the experiment.

The overall reaction for stoichiometric dissolution of K- and Na-compreignacite minerals can be stated as:

where M = K or Na. Optimization of k_m using the TST rate law and parameter estimation in the RT model (Eq. 6) included no dependence of the rate equation on the concentration of other solution species and applied stoichiometric dissolution to Eq. 1. Interlayer cation exchange or preferential leaching from the compreignacite structure was not included in the RT simulations. The calculated overall dissolution rates using either the SSD (R_n , Eq. 7) or RT-TST (R_s , Eq. 2)

methods were each normalized to the initial specific surface area (A_s) of the mineral and were dependent only on the total effluent U concentration. The difference between these two methods for calculating R was, in the RT-TST optimization, the inclusion of sorption of aqueous uranyl on quartz and flow through a porous medium. Based on the surface site concentration (Table S4 in SI) and U effluent concentrations, a maximum of 8-9% and 18-19% of the total U dissolved from K- and Na-compreignacite columns, respectively, could have sorbed on quartz (also suggested by the EXAFS LC fits), and thus reduce the total U concentration measured in the effluent solution. Inclusion of uranyl sorption in the RT-TST estimations should have resulted in an optimized R_s that was higher compared to the estimation of R_n in SSD, for which all effluent U was attributed to dissolution, since U that is dissolved and then sorbed is retained in the column. However, using the same range of experimental effluent data, calculated rates were significantly lower for RT-TST optimization than using the SSD equation (~7 times lower for K-compreignacite and ~1.4 times lower for Na-compreignacite columns), which indicates that uranyl sorption does not account for the observed differences in calculated rates. The lack of change in optimized R_s between RT-TST and RT-TST-VF calculations is consistent with the small fraction of mineral dissolved (<1% of total mass) and thus lack of change in porosity and flow characteristics during dissolution. None of the rate calculations included interlayer cation exchange and all assumed stoichiometric dissolution of compreignacite (Eq. 8). Slightly faster dissolution rates calculated by all methods for Na-compreignacite compared with K-compreignacite (Table 6) indicate that overall rates are relatively insensitive to the exchange of interlayer cations. These observations support the interpretation that the molecular-scale rate-determining step is detachment of the uranyl group from the polyhedral layers of the mineral structure (Fig. 8 A), which occurs after H^+ , OH^- or ions in solution bond to surface O-atoms and weaken the corresponding U-O-U bonds until separation (Schindler et al., 2004). The lower rates calculated using the RT-TST governing equation to include flow through porous media compared to the SSD method demonstrates the influence of pore-scale transport in reducing apparent rates for a steady-state system in which net mineral dissolution is small and transport properties are relatively constant.

4.3 Effect of dissolved carbonate on dissolution mechanism

Increasing the concentration of dissolved carbonate in general accelerates the dissolution of uranyl minerals, particularly above pH 7 (de Pablo et al., 1999; Gudavalli et al., 2013; Ilton et al., 2006; Pérez et al., 2000; Pérez et al., 1996; Sowder et al., 2001). In this study, an increase of one order-of-magnitude in the dissolved carbonate concentration resulted in faster dissolution rates by 2-3 orders-of-magnitude (Table 6) and net removal of U from the columns of 58-87% of the initial mass (Table 2). Electron microscopy of column material showed removal of fine particles and relatively clean quartz surfaces after reaction with high carbonate solutions (Fig. 5 B3-C3). Results from EXAFS analysis indicated a reduction in long-range atomic scattering from U and changes in the distribution of U-O_{eq} bonding compared with compregnacite reacted in low carbonate BPW solutions. These results are consistent with a faster dissolution rate and congruent dissolution (i.e., no build-up of an extensive leached or altered surface layer) compared with low carbonate BPW experiments.

The effect of dissolved carbonate on enhancing dissolution has been reported for other uranyl minerals (e.g. Sowder et al. (2001)), yet the exact role of carbonate species on the dissolution mechanism is not always elucidated. For example in Ilton et al. (2006), the solubility of Na-boltwoodite was strongly enhanced by dissolved carbonate, but the relative importance or molecular details of the mechanism controlling the dissolution rate was not reported. Some studies inferred molecular mechanisms from aqueous speciation calculations. For example, Gudavalli et al. (2013) showed that during dissolution of Na- and Ca-autunite, buffered bicarbonate solutions were undersaturated thermodynamically with respect to becquerelite, and uranyl carbonate and Ca-uranyl carbonate complexes were the predominant aqueous species, which were postulated to control mineral dissolution. Uranyl carbonate and alkaline-earth uranyl carbonate complexes are highly soluble and stable species that dominate the uranyl aqueous speciation between pH 7 and 11 (Bernhard et al., 1996; Bernhard et al., 2001; Kalmykov and Choppin, 2000) and also uranyl adsorption onto sediment and soils (Stewart et al., 2010). Indeed, breakthrough of U(VI) was noticeably retarded by sorption to quartz in control columns with low carbonate BPW compared to high carbonate BPW systems (Control 2, Fig. 1 A1-B1, and Fig. S6 in SI). A recent review concluded that reported differences in the inorganic speciation of U in natural waters were caused by whether or not the species $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$,

