Electronic Supplementary Information

Uranyl adsorption on solvated edge surfaces of pyrophyllite. A DFT model study

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Two conventions exist for choosing the unit cell of pyrophyllite. Figure S1 shows the top view of a pyrophyllite layer, from direction [001]. The grey rectangle indicates the conventional choice of the unit cell for pyrophyllite. The red rectangle represents the montmorillonite-like convention for the unit cell. The montmorillonite-like unit cell is rotated by 60º with respect to the pyrophyllite one.

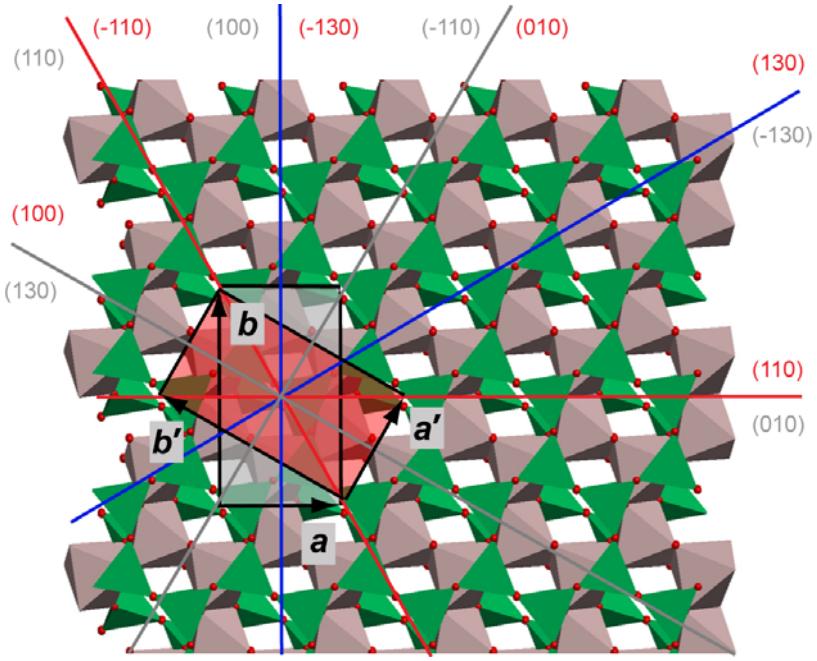

Figure S1. Top view of a pyrophyllite layer, from direction [001]. Si tetrahedra are in green, Al octahedra in brown. The grey rectangle indicates the conventional choice of the unit cell for pyrophyllite. The montmorillonite-like unit cell is indicated as red rectangle. Similarly, Miller indices of pyrophyllite-type surfaces are labeled in grey, montmorillonite-type surfaces in red.

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Periodic bond chain theory[1-3] predicts six preferred edge surfaces for pyrophyllite, (010), (100), (±110), and (±130), which are obtained when the crystal is cut in a way that preserves the chains of Si tetrahedra and Al octahedra which make up the structure. All six edges are indicated in Fig. S1. Edge surfaces can be named according to either of the two conventions mentioned above. The labels in grey color correspond to the pyrophyllite convention, the labels in red to the montmorillonite convention.

Pyrophyllite exhibits a pseudohexagonal structure, as the Si atoms form hexagons in the upper and lower sheets; also, Al atoms form hexagons in the middle sheet. Because of the pseudohexagonal structure vector *b* of the unit cell equals almost exactly $a^*\sqrt{3}$. In other words, there will be a pair of coinciding diagonals of the two unit cells after rotation by 60°; see Fig. S1, (110) according to pyrophyllite convention (red line). The conjugate diagonal of the pyrophyllite unit cell [grey label (-110)] will be perpendicular to vector *b* of the montmorillonite unit cell, and vice versa (Fig. S1).

From here on, as in the main text, we will name surfaces according to the conventional montmorillonite-like unit cell. The labels according to the pyrophyllite convention can always be obtained from Fig. S1.

There are six orientations of edge facet. However, in case of a simplified orthogonal unit cell only four of the corresponding surfaces are different from each other. Below we will discuss this in detail. Blue and red lines in Fig. S1 indicate structurally very similar edge surfaces of pyrophyllite which are pairwise identical with the approximation of an orthogonal unit cell. For example, the surfaces (130) and (-130) of the montmorillonite convention are very similar in general and identical in case of orthogonality.

