Electronic Supplementary Information: Hydration structure and water exchange kinetics at xenotime-water interfaces: Implications for rare earth minerals separations

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EXPERIMENTS

In order to study the surface energy of xenotime, water adsorption calorimetry was applied to investigate yttrium phosphate (YPO_4). A commercial sample of YPO_4 (Aldrich, 100 nm) was used. XRD, DSC, and BET have been performed to characterize the sample phase, thermal behavior and surface area. The data from water adsorption calorimetry and surface area measurement (BET) have been used to calculate the surface energy of YPO_4 as 1.16 J/m^2.

XRD. Powder X-ray diffraction (XRD) was performed for sample on Bruker D8 Advance diffractometer with Cu Kα radiation, $\lambda= 1.5418$ Å, to determine the crystalline phases. The data were collected in range of 10-70° 2θ, with step size 0.02° and 1s per step. Results are shown in Figures 1. The XRD pattern (Figure S5)shows that the main phase matches YPO_4 but the sample contains about 3 % of a $Y(PO_3)_3$ phase. This small impurity should not affect the water adsorption experiment significantly.

DSC-TG. Differential scanning calorimetry coupled thermogravimetry (DSC-TG) have been performed on a Setaram Labsys instrument. Sample powder weighing about 20 mg was pressed into a pellet and placed in Pt crucible in the DSC. The sample was heated from 20 to 1200 °C at 10 °C/min in Ar. The results show a broad endothermic peak and weight loss at 20-300 °C which indicates the dehydration is occurred (Figure S6). A sharp exothermic peak at 900 °C may indicate coarsening of the sample or some other change to a more stable state. This is not relevant to the present study and was not investigated further. According to this information, a degas temperature of 300 °C was chosen for the water adsorption calorimetry. The degas process was aimed to remove all the water from the surface of the sample.

BET. Cryogenic N_2 gas adsorption (BET method) showed that the powders had a surface area of 13.0 m^2/g.

Water adsorption calorimetry. Water adsorption calorimetry has been performed on ASAP 2020 Mircomeritics, equipped with turbo pumps and a furnace for degassing at elevated temperatures, coupled with a Calvet microcalorimeter (Setaram DSC-111). The ASAP 2020 measures the pressures and adsorbed water quantities while the microcalorimeter measures the heat evolved during the adsorption process (that combined with the adsorption data gives enthalpies of adsorption). The results are summarized in Table S3. The isotherm and differential enthalpies have been graphed in Figures S7 and S8.

The experiment was performed as follows. The sample weighing about 80 mg pressed pellet was placed in the one side of a forked tube. The tube was placed inside the twin chambers of the DSC111 Calvet microcalorimeter and plugged into the analysis port of a Micromeritics ASAP 2020 analyzer. A degas procedure was processed in which the sample was heated at 300 °C for 2h under vacuum to remove all the surface water and any other adsorbed molecules. Water vapor was dosed into the forked tube in increments of 2 μmol of H_2O per dose using the ASAP 2020 analyzer. The amount of adsorbed water vapor on the sample was determined from the pressure drop (relative pressure P/P_0) as the water vapor is removed from the sample chamber onto the sample surface. Each water dose generates a distinct calorimetric peak due to heat effect associated with water adsorption. The integral of the area under the peak provides the corresponding heat of adsorption (differential enthalpy). A blank with an empty tube was run to correct the data for water adsorbed on the forked tube wall.