CaUO₂(CO₃)₃²⁻, and MgUO₂(CO₃)₃²⁻ were included in the thermodynamic database for the equilibrium speciation calculations (Vercouter et al., 2015). Formation data for these ternary species have been determined in the last decade (Dong and Brooks, 2006, 2008; Geipel et al., 2008; Lee and Yun, 2013), but few compiled thermodynamic databases have included them (e.g., they have been recently added to Thermochimie, www.thermochimie-tdb.com). In this study, equilibrium speciation calculations of effluent column solutions, which included all recently reported uranyl carbonate species (Table S3 in SI; Dong and Brooks (2006)), indicated that the thermodynamically most stable aqueous uranyl species were Ca₂UO₂(CO₃)₃(aq), CaUO₂(CO₃)₃²⁻, and MgUO₂(CO₃)₃²⁻, comprising over 99% of dissolved uranyl in the high carbonate BPW solutions (Fig. S9 in SI). Calculations also showed that K- and Na-compreignacite and other common uranyl oxyhydroxide and carbonate phases were highly undersaturated (by orders-of-magnitude) in these solutions.

In high carbonate BPW systems of pH > 8 and relatively high concentration of Ca (2.7 mmol L⁻¹) and Mg (0.83 mmol L⁻¹), we postulate that the dissolution of K- and Na-compreignacite was driven by the formation of ternary Ca-uranyl carbonate complexes, and possible Mg-uranyl carbonate complexes (Fig. 8 B). A proposed molecular mechanism can be formulated from the process presented by Gudavalli et al. (2013) and de Pablo et al. (1999) for the dissolution of Na- and Ca-autunite and UO₂ minerals, respectively, in the presence of dissolved carbonate. The two-step process consists of surface coordination of Ca²⁺, CO₃²⁻ and HCO₃⁻ on the U(VI)-oxygen polyhedral in the mineral layers, perhaps mostly on the edge sites, and then detachment of the Ca-uranyl carbonate complexes from the surface into solution. Given the lack of evidence for development of a surface leached or altered layer, it is likely that the overall adsorption/desorption process is relatively fast, with the bond breaking of uranyl polyhedral as the rate-determining step. The significant increase in dissolution rate between low and high carbonate solutions suggests that the TST rate law (Eq. 1) used to describe overall mineral dissolution should be modified to include a dependence on, for example, the concentration of total carbonate or the concentrations of aqueous or adsorbed uranyl carbonate species (Ca₂UO₂(CO₃)₃(aq), CaUO₂(CO₃)₃²⁻, MgUO₂(CO₃)₃²⁻). Additional experimental data over a range of dissolved carbonate concentrations are needed to adequately parameterize a rate law that captures this mechanism in order to derive an intrinsic rate constant (k_m) from fitting of the overall rate (R_m).

Dissolution rates for both K- and Na-compreignacite calculated by the RT-TST model (R_s) were faster than the rates calculated with the SSD equation (R_n), but this difference is likely due to the small data range used for the latter since constant release of U was not achieved by the end of the experiment. The RT-TST optimization failed to adequately capture U effluent behavior over the entire experiment because the rapid rate of dissolution and uranyl transfer to solution required correction for changing volume and reactive surface area of the mineral as dissolution proceeded. The initial volume fraction of either K- or Na-compreignacite was <1% of the total column volume. As such, removal from columns of >60% of initial U would have little effect on total porosity or bulk transport properties, which are controlled by the quartz matrix. Transport properties calculated from Br tracer fits showed differences of < 5% between the beginning and the end of each experiment, and control and experimental columns had a similar range of values for fluid velocity and dispersivity (Table 2, Fig. S1 in SI). Calculated changes in total porosity by the end of the experiment due to mineral dissolution were < 0.6%. Although variation in mineral volume fraction (ϕ_m) affects total porosity (ϕ) (Eq. 4), and thus transport properties in the column (Eq. 6), variation in physical properties among different column packing of quartz was greater on average than the change in porosity from uranyl mineral dissolution alone. Therefore, optimization of ϕ_m in the RT-TST-VF calculation was used to account primarily for the effect of changing particle mass, volume, and surface area over the course of the experiment in the absence of a constant U effluent concentration. Derivation of dissolution rates using a RT model while accounting for dynamic changes in reactive surface area captures an average rate that does not require the system to exhibit constant effluent concentrations (i.e., “steady-state”).

