

# Neptunium<sup>V</sup> Retention by Siderite under Anoxic Conditions: Precipitation of NpO<sub>2</sub>-Like Nanoparticles and of Np<sup>IV</sup> Pentacarbonate

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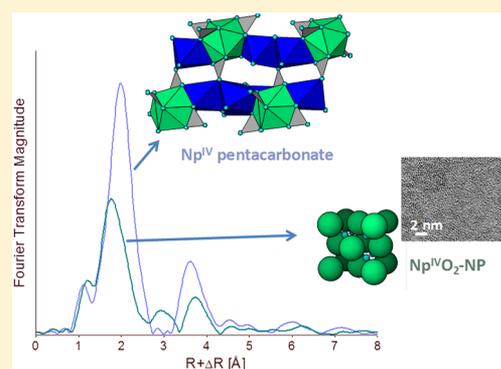
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## Supporting Information

**ABSTRACT:** The Np<sup>V</sup> retention by siderite, an Fe<sup>II</sup> carbonate mineral with relevance for the near-field of high-level radioactive waste repositories, was investigated under anoxic conditions. Batch sorption experiments show that siderite has a high affinity for aqueous Np<sup>V</sup>O<sub>2</sub><sup>+</sup> across pH 7 to 13 as expressed by solid-water distribution coefficients,  $\log R_d > 5$ , similar to the  $\log R_d$  determined for the (solely) tetravalent actinide Th on calcite, suggesting reduction of Np<sup>V</sup> to Np<sup>IV</sup> by siderite. Np L<sub>3</sub>-edge X-ray absorption near edge (XANES) spectroscopy conducted in a pH range typical for siderite-containing host rocks (7–8), confirmed the tetravalent Np oxidation state. Extended X-ray absorption fine-structure (EXAFS) spectroscopy revealed a local structure in line with NpO<sub>2</sub>-like nanoparticles with diameter < 1 nm, a result further corroborated by high-resolution transmission electron microscopy (HRTEM). The low solubility of these NpO<sub>2</sub>-like nanoparticles ( $\sim 10^{-9}$  M), along with their negligible surface charge at neutral pH conditions which favors particle aggregation, suggest an efficient retention of Np in the near-field of radioactive waste repositories. When Np<sup>V</sup> was added to ferrous carbonate solution, the subsequent precipitation of siderite did not lead to a structural incorporation of Np<sup>IV</sup> by siderite, but caused precipitation of a Np<sup>IV</sup> pentacarbonate phase.



## INTRODUCTION

Nuclear power generation has left behind a legacy of high-level radioactive waste, which needs to be kept safe for hundreds of thousands of years. The disposal of this waste in deep geological formations behind multiple barriers is a concept favored by many nuclear power producing countries to ensure a lasting protection of people and the environment. The multiple barrier system consists of three principal parts, an engineered barrier (copper or stainless steel containers), a geo-engineered barrier (cement or clay-based backfill-material, e.g. bentonite), and the geological barrier (argillaceous, granitic or salt host rock).<sup>1</sup> Many of these components contain or form Fe<sup>II</sup>-bearing minerals, which may act as scavenger for potentially released radionuclides by their reducing power and sorption capacity. Steel containers are likely to corrode under near-field conditions, forming for instance magnetite, siderite, chukanovite and Fe-phyllsilicates in contact with clay backfill,<sup>2,3</sup> magnetite and hydrous Fe<sup>II</sup> oxides in contact with brine,<sup>4</sup> and Fe<sup>II</sup> sulfides in the presence of sulfate reducing bacteria.<sup>5</sup> Such Fe<sup>II</sup>-bearing minerals also occur naturally in clay rocks; for example, MX80 bentonite considered as backfill material contains 0.7% siderite and 0.3% pyrite, and Opalinus clay considered as host rock in Switzerland contains 6% siderite and 0.9% pyrite.<sup>6,7</sup>

Spent nuclear fuel consists mainly of the original uranium dioxide ( $\sim 95\%$ ) and its fission products (lanthanides, technetium, selenium, noble gases, and cesium,  $\sim 4\%$ ). Neutron absorption and decay reactions lead to the formation of plutonium ( $\sim 1\%$ ) and the minor actinides neptunium, americium and curium ( $< 0.1\%$  of typical burnt fuel). The redox-sensitive elements uranium, plutonium, technetium, selenium have been shown to be efficiently immobilized by sorption and redox reactions on Fe<sup>II</sup>-bearing minerals.<sup>4,8–14</sup> Much less work has been conducted on the redox-driven (anoxic) immobilization of the minor actinide neptunium, although its major radionuclide <sup>237</sup>Np has a very long half-life (2.14 Mio years) and contributes significantly to the long-term radiotoxicity of spent fuel. Work attempting to elucidate the mechanisms of Np reduction by mineral surfaces is even more scarce. Np<sup>V</sup> was found to be much more strongly retained by magnetite under anoxic conditions than under atmospheric conditions; using a liquid extraction technique, Np associated with the solid phase was determined to be tetravalent.<sup>15</sup> In

