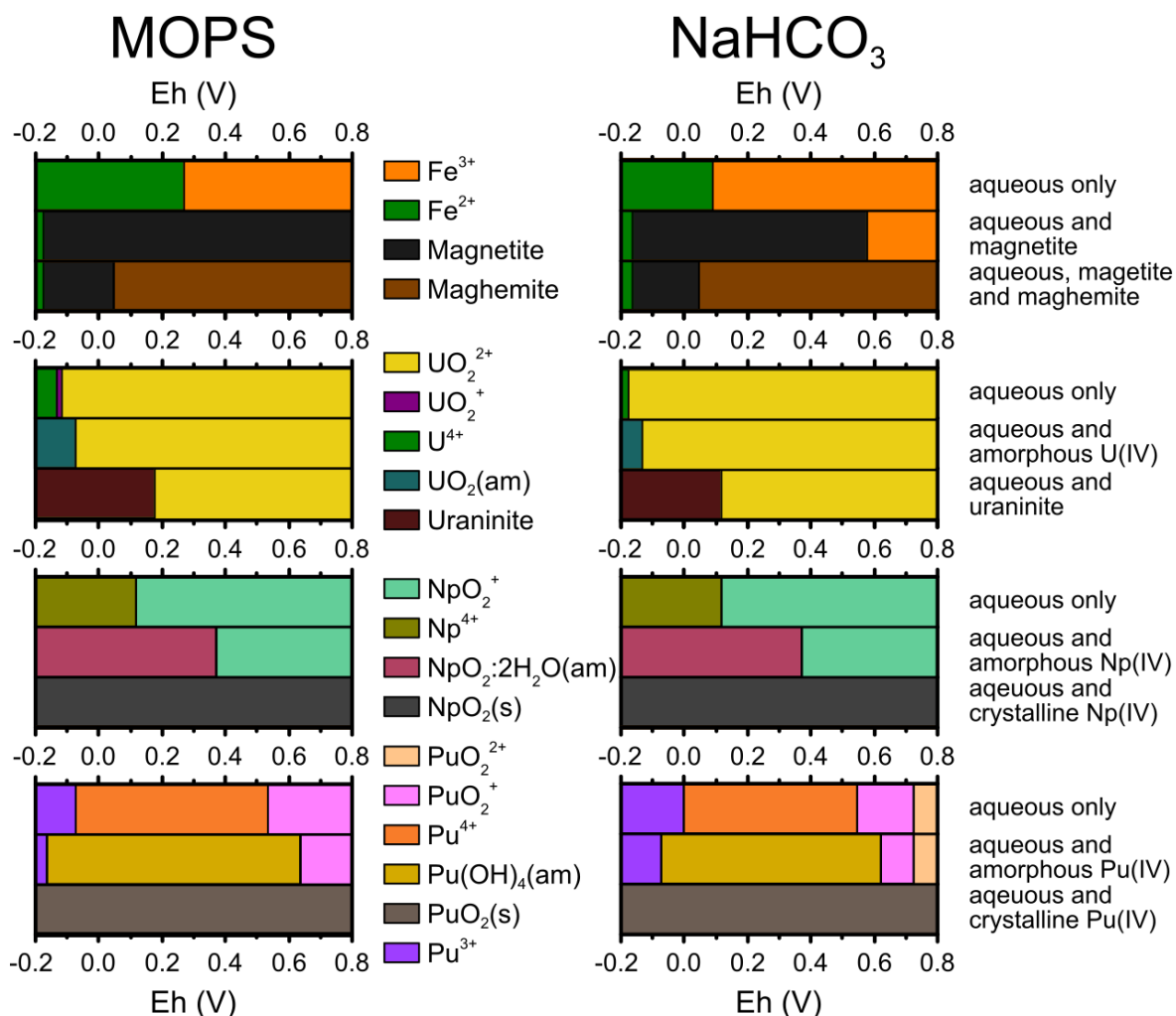


1 **Supporting information**

2



3

4 **Figure S1. Stability fields (Eh) of the dominant redox species for Fe, U, Np and Pu in the presence of MOPS or NaHCO₃ at**
 5 **pH = 7, 0.1 mM Fe, 42 μM U, 25 μM Np and 25 nM Pu, based on PHREEQC calculations using the SIT database mimicking**
 6 **the experimental conditions, the calculations were first performed on aqueous species only and second allowing the**
 7 **formation of several solid phases; the coloured boxes represent the dominant redox species / solid; (am) represent**
 8 **amorphous / poorly crystalline solid species and (s) represents crystalline solid species and the ionic species refer to the**
 9 **sum of all aqueous complexes that include the ions listed in the legends (Table S1).**

10

11

12

13

14

15

16
17
18
19
20
21

Table S1 Predicted aqueous actinide speciation in the experimental conditions during the MOPS and NaHCO₃ experiments for the different redox species of uranium, neptunium and plutonium, based on the PHREEQC calculations without equilibration with solid phases (Figure S1); the aqueous species included are the species contributing ≥ 1% of the redox species.

