Supplementary materials for

Interfacial structure and acidity of orthoclase (001) surface: understanding the effect of surface metal cation

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Number of pages: 4
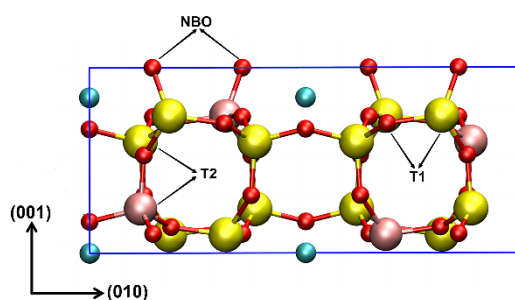
Number of figures:3

Number of tables :1

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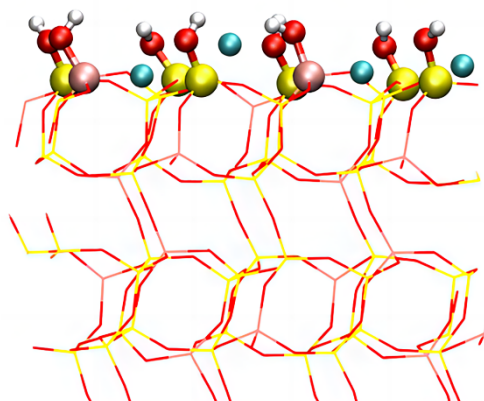**Figure S1.** Snapshot of the orthoclase unit cell.

Figure S2. Snapshot of the hydroxyl sites on orthoclase (001) surface.

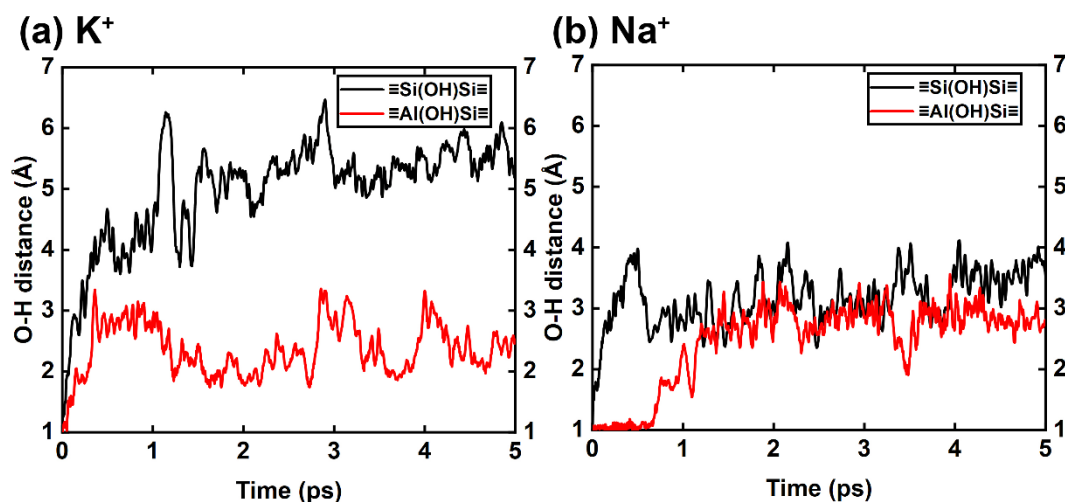**Figure S3.** Trajectories of Ob-H distances on orthoclase (001) surface

Table S1. The parameters used in restraining the dummy atoms

Figure S1. Schematic view of the orthoclase unit cell structure with perspective views of (001) and (010) cleavage surfaces. Also shown are the T1 and T2 sites and non-bridging oxygens (NBO) resulting from cleavage of either surface. The unit cell contains 12 Si atoms and 4 Al atoms (including 2 Al atoms in T1 site and 2 Al atoms in T2 site), and the non-bridging oxygen (NBO) sites expressed on the (001) surfaces are all T1 sites. O = red, H = white, Si = yellow, K = cyan, and Al = pink.

Figure S2. Snapshots of the orthoclase (001) surface with K^+ as the surface cations. 6 $\equiv$SiOH and 2 $\equiv$AlOH are presented in this picture. The mineral framework is shown in stick; K^+, Si, Al and surface hydroxyl are shown in ball and stick. O = red, H = white, Si = yellow, K = cyan and Al = pink.

Figure S3. Trajectories of Ob-H distances on orthoclase (001) surface with (a) K^+ and (b) Na^+ as the surface cations. The length of Ob-H bond has already been restrained at 1.0 Å for 5.0 ps before production run. After the constraint removed, the distance

between Ob-H can exceed 2.0 Å within 1.0 ps, which represent that the OH in both

$\equiv$Si(OH)Si$\equiv$ and $\equiv$Al(OH)Si$\equiv$ can dissociate quickly. The average distance of Ob-H is

beyond 2.0 Å, which means that the H atom has completely separated from the Ob.

Table S1. The parameters used in restraining the dummy atoms (harmonic potentials (V_r) which was defined in Eq. (1) below). H_d represents the dummy atom. n_d and n_θ mean the number of restrained bonds and angles, respectively. d_0 stands for equilibrium bond lengths (in Bohr), and θ_0 stands for equilibrium angles (in radian).

Surface	Group	n_d	d_0	k_d	n_θ	θ_0	k_θ
(001) with surface K^+	$\equiv$SiOH	1	1.87	1.0	1	2.18 (Si-O-H$_d$)	0.1
	$\equiv$AlOH	1	1.87	1.0	1	2.10 (Al-O-H$_d$)	0.1
	$\equiv$AlOH$_2$	2	1.97	1.0	2	1.88 (H-O-H$_d$)	0.1
			1.93	1.0		2.17 (Al-O-H$_d$)	0.1
	H_3O^+	3	1.89	1.0	2	1.94 (H-O-H$_d$)	0.1
			1.89	1.0		1.94 (H-O-H$_d$)	0.1
			1.89	1.0			
(001) with surface Na^+	$\equiv$SiOH	1	1.87	1.0	1	2.18 (Si-O-H$_d$)	0.1
	$\equiv$AlOH	1	1.87	1.0	1	2.10 (Al-O-H$_d$)	0.1
	$\equiv$AlOH$_2$	2	1.97	1.0	2	1.88 (H-O-H$_d$)	0.1
			1.93	1.0		2.17 (Al-O-H$_d$)	0.1
	H_3O^+	3	1.89	1.0	2	1.94 (H-O-H$_d$)	0.1
			1.89	1.0		1.94 (H-O-H$_d$)	0.1
			1.89	1.0			

$$V_r = \sum_{bonds} \frac{1}{2} k_d (d - d_0)^2 + \sum_{angles} \frac{1}{2} k_\theta (\theta - \theta_0)^2 \qquad (1)$$