Supporting Information

Dynamic dissolution of Cm^{3+} ions incorporated at the calcite–water interface: an *ab initio* molecular dynamics simulation study

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Table of Contents

Section S1 Supplementary Methods

Section S1.1 AIMD calculation details

The incorporated Cm^{3+} ion species in the calcite-water systems were investigated by using AIMD simulations (see the models in Figure S1). We first performed a 5 ps NVT ensemble of AIMD simulations at 300 K, followed by a slow anneal to 0 K with a rescaling factor equal to 0.997 for the annealing rate, and finally a geometry optimization. A time step of 1 fs was set. The optimized geometrical parameters were summarized in Table S1.

For equilibrium state before the detachment of the $Cm_{t/s}$, the 15 ps NVT AIMD simulations at 300 K were performed. For equilibrium state after the detachment of the $Cm_{t/s}$ from its initial position to the state of D/D', the 10 ps NVT AIMD simulations at 300 K were performed. The structural of the hydrated Cm^{3+} ion and the water/$CaCO_3$ interface were analyzed by using the the above equilibrated AIMD trajectories of 5-10 ps (see Figure S9). The geometrical parameters of hydrated Cm^{3+} ion at equilibrium were summarized in Table S4.

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Section S1.2 Metadynamics simulations

During *ab initio* molecular dynamics (AIMD), various geometries are sampled as a function of simulation time t and can be described by a generalized coordinate q(t). Metadynamics response is to keep adding a bias potential to the original (unbiased) system during the MD simulation, with the aim of lifting the potential energy surface until the entire surface is filled in. Here, the added bias potential is along the selected geometric parameters (distance, angle, dihedral or any parameter that depends on q(t)), and these are called collective variables (CV(ξ)). Its purpose is to control our enhanced sampling. The metadynamics hamiltonian is written as:[1]

$$H(p,q,t) = H(p,q) + V(t,\xi),$$

where $H(p,q)$ is the Hamiltonian for the original (unbiased) system, $V(t,\xi)$ is the time-dependent bias potential. The bias potential is defined as:

$$\tilde{V}(t,\xi) = h \sum_{i=1}^{\left|\frac{t}{t_G}\right|} exp\left[-\frac{|\xi^{(t)}-\xi^{(i \cdot t_G)}|^2}{2\omega^2}\right],$$

where h is the height of a Gaussian hill, ω is the width of the Gaussian hill and the t_G sets frequency of a bias potential to be added. In this work, we chose coordination numbers as collective variables. Thus, the coordination of Cm(III) with a set of oxygen atoms [2-4], i.e., CV(Cm, O_{set}), is defined by:[5]

$$CV(Cm, O\text{set}) = \sum s_{ij} = \sum \frac{1 - \left(\frac{r_{ij}}{r_0}\right)^{NN}}{1 - \left(\frac{r_{ij}}{r_0}\right)^{ND}}$$

where r_{ij} is the inter-atomic distance between atom Cm and atom O, $s_{ij}(r_{ij})$ is the switching function describing the coordination between atom i and j, r_0 is the Cm-O equilibrium distance, and the two integer exponents, i.e., NN and ND, determines the curve. The value of r_0 for Cm-O_S is 2.50 Å, for Cm-O_W is 2.48 Å for terrace surface system and the value of r_0 for Cm-O_S is 2.51 Å, for Cm-O_W is 2.47 Å for stepped surface system. (O_S belongs to the surface of calcite

bulk, O_W belongs to water molecule in solution aqueous). The ratio NN/ ND determines the curvature of the switching function s_{ij} and finally control the CV value. The CV describes the interaction between Cm atom and the coordinate oxygen atoms from calcite or water molecules. It should be approximately zero when the oxygen atoms are far from the curium atom. When one or more oxygen atoms are close to the curium atom, it will be greater than zero, but always less than 1. The switching function s_{ij} is plotted for a given value of r_0 and various ratios *NN/ND* to illustrate the effect of those parameters on its shape in Figure S2. Here, a ratio of 4/7 (NN=8, ND=14) was chosen in this work, and correspondingly, the CV starts to be greater than zero when the Cm-O distance is less than 5 Å.

The relevant information of the dissolution pathway of Cm from the terrace/stepped surface system revealed by ab initio metadynamics simulations was displayed in Figures S3-S8. The convergence tests for the free energy surfaces and the error analyses were summarized in Figures S5 and S8 and Tables S2 and S3.

