A Comparative Study of Surface Energies and Water Adsorption on Ce-Bastnästite, La-Bastnästite, and Calcite via Density Functional Theory and Water Adsorption Calorimetry

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Electronic Supplementary Information (ESI) Available: Geometric features of Ce-bastnäsite surfaces computed using the large-core pseudopotential, overlays of cleaved and optimized structures of Ce-bastnäsite and calcite surfaces, crystallographic information files containing optimized structures of the studied surfaces obtained from VASP calculations, and adsorption isotherm for $CeFCO_3$ with corresponding calorimetric trace.

Table S1: C-O and Ce-F bond lengths in Ce-Bastnäsite computed using the large-core pseupopotential.

Structure	r_{C-O}^{min}(Å)	r_{C-O}^{max}(Å)	r_{C-O}^{avg}(Å)	r_{Ce-F}^{min}(Å)	r_{Ce-F}^{max}(Å)	r_{Ce-F}^{avg}(Å)	$\Delta_{C-O}(\%)$	$\Delta_{Ce-F}(\%)$	$\delta_{C-O}(\%)$	$\delta_{Ce-F}(\%)$
Ce – Bastnäsite with *'f'* electrons included in the core										
Bulk	1.289	1.292	1.291	2.394	2.407	2.399	0	0	0.26	0.54
$[10\bar{1}0]$-(a)	1.275	1.314	1.291	2.297	2.452	2.383	0.04	-0.65	3.07	6.49
$[10\bar{1}0]$-(b)	1.277	1.326	1.291	2.297	2.478	2.383	0.02	-0.65	3.78	7.60
$[10\bar{1}1]$–CO_3^{2-}	1.257	1.350	1.294	2.262	2.566	2.388	0.26	-0.45	7.18	12.73
$[10\bar{1}1]$ –Ce^{3+}	1.258	1.352	1.295	2.297	2.594	2.397	0.29	0.10	7.29	14.05
$[10\bar{1}1]$–F^-	1.245	1.365	1.295	2.108	2.556	2.380	0.35	-0.80	9.26	18.84
$[10\bar{1}1]$–CeF^{2+}	1.265	1.347	1.294	2.247	2.568	2.389	0.23	-0.43	6.32	13.46
$[10\bar{1}1]$–$CeFCO_3$	1.261	1.354	1.295	2.231	2.583	2.388	0.29	-0.44	7.19	14.72
$[10\bar{1}2]$	1.257	1.358	1.294	2.283	2.475	2.393	0.21	-0.23	7.84	8.06
[0001]– CO_3^{2-}	1.256	1.392	1.298	2.308	2.571	2.428	0.58	1.20	10.48	10.85
[0001]–CeF^{2+}	1.253	1.364	1.295	2.123	2.435	2.352	0.34	-1.94	8.58	13.26
$[11\bar{2}2]$	1.238	1.358	1.296	2.287	2.589	2.365	0.40	-1.40	9.28	12.77
$[10\bar{1}4]$	1.212	1.430	1.295	2.296	2.598	2.413	0.34	0.58	16.84	12.53

The percentage change in the average C–O and Ce–F bond lengths with respect to the bulk, $\Delta_{C\text{-}O}$ and $\Delta_{Ce\text{-}F}$, is calculated using equation (3). The percentage of spread in the C–O and Ce–F bond lengths with respect to the average C–O and Ce–F bond lengths in each structure, $\delta_{C\text{-}O}$ and $\delta_{Ce\text{-}F,}$ is calculated using equation (4).