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comparison to reduction by aqueous  $\text{Fe}^{\text{II}}$ , reduction by magnetite was 3 orders of magnitude faster.<sup>16</sup> A pioneering study employing EXAFS spectroscopy showed that  $\text{Np}^{\text{V}}$  was only weakly taken up by mackinawite, forming rather surprisingly a mononuclear  $\text{Np}^{\text{IV}}$  sorption complex coordinated to both O and S.<sup>17</sup> In the presence of green rust,  $\text{Np}^{\text{V}}$  was rapidly sorbed and reduced to  $\text{Np}^{\text{IV}}$  at the edges of the hexagonal platelets; the authors suggest formation of  $\text{Np}^{\text{IV}}$  particles, but their identification by TEM remained elusive.<sup>18</sup>  $\text{Np}^{\text{V}}$  reacted with Opalinus clay was reduced to  $\text{Np}^{\text{IV}}$  and showed a strong association with pyrite particles embedded in the clay matrix; the exact nature of the reduced  $\text{Np}^{\text{IV}}$  could not be identified, but the authors excluded formation of  $\text{NpO}_2$  due to the absence of Np-Np backscattering contributions in  $\text{Np}$   $L_{3-}$  edge EXAFS spectra.<sup>19</sup> Biotite and chlorite with structural  $\text{Fe}^{\text{II}}$  fully reduced  $\text{Np}^{\text{V}}$  to  $\text{Np}^{\text{IV}}$ , and nanoparticulate  $\text{NpO}_2$  formed as identified by EXAFS.<sup>20</sup> In the presence of Ti-doped magnetite, sorption of Np was high at pH values 5 and 7, while the sorption at pH 3 was low, but increased with Ti-doping most likely because of the increasing  $\text{Fe}^{\text{II}}$  fraction to counterbalance the charge of structural  $\text{Ti}^{\text{IV}}$ . Using Np  $L_{3-}$  edge XANES and EXAFS, the reaction product could be identified as a  $\text{Np}^{\text{IV}}$  species, while the absence of Np-Np backscattering contradicted formation of  $\text{NpO}_2$ .<sup>21</sup> The authors claim formation of an inner-sphere sorption complex, but fitted Np-Fe and Np-Ti coordination numbers between 5 and 7 would rather suggest structural incorporation by magnetite or a secondary Fe phase. In conclusion, the few studies on Np uptake by  $\text{Fe}^{\text{II}}$ -bearing minerals under anoxic conditions show sorption and reduction to  $\text{Np}^{\text{IV}}$ , but the reaction mechanism and the end product, that is, sorption complexation vs structural incorporation vs  $\text{NpO}_2$  precipitation, often remain elusive.

The objective of our study was therefore, to investigate the Np reduction products on siderite under strictly anoxic atmosphere by Np  $L_{3-}$  edge XANES and EXAFS spectroscopy and electron microscopy. The  $\text{Fe}^{\text{II}}$  carbonate siderite was selected because of its relevance for many high-level radioactive waste scenarios as outlined above. In comparison to other  $\text{Fe}^{\text{II}}$ -bearing phases like green rust, magnetite and mackinawite, the electron transfer provided by siderite (or by the hydroxocarbonate chukanovite) generally seems to be smaller, as revealed by a lesser amount of reduction, smaller reduction kinetics, or reduction not to the lowest possible but to an intermediate oxidation state only. This has been demonstrated for instance for uranium, plutonium, and selenium.<sup>11,22–24</sup> A reason for this is certainly the larger electronic bandgap of siderite as compared to green rust, magnetite and mackinawite with their almost metal-like electron conduction, which strongly limits the supply of electrons from the mineral structure to adsorbed (metal) oxidants.<sup>24</sup> An additional reason might be that dissolved carbonate forms complexes with  $\text{Fe}^{\text{II}}$  and potentially also with the metal oxidant, thereby competing with the Fe/oxidant redox reaction.<sup>11,22–26</sup> Therefore, the purpose of our study was to investigate, whether or not  $\text{Np}^{\text{V}}$  is reduced by siderite, to characterize the oxidation state and local structure of the reaction product and to decipher, if possible, the reaction pathway.

## MATERIALS AND METHODS

**Caution!**  $^{237}\text{Np}$  is a radioactive isotope and an  $\alpha$ -emitter. It should be handled in dedicated facilities with appropriate

equipment for radioactive materials to avoid health risks caused by radiation exposure.

Generally, all sample manipulations, including mineral synthesis and washing, UV-vis measurements, and preparation of samples for XAS measurements, were carried out under anoxic conditions in a nitrogen glovebox with 0–5 ppmv  $\text{O}_2$ . Experiments were carried out at RT ( $23 \pm 3$  °C); deionized (18.2 M $\Omega$  cm Milli-Q), degassed ( $\text{O}_2$  and  $\text{CO}_2$  free) water was used for all purposes. Eh measurements were performed by dipping a conventional ORP (oxidation–reduction potential) electrode with platinum disc (Sentix, WTW) in the unstirred suspensions. pH measurements were performed with glass electrodes with 3 M KCl (Sentix Micro, WTW) calibrated against standard pH buffers. No ionic strength correction was done for measurements at  $I = 1.0$  M NaCl. According to Felmy et al. the estimated difference between  $\text{pH}_{\text{exp}}$  and  $\text{pH}_c$  ( $= -\log[\text{H}^+]$ ) is smaller than 0.15 pH units.<sup>27</sup>

**Siderite Synthesis and Characterization.** A siderite ( $\text{Fe}^{\text{II}}\text{CO}_3$ ) suspension ( $[\text{Fe}_{\text{tot}}] = 0.2$  M) was prepared by slowly mixing 100 mL of a 0.4 M  $\text{Fe}^{\text{II}}\text{Cl}_2$  solution with 100 mL of a 0.8 M  $\text{Na}_2\text{CO}_3$  solution.<sup>28</sup> The light gray precipitate was washed with 0.1 M NaCl (at least 3 washing cycles) and kept in suspension in 0.1 M NaCl. Siderite is extremely oxidation-sensitive and not stable in suspension with an ionic strength ( $I$ ) lower than 0.1 M, as indicated by the rapid appearance of brownish  $\text{Fe}^{\text{III}}$  oxyhydroxides like goethite.<sup>29,30</sup> Raman spectroscopic measurements were carried out with a Raman-microscope (HORIBA Jobin Yvon LabRAM Aramis Vis) using an argon-ion laser (437 nm) with an output energy of 0.2 mW as light source and confirmed the phase identity and purity of the siderite stock suspension (see Figure S1 in the Supporting Information (SI)). An isoelectric point of 10.1 was determined by zeta potential measurements using a laser-doppler-electrophoresis instrument (Zetasizer nano-ZS, Malvern Instruments Ltd.) (SI Figure S2).