5. CONCLUSIONS

This study reports for the first time dissolution rates of two environmentally relevant uranyl oxyhydroxide minerals, K-compreignacite and Na-compreignacite. The overall dissolution rates reported here were determined from packed-column experiments of the synthetic mineral endmember mixed with quartz to simulate reaction dynamics in a porous medium. A reactive transport model (CrunchFlow) was used to calculate overall dissolution rates normalized to surface area (R_s) while accounting for variation in reactive surface area and fluid transport over the course of the dissolution experiment, rather than attempting to quantify a kinetic rate constant

(k_m) that relates to elementary reaction steps (e.g., Lichtner (2016)). Characterization of column material before and after reaction by a combination of bulk methods, microscale imaging, and EXAFS spectroscopy provided insight into molecular-scale processes.

Findings of this study show that during flow-through reactive dissolution in low carbonate solutions:

1. Interlayer cations were initially leached out from the minerals. In Na-compreignacite, K and minor divalent cations are exchanged for Na and incorporated into the interlayer, destabilizing the mineral structure and slightly increasing the dissolution rate. Characterizations suggest that, after reaction, both K- and Na-compreignacite resemble disordered K-compreignacite with altered surfaces.
2. The total fraction of U dissolved over the course of the experiments was <1% of initial mass, and thus mineral mass and transport properties did not change during the experiment. Dissolution rates calculated using a fully transient reactive transport model were slower than those calculated using a steady-state dissolution assumption, demonstrating the effect of including pore-scale transport on overall rates of mineral dissolution.
3. Calculated dissolution rates did not consider exchange of interlayer cations and assumed stoichiometric dissolution. If the molecular-scale rate-determining step is detachment of the uranyl group from the polyhedral layers of the mineral structure, this process is relatively insensitive to bonding with interlayer cations and results in similar overall dissolution rates.

For flow-through reactive dissolution in high carbonate solutions:

4. A 10-fold increase in dissolved total carbonate concentration and corresponding increase in pH (from 6.65 to 8.4) resulted in about 2.5-3 orders-of-magnitude faster dissolution rate for K- and Na-compreignacite, net removal of 58-87% of initial U mass from the columns, and lack of development of a surface leached or altered layer.
5. Faster dissolution and non-steady-state U release required a model that accounted for decrease in U mass, volume, and reactive surface area over the course of the experiments. Optimization of both dissolution rate and mineral volume fraction in the reactive transport model resulted in faster rates compared with a steady-state dissolution assumption, with Na-compreignacite dissolving slightly faster than K-compreignacite ($\log R = -9.24$ vs. -9.81 mol

m² s⁻¹). The small uranyl mineral mass and volume fraction (< 1%) compared to the quartz matrix in the columns did not affect column transport properties. Thus, calculated dissolution rates captured an average rate that accounted for significant change in particle volume and reactive surface area over the course of the experiment.

6. We postulate that faster dissolution of K- and Na-compreignacite was driven mostly by the formation of ternary Ca-uranyl carbonate complexes. These aqueous complexes dominate uranyl speciation in solution and increase in stability with increasing pH. It is likely that adsorption of Ca²⁺, CO₃²⁻ and HCO₃⁻ on U(VI)-oxygen surface sites is a relatively fast process, whereas the detachment of Ca-uranyl carbonate complexes from mineral polyhedral layers was the rate-determining step.

Uranyl oxyhydroxide minerals such as compreignacite are formed easily from oxidation of reduced U minerals (compared to uranyl phosphates and silicates) and precipitate readily from saturated solutions (Hunter and Bertsch, 1998; Kanematsu et al., 2014; Morris et al., 1996). Their fast dissolution rates in natural waters, especially in the presence of high dissolved carbonate, compared with uranyl phosphate and silicate phases emphasizes the need for quantification of coupled reaction and transport processes that control the concentration and fate of U in surface and subsurface environments.

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Figures

Rates and mechanisms of uranyl oxyhydroxide mineral dissolution

Estela REINOSO-MASET, Carl I. STEEFEL, Wooyong UM, Jon CHOROVER, Peggy A. O'DAY

Figure 1. Duplicated control columns with quartz and no solid uranyl phases. Input solutions of background porewater (BPW) in Control 1 columns (green symbols) contain no U(VI); Control 2 columns (orange symbols) contain BPW with the addition of dissolved U(VI) ($3.74 - 4.06 \mu\text{mol L}^{-1}$). Dashed lines represent concentrations and pH of BPW input solutions with (A) low ($0.30 - 0.38 \text{ mmol L}^{-1}$) and (B) high ($2.17 - 2.21 \text{ mmol L}^{-1}$) total carbonate. **A1, B1:** dissolved U concentration (in $\mu\text{mol L}^{-1}$), **A2, B2:** pH, and **A3, B3:** dissolved total carbon (mmol L^{-1} TC) from effluent solutions as a function of time in pore volume (PV).

Figure 2. Concentration of released U (in $\mu\text{mol L}^{-1}$), effluent pH, and total dissolved carbon (TC), Na, Mg, K, Ca, Cl and SO₄ effluent concentrations respect to input solution measured over time (in pore volumes, PV) for duplicate K-compreignacite (red circles) and Na-compreignacite (blue squares) flow-through columns reacted with low carbonate BPW (0.21 mmol L⁻¹ TC). The insets in U and K figures show data points for the first 50 and 125 PV respectively.

