Supporting Information

Competitive Reaction of Neptunium(V) and Uranium(VI) in Potassium Sodium Carbonate Rich Aqueous Media – Speciation study with focus on high resolution X-ray spectroscopy

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Figures 11

Table 1

Table of Contents

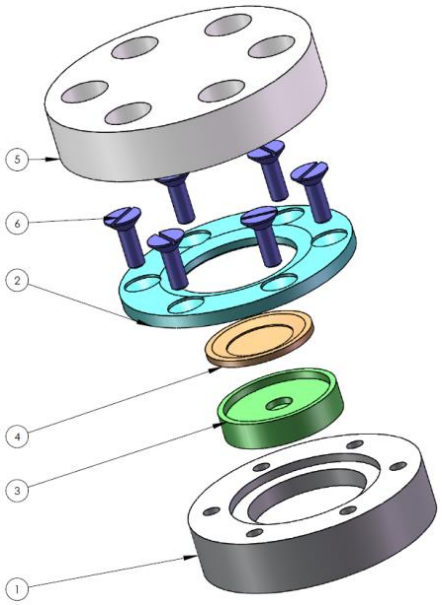

Figure S1. Sample holder for An $M_{4,5}$ edges HR-XANES measurements (original design from JRC Karlsruhe): (1) First containment (Al); (2) outer containment ring with 13 µm Kapton foil; (3) inner containment (Al) with a 3 mm cavity for An sample; (4) inner containment ring with 8 µm Kapton foil; (5) Window cover during transportation; (6) Screws for the outer containment ring.