**$\text{Np}^{\text{V}}$  Stock solution.** A 0.056 M  $\text{Np}^{\text{VI}}$  stock solution in 1.0 M  $\text{HClO}_4$  was prepared from neptunium ( $^{237}\text{Np}$ ) dioxide (CEA-Marcoule, France), according to a previously reported procedure.<sup>31</sup> The pentavalent oxidation state of Np was prepared by electrochemical reduction from  $\text{Np}^{\text{VI}}$  and verified by UV-vis-NIR spectroscopy. This solution was diluted with degassed deionized water to obtain a stock solution of  $10^{-3}$  M  $\text{Np}^{\text{V}}$  used for the sorption experiments.

**Np Sorption on Siderite.** The  $\text{Np}^{\text{V}}$  retention by siderite was investigated in the pH range 7 to 13 by batch experiments. For pre-equilibration, siderite suspensions (S/L ratio of 1 g/L) were prepared in either 0.1 M NaCl or 0.1 M  $\text{Na}_2\text{CO}_3$  background electrolyte ( $V = 10$  mL) and continuously shaken on a horizontal shaker for 48 h, with pH values initially adjusted and readjusted if necessary. Then, aliquots of the  $\text{Np}^{\text{V}}$  stock solution were added to the siderite suspensions to obtain the final  $\text{Np}^{\text{V}}$  concentration of  $2 \cdot 10^{-5}$  M. The pH values were readjusted immediately by addition of NaOH or HCl. The samples were shaken up to 3 weeks, whereby the pH was monitored and readjusted if necessary. Finally, the remaining suspensions were centrifuged for phase separation (60 min, 3200g). The final Np concentration in the supernatant was determined by liquid scintillation counting (LSC, Winspectral  $\alpha/\beta$ , Wallac 1414, Perkin-Elmer) using  $\alpha/\beta$  discrimination with a lower detection limit  $\leq 10^{-9}$  M. The distribution coefficient  $R_d$  in L/kg was calculated as follows

$$R_d = \frac{c_{\text{ini}} - c_{\text{eq}}}{c_{\text{eq}}} \cdot \frac{V}{m}$$

where  $c_{\text{ini}}$  and  $c_{\text{eq}}$  (mol/L) are the initial and equilibrium Np concentration in solution,  $V$  (L) the sample volume and  $m$  (kg) the mass of siderite. Note that the sorption conditions were chosen to obtain samples with sufficient Np concentration to be measured by EXAFS spectroscopy (see below).

**Np Siderite Coprecipitation.** In addition to the batch sorption experiments, where  $\text{Np}^{\text{V}}$  was added to presynthesized siderite, we also conducted a  $\text{Np}^{\text{V}}$ -siderite coprecipitation experiment at pH 10.5 to study the eventual structural incorporation of Np. This experiment was performed like the pure mineral synthesis described before, except that an appropriate aliquot of the Np stock solution to obtain a nominal Np loading on siderite of 4705 mg/kg was slowly added to the  $\text{Fe}^{\text{II}}\text{Cl}_2$  solution, before adding the  $\text{Na}_2\text{CO}_3$  solution to initiate the siderite precipitation. The sample was examined by XANES and EXAFS after a washing step with 0.1 M NaCl without any further aging.