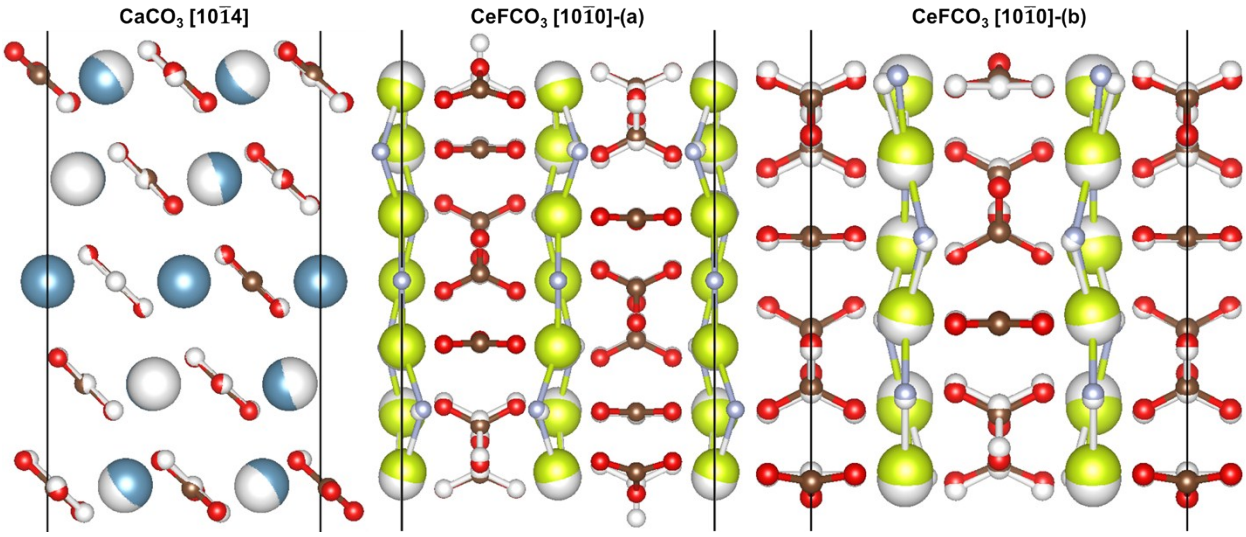

Figure S1: Optimized structure of calcite [10$\bar{1}$4] and Ce-bastnäsite [10$\bar{1}$0]-(a) and [10$\bar{1}$0]-(b) surfaces. Ca atoms are blue, Ce atoms are yellow, O atoms are red. C atoms are brown, F atoms are blue. Atoms from the cleaved structure are superimposed using white spheres.

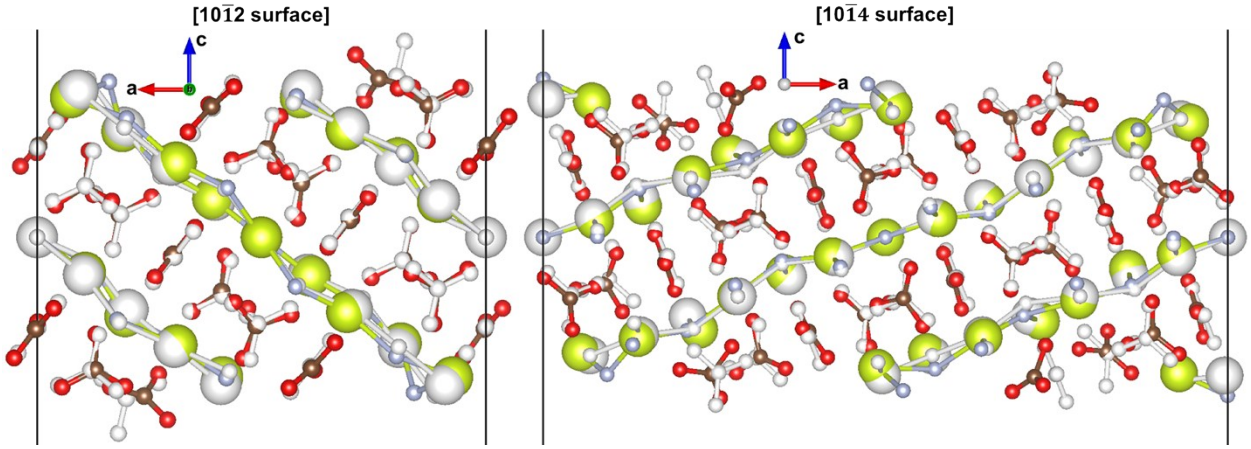

Figure S2: Optimized structure of the Ce-bastnäsite [10$\bar{1}$2] and [10$\bar{1}$4] surfaces. Ce atoms are yellow, O atoms are red. C atoms are brown, F atoms are blue. Atoms from the cleaved structure are superimposed using white spheres.