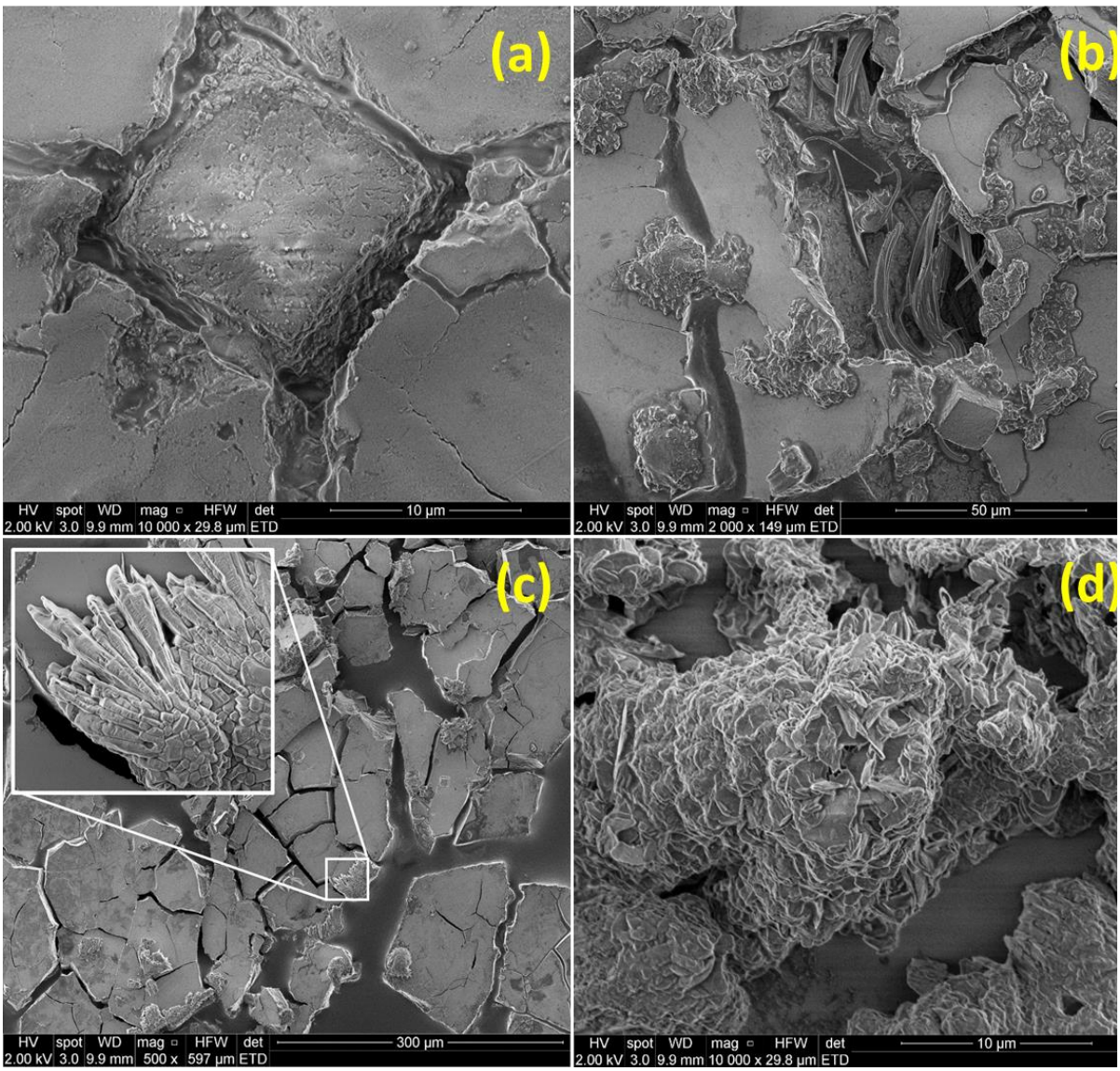

Figure S2. SEM secondary electron images of the K-Np-CO_3 precipitate and K_2CO_3 crystals (a,b) formed after drying and preparation for SEM analysis (K_2CO_3 crystals are identified by the squares in c, and zoomed in d).