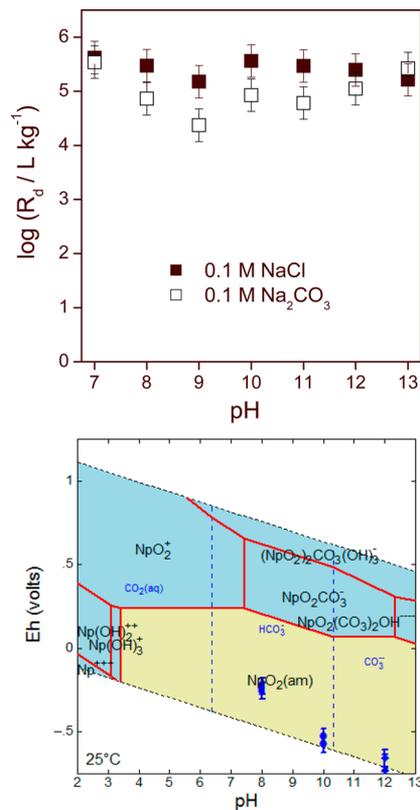
**X-ray Absorption Spectroscopy (XAS).** We selected three different types of samples (see SI Table S1): (i) to investigate the influence of reaction time on sorption a time series collected after 1 hour, 1 day, 7 and 21 days, at pH  $7.7 \pm 0.3$ , that is, in the pH range predominant in siderite-containing host rocks,<sup>6,7,32</sup> and an ionic strength of 0.1 M; (ii) to investigate the influence of ionic strength on sorption two additional samples in 0.001 and 1 M NaCl background electrolyte at the same pH and after a reaction time of 7 days; (iii) to investigate the potential incorporation of Np by siderite the coprecipitation sample as described before. After phase separation by centrifugation, the solids were filled into double-confinement, heat-sealed polyethylene sample holders inside the anoxic glovebox. The samples were then removed from the glovebox and immediately flash-frozen in  $\text{LN}_2$  and stored in an  $\text{LN}_2$  dewar to prevent oxygen diffusion into the samples and to freeze-in chemical reactions until XAS measurements. After transport to the Rossendorf Beamline at ESRF (Grenoble, France), the samples were individually removed from the  $\text{LN}_2$  dewar and transferred to a closed-cycle He cryostat operating at 10 K within less than 30 s for the XAS measurements. XAS (XANES and EXAFS) measurements were carried out in fluorescence mode at the Np- $L_3$  edge (17 610 eV) using a 13-element high-purity Ge solid state detector (Canberra) with digital signal analysis (XIA XMap). The polychromatic synchrotron beam was monochromatized using a pair of water-cooled Si(111) crystals, and higher-order harmonics were rejected by a Rh-coated 1.3-m long collimating mirror before the double-crystal monochromator, and a 1.2-m long Rh-coated toroidal mirror after the monochromator. Between 6 and 12 individual XAS scans were energy-calibrated against a simultaneously measured Y foil (17 038 eV), corrected for fluorescence deadtime and averaged using SIXpack, while subsequent data reduction steps and shell fits were conducted using WinXAS.<sup>33,34</sup> Theoretical backscattering paths were calculated with FEFF8.2 using crystal structures of  $\text{NpO}_2$  and siderite (with one Fe replaced by Np).<sup>35–37</sup> Shell fits were performed with an amplitude reduction factor,  $S_0^2$ , of 0.9 in the  $k$ -range 2.0 to 11.5  $\text{\AA}^{-1}$ . Reference spectra for the  $\text{Np}^{\text{IV}}$  aquo complex<sup>38</sup> and for  $\text{NpO}_2^+$  were downloaded from AcReDaS, the online actinide reference database for spectroscopy.<sup>40</sup>

**Transmission Electron Microscopy (TEM).** A sample ( $[\text{Np}^{\text{V}}]_{\text{ini}} = 2 \cdot 10^{-5}$  M,  $S/L = 0.1$   $\text{g}\cdot\text{L}^{-1}$ ,  $I = 0.1$  M (NaCl),

reacted for 7 days under anoxic conditions) was prepared by disposing a drop of the Np-siderite suspension on a carbon-coated copper grid (400 mesh, S 160, Plano GmbH) and drying it under inert gas atmosphere. Bright-field TEM and high-resolution TEM (HRTEM) images were collected on an image  $C_s$ -corrected Titan 80–300 electron microscope (FEI) operated at 300 kV. Reciprocal space diffractograms were derived from the HRTEM micrographs by Fast Fourier Transform (FFT) analysis. Energy-dispersive X-ray spectroscopy (EDXS) was performed in scanning TEM mode with a Li-drifted silicon detector (EDAX).