Figure S2 shows the unit cell according to the montmorillonite convention together with three orientations of edge surface: (100), (130), and (-130). The hexagon rendered in

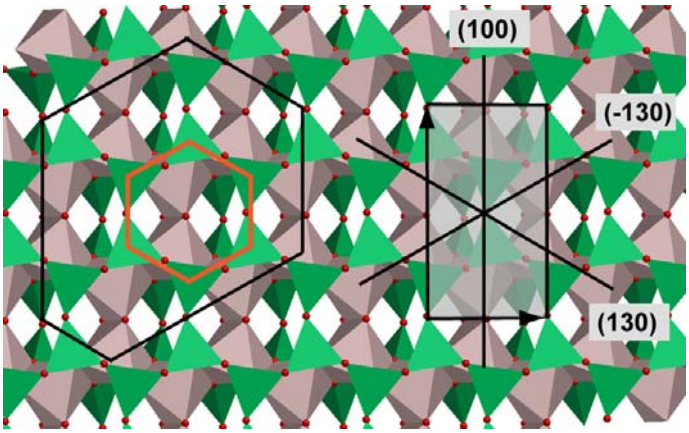

Figure S2. Top view of a pyrophyllite layer. The conventional montmorillonite-like unit cell is indicated as gray rectangle on the right side. The directions of three edge facets are shown as solid black lines: (100), (130), and (-130).

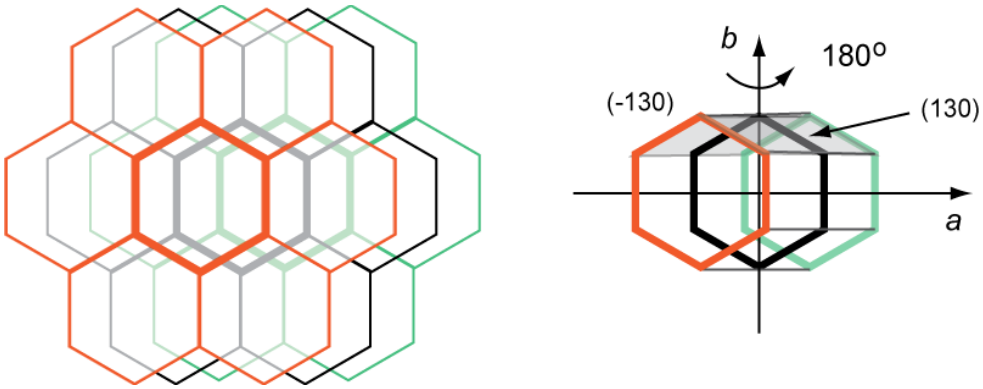

Figure S3. Schematic hexagonal representation of the pyrophyllite structure. Orange hexagons represent the upper sheet of Si tetrahedra, the black sheet of hexagons indicates the Al octahedra, the green correspond to the lower Si sheet. On the right side the directions *a* and *b* of the unit cell are shown together with a single stack of three hexagons.

orange in Fig. S2 is formed by Si atoms. Such hexagons, formed by either Si or Al atoms in each of three sheets are shifted with respect to each other in the direction *a*, forming a stack (Fig. S3). The shift between the upper Si hexagon and the Al hexagon is just opposite to that between the lower Si hexagon and the Al hexagon.

When the unit cell is approximated as orthogonal and vector *c* is perpendicular to the basal surface, spanned by vectors *a* and *b*, the (130) and (-130) planes are identical. These surfaces transform into each other when the pyrophyllite layer is rotated by 180º around vector *b*.

In the simplified structure of pyrophyllite, three nets of hexagons are stacked in direction *c* and shifted with respect to each other in direction *a* (right-hand side of Fig. S3). If one now takes vector *b* in the central plane of Al hexagons as rotation axis (rendered in black in Fig. S2) and rotates the whole structure by 180º, the Al net will be transformed onto itself while the green and the orange nets of Si hexagons will be transformed into each other. For a stack of three suitable hexagons, this is shown on the right-hand side of Fig. S3.