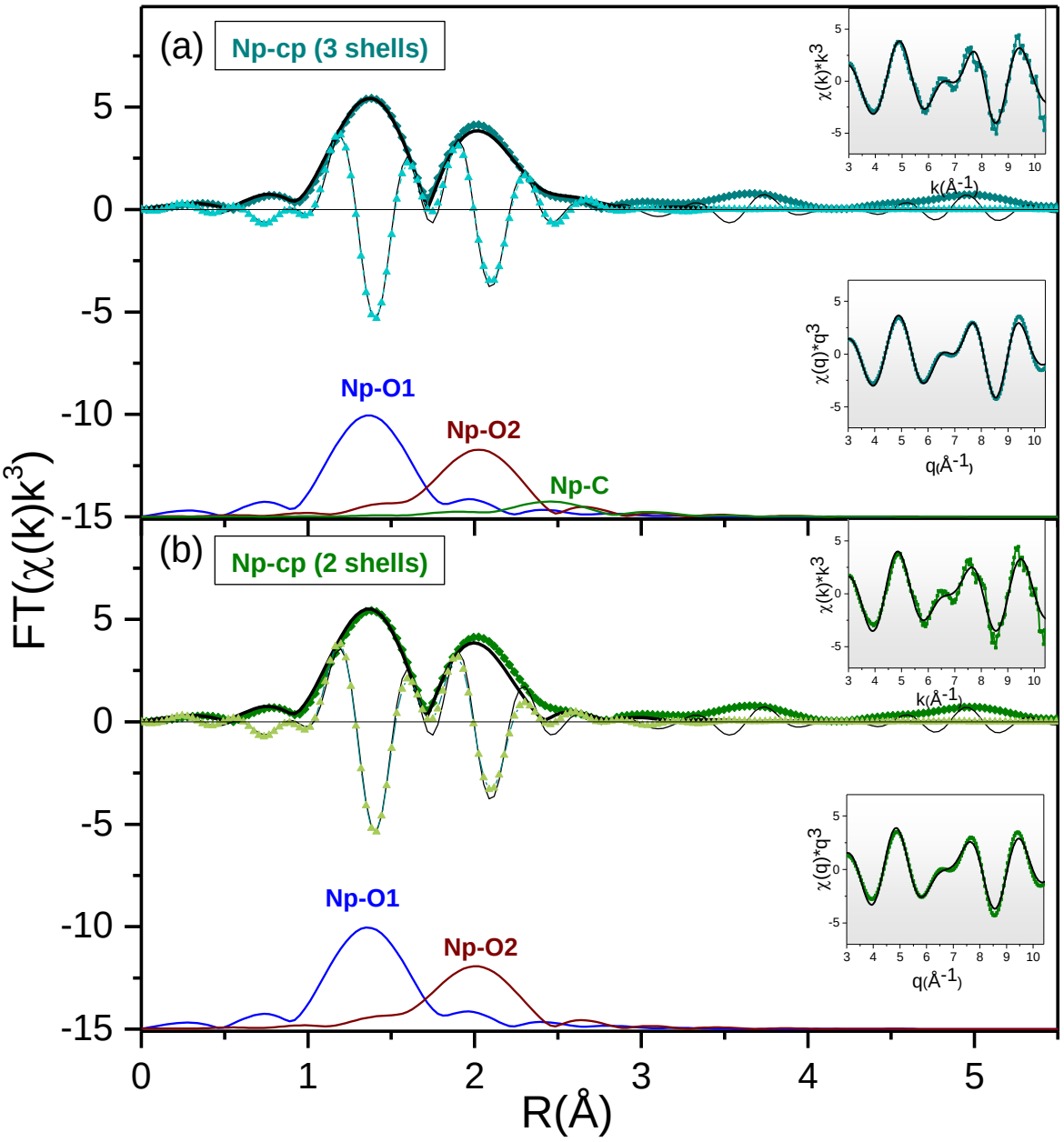

Figure S3. R-space fit results for the Np-cp fitted with 3 (a) and 2 (b) shells. Magnitude of the FT-EXAFS (colored rhombs) and their best fits (black dash dot line) and single scattering paths; imaginary parts of the FT-EXAFS (light colored triangles) and the best fits (black dash line) (top inset); k^3-weighted filtered χ(k)-function (colored rhombs) and their best fits (black solid line); back FT-EXAFS and fits (down inset). k = 1.0-3.0 $Å^{-1}$ was used for 3 shell fit and k = 1.0-2.6 $Å^{-1}$ for 2 shells.

Table S1. EXAFS fit results for the **Np-cp** sample fitted with 3 and 2 shells (SP denotes scattering path, N – coordination number, R – bond distance, σ^2 - Debye-Waller factor, ΔE_0 – energy shift of the ionization potential, S_0^2 – amplitude reduction factor and r - goodness of fit. Uncertainties are given in the parentheses as the last decimal in the fit value, ^{f} – paramters are fixed).

Shells	SP	N	R, [Å]	$\sigma^2 \cdot 10^{-3}$, [Å^2]	ΔE_0, [eV]	r, %
3	Np-O1	2^f	1.83 (1)	0.8 (7)	7.4 ± 1.1	**0.5**
	Np-O2	5.4 (4)	2.53 (1)	6 (1)		
	Np-C	2.9 ± 1.0	2.99 (4)	6 (1)		
2	Np-O1	2^f	1.82 (2)	0.6 (9)	6.4 ± 1.3	**1.4**
	Np-O2	5.9 (5)	2.52 (2)	7 (2)		