Section S1.3 Structural analysis

To show the difference in the atomic density distribution for O_W and H, the atomic excess (*AE*) is defined as: $AE = \frac{2[O_W]-[H]}{2[O_W]-[H]}$, where $[O_W]$ and $[H]$ are atomic density for O_W and H, respectively. The negative value for *AE* indicates an excess of H, while the positive one indicates an excess of O_W.

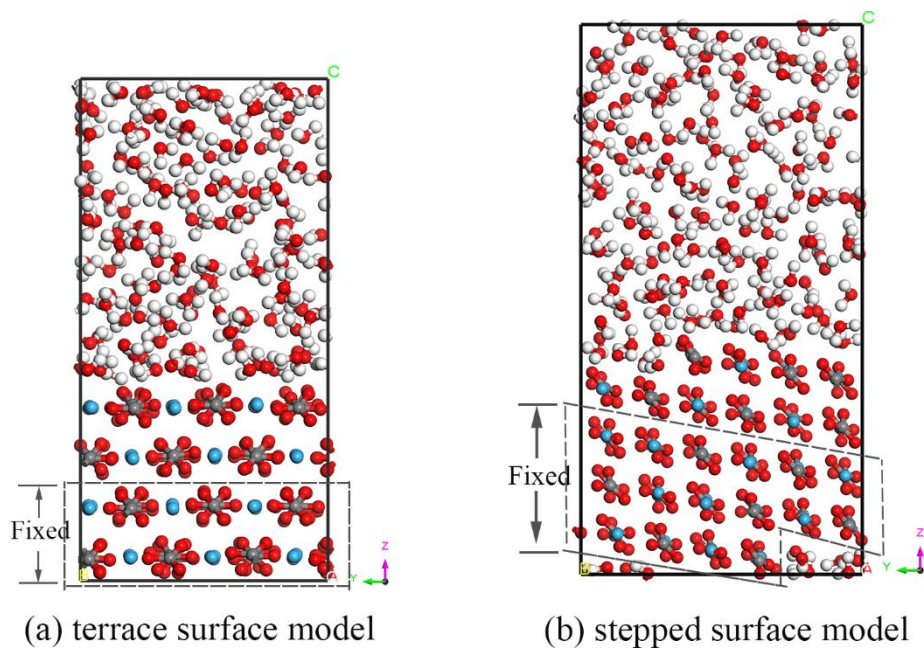(a) terrace surface model   (b) stepped surface model

Figure S1. Two surface models of water-calcite system: (a) the terrace–water surface model and (b) the stepped–water surface model, respectively. The minerals in the dashed box are fixed. The white, red, gray and purple balls indicate hydrogen, oxygen, carbon and curium atoms, respectively.
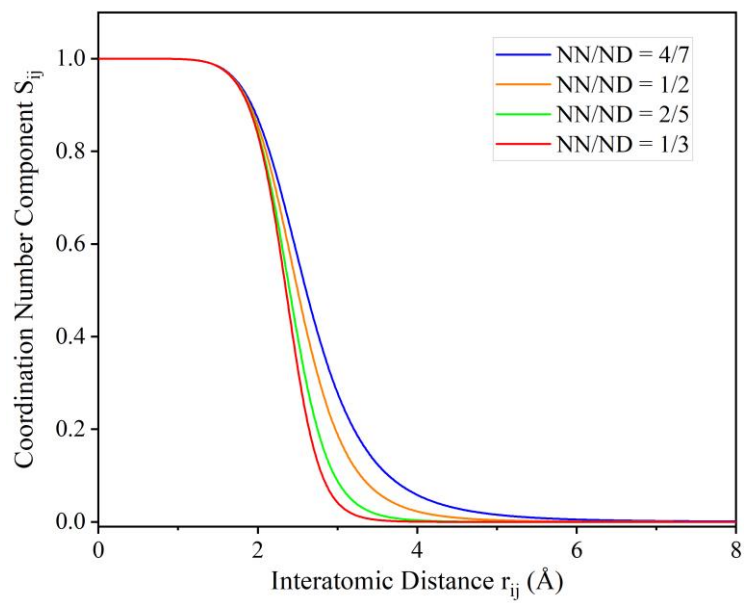
Figure S2. Switching function s_{ij} for r_0=2.5 Å and n/m ratio with NN=8. See the corresponding mathematical definition in the text.