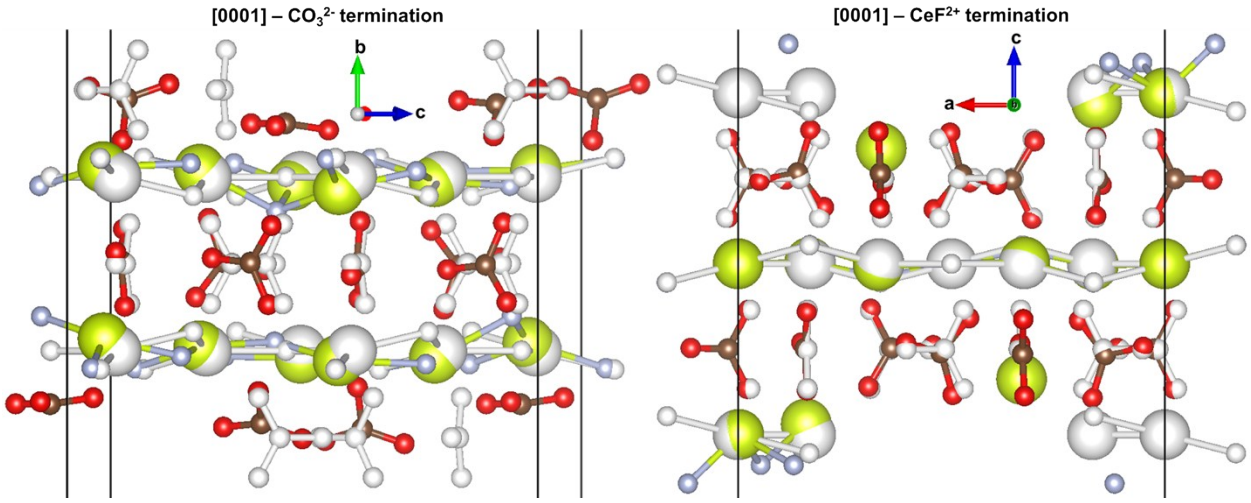

Figure S3: Optimized structure of the CO_3^{2-}- and CeF^{2+}-terminated Ce-bastnäsite [0001] surfaces. Ce atoms are yellow, O atoms are red. C atoms are brown, F atoms are blue. Atoms from the cleaved structure are superimposed using white spheres.