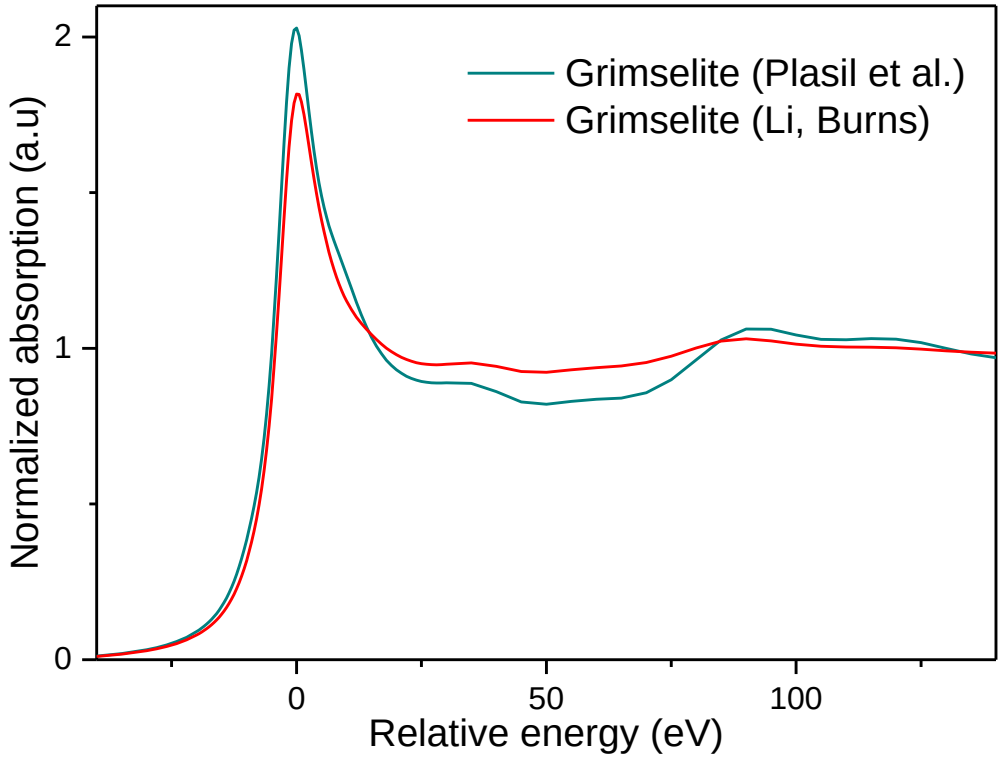

Figure S4. U L_3 edge XANES spectra of grimselite ($K_3Na[(UO_2)(CO_3)_3]\cdot H_2O$) calculated with the FDMNES program using the two published crystal structures of grimselite: Li, Burns - AMCSD 0005731 (red line) and Plasil et al. - ICSD 186867 (blue line).

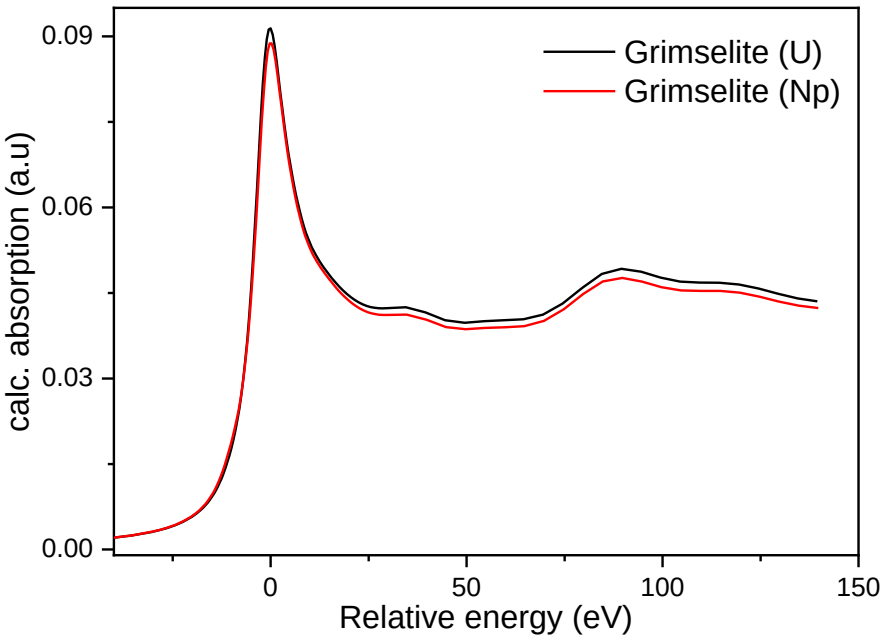

Figure S5. U (black line) and Np (red line) L_3 edge XANES spectra of grimselite ($K_3Na[(UO_2)(CO_3)_3]\cdot H_2O$, ICSD 186867) calculated with the FDMNES program. The U atoms are substituted with Np atoms for the calculation of the Np L_3 edge XANES spectrum (red line).