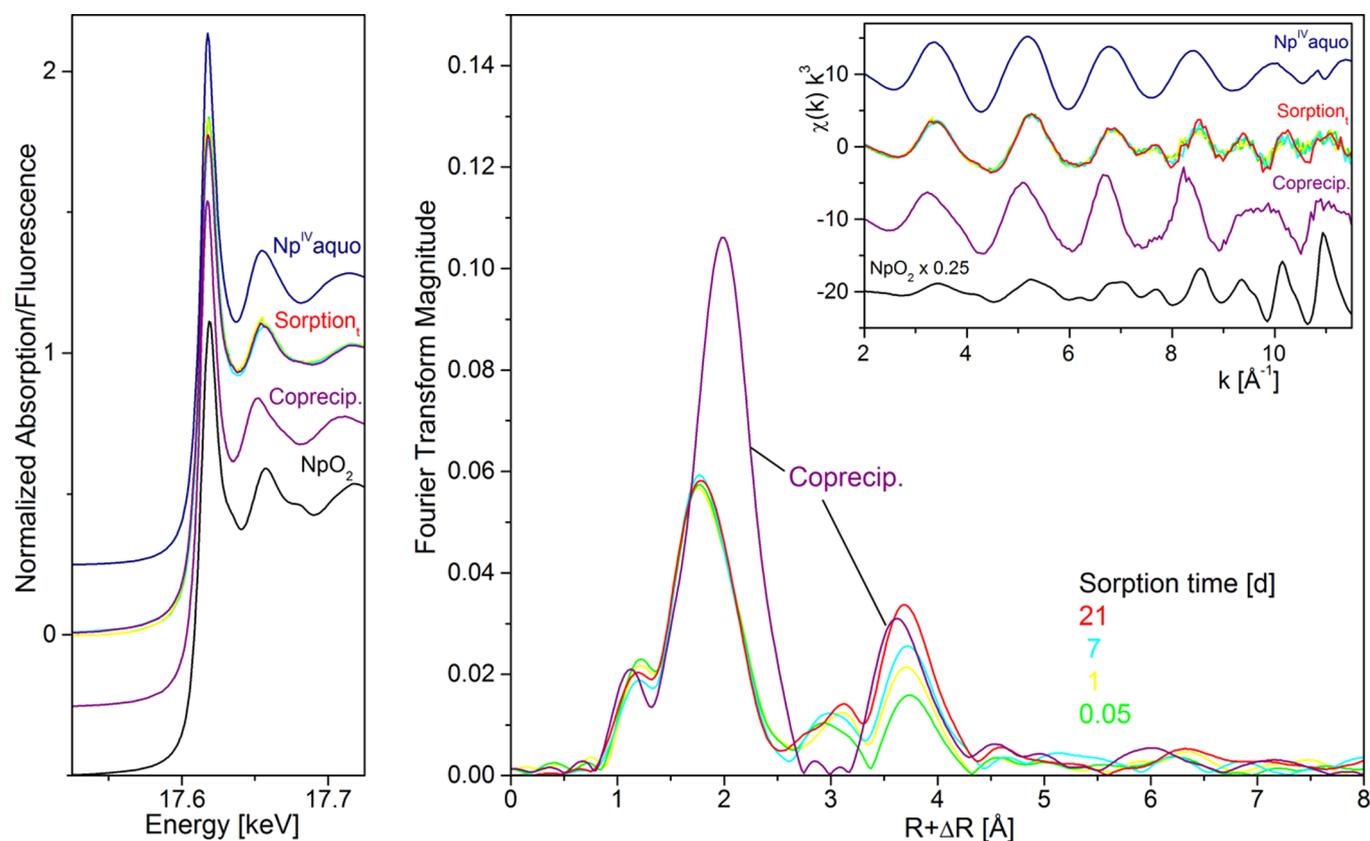
## RESULTS AND DISCUSSION

The  $\text{Np}^{\text{V}}$  uptake by siderite during the sorption experiments is very high with  $\log R_d$  values always above 5 and little variation across the pH range 7 to 13 (Figure 1 top). The addition of 0.1



**Figure 1.** Top: Np solid/liquid distribution coefficient in the siderite system as function of pH.  $[\text{Np}^{\text{V}}]_{\text{ini}} = 2 \cdot 10^{-5}$  M,  $S/L = 1$   $\text{g}\cdot\text{L}^{-1}$ ,  $I = 0.1$  M NaCl or  $\text{NaCO}_3$  as indicated, after 1 week reaction time under anoxic  $\text{N}_2$ . Bottom: Eh-pH diagram calculated for the chemical system  $2 \cdot 10^{-5}$  M  $\text{Np}^{\text{V}}$  in 0.1 M NaCl solution in presence of siderite under anoxic conditions at 25 °C (carbonate activity determined by siderite solubility). Thermodynamic data of the Lawrence Livermore National Laboratory thermo database were supplemented by the most recent NEA database.<sup>44,45</sup> Results of batch experiments are represented by blue symbols.

M carbonate reduced Np uptake significantly between pH 8 and 11, that is, in the pH region where siderite solubility is low (Figure S3). In comparison to the  $\text{Np}^{\text{V}}$  uptake by the (redox-inactive) Ca carbonate calcite, these  $\log R_d$  values are 2–3 orders of magnitude higher,<sup>41</sup> and much more similar to values obtained for the tetravalent actinide, Th, on calcite,<sup>42</sup> in both cases at comparable pH. Hence the high  $R_d$  values are a first



**Figure 2.** Neptunium  $L_3$ -edge XAS spectra of selected siderite sorption and coprecipitation samples ( $\text{pH } 7.7 \pm 0.3$ ) along with Np references. Left: XANES spectra, right: EXAFS Fourier transform magnitude and corresponding  $\chi(k)$  spectra as insert.

**Table 1.** Np- $L_3$  XANES Edge Energies and EXAFS Fit Results of Np Siderite Samples and References.

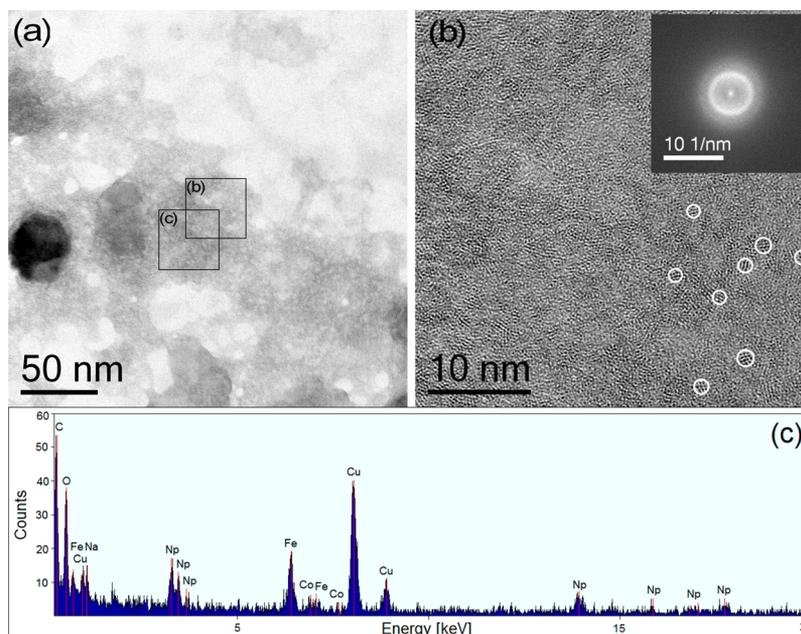
sample	$E_0$ [eV]	first shell			second shell			$\Delta E_0$ [eV]	$\chi^2_{\text{res}} \%$
		CN <sup>a</sup>	$R^b$ [Å <sup>2</sup> ]	$\sigma^{2c}$ [Å]	CN	$R$ [Å]	$\sigma$ [Å <sup>2</sup> ]		
sorp. 1 h (0.1 M)	17613.3	8.0 O	2.35	0.0100	2.1 Np	3.83	0.0026	7.1	19.3
sorp. 1 d (0.1 M)	17613.4	7.7 O	2.35	0.0100	4.4 Np	3.84	0.0100	7.6	19.8
sorp. 7 d (0.1 M)	17613.3	7.8 O	2.34	0.0100	3.9 Np	3.83	0.0054	7.4	16.4
sorp. 21 d (0.1 M)	17613.5	7.9 O	2.34	0.0100	3.8 Np	3.82	0.0034	7.0	13.8
sorp. 0.001 M (7 d)	17613.6	8.4 O	2.35	0.0100	3.4 Np	3.83	0.0027	7.4	14.6
sorp. 1 M (7 d)	17613.6	8.0 O	2.34	0.0100	3.6 Np	3.83	0.0060	7.3	15.5
coprecipitate	17613.8	9.6 O	2.41	0.0048	4.2 C <sub>bid</sub>	2.87	0.0010	14.6	12.8
					4.2 <sup>d</sup> O <sub>dist</sub>	4.14 <sup>d</sup>	0.0016 <sup>d</sup>		
					8.4 <sup>2d</sup> C <sub>bid</sub> -O <sub>dist</sub>	4.14 <sup>d</sup>	0.0016 <sup>d</sup>		
					4.2 <sup>d</sup> C <sub>bid</sub> -O <sub>dist</sub> -C <sub>bid</sub>	4.14 <sup>d</sup>	0.0016 <sup>d</sup>		
Np <sup>IV</sup> aquo	17613.8	11.6 O	2.39	0.0083				9.4	5.2
NpO <sub>2</sub>	17613.6	8 O	2.35	0.0043	12 Np	3.85	0.0010	9.6	19.4
					24 O	4.48	0.0010		
NpO <sub>2</sub> crystal structure <sup>47</sup>		8 O	2.35		12 Np	3.84			
					24 O	4.51			