The discussion above is only valid for the orthogonal unit cell. As the perturbation from orthogonality is small in the pyrophyllite unit cell, the surfaces (130) and (-130) will be similar, but not identical, in the triclinic unit cell. However, these surfaces will be terminated by the same arrangement of Si tetrahedral and Al octahedral and exhibit the same active surface groups. The same argument is applies to the three facets (010), (110), and (-110); see Fig. S4 which is analogous to Fig. S2.

Note that in case of the conventional pyrophyllite-like unit cell, the two pairs of edge surfaces (100) and (-130) as well as (010) and (110) will be similar. In the convention of the pyrophyllite unit cell, the edge surfaces studied in the present work carry the labels (-110) and (010).

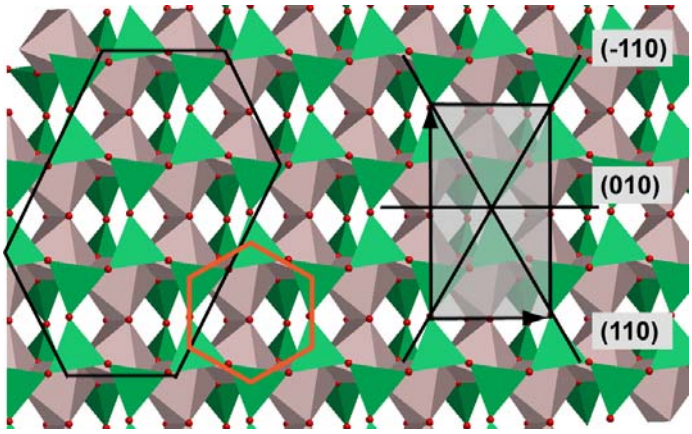

Figure S4. Top view of a pyrophyllite layer. The conventional montmorillonite-like unit cell is indicated as gray rectangle on the right-hand side. The directions of three edge facets are shown as solid black lines: (010), (110), and (-110).

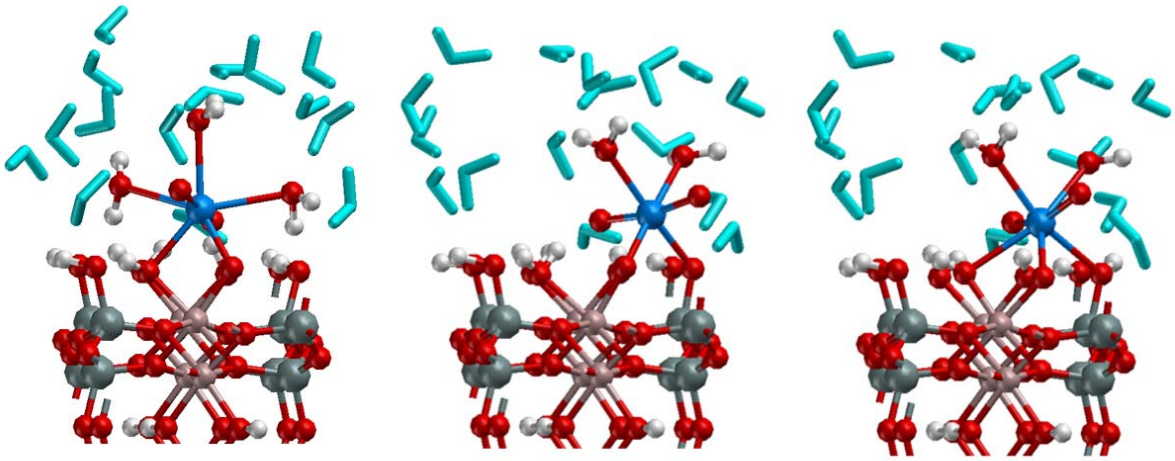

Figure S5. Optimized adsorption complexes of uranyl on solvated (010) pyrophyllite surface.