Surface energy. The differential enthalpy of adsorption for the first dose at near-zero coverage is -144.22 kJ/mol, indicating strong chemisorption of water on the xenotime surface. With increasing surface coverage, the differential enthalpy becomes less exothermic with successive doses and finally reaches the value of enthalpy of condensation of bulk water at 25 °C (-44 kJ/mol) in about 7-8 doses. The average water coverage value on the xenotime surface at this point is 8.99 H_2O/nm^2. The water adsorbed up to this coverage is strongly bound and can be considered to be chemisorbed. The remaining water, with a differential enthalpy of -44 kJ/mol, can be treated as physisorbed water. The integral enthalpy of adsorption, which is the sum of the differential enthalpies of adsorption, divided by the total water up to this coverage, corresponds to the enthalpy of chemisorbed water. At higher dosing, the enthalpy appears to become even less exothermic but this is probably related to condensation of water on the rest of the sample tube after the mineral surface is saturated and is considered an artifact. The surface energy γ has been calculated by the equation below:

$$S_{\mathrm{A}} \times d\gamma = -\theta d\mu_{\mathrm{ads}} + d\mu_{\mathrm{ads}} \sum_{\beta} \sum_{i} \theta_i \simeq -\theta d\mu_{\mathrm{ads}}, \tag{1}$$

where,

$$\gamma = \sum_{i=0}^{n} -\frac{\theta_i}{S_{\mathrm{A}}} d\mu_{\mathrm{ads}}. \tag{2}$$

Here S_{A} is the surface area, γ is the surface energy; θ_i is the water coverage; μ_{ads} is the differential adsorption enthalpy. The surface energy of yttrium phosphate is calculated as 1.16 $\mathrm{J/m^2}$. Further details regarding use of water adsorption for calculating surface energy can be found elsewhere.[1]