Table S1. The DFT/PBE calculated Cm-O bond length (in Å) for the first coordination shell of the incorporated Cm^{3+} ion in the calcite bulk, where O_C and O_W are the coordinated oxygen atoms from carbonate groups and water, respectively. Those marked with bold italics are the bond distances between Cm^{3+} ion and the O_C from the second layer of calcite. The average bond length (in Å) for each type of Cm-O bond is shown in parathesis.

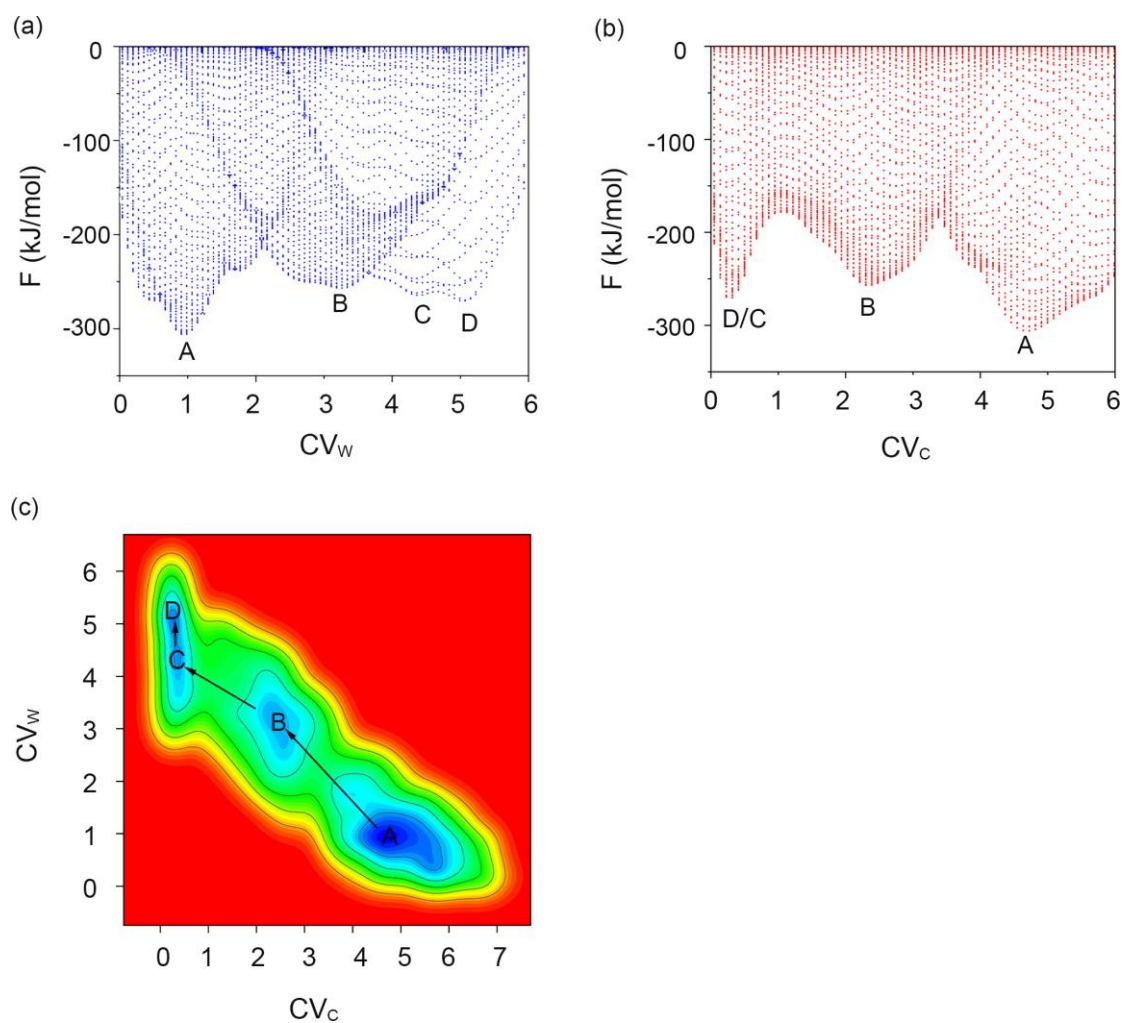| Adsorption Surface	R(Cm-O$_c$)		R(Cm-O$_w$)
	Bidentate mode	**Monodentate mode**	
Terrace Surface	2.45/2.62, 2.44/2.70 (2.55)	2.42 2.37 ***2.51*** (2.43)	2.48
Stepped Surface	2.43/2.78, 2.49/2.55 (2.56)	2.38 ***2.44 2.48*** (2.43)	2.47