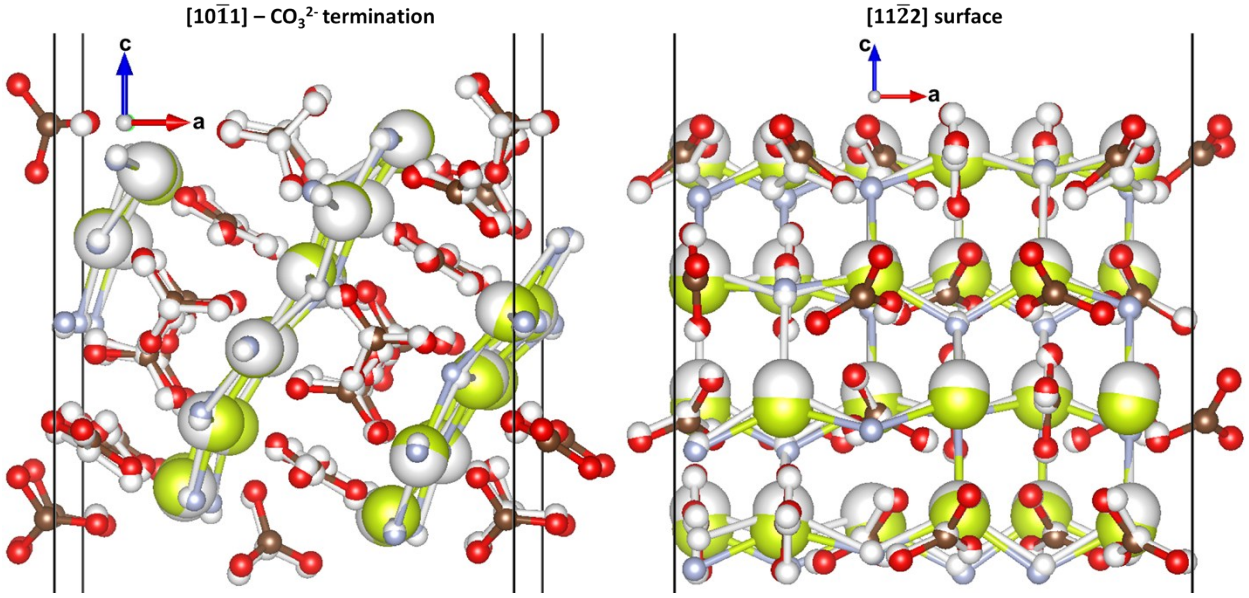

Figure S4: Optimized structure of the CO_3^{2-}terminated Ce-bastnäsite [$10\bar{1}1$] and Ce-bastnäsite [$11\bar{2}2$] surfaces. Ce atoms are yellow, O atoms are red. C atoms are brown, F atoms are blue. Atoms from the cleaved structure are superimposed using white spheres.

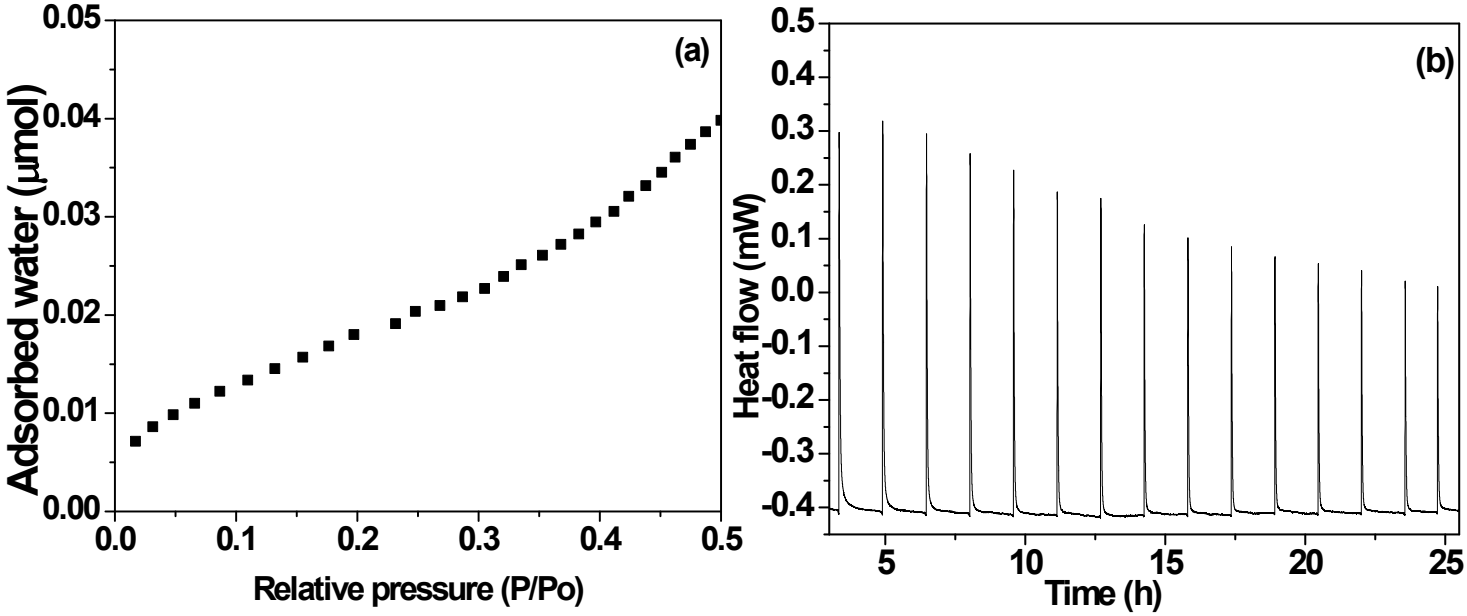

Figure S5: (a) Water adsorption isotherm and (b) corresponding calorimetry trace for $CeFCO_3$