Figure 3. Concentration of released U (in $\mu\text{mol L}^{-1}$), effluent pH, and total dissolved carbon (TC), Na, Mg, K, Ca, Cl and SO_4 effluent concentrations respect to input solution measured over time (in pore volumes, PV) for duplicate K-compreignacite (red triangles) and Na-compreignacite (blue diamonds) flow-through columns reacted with high carbonate BPW (2.78mmol L^{-1} TC). The inset of U and K figures show the data points for the first 25 and 50 PV respectively.

Figure 4. Characterization of unreacted solid phases: X-ray diffractograms for (A1) K-compreignacite and (A2) Na-compreignacite with their corresponding ICDD XRD reference patterns (black line spectra, ICDD card code number 01-089-5409 for K-compreignacite and 00-053-0876 for Na-compreignacite); FT-IR (B) and Raman (C) spectra of K-compreignacite (red lines) and Na-compreignacite (blue lines); DSL particle size distribution for (D1) K-compreignacite and (D2) Na-compreignacite.

Figure 5. Representative SEM images of control and uranyl oxyhydroxide mineral columns before and after reaction with low (0.21 mmol L^{-1} TC) and high (2.78 mmol L^{-1} TC) carbonate background porewater (BPW). Pure K-compreignacite and Na-compreignacite minerals are shown in **B** and **C** images respectively. Images of unreacted column mixtures (**A1, B1, C1**), column mixtures after reaction with low carbonate BPW (**A2, B2, C2**) and column mixtures after reaction with high carbonate BPW (**A3, B3, C3**) are shown for quartz only (**A1-3**), K-compreignacite with quartz (**B1-3**) and Na-compreignacite with quartz (**C1-3**).

Figure 6. Uranium L_{III} -edge EXAFS spectra and Fourier Transforms (FT) of unreacted K-compreignacite (A), Na-compreignacite (B) and becquerelite (C), U(VI) sorbed on quartz (D), reacted K-compreignacite with low (E) and high (F) carbonate BPW and reacted Na-compreignacite with low (G) and high (H) carbonate BPW. Total dissolved carbon for low and high carbonate BPW solutions was 0.21 and 2.78 mmol L^{-1} TC respectively. Overlapping dashed black lines represent the non-linear least-squares fits (numerical fit results shown in Table 4 and 5) obtained by shell-by-shell fit. For detailed fit deconvolutions see Fig. S3 and S4 in SI.

Figure 7. Reactive transport model simulations of effluent U concentration (**A1, B1**), pH (**A2, B2**) and TC concentration (as HCO_3^- for the model) (**A3, B3**) for K-compreignacite (**A1-3**) and Na-compreignacite (**B1-3**) columns reacted with low and high carbonate background porewater (BPW). Symbols represent experimental data of duplicated columns. Note that y-axes for U and TC concentrations are broken for clarity. Solid and dashed lines represent averaged reactive transport model simulations (RT-TST-VF approach, Table 6) of duplicated columns for low and high carbonate BPW systems respectively, except for high carbonate BPW Na-compreignacite columns in **B1**, where individual simulations are plotted. Grey rectangle areas in **A1** and **B1** indicate data points used for dissolution rate calculations using the SSD approach (Table 6).

Figure 8. Schematic diagram showing the dissolution mechanisms for K- and Na-compreignacite mineral particles in low (A) and high (B) carbonate BPW flow-through column systems: [1] flush out of < 0.20 μm mineral particles and [2] preferential leaching of interlayer cation in the first 200 PV; [3] cation exchange and/or incorporation into the mineral structure; [4] detachment of uranyl from mineral structure and formation of uranyl aqueous species (only the most abundant species are shown, Fig. S9 in SI); [5] formation and detachment of ternary Ca and Mg uranyl carbonate complexes. Dashed lines represent particle size by the end of the dissolution experiment (ca. 99% and 40% of original size in A and B, respectively).

Tables

Rates and mechanisms of uranyl oxyhydroxide mineral dissolution

Estela REINOSO-MASET, Carl H. STEEFEL, Wooyong UM, Jon CHOROVER, Peggy A. O'DAY

Table 1. Measured composition and pH of synthetic background porewater (BPW) used as input solutions in control and uranyl minerals flow-through column experiments.

Concentration (mmol L ⁻¹) ^a						
Low carbonate BPW				High carbonate BPW		
Column set	Controls	Controls + U(VI)	U-minerals	Controls	Controls + U(VI)	U-minerals
Column label	Ctl1_A/B	Ctl2_A/B	K-Comp_A/B Na-Comp_A/B	Ctl1_C/D	Ctl2_C/D	K-Comp_C/D Na-Comp_C/D
Na	3.05	2.92	3.09	3.56	3.61	9.51
Mg	1.17	1.04	0.95	0.89	0.90	0.83
K	0.43	0.37	0.34	0.32	0.33	0.36
Ca	3.38	3.36	3.14	1.77	1.85	2.70
Cl	9.77	8.96	8.42	3.41	3.34	11.06
SO₄	2.46	2.24	2.01	2.25	2.16	1.69
TC^b	0.38	0.30	0.21	2.17	2.21	2.78
U^c	n/a	4.06·10 ⁻³	n/a	n/a	3.74·10 ⁻³	n/a
pH^d	6.95	7.00	6.65	7.84	7.79	8.40
I^e	0.019	0.018	0.017	0.013	0.013	0.020

^aErrors associated with measurements were ≤2% RSD for Na, Mg, K, Ca, and U concentrations, and ≤3% RSD for Cl, SO₄, and TC concentrations.