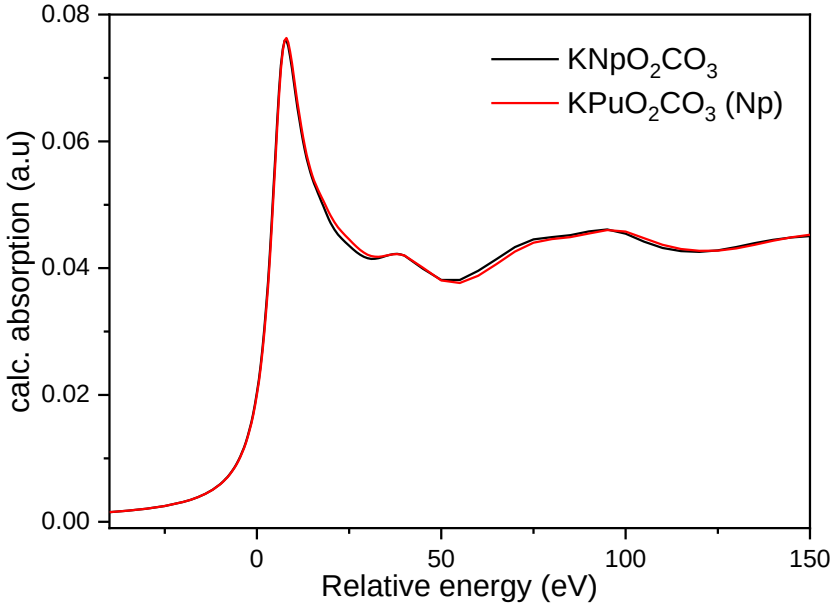

Figure S6. Np L_3 edge XANES spectra of $K[NpO_2CO_3]$ calculated with the FDMNES program: ICSD 15685, Pu is exchanged with Np, lattice parameters a = b = 5.09, c = 9.83 Å (red line); the same crystal structure but the lattice parameters: a = b = 5.12, c = 9.971 Å reported for $K[NpO_2CO_3]$ by Keenan and Kruse [1] are applied (black line).

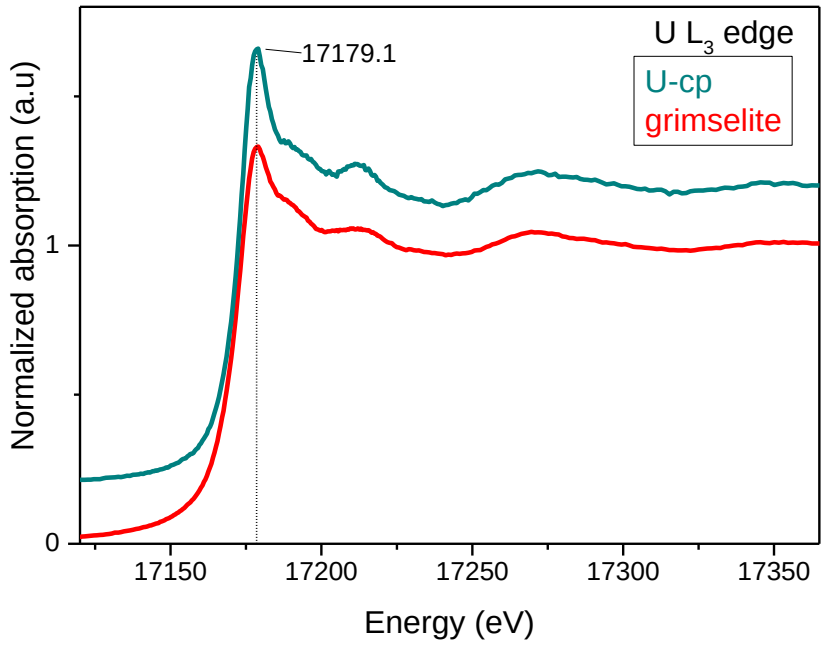

Figure S7. U L_3 edge XANES spectra of U-cp and grimselite ($K_3Na[(UO_2)(CO_3)_3]\cdot H_2O$).