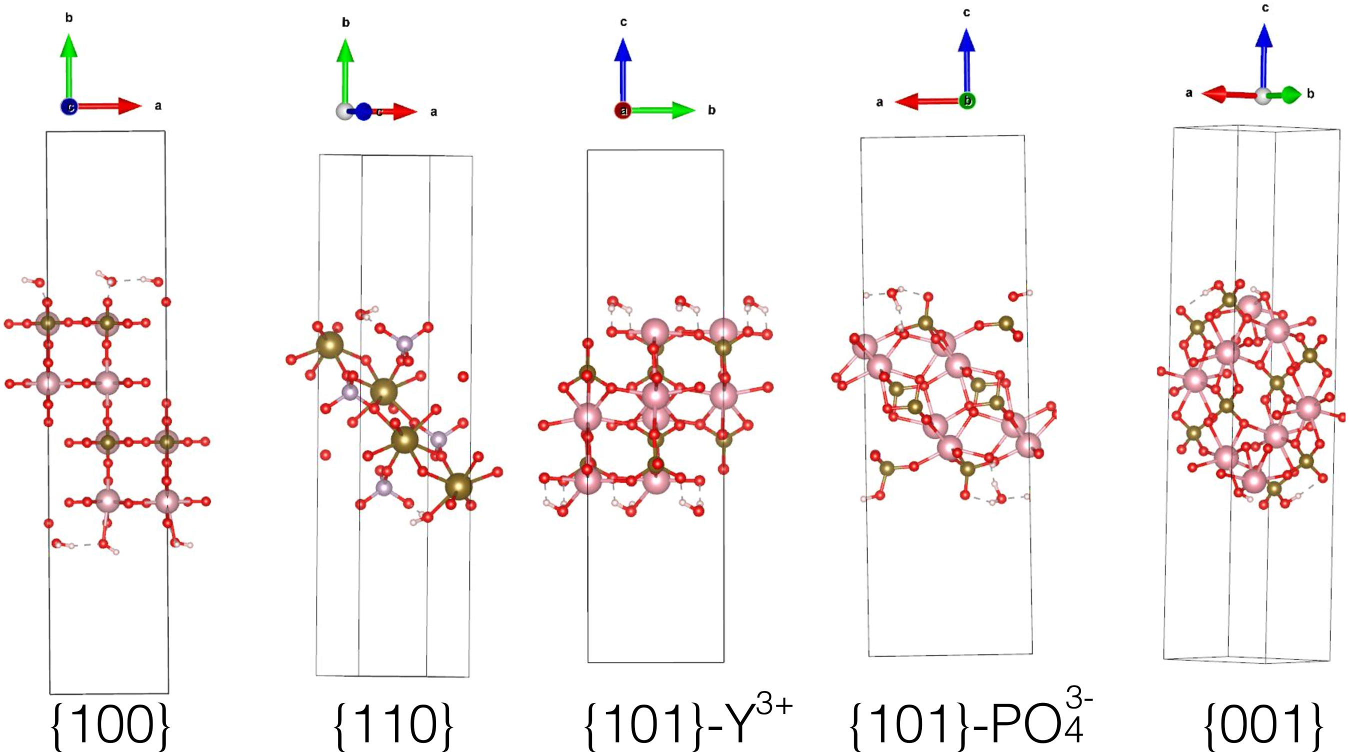

Figure S1. Structures of different surfaces of xenotime at 100% coverage, of which only {100} and phosphate-terminated {101} surfaces are observed in the crystal morphology. The other surfaces are less stable, including {001} where water molecules are dissociated.

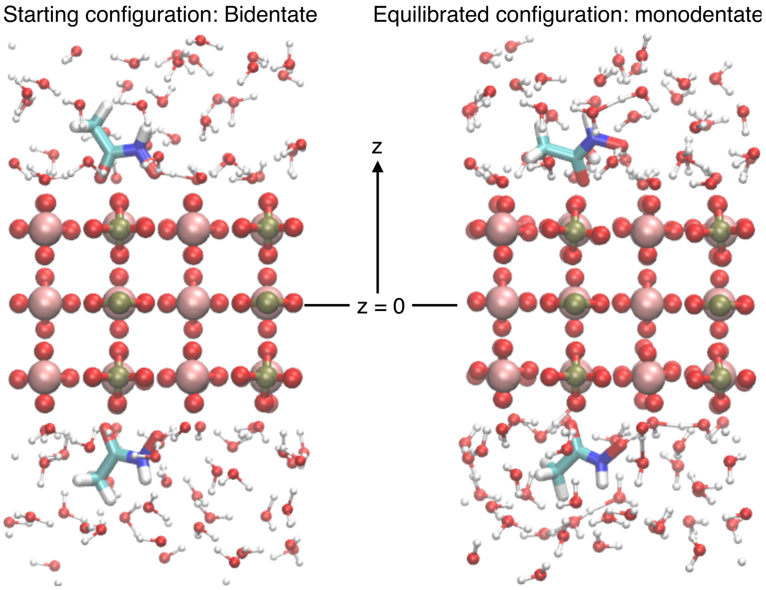

Figure S2. The starting and equilibrated configurations of Config B in the AIMD simulation.

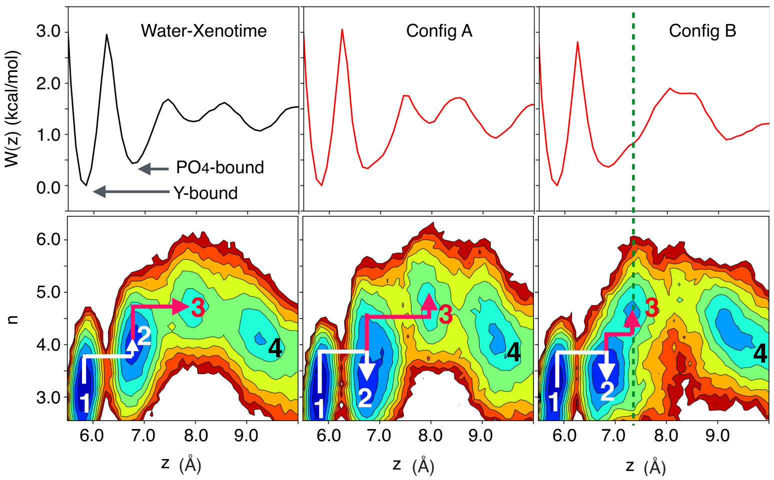

Figure S3. The 1D and 2D free energy surfaces (together with Marcus pathways indicated by the arrows) for the xenotime-water interface without (left) and with (middle and right) the presence of the ligand bound to the surface in Config A and Config B. 10 contours are plotted between 0 and 3.5 kcal/mol on the 2D-free energy surfaces.