^bTC corresponds to dissolved total carbon.

^cn/a: not applicable, input solutions containing no dissolved U(VI).

^dSolution pH after transport through tubing.

^eI corresponds to ionic strength of the input solutions in mol L⁻¹.

Table 2. Experimental conditions for control and K- and Na-compreignacite dissolution flow-through columns reacted with low and high carbonate background porewater (BPW) as influent solutions.

Column conditions	Label	Experiment duration		Mass in column		Fluid volume (V) ^a (mL)	Volume fraction (ϕ_m) ^b		Porosity (ϕ) ^b	Volumetric flow rate (Q) ^c ($\leq 2\%$ RSD) (mL min ⁻¹)	Linear fluid velocity (v) ^d (± 0.003) (cm min ⁻¹)	Dispersion coefficient (D _L) ^d (± 0.001) (cm ² min ⁻¹)	Dispersivity (α_L) ^d (± 0.011) (cm)	Peclet number ^d	Initial U _{total} ^e (mol)	Dissolved U _{total} ^f (mol)	Remaining U _{total}	
		(h)	(PV)	Mixture (g)	U-mineral (g)		Quartz	U-mineral									(mol)	% of initial
Quartz + low CO ₃ BPW	Ctl1_A	154	905	1.7495	-	0.3451	0.6567	-	0.3433	0.035	0.068	0.006	0.083	24	-	-	-	-
	Ctl1_B	154	979	1.8421	-	0.3102	0.6915	-	0.3085	0.034	0.068	0.004	0.053	38	-	-	-	-
Quartz + low CO ₃ BPW + 4 μ M U(VI)	Ctl2_A	154	991	1.8181	-	0.3192	0.6825	-	0.3175	0.044	0.084	0.004	0.051	39	-	-	-	-
	Ctl2_B	154	1225	1.8524	-	0.3063	0.6953	-	0.3047	0.034	0.068	0.003	0.043	47	-	-	-	-
Quartz + high CO ₃ BPW	Ctl1_C	112	601	1.8651	-	0.3015	0.7001	-	0.2999	0.027	0.050	0.002	0.041	50	-	-	-	-
	Ctl1_D	112	890	1.8351	-	0.3128	0.6888	-	0.3112	0.042	0.090	0.004	0.043	47	-	-	-	-
Quartz + high CO ₃ BPW + 4 μ M U(VI)	Ctl2_C	112	894	1.8558	-	0.3050	0.6966	-	0.3034	0.041	0.089	0.006	0.065	31	-	-	-	-
	Ctl2_D	112	607	1.8730	-	0.2985	0.7031	-	0.2969	0.027	0.051	0.002	0.048	42	-	-	-	-
K-comp. + quartz + low CO ₃ BPW	K-Comp_A	173	1392	1.9433	0.2363	0.3163	0.6407	0.0446	0.3147	0.037	0.063	0.002	0.036	55	6.88·10 ⁻⁴	3.36·10 ⁻⁶	6.84·10 ⁻⁴	99.5
	K-Comp_B	173	1381	1.9332	0.2351	0.3199	0.6374	0.0444	0.3182	0.037	0.060	0.002	0.039	52	6.84·10 ⁻⁴	3.06·10 ⁻⁶	6.81·10 ⁻⁴	99.6
Na-comp. + quartz + low CO ₃ BPW	Na-Comp_A	173	1291	1.8735	0.1463	0.3253	0.6483	0.0281	0.3236	0.037	0.062	0.003	0.054	37	4.33·10 ⁻⁴	1.53·10 ⁻⁶	4.31·10 ⁻⁴	99.6
	Na-Comp_B	173	1321	1.8806	0.1469	0.3228	0.6508	0.0282	0.3211	0.038	0.067	0.003	0.049	45	4.34·10 ⁻⁴	1.44·10 ⁻⁶	4.33·10 ⁻⁴	99.7
K-comp. + quartz + high CO ₃ BPW	K-Comp_C	190	1208	1.8109	0.0510	0.3314	0.6606	0.0098	0.3296	0.035	0.059	0.002	0.030	59	1.49·10 ⁻⁴	9.26·10 ⁻⁵	5.59·10 ⁻⁵	37.7
	K-Comp_D	190	1389	1.8598	0.0524	0.3132	0.6784	0.0100	0.3115	0.037	0.067	0.002	0.037	67	1.53·10 ⁻⁴	8.87·10 ⁻⁵	6.38·10 ⁻⁵	41.7
Na-comp. + quartz + high CO ₃ BPW	Na-Comp_C	190	1238	1.8153	0.0264	0.3252	0.6715	0.0051	0.3234	0.035	0.063	0.002	0.031	63	7.80·10 ⁻⁵	6.79·10 ⁻⁵	1.04·10 ⁻⁵	12.9
	Na-Comp_D	190	1249	1.8062	0.0263	0.3286	0.6681	0.0050	0.3268	0.035	0.064	0.002	0.030	64	7.76·10 ⁻⁵	4.56·10 ⁻⁵	3.20·10 ⁻⁵	41.3