<sup>a</sup>CN: coordination number, error  $\pm 25\%$ . <sup>b</sup> $R$ : Radial distance, error  $\pm 0.01$  Å. <sup>c</sup> $\sigma^2$ : Debye–Waller factor, error  $\pm 0.0005$  Å<sup>2</sup>. <sup>d</sup>Values correlated during fit.

indication that Np<sup>V</sup> was reduced to Np<sup>IV</sup> by siderite. Further support comes from by the thermodynamic calculation, showing that the equilibrium should be dominated by NpO<sub>2</sub> at the Eh values measured at pH 8, 10, and 12 (Figure 1 bottom).

Figure 2 shows the Np- $L_3$  edge XANES spectra of the siderite sorption time series at  $\text{pH } 7.7 \pm 0.3$ , and of the coprecipitation sample. All spectra are well aligned and correspond both in edge and white-line position with the two

Np<sup>IV</sup> references, NpO<sub>2</sub> and the Np<sup>IV</sup> aquo complex.<sup>38,39</sup> This is further confirmed by the XANES edge energies as determined by the knot of the second derivative, which vary by less than 0.3 eV from the average of 17 613.5 eV (Table 1). Furthermore, iterative transformation factor analysis performed with the software package ITFA on the XANES spectra revealed only one spectral component for the sorption samples, indicating that possible traces of Np<sup>V</sup> remain below 5%.<sup>43</sup> Therefore, Np<sup>V</sup>



**Figure 3.** (a) Bright-field TEM micrograph of a 7-d sorption sample. (b) HRTEM image of area (b) with corresponding Fast Fourier Transform (FFT) in the inset. Some nanocrystals are marked by circles. (c) Energy-dispersive X-ray (EDX) spectrum obtained in scanning TEM mode from the area (c).

is reduced to  $\text{Np}^{\text{IV}}$  in all systems, even already after the shortest sorption time of 1 h, and also in the coprecipitation sample.

The EXAFS Fourier transform magnitudes of the sorption samples show a coordination shell at  $R + \Delta R = 1.8 \text{ \AA}$  (uncorrected for phase shift), which is fitted by about 8 oxygen atoms at a distance of  $2.34 - 2.35 \text{ \AA}$ . Note that the small peak at the left side of this coordination shell cannot be fitted with a Np–O distance of  $1.87 \text{ \AA}$  as would be expected for the  $-\text{yl}$  group of  $\text{Np}^{\text{V}}$ ; they constitute instead a truncation artifact of the Fourier transformation arising from the relatively short  $k$ -range. A second peak at  $R + \Delta R = 3.7 \text{ \AA}$  increases in height with sorption time. Wavelet analysis of this peak reveals an amplitude maximum at  $k > 10 \text{ \AA}^{-1}$ , in line with backscattering by a heavy element.<sup>46</sup> Correspondingly, this shell could be fitted with Np atoms at a distance of  $3.82 - 3.84 \text{ \AA}$  (see exemplary fit in Figure S4).

The interatomic distances ( $R$ ) for these nearest Np–O and Np–Np shells are close to those of  $\text{NpO}_2$ . This is also true for the coordination numbers (CN) of the Np–O coordination shell, which are close to 8 as in the cubic  $\text{NpO}_2$  structure. In contrast, the CNs of the Np–Np path are much lower, and their Debye–Waller factors ( $\sigma^2$ ) as measure of static disorder much larger, than those of  $\text{NpO}_2$ , suggesting formation of nanoparticles.<sup>47</sup> Assuming  $\text{NpO}_2$  particles with 1 nm diameter, one can calculate an average Np–Np coordination number of 5.5 ( $12 \times 5 + 1 \times 12$ ) for the cluster containing 13 Np atoms. This coordination number is significantly higher than the ones derived from the EXAFS shell fit (3.5 per average for all sorption samples), suggesting an even smaller average particle size, or cation vacancies. Similar trends were observed for nanocrystalline Np dioxide particles formed after dilution of aqueous  $\text{Np}^{\text{IV}}$  carbonate complexes<sup>39</sup> and for other  $\text{An}^{\text{IV}}$  oxide/hydroxide species.<sup>48–50</sup> Therefore, the EXAFS analysis suggests that  $\text{Np}^{\text{V}}$  reduction at the siderite surface leads to the formation of either small particles of crystalline  $\text{NpO}_2$  or to structurally disordered  $\text{Np}^{\text{IV}}$  oxide/hydroxide. While the peak height of the Np–Np shell increases with increasing sorption time, suggesting

