Investigating the nanoscale hydration landscape of kaolinite, a key material in technology

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I. Introduction

The interface between aqueous solutions and kaolinite mineral surface is crucial in technology from tribology to ceramics, nuclear waste treatment and medical devices[1-4]. This is thanks to its layered structure with the two basal surfaces exhibiting different properties. As a result, kaolinite forms a stable, compact interlayer spacing, highly functional for chemical- physical processes[1].

Open questions: existing studies show a dependence of kaolinite's surface properties on its hydration structure[2-4], but no experimental results have systematically investigated hydration landscape of both facets.

Aims: close this gap using a combination of high-resolution atomic force microscopy (AFM) and molecular dynamics (MD) simulations over both facets.

II. Materials and methods

Sample preparation: selective absorption of the two kaolinite facets on the substrate (mica or sapphire)[2]

⊕ charged aluminol facet of attracted to ⊖ charged mica

⊖ charged siloxane facet attracted to ⊕ charged sapphire

Amplitude modulation AFM imaging:

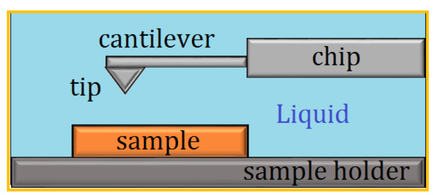
structural characterisation of the interactions of water molecules with kaolinite facets[6]

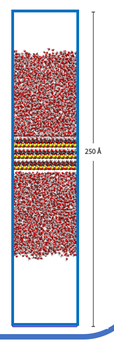
Amplitude modulation AFM spectroscopy

Vibrating tip driven at oscillation amp. ~0.2nm(<single hydration layer thickness)[7]. Dynamic information on the interactions of water molecules with the surface[7]

MD simulations

3 layers of kaolinite in the centre of simulation box



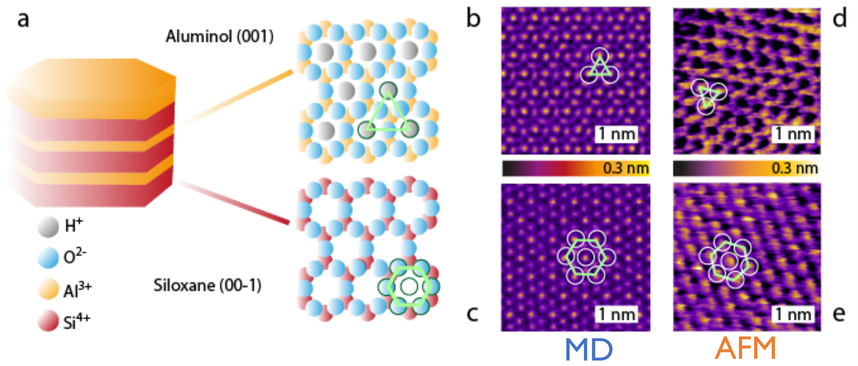


1. Hao *Nat. Commun.* **2021**, 12
2. Kumar *Langmuir* **2017**, 33
3. Klaassen Langmuir **2022**, 38
4. Underwood *J. Phys. Chem. C*, **2016**, 120

References

5. Santha *Minerals* **2017**, 7
6. Cafolla *Sci.Adv.* **2020**, 6
7. Hofmann *Sci. Rep.* **2016**, 6

III. Mapping the main hydration layer at equilibrium



Aluminol: ordering of water molecules in triangular-like

Siloxane: pseudo-hexagonal arrangement of water molecules; on siloxane more disordered & denser hydration layer

IV. Probing hydration water density & mobility the method

MD density profiles of hydration layers for the 2 facets (**a**)

AFM spectroscopy phase curves (siloxane facet in water) (**b-d**)

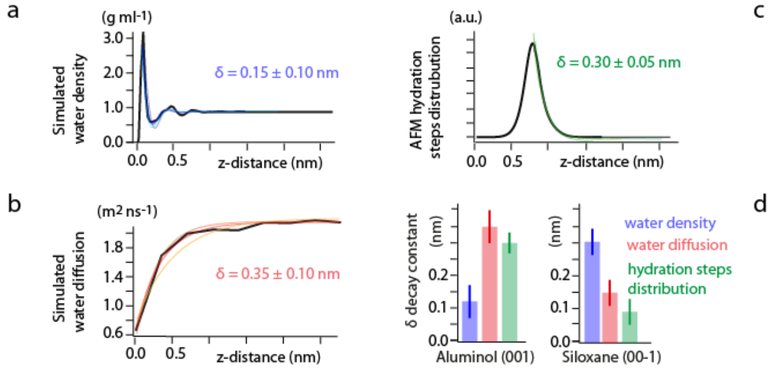
i. Tip approaching surface, dampening by hydration layers (**b**)

ii. Oscillations isolated subtracting sigmoidal from raw phase(**b**)

iii. Curves from same experiment, offset to help inspection (**c**)

iv. Align & Average gaussians for each phase curve (in red): solid grey curve (**d**)

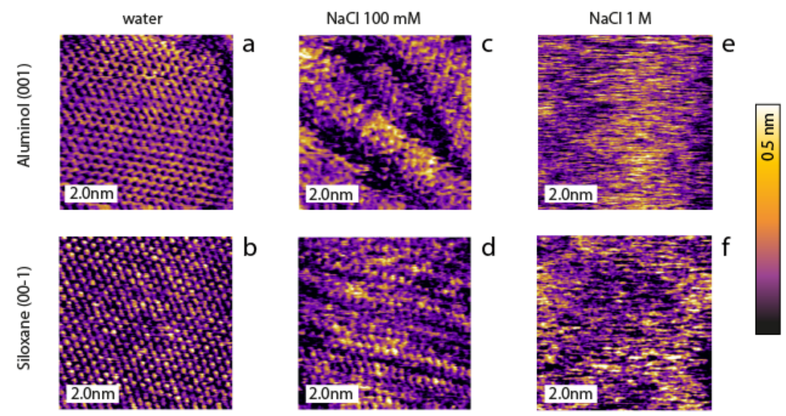
V. Probing hydration water density & mobility