Figure S3. Dissolution information of Cm_t in the terrace-water surface system: the one-dimensional free energy profiles with respect to (a) $CV_W(Cm\text{-}O_W)$ and (b) $CV_C(Cm\text{-}O_C)$, respectively, and (c) the two-dimensional free energy surface with variables of $CV_C(Cm\text{-}O_C$ bond) and $CV_W(Cm\text{-}O_W)$.
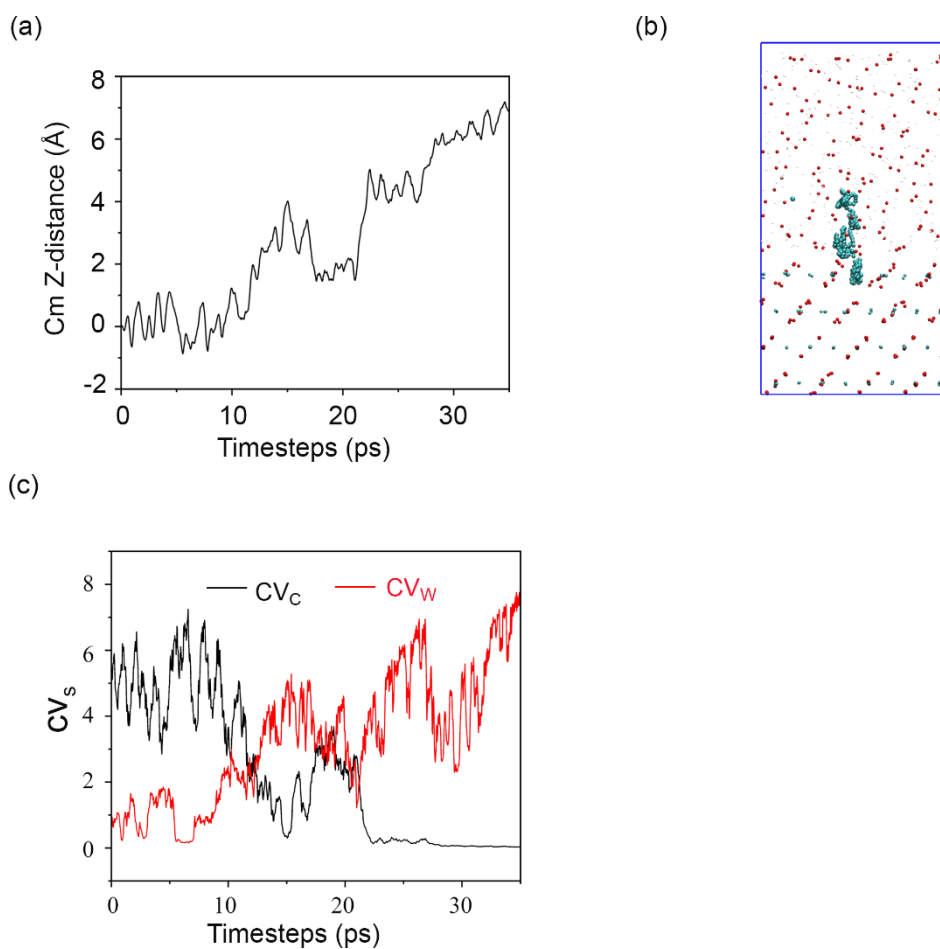
Figure S4. Dissolution pathway of Cm_t from the terrace-water surface system revealed by ab initio metadynamics simulations. (a) The change in the distance of dissociated Cm_t from original site towards aqueous solution along the Z-axis during simulation; (b) The dynamic trajectories of Cm_t; (c) Time evolution of $CV_C(Cm-O_C)$ and $CV_W(Cm-O_W)$ with black line for CV_C and red line for CV_W, respectively, during the whole simulation time.
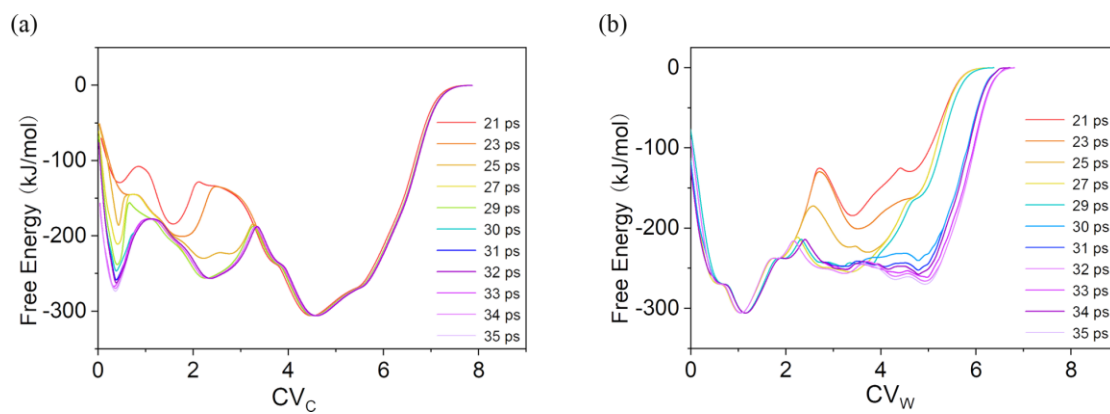
(a)