the growth of nanoparticles with time, the shell fit data suggest a more complicated process: between 1 hour and 1 day sorption time, the CN doubles from 2 to 4, but then remains constant. At the same time, the Debye–Waller factor increases from  $0.0026$  to  $0.0100 \text{ \AA}^2$ , and decreases thereafter with increasing equilibration time to  $0.0034 \text{ \AA}^2$ . This suggests that the initial particles are small, but well ordered, and then grow with high disorder, which subsequently obtain a higher degree of order with equilibration time. Ionic strength of the background electrolyte also shows a significant effect on the Debye–Waller factor, which increases from  $0.0027$  to  $0.0054$  to  $0.0060 \text{ \AA}^2$ , when the ionic strength increases from  $0.001$  to  $1 \text{ M}$  for a constant reaction time of 7 days. Therefore, increasing background electrolyte concentrations increasingly interferes with the crystallization process.

To further characterize the microstructure of the  $\text{Np}^{\text{IV}}$  phase, a 7-d sorption sample was analyzed using TEM. A typical bright-field TEM micrograph is shown in Figure 3a. While the black particle with a diameter of approximately  $40 \text{ nm}$  is siderite, the gray areas arise from particles much smaller. The HRTEM micrograph (Figure 3b) shows periodic structures with diameters  $\leq 1\text{--}2 \text{ nm}$  (marked by circles). The diffractogram based on Fast Fourier Transform (FFT) analysis of the HRTEM image consists of diffuse rings as expected for such nanocrystalline material, which are not accessible to structure analysis. However, the dominant presence of Np and O determined in an adjacent region by energy-dispersive X-ray (EDX) spectroscopy (Figure 3c) confirms that these small particles constitute indeed the Np phase (Note that C and Cu contributions stem from the TEM support grid, and Fe and Co from the objective lens pole piece). Extended electron irradiation ( $1\text{--}2 \text{ min.}$ ) induced particle growth, and the FFT-derived diffractograms produced now distinctive rings in agreement with the fluorite-type  $\text{NpO}_2$  structure ( $Fm\bar{3}m$ ) (SI Figure S5).<sup>51</sup> Thus, the TEM-derived particle size of the unaltered material and the phase identification after the electron-induced particle growth support the EXAFS analysis

that  $\text{Np}^{\text{IV}}$  is precipitated as  $\text{NpO}_2$  or a hydrated precursor phase with particle sizes around 1 nm or even smaller.

In contrast to the sorption samples, the EXAFS Fourier transform magnitude of the coprecipitation sample shows a much higher and more distant coordination shell (Figure 2 right), which could be fitted with  $\sim 10$  oxygen atoms at a distance of 2.41 Å, that is, not commensurate to the cubic  $\text{NpO}_2$  structure (Table 1). Furthermore, the second shell is at a shorter distance than the Np-Np shell of  $\text{NpO}_2$ . Wavelet analysis of this shell shows a maximum of  $k$  at about  $8 \text{ \AA}^{-1}$ , and hence discards that this peak arises from Np-Np backscattering. The spectrum is in fact similar to compounds where carbon is bidentately coordinated, like in  $\text{Ce}^{\text{IV}}$  or  $\text{U}^{\text{IV}}$  carbonate compounds.<sup>52</sup> This was confirmed by a shell fit based on this bidentate arrangement, which gives rise to very characteristic multiple scattering paths involving the nearest bidentately coordinated C ( $C_{\text{bid}}$ ) and the next nearest, distal O ( $O_{\text{dist}}$ ) atom of the carbonate molecule. The Np-O coordination number of  $\sim 10$  as well as the Np- $C_{\text{bid}}$  coordination number of 4.2 (theoretically 5) confirm the formation of  $\text{Np}^{\text{IV}}(\text{CO}_3)_5$  units very similar to those found for  $\text{U}^{\text{IV}}$  and  $\text{Pu}^{\text{IV}}$  before, in line with the similar complex formation constants of all three actinides.<sup>45,52,53</sup> As expected for the slightly smaller ionic radius of  $\text{Np}^{\text{IV}}$  versus  $\text{U}^{\text{IV}}$ , the fitted radial distances are about 0.02 Å shorter than for the  $\text{U}^{\text{IV}}$  carbonate unit (Table 1). Analogous to  $\text{U}^{\text{IV}}$ , the  $\text{Np}^{\text{IV}}$  pentacarbonate unit may exist either as aquo-anion complex,<sup>39</sup> or in the solid state with, for example, Na for charge compensation and crystal water.<sup>52</sup> The relatively strong association of this  $\text{Np}^{\text{IV}}$  species with the solid phase ( $\log R_d = 4.0$ ) leaves little doubt about the solid-state nature of this  $\text{Np}^{\text{IV}}$  carbonate species, since the expected 6-fold negative charge of the corresponding pentacarbonate aquo ion would prevent strong sorption to the siderite surface. Furthermore, a fit of the spectrum assuming that  $\text{Np}^{\text{IV}}$  resides in the octahedrally coordinated position of  $\text{Fe}^{\text{II}}$  in siderite failed due to the fact that no Np-C shell at a distance of 3.0–3.4 Å could be fitted, which would be characteristic for the monodentate coordination of carbon in siderite. Therefore, our results demonstrate that  $\text{Np}^{\text{IV}}$  is not entrapped in the siderite structure by coprecipitation, but forms instead a  $\text{Np}^{\text{IV}}$  carbonate precipitate. Evidently, the strong complexation of Np with dissolved carbonate prevented the incorporation by siderite.<sup>45</sup>