MOPS		U(V)		U(IV)			
U(VI)							
(UO ₂) ₃ (OH) ₅ ⁺	72%	UO ₂ ⁺	100%	U(OH) ₄ ⁰	98%		
(UO ₂) ₄ (OH) ₇ ⁺	22%			U(OH) ₃ ⁺	2%		
UO ₂ (OH) ₂ ⁰	4%						
UO ₂ (OH) ⁺	3%						
NaHCO₃		U(V)		U(IV)			
U(VI)							
UO ₂ (CO ₃) ₂ ²⁻	51%	UO ₂ ⁺	100%	U(OH) ₄ ⁰	98%		
UO ₂ (CO ₃) ₃ ⁴⁻	34%			U(OH) ₃ ⁺	2%		
(UO ₂) ₂ (CO ₃)(OH) ₃ ⁻	10%						
UO ₂ (CO ₃) ⁰	5%						
MOPS		Np(V)		Np(IV)			
Np(VI)							
NpO ₂ (OH) ⁺	57%	NpO ₂ ⁺	100%	Np(OH) ₄ ⁰	97%		
NpO ₂ (OH) ₂ ⁰	42%			Np(OH) ₃ ⁺	3%		
NpO ₂ ²⁺	1%						
NaHCO₃		Np(V)		Np(IV)			
Np(VI)							
NpO ₂ (CO ₃) ₂ ²⁻	97%	NpO ₂ ⁺	86%	Np(OH) ₄ ⁰	77%		
NpO ₂ (CO ₃) ⁰	3%	NpO ₂ (CO ₃) ⁻	14%	Np(CO ₃)(OH) ₃ ⁻	19%		
				Np(OH) ₃ ⁺	3%		
				Np(OH) ₂ (CO ₃) ₂ ²⁻	1%		
MOPS		Pu(V)		Pu(IV)		Pu(III)	
Pu(VI)							
PuO ₂ (OH) ⁺	82%	PuO ₂ ⁺	100%	Pu(OH) ₄ ⁰	85%	Pu ³⁺	53%
PuO ₂ (OH) ₂ ⁰	15%			Pu(OH) ₃ ⁺	15%	Pu(OH) ²⁺	47%
PuO ₂ ²⁺	3%						
NaHCO₃		Pu(V)		Pu(IV)		Pu(III)	
Pu(VI)							
PuO ₂ (CO ₃) ⁰	73%	PuO ₂ ⁺	81%	Pu(OH) ₄ ⁰	53%	Pu(CO ₃) ⁺	84%
PuO ₂ (CO ₃) ₂ ²⁻	27%	PuO ₂ CO ₃ ⁻	19%	Pu(CO ₃) ₂ (OH) ₂ ²⁻	38%	Pu(CO ₃) ₂ ⁻	12%
				Pu(OH) ₃ ⁺	9%	Pu ³⁺	2%
						Pu(OH) ²⁺	2%

22

Table S2 XPS results; fitted binding energy in eV of the main peaks for the actinide 4f transitions

Transition	U(IV)		U(VI)		Pu(III)		Pu(IV)		Np(IV)	
	4f 7/2	4f 5/2	4f 7/2	4f 5/2	4f 7/2	4f 5/2	4f 7/2	4f 5/2	4f 7/2	4f 5/2
U MOPS – 1	380.3	391.1	382.0	392.9	-	-	-	-	-	-
U MOPS – 2	380.7	391.6	382.2	393.0	-	-	-	-	-	-
U NaHCO ₃	380.5	391.3	382.2	393.1	-	-	-	-	-	-
Np / Pu MOPS	-	-	-	-	424.8	437.7	426.6	439.4	403.2	415.0
Np / Pu NaHCO ₃	-	-	-	-	424.7	437.6	426.5	439.3	403.4	415.2

24