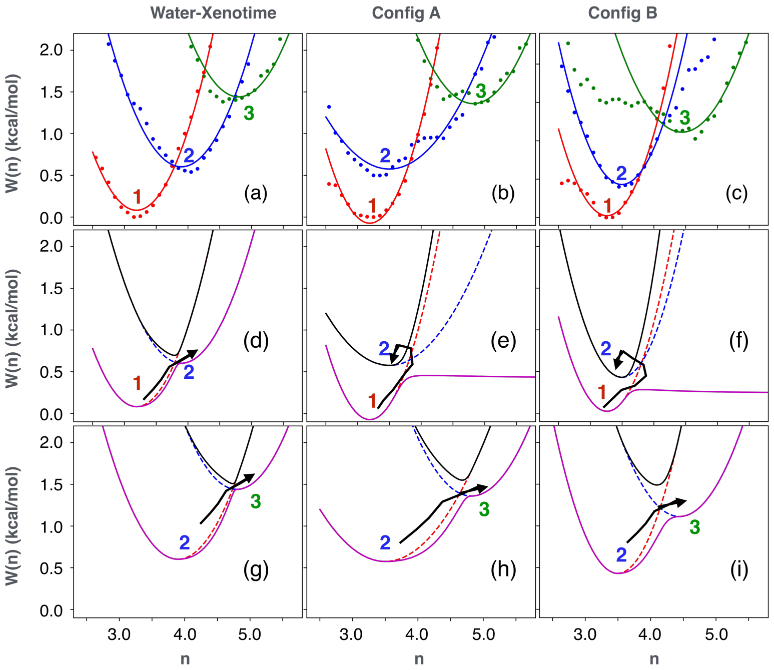

Figure S4. Marcus parabolas defining the transitions between different layers of water at the xenotime-water interface without (left) and with (middle and right) the presence of the ligand bound to the surface in Config A and Config B.

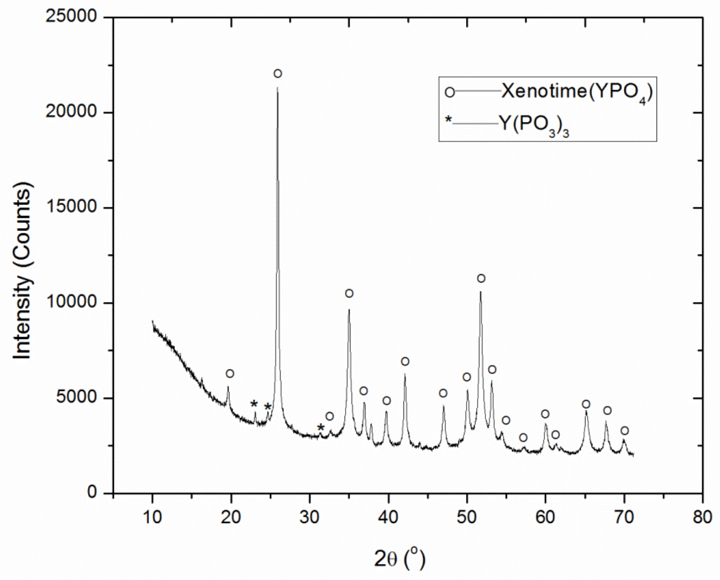

Figure S5. XRD pattern of YPO4 used in this study.