## ENVIRONMENTAL IMPLICATIONS

After reaction of  $\text{Np}^{\text{V}}$  with siderite in the pH range 7–8 most relevant for siderite-containing clay rocks,<sup>54</sup> we could demonstrate for the first time the formation of  $\text{NpO}_2$ -like nanoparticles. The formation of a  $\text{NpO}_2$ -like phase by a surface-mediated redox reaction is in line with results by a recent study showing  $\text{Np}^{\text{V}}$  reduction by biotite and chlorite with reduced structural iron.<sup>20</sup> It is also in line with formation of  $\text{UO}_2$ -like nanoparticles upon  $\text{U}^{\text{VI}}$  sorption to, for example, magnetite and mackinawite.<sup>55,56</sup> Formation of monomeric  $\text{Np}^{\text{IV}}$  sorption complexes was not observed at the given reaction conditions, but may form when initial Np concentrations remain below the solubility of  $\text{NpO}_2(\text{am})$ . Interestingly, the strong affinity of  $\text{Np}^{\text{IV}}$  toward carbonate did not prevent the precipitation of the  $\text{NpO}_2$ -like phase, likewise to the formation of  $\text{PuO}_2$  after reaction of  $\text{Pu}^{\text{V}}$  with the  $\text{Fe}^{\text{II}}$  hydroxocarbonate chukanovite.<sup>11</sup> This can be explained by the relatively low siderite solubility in the investigated pH range. Only during coprecipitation (i.e., when  $\text{Np}^{\text{V}}$  was added to the 0.8 M carbonate solution prior to

siderite precipitation), strong carbonate complexation and subsequent precipitation of a  $\text{Np}^{\text{IV}}$  pentacarbonate took place. Since such high carbonate concentrations are not to be expected under radioactive waste conditions, formation of  $\text{NpO}_2$ -like nanoparticles is certainly more relevant for the safety case.

For equilibration periods up to one day, the measured equilibrium concentrations of Np were found to be 2 orders of magnitude larger than those expected in equilibrium with  $\text{NpO}_2(\text{am})$  ( $[\text{Np}] = 10^{-9} \text{ M}$ ).<sup>45</sup> This effect is explained by formation of colloidal  $\text{NpO}_2(\text{am})$  in agreement with other amorphous actinide(IV) oxyhydroxide colloids.<sup>57</sup> After 7 days of equilibration, however, the Np concentrations decreased almost to the value of  $\text{NpO}_2(\text{am})$  (SI Table S1). Interestingly, this lower solubility coincides with a higher static order as reflected by lower Debye–Waller factor of the Np-Np paths as compared to the 1 day sample (Table 1). Even addition of a high concentration of carbonate (0.1 M) had only a relatively small influence on Np retention, in line with previous results.<sup>58,59</sup>

The observed high retention of Np by siderite across a relatively wide pH range is encouraging. However, the potential mobilization of the formed  $\text{NpO}_2$ -like nanoparticles as colloids may significantly raise the risk of Np migration away from the waste disposal site.<sup>60,61</sup> In case of the redox sensitive uranium, the two-electron transition from  $\text{U}^{\text{VI}}$  to  $\text{U}^{\text{IV}}$  requires the formation of a chemical bond with an electron-donor surface, whereas the formation of aqueous Fe-U ion pairs can provide only one electron, thereby hindering the redox reaction kinetically.<sup>62</sup> Not surprising, TEM images of surface-catalyzed  $\text{UO}_2$  show an intimate spatial association with the most reactive sites on mineral surfaces.<sup>55,56</sup> This is not the case for the  $\text{NpO}_2$  particles, which are diffusely distributed between the siderite particles (Figure 3 a), thereby suggesting that the single electron required for the  $\text{Np}^{\text{V}}$  reduction might be provided by dissolved  $\text{Fe}^{\text{II}}$  species. This is further supported by the high isoelectric point of siderite (pH 10.1), leading to charge repulsion between the (net) positively charged siderite surface and the cationic  $\text{Np}^{\text{VO}_2^+}$  species prevailing below pH 10, which should also favor the redox reaction between dissolved  $\text{Np}^{\text{V}}$  and  $\text{Fe}^{\text{II}}$  species. Therefore, the  $\text{NpO}_2$ -like nanoparticles formed in presence of siderite may have a significant tendency to become detached from the mineral assembly. This does not necessarily mean that they also have a strong tendency to form mobile colloids, since their surface charge is low at circumneutral conditions, which favors their coagulation and causes a relatively fast settling.<sup>39</sup> This, however, may change in the presence of dissolved silica, since then amorphous  $\text{NpO}_2$  silica structures can form, whose negatively charged silanol surface groups may provide rather stable colloidal suspensions.<sup>63</sup>

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b02399.

Raman spectrum of synthetic siderite; table of XAFS samples; Zeta potential of synthetic siderite; carbonate and Fe solubility in equilibrium with siderite; Np  $L_{3\text{-edge}}$  EXAFS fits; HRTEM micrograph and its FFT of 7-d sorption sample after electron irradiation induced changes (PDF)

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### Notes

The authors declare no competing financial interest.

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