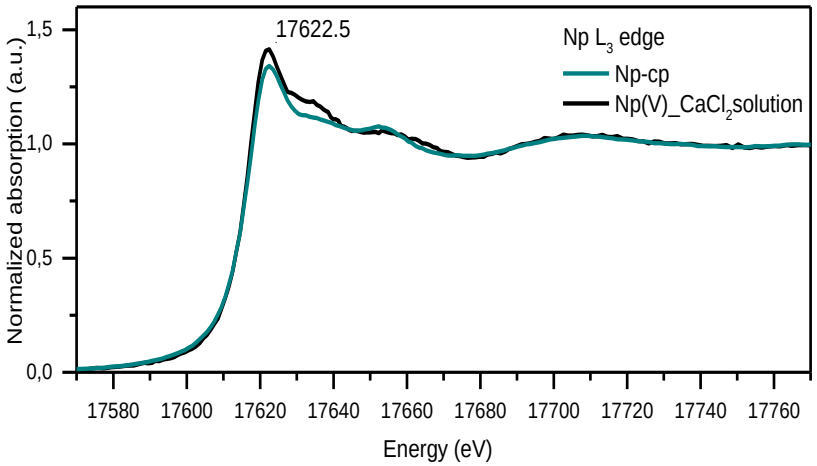

Figure S8. Np L_3 edge XANES spectra of Np-cp and Np(V) in $CaCl_2$ solution.

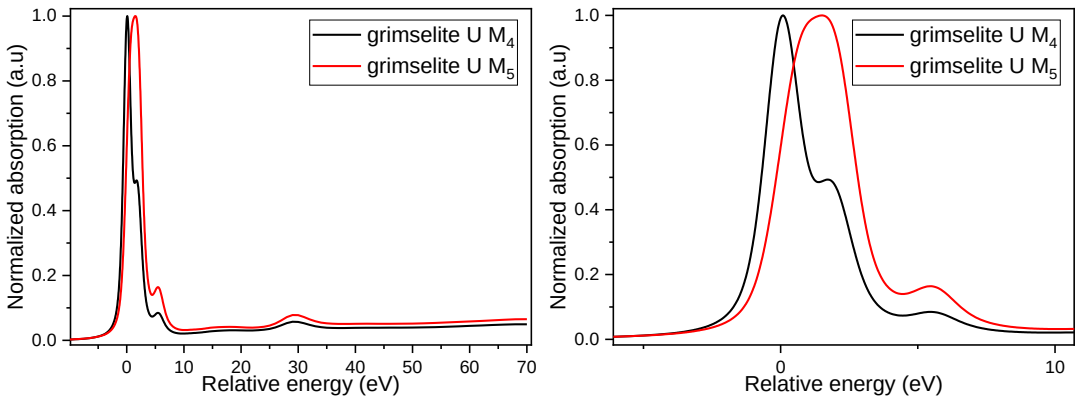

Figure S9. U M_4 and M_5 edge HR-XANES spectra of grimselite ($K_3Na[(UO_2)(CO_3)_3]\cdot H_2O$) computed with the FDMNES code.

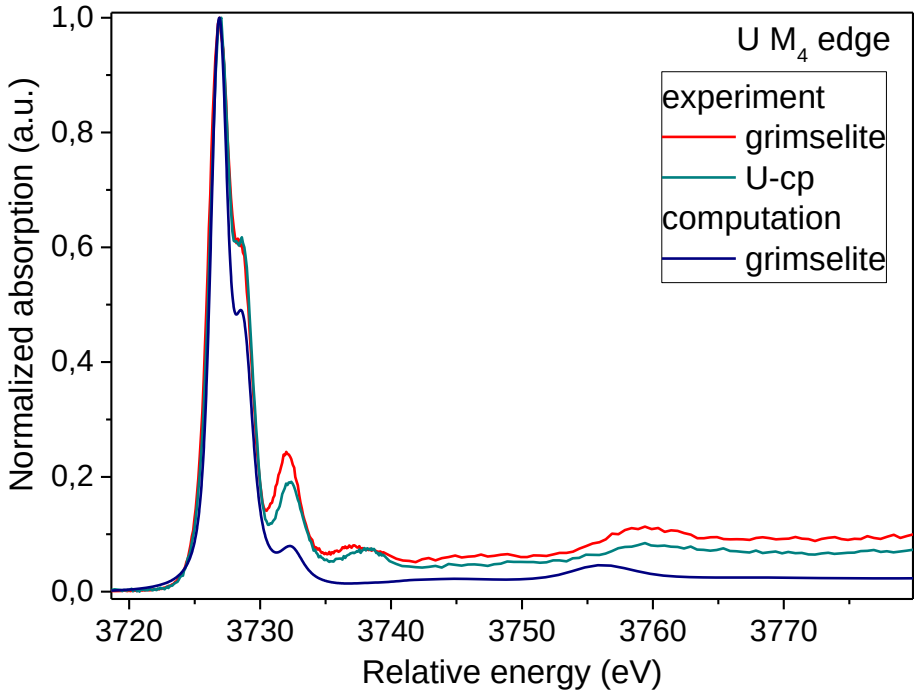

Figure S10. U M_4 edge HR-XANES spectra of grimselite ($K_3Na[(UO_2)(CO_3)_3]\cdot H_2O$) and U-cp and the grimselite spectrum computed with the FDMNES code.