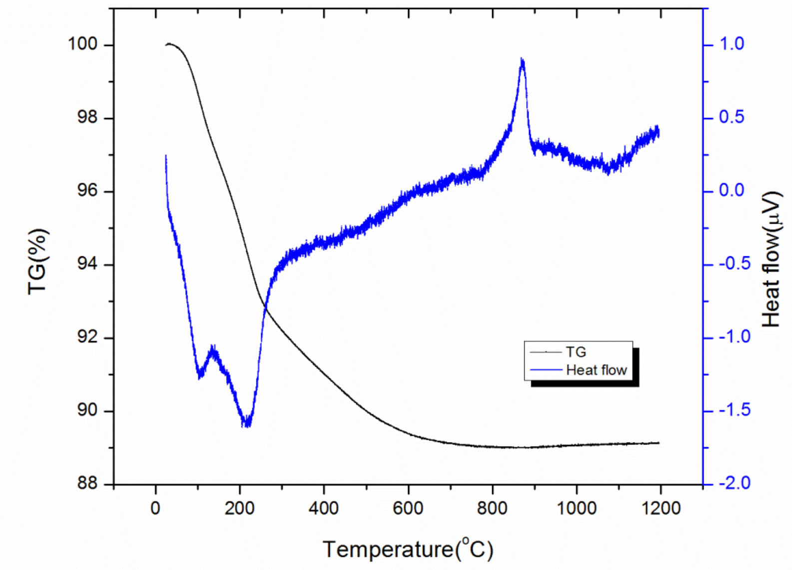

Figure S6. DSC-TG of YPO_4 scanning at range of 20-1200 °C in argon.

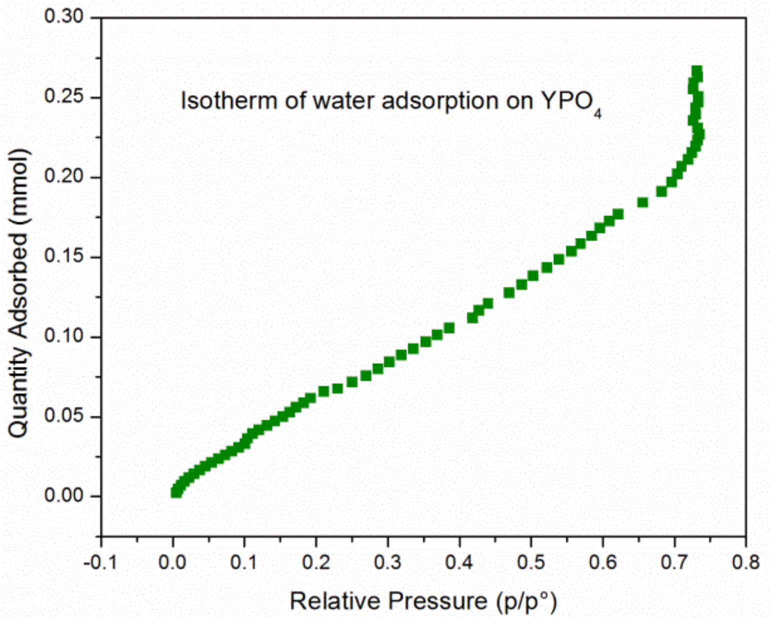

Figure S7. Isotherm of water adsorption on YPO_4.

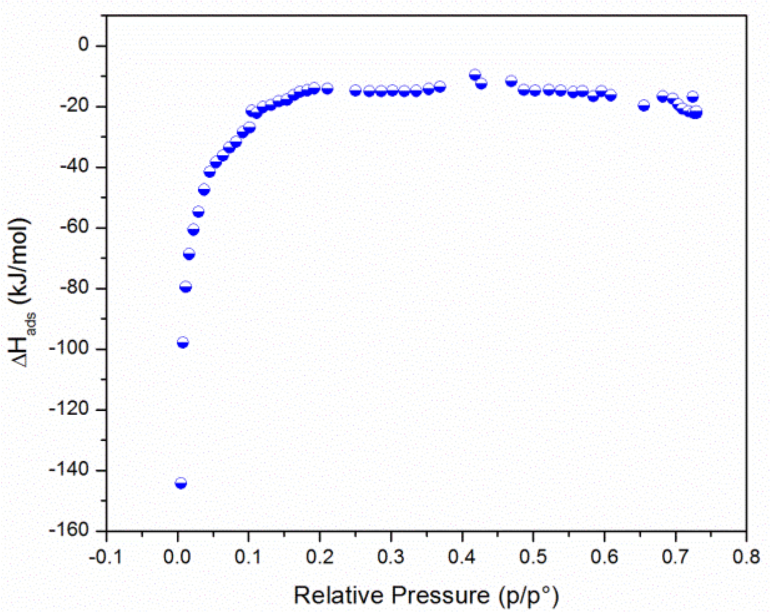

Figure S8. Differential enthalpies of water adsorption on YPO_4.