^a Fluid volume (mL) or pore volume (cm³) = total column volume – quartz volume – U-mineral volume; total column volume = 1.0053 cm³; quartz volume = g of quartz / quartz density; quartz density = 2.65 g/cm³; U-mineral volume = (g of U-mineral / molecular weight) * U-mineral molar volume; compreignacite molar volume = 391.3 cm³/g (from <http://database.iem.ac.ru/mincryst/>).

^b Volume fraction = solid phase volume / total column volume; porosity = pore volume / total column volume.

^c Determined by weight of effluent column samples.

^d Determined from fits of Br tracer breakthrough curves (Fig. S1 in SI); dispersivity $\alpha_L = D_L/v$; peclet number = $(v*L/D_L)$ with L (column length) = 2 cm

^e Calculated from U-mineral quartz mixture preparation.

^f Calculated from the curve area integration of U released during dissolution.

Table 3. Solid phase characterization of K- and Na-compreignacite synthetic minerals, uranyl mineral and quartz column mixtures, and quartz-only control columns, unreacted and reacted with low and high carbonate background porewater (BPW).

		<i>Elemental analysis ($\mu\text{mol g}^{-1}$)^d</i>						
<i>Sample</i>		<i>N₂-BET SSA^c</i> ($\text{m}^2 \text{g}^{-1}$)	[Na]	[Mg]	[K]	[Ca]	[U]	U:cation ratio^e
Quartz	unreacted columns	0.128 ± 0.015	6.1 ± 0.7	1.0 ± 0.1	1.2 ± 0.4	18.5 ± 0.5	< LOD	n/a
	reacted low CO ₃ BPW	0.115 ± 0.005	1.1 ± 0.4	0.2 ± 0.2	0.6 ± 0.2	3.0 ± 0.1	1.3 ± 0.4	n/a
	reacted high CO ₃ BPW	0.132 ± 0.008	1.3 ± 0.9	0.5 ± 0.4	0.7 ± 0.4	6.2 ± 0.1	0.1 ± 0.1	n/a
K-compreignacite K ₂ (UO ₂) ₆ O ₄ (OH) ₆ ·nH ₂ O 6.60% mass loss (n = 8) ^a MW ^b = 2008.25	pure compound	9.645 ± 0.520	< LOD	< LOD	1233 ± 24	< LOD	2621 ± 52	2.13 ± 0.05
	unreacted column	0.196 ± 0.039	1.6 ± 0.5	< LOD	125 ± 16	< LOD	252 ± 5	2.02 ± 0.22
	reacted low CO ₃ BPW	0.351 ± 0.024	0.3 ± 0.1	< LOD	29.0 ± 0.3	< LOD	75.9 ± 0.2	2.59 ± 0.02
	reacted high CO ₃ BPW	0.122 ± 0.004	< LOD	< LOD	6.6 ± 2.5	< LOD	16.2 ± 1.7	2.67 ± 0.93
Na-compreignacite Na ₂ (UO ₂) ₆ O ₄ (OH) ₆ ·nH ₂ O 7.29% mass loss (n = 8) ^a MW ^b = 1976.03	pure compound	3.534 ± 1.798	662 ± 13	< LOD	< LOD	< LOD	2499 ± 50	3.78 ± 0.05
	unreacted column	0.291 ± 0.008	51 ± 25	< LOD	< LOD	< LOD	194 ± 110	3.70 ± 0.29
	reacted low CO ₃ BPW	0.284 ± 0.033	18 ± 2	0.3 ± 0.1	67.5 ± 1.5	18.0 ± 0.3	225 ± 5	2.72 ± 0.48
	reacted high CO ₃ BPW	0.104 ± 0.009	< LOD	< LOD	0.5 ± 0.4	< LOD	3.8 ± 1.1	n/a

^a From thermogravimetric analysis (TGA, n = number of H₂O molecules associated with mass loss at temperature range 20-400°C).

^b Molecular weight with nH₂O.

^c SSA = specific surface area from N₂-BET measurements.

^d Element concentrations from acid digestion and ICP-MS analysis; LOD: limit of detection.

^e Average of U:sum(cations) ratios of replicated measurements, accounting for charge balance (1 for +1 ions and 0.5 for +2 ions); n/a: not applicable.

