## **Supplementary Information of** Surface phase diagram of hematite pseudocubes in hydrous environments

## Haibo Guo\*a and Amanda S. Barnarda

The configurations of surface hydroxylation can be divided into categories according to the non-hydrogenated terminations. To obtain the non-hydrogenated terminations, we truncate bulk hematite at different (012) atomic planes, and if possible, remove sub-surface iron atoms from the truncated structures. However, we have found that only the clean surface can derive a new termination type by removing the sub-surface Fe layer, and all other truncated terminations may not have sub-surface Fe layer removed because (i) for Fe-terminated surfaces it is unreasonable to remove the sub-surface Fe layer while keeping the top-surface Fe termination, and (ii) for Oterminated surfaces removing sub-surface Fe layer leads to desorption of O atoms and is equivalent to another truncated termination. The the terminations with sub-surface Fe atoms removed from the stoichiometric clean surface are referred to as A, and by hydrogenating the triply coordinated oxygen atoms at the clean surface we arrived at the B termination. As mentioned in the main texts, by truncating at different (012) atomic planes we get terminations C-F, and by removing half of the surface atoms, G-I. The terminations C-F are referred to as dense hydroxylated terminations, and G-I are sparse hydroxylated terminations. The densities of unsaturated oxygen atoms (whose coordination number is below 4) of these categories are summarized in Table 1.

Table 1 The densities of unsaturated oxygen atoms at the surfaces of different terminations. "S" stands for singly, "D" for doubly, and "T" for triply coordinated oxygen atoms. Unit:  $nm^{-2}$ .

	S	D	Т
A	7.2	7.2	7.2
В	0.0	0.0	7.2
С	0.0	0.0	0.0
D	0.0	7.2	7.2
Ε	0.0	0.0	7.2
F	7.2	0.0	7.2
G	0.0	0.0	10.8
Н	0.0	3.6	7.2
Ι	0.0	7.2	3.6
J	3.6	0.2	7.2

We consider the geometry freedoms of singly and doubly coordinated hydroxyl groups as the terminal hydrogen atoms







(c) AC: S-,D-OH







S-OH2, D-, T-OH







[100].

Fig. 1 Configurations of hydroxylation of the A termination. O atoms are in red, Fe in grayish blue, and H in white. Viewed along

may rotate or flip around the oxygen atoms. We also consider attaching two hydrogen atoms to a singly coordinated oxygen atom to create a hydrated surface. In constructing the hydroxylation configurations we avoid close contact of adjacent H atoms because they are energetically unstable due to the strong electrostatic interactions. Hydrogen-bonds are identified by



**Fig. 2** Configurations of hydroxylation of the *D* termination. The doubly coordinated hydroxyl groups in configuration *DA* and *DB* points to different directions. Viewed along [100].



Fig. 3 Configurations of hydroxylation of the *F* termination. The configurations *FA* and *FB* contain singly coordinated hydroxyl groups which point outward (that is, towards the vacuum) and inward (that is, towards the surface), but they have the same density of surface hydroxyl groups, and after geometry optimization, the two configurations are almost isostructural (see Fig. 6 of the main text) and have the same surface energy. So do the configurations *FC* and *FD*. Viewed along  $[12\overline{1}]$ .

measuring the distances between a H atom and possible donor O atoms.

Among all the terminations in Table 1, A and E only have triply coordinated oxygen atoms and therefore has definite hydrogenated structure, C has no under-saturated oxygen atom and it is therefore impossible to add hydrogen atoms. The hydrogenated structures of other terminations are presented in the the figures 1–7, as projections of near-surface atoms along the crystallographic [100] or  $[12\overline{1}]$  direction.



**Fig. 4** Configurations of hydroxylation of the *G* termination. There are three triply coordinated oxygen atoms. If all the

under-coordinated oxygen atoms were hydrogenated, there would be close-contacting hydrogen atoms. Therefore, the two configurations (*GA* and *GB*) are not fully passivated. Viewed along [100].



**Fig. 5** Configurations of hydroxylation of the *H* termination. The configurations *HB* and *HC* differ by the positions of the doubly coordinated hydroxyl groups. Viewed along [100].



**Fig. 6** Configurations of hydroxylation of the *I* termination. The configurations *IB* and *IC*, and *ID* and *IE* differ by the directions of the doubly coordinated hydroxyl groups. Viewed along [100].



**Fig.** 7 Configurations of hydroxylation of the *J* termination. The configurations *JA* and *JB* differ in the direction of the singly coordinated hydroxyl groups. After geometry optimizations the two configurations are almost isostructural and have the same surface energy. So do the configurations *JD* and *JE*. Viewed along  $[12\overline{1}]$ .