(b)

Figure S5. Convergence tests for metadynamics simulations of Cm dissolution: the one-dimensional free energy profiles with respect to (a) CV_C(Cm-O_W) and (b) CV_W(Cm-O_C) for the terrace-water system.

Table S2. Free energy difference (kJ/mol) between the first and the last basin along CV_C or CV_W on the free energy profile in the terrace-water system and the corresponding standard deviation (*SD*) and standard error (*SE*).[a] The free energy profiles are shown in Figure S5.

Timestep (ps)	31	32	33	34	35
$\Delta G(CV_C)$	46	42	39	33	29
$\Delta G(CV_W)$	52	47	43	39	36
SD(CV_C)	6				
SD(CV_W)	6				
SE(CV_C)	3				
SE(CV_W)	3				

[a]The standard deviation (*SD*) is defined by $SD = \sqrt{\frac{\Sigma(x_i - \bar{x})^2}{n}}$, where x_i represent each $\Delta G(CV_{C/W})$ value in the table, $\bar{x}$ is the mean of $\Delta G(CV_{C/W})$, n is the number of $\Delta G(CV_{C/W})$ data and equals to 5. The standard error (*SE*) can be obtained by $SE = \frac{SD}{\sqrt{n}}$
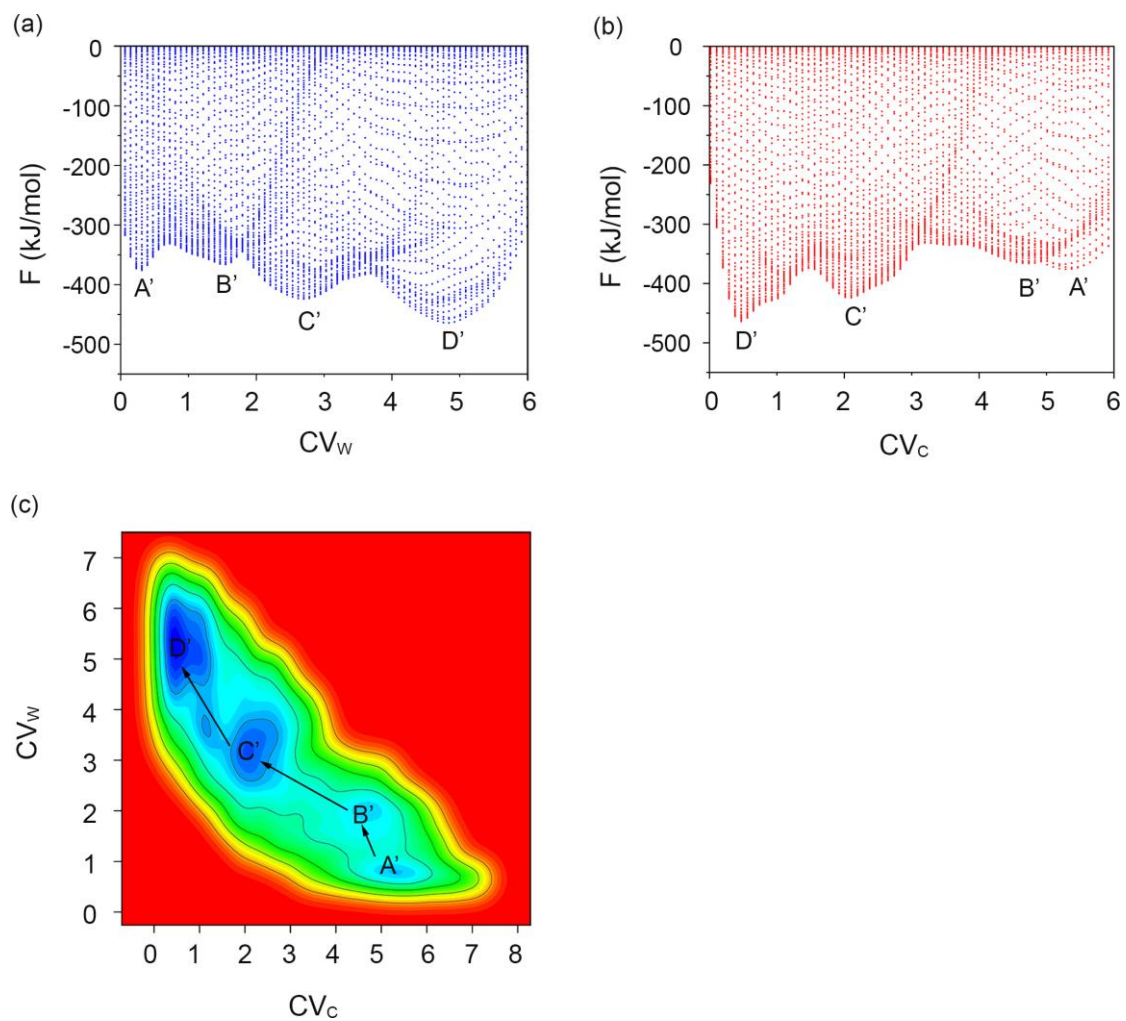
Figure S6. Dissolution pathway information of Cm_s in the stepped-water surface system: the one-dimensional free energy profiles with respect to (a) CV_W(Cm-O_W) and (b) CV_C(Cm-O_C), respectively, and (c) the two-dimensional free energy surface with variables of CV_C (Cm-O_C bond) and CV_W(Cm-O_W).