Table 4. Uranium L_{III}-edge EXAFS shell-by-shell fit results for unreacted uranyl minerals and U(VI) sorbed on quartz compared with interatomic distances reported in prior studies.

U-L _{III} EXAFS fits ^a					XRD ^d	
Sample	A-B	N ^b	R (Å)	σ ²	N	R (Å)
K-compreignacite (N _{Usite} = 2) ΔE ₀ (eV) = 0.30 R-factor = 0.004	U-O _{ax}	2.0	1.82	0.0028	2	1.79-1.81
	MS _{Oax}	4.0	3.65 ^c	0.0073	2	3.59-3.62
	U-O _{eq}	2.0	2.24	0.0047	2	2.20-2.27
	U-O _{eq}	2.0	2.38	0.0076	2	2.40-2.46
	U-O _{eq}	1.0	2.50	0.0049	0.67 0.33	2.57 2.85
	U-U	1.5	3.69	0.0078	1.33	3.82
	U-U	2.5	3.89	0.0078 ^c	1.33 1.33	3.88 3.94
	U-U	2.0	4.62	0.0086	2	4.61-4.63
Na-compreignacite (N _{Usite} = 2) ΔE ₀ (eV) = 0.20 R-factor = 0.004	U-O _{ax}	2.0	1.81	0.0031		
	MS _{Oax}	4.0	3.64 ^c	0.0059		
	U-O _{eq}	2.0	2.24	0.0052		
	U-O _{eq}	2.0	2.37	0.0083		
	U-O _{eq}	1.0	2.50	0.0045		
	U-U	4.0	3.89	0.0091		
	U-U	2.0	4.59	0.0087		
Becquerelite^e (N _{Usite} = 6) ΔE ₀ (eV) = -0.94 R-factor = 0.010	U-O _{ax}	2.0	1.82	0.0028	2	1.77-1.82
	MS _{Oax}	2.0	3.64 ^c	0.0031	2	3.49-3.66
	U-O _{eq}	3.0	2.26	0.0072	3	2.22-2.39
	U-O _{eq}	2.0	2.47	0.0072 ^c	2	2.39-2.80
	U-U	4.0	3.88	0.0061	4	3.79-3.92
	U-U	1.5	4.64	0.0108	1.5	4.52-4.64
U(VI) sorbed on quartz^f ΔE ₀ (eV) = -0.98 R-factor = 0.036	U-O _{ax}	2.0	1.81	0.0029		1.76-1.79
	MS _{Oax}	4.0	3.62 ^c	0.0041		
	U-O _{eq}	2.45	2.28	0.0053		2.24-2.26
	U-O _{eq}	2.12	2.48	0.0053 ^c		2.48-2.50

^aA-B is the absorber-backscatterer pair (MS = multiple scattering for 4 leg paths), N is the coordination number, R is the interatomic distance in Å, σ² (Debye-Waller factor) is the absorber-backscatterer mean-square relative displacement, ΔE₀ is the energy shift in eV from the least-squares fit, and R-factor is a goodness-of-fit parameter.

^bParameter fixed or constrained in least-squares fit.

^cParameter linked in the fit to the parameter directly above.

^dInteratomic distances calculated from published crystal structure refinements from X-ray diffraction: i) K-compreignacite from Burns (1998) and ii) becquerelite from Burns and Li (2002).

^eBecquerelite spectrum obtained from Kanematsu et al. (2014); shell-by-shell parameters were re-fit for this work.

^fInteratomic distances (R) and N for U(VI) sorbed on quartz were based on EXAFS fit results reported in Sylwester et al. (2000) and Batuk et al. (2011) for sorbed aqueous uranyl on silica and silica colloids in pH 6.46 and 6.5 experiments, respectively.

Table 5. Linear combination and shell-by-shell fits of U L_{III}-edge EXAFS for K-compreignacite and Na-compreignacite reacted with low and high carbonate background porewater (BPW).