Table S1. Computed surface energies ($E^{\mathrm{i}}_{\mathrm{surf}}$) of the xenotime mineral with varying number of layers (i) and water coverage.

Surface Energy (J/m^2)	(100)	(110)	(101) (Y-truncated)	(101) (PO$_4$-truncated)	(001)
0% water coverage					
E^4_{surf}	0.832	1.089	1.302	1.576	
E^8_{surf}	0.831	1.090	1.304	1.600	2.553
E^{16}_{surf}					2.583
100% water coverage					
E^4_{surf}	0.539	0.758	1.030	0.844	
E^8_{surf}	0.538	0.758	1.030	0.849	1.409
E^{16}_{surf}					1.416

Table S2. Computed number of water molecules adsorbed per unit surface area (N_{A}) and the adsorption energy of a water molecule ($E^{\mathrm{i}}_{\mathrm{ads}}$) on the xenotime mineral surfaces with varying number of layers (i) and water coverage.

N_{A} (1/nm^2) or $E^{\mathrm{i}}_{\mathrm{ads}}$ (kJ/mol)	(100)	(110)	(101) (Y-truncated)	(101) (PO$_4$-truncated)	(001)
100% water coverage					
N_{A}	4.787	3.385	3.150	3.150	2.092
E^4_{ads}	-98.345	-120.432	-113.505	-201.409	
E^8_{ads}	-98.346	-120.551	-114.014	-205.307	-390.722
E^{16}_{ads}					-397.534

Table S3. Water adsorption calorimetry results of xeotime (YPO$_4$).

Sample	Surface area (m^2/g)	Sample mass (mg)	First dose adsorption enthalpy (kJ/mol)	Total adsorbed amount of water (mmol/g)	Integral enthalpy of adsorption (kJ/mol)	Water Coverage H$_2$O/nm^2)
YPO$_4$	13.0	85	-144.22	0.49	-74.14	8.99

Table S4. Parameters used in the Marcus model and the transition timescales.

	Xenotime-water	Config A	Config B
1→2 transition			
K_{R} (kcal/mol)	2.92	3.72	3.89
K_{P} (kcal/mol)	2.40	1.25	3.72
ΔW (kcal/mol)	0.52	0.65	0.41
λ (kcal/mol)	0.73	0.18	0.11
C (kcal/mol)	0.082	0.206	0.333
v_n (fs^{-1})	0.014	0.015	0.015
$\Delta W^{\dagger} + \Delta W_z^{n\dagger}$ (kcal/mol)	2.97	3.31	2.66
κ_{LZ}	0.17	0.50	0.08
τ (ps)	144.63	86.17	175.76
2→3 transition			
K_{R} (kcal/mol)	2.40	1.25	3.72
K_{P} (kcal/mol)	2.42	2.08	2.04
ΔW (kcal/mol)	0.84	0.79	0.67
λ (kcal/mol)	0.97	1.09	1.38
C (kcal/mol)	0.063	0.163	0.20
v_n (fs^{-1})	0.016	0.017	0.015
$\Delta W^{\dagger} + \Delta W_z^{n\dagger}$ (kcal/mol)	1.40	1.91	1.31
κ_{LZ}	0.09	0.46	0.45
τ (ps)	19.19	8.65	3.29

References

(1) Drazin, J. W.; Castro, R. H. R. Water Adsorption Microcalorimetry Model: Deciphering Surface Energies and Water Chemical Potentials of Nanocrystalline Oxides. *J. Phys. Chem. C* 2014, **118**, 10131–10142.