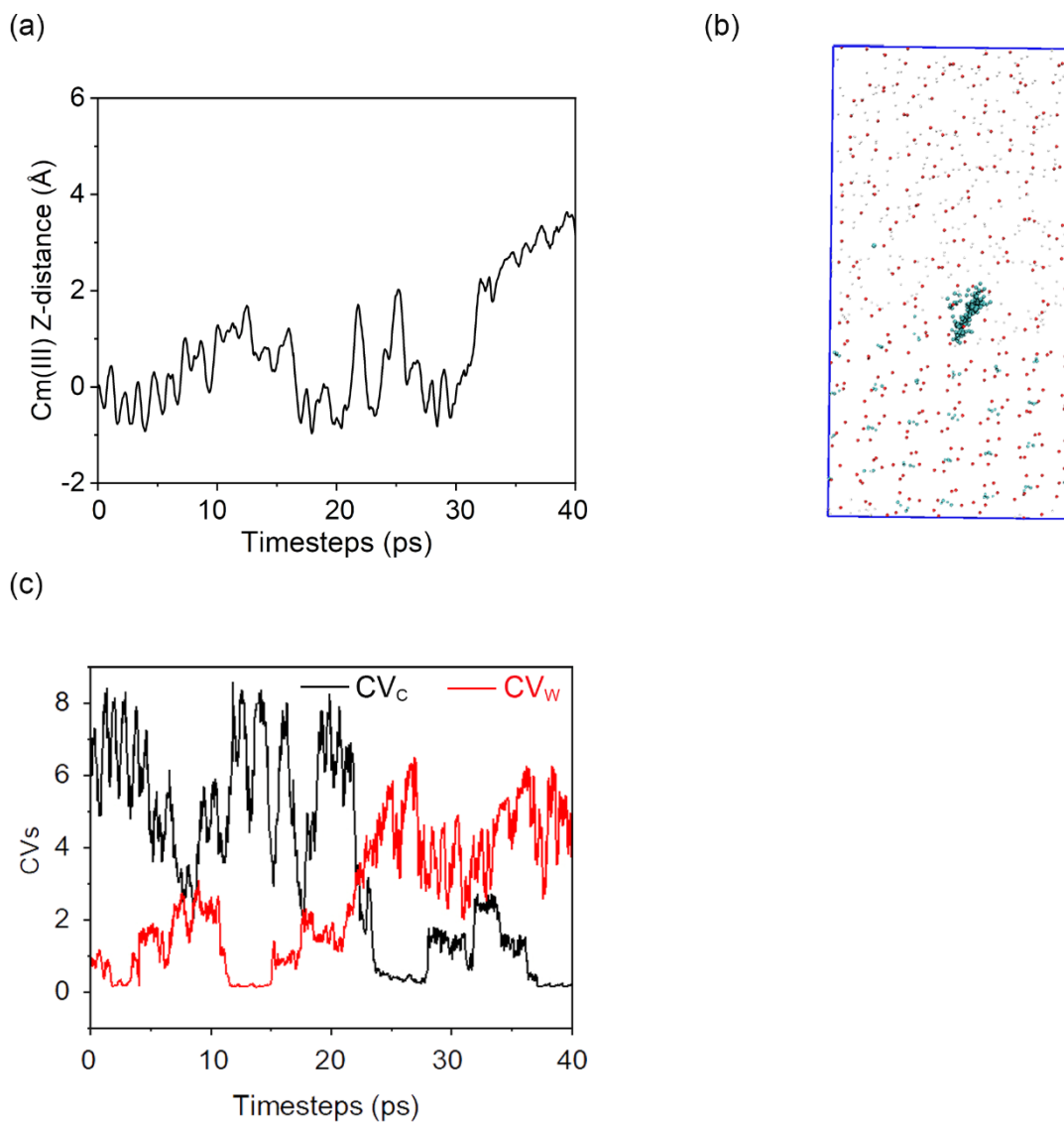
Figure S7. Dissolution pathway of Cm_S from the stepped-water surface system revealed by ab initio metadynamics simulations. (a) The change in the distance of dissociated Cm_S from original site towards aqueous solution along the Z-axis during simulation; (b) The dynamic trajectories of Cm_S, (c) Time resolution of CV_C(Cm-O_C) and CV_W(Cm-O_W) with black line for CV_C and red line for CV_W, respectively, during the whole simulation time.
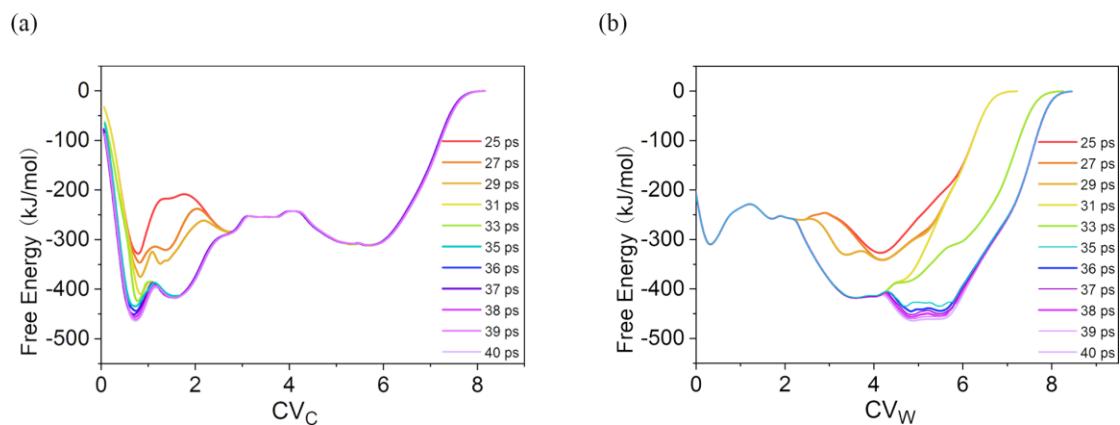
(a)   (b)