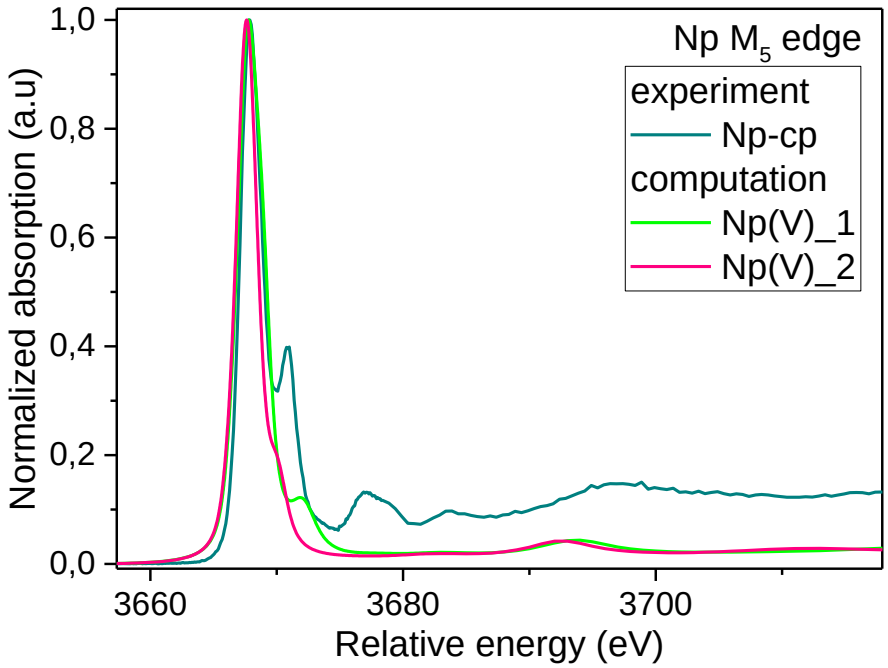

Figure S11. Np M_5 edge HR-XANES spectra of Np-cp and computed spectra of $K_3[NpO_2(CO_3)_2]\cdot nH_2O_{(cr)}$ (Np(V)_1), and $K[NpO_2CO_3]_{(cr)}$ (Np(V)_2) using the FDMNES code.

An example of an input file used for the FDMNES calculations of U L3 edge HR-XANES and DOS spectra

```
! Fdmnes indata file

 Filout
   Grimselite/grimselite_UL3_rel_green_out
Edge
 L3
 Range                    ! Energy range of calculation (eV)
 -100 5 -20 2 -10. 0.5 20 1 40 5 150
 Radius
 6
Green
 Spinorbit
Density
state_all
 SCF
 Z_absorber
 92
Cif_file
Grimselite_186867.cif
Convolution
 End
```

An example of an input file used for the FDMNES calculations of U M4 edge HR-XANES and DOS spectra

```
! Fdmnes indata file
 Filout
   M_edge/Grimselite_M4
Range
-4 0.02 4 0.05 10 0.2 15 1 40 2 70
Quadrupole
S-10
```

```
SCF
Relativiste
Spinorbite
Density
Edge
M4
Radius
3.5
Z_absorber
 92
Cif_file
Grimselite_186867.cif
 End

!Indata file for FDMNES-Convolution step
Calculation
M_edge/KNpO2CO3_NpM5.txt
EFermi
-0.8
Gamma_max
3
Gamma_hole
0.8
Gaussian
1.0
Conv_out
M_edge/KNpO2CO3_NpM5_conv_new2
Convolution
Estart
-20
End
```

[1] Keenan, T. K.; Kruss, F. H. Potassium Double Carbonates of Pentavalent Neptunium, Plutonium, and Americium. *Inorg. Chem.*1964, *39*, 1231-1232.