Sample	Linear combination fits ^a			Shell-by-shell fits ^b					
	K-comp	Sorbed U(VI)	Sum	R-factor		A-B	N	R (Å)	σ^2
Reacted K-compreignacite low CO₃ BPW	0.788	0.197	0.985	0.070	ΔE_0 (eV) = 0.44	U-O _{ax}	2.0 ^c	1.80	0.0028
					R-factor = 0.011	MS _{Oax}	4.0 ^c	3.61 ^d	0.0030
						U-O _{eq}	1.7	2.26	0.0057 ^c
						U-O _{eq}	2.6	2.40	0.0057 ^d
						U-O _{eq}	0.9	2.59	0.0057 ^d
						U-O _{eq}	0.9	2.88	0.0057 ^d
						U-U	1.6	3.91	0.0078 ^c
Reacted K-compreignacite high CO₃ BPW	0.884	0.146	1.030	0.077	ΔE_0 (eV) = 0.75	U-O _{ax}	2.0 ^c	1.82	0.0026
					R-factor = 0.017	MS _{Oax}	4.0 ^c	3.65 ^d	0.0026 ^d
						U-O _{eq}	2.5	2.26	0.0057 ^c
						U-O _{eq}	1.3	2.37	0.0057 ^d
						U-O _{eq}	1.9	2.52	0.0057 ^d
						U-O _{eq}	1.2	2.81	0.0057 ^d
						U-U	1.5	3.92	0.0078 ^c
Reacted Na-compreignacite low CO₃BPW	0.583	0.331	0.914	0.180	ΔE_0 (eV) = 0.86	U-O _{ax}	2.0 ^c	1.81	0.0035
					R-factor = 0.061	MS _{Oax}	4.0 ^c	3.62 ^d	0.0035 ^d
						U-O _{eq}	2.6	2.30	0.0053 ^c
						U-O _{eq}	0.9	2.46	0.0053 ^d
						U-O _{eq}	1.6	2.57	0.0053 ^d
						U-O _{eq}	2.0	2.85	0.0053 ^d
						U-U	2.4	3.88	0.0091 ^c
Reacted Na-compreignacite high CO₃BPW	1.000		1.000	0.250	ΔE_0 (eV) = -0.30	U-O _{ax}	2.0 ^c	1.84	0.0034
					R-factor = 0.011	MS _{Oax}	4.0 ^c	3.66 ^d	0.0034 ^d
						U-O _{eq}	2.7	2.22	0.0060 ^c
						U-O _{eq}	2.2	2.39	0.0060 ^d
						U-O _{eq}	0.5	2.90	0.0060 ^d
						U-U	1.0	3.89	0.0078 ^c

^a Linear combination fits were performed using K-compreignacite (K-comp), Na-compreignacite (Na-comp), becquerelite, schoepite, uranyl nitrate and U(VI) sorbed on quartz (sorbed U(VI)) reference spectra (from this work and Kanematsu et al. (2014)). Spectra contributing less than 10% to the fit were discarded.

^b A-B is the absorber-backscatterer pair (MS = multiple scattering for 4 leg paths), N is the coordination number, R is the interatomic distance in Å, σ^2 (Debye-Waller factor) is the absorber-backscatterer mean-square relative displacement, ΔE_0 is the energy shift in eV from the least-squares fit, and R-factor is a goodness-of-fit parameter.

^c Parameter fixed or constrained in least-squares fits; σ^2 of U-O_{eq} shells were obtained from averaging σ^2 of reference spectra fits (Table 4).

^d Parameter linked in the fit to the parameter directly above.

Table 6. Dissolution rates normalized to mineral specific surface area (R , $\text{mol m}^{-2} \text{s}^{-1}$) for K- and Na-compreignacite columns reacted with low and high carbonate background porewater (BPW) calculated from experimental U effluent concentrations using either a steady-state rate calculation or an optimization with CrunchFlow/PEST to include reactive transport through porous media and changes in mineral volume fraction (ϕ_m), porosity and chemical composition.

	method ^a	low CO_3 BPW			high CO_3 BPW		
		ϕ_m ^b	R ^c ($\text{mol m}^{-2} \text{s}^{-1}$)	$\log R$ ^c	ϕ_m ^b	R ^c ($\text{mol m}^{-2} \text{s}^{-1}$)	$\log R$ ^c
K-compreignacite	SSD	0.0445	$8.46 \cdot 10^{-13}$	-12.07 ± 0.02	0.0099	$6.02 \cdot 10^{-11}$	-10.22 ± 0.07
	RT-TST	0.0445	$1.24 \cdot 10^{-13}$	-12.91 ± 0.03	0.0099	$8.31 \cdot 10^{-11}$	-10.08 ± 0.04
	RT-TST-VF	0.0430	$1.28 \cdot 10^{-13}$	-12.89 ± 0.01	0.0058	$1.57 \cdot 10^{-10}$	-9.81 ± 0.07
Na-compreignacite	SSD	0.0282	$5.01 \cdot 10^{-13}$	-12.30 ± 0.04	0.0051	$8.11 \cdot 10^{-11}$	-10.09 ± 0.32
	RT-TST	0.0282	$3.63 \cdot 10^{-13}$	-12.44 ± 0.03	0.0051	$4.06 \cdot 10^{-10}$	-9.39 ± 0.03
	RT-TST-VF	0.0275	$3.71 \cdot 10^{-13}$	-12.43 ± 0.03	0.0038	$5.79 \cdot 10^{-10}$	-9.24 ± 0.11

^a SSD: steady-state dissolution (Eq. 7); RT-TST: reactive transport-transition state theory with optimization of rate constant (k_m) (Eq. 2 and 6); RT-TST-VF: reactive transport-transition state theory with simultaneous optimization of k_m and ϕ_m (Eq. 2, 3 and 6).

^b Volume fraction calculated from initial mineral mass loaded in columns (average of duplicated columns); for RT-TST-VF method, reported values are the ϕ_m after CrunchFlow/PEST optimization.

^c Reported values are average of duplicate columns.

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