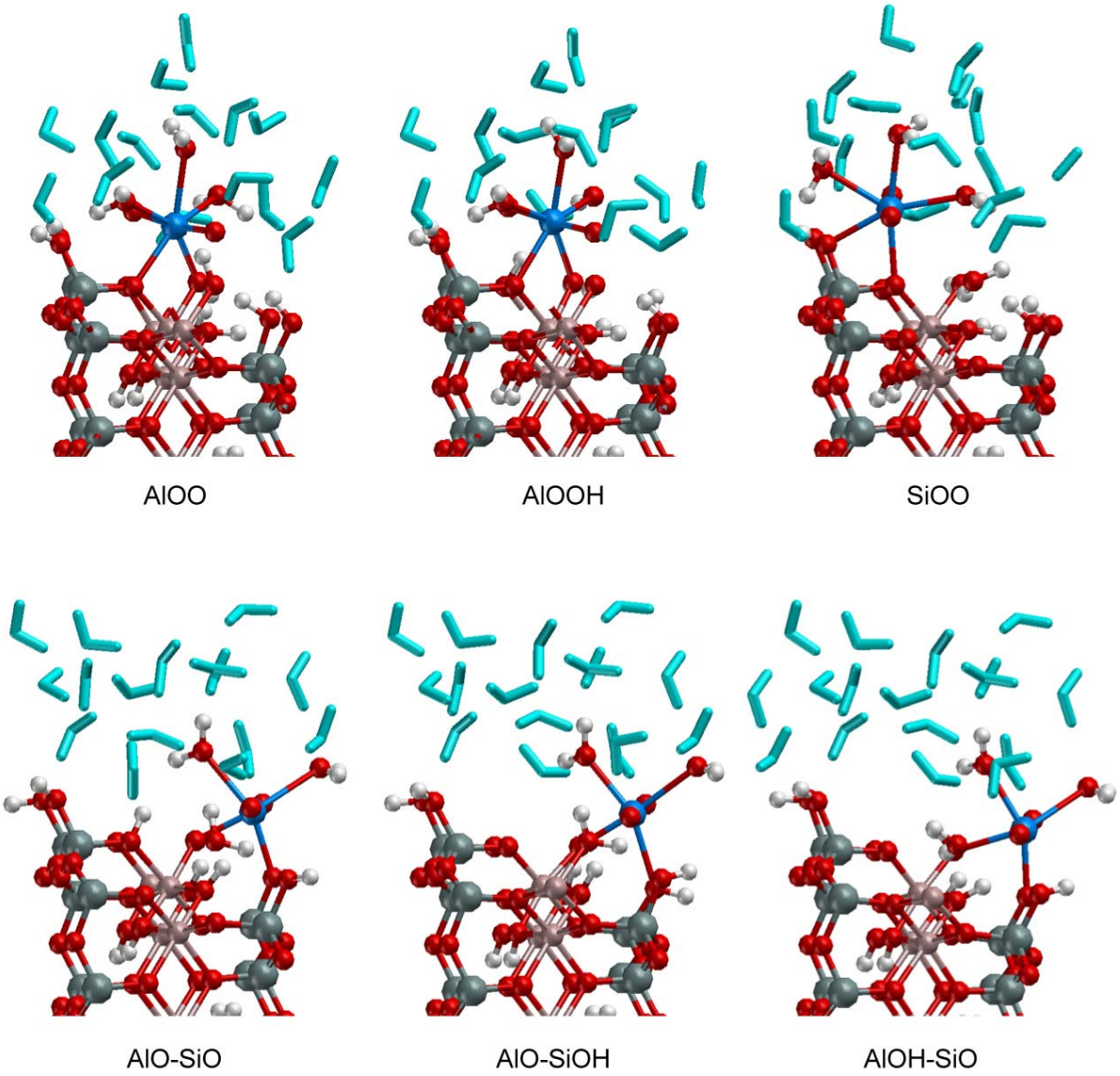

Figure S6. Optimized adsorption complexes on solvated (110) pyrophyllite surface.

References

1 P. Hartmann and W. G. Pedrock, *Acta Cristallographica*, **1955**, *8*, 49.
2 P. Hartmann and W. G. Pedrock, *Acta Cristallographica*, **1955**, *8*, 521.
3 P. Hartmann and W. G. Pedrock, *Acta Cristallographica*, **1955**, *8*, 525.