Figure S8. Convergence tests for metadynamics simulations of Cm dissolution: the one-dimensional free energy profiles with respect to (a) CV_C(Cm-O_W) and (b) CV_W(Cm-O_C) for the stepped-water system.

Table S3. Free energy difference (kJ/mol) between the first and the last basin along CV_C or CV_W on the free energy profile in the stepped-water system system and the corresponding standard deviation (*SD*) and standard error (*SE*). [a] The free energy profiles are shown in Figure S8.

Timestep (ps)	36	37	38	39	40
$\Delta G(CV_C)$	-135	-139	-144	-149	-152
$\Delta G(CV_W)$	-135	-140	-144	-148	-152
$SD(CV_C)$	6				
$SD(CV_W)$	6				
$SE(CV_C)$	3				
$SE(CV_W)$	3				

[a]The standard deviation (*SD*) is defined by $SD = \sqrt{\frac{\Sigma(x_i - \bar{x})^2}{n}}$, where x_i represent each $\Delta G(CV_{C/W})$ values in the table, $\bar{x}$ is the mean of $\Delta G(CV_{C/W})$, n is the number of $\Delta G(CV_{C/W})$ data and equals to 5. The standard error (*SE*) can be obtained by $SE = \frac{SD}{\sqrt{n}}$

Table S4. The Cm-O bond length (in Å) in the first coordination shell of Cm^{3+} ion corresponding to the last snapshot of 10 ps equilibrium AIMD simulation after Cm dissolution. The O_W and O_{OH} are the coordinated oxygen atoms from water and hydroxide, respectively.

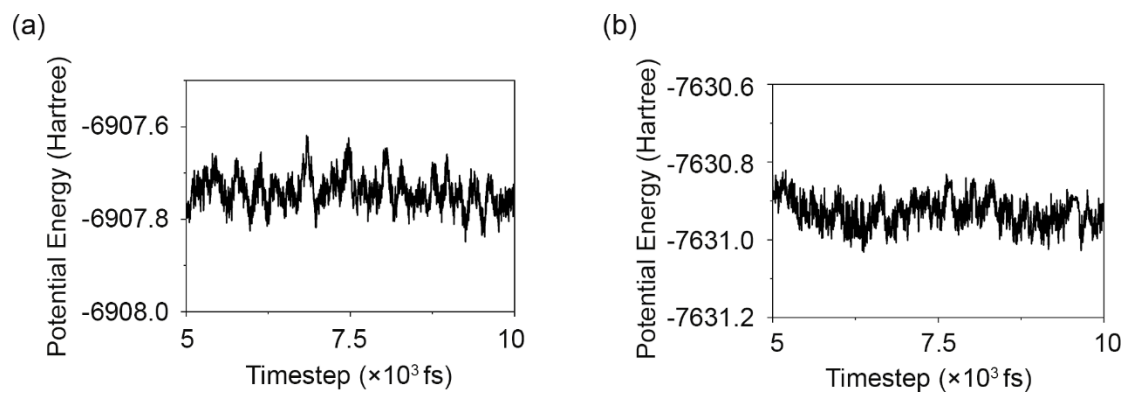| Equilibrium state after Cm dissolution	R(Cm-O$_W$)	R(Cm-O$_{OH}$)
Terrace surface system	2.44 2.49 2.49 2.58 2.55 2.61	2.20
Stepped surface system	2.40 2.48 2.40 2.38 2.80 2.31	2.35

Figure S9. Potential energy plot for the AIMD trajectories of the equilibrium state for (a) terrace surface system and (b) stepped surface system after Cm dissolution.

References

1.   Laio, A.; Parrinello, M., Escaping Free-energy Minima. *Proceedings of the National Academy of Sciences* **2002,** *99* (20), 12562-12566.

2.   Thompson, D. W.; Pownall, P. G., Surface Electrical Properties of Calcite. *Journal of Colloid and Interface Science* **1989,** *131* (1), 74-82.

3.   Cao, X.;   Hu, L.;   Wang, J.; Wang, J., Regional Groundwater Flow Assessment in a Prospective High-level Radioactive Waste Repository of China. *Water* **2017,** *9* (7), 551.

4.   Stumpf, T.;   Bauer, A.;   Coppin, F.; Kim, J. I., Time-resolved Laser Fluorescence Spectroscopy Study of the Sorption of Cm (III) onto Smectite and Kaolinite. *Environmental Science & Technology* **2001,** *35* (18), 3691-3694.

5.   Bal, K. M.;   Fukuhara, S.;   Shibuta, Y.; Neyts, E. C., Free Energy Barriers from Biased Molecular Dynamics Simulations. *The Journal of Chemical Physics* **2020,** *153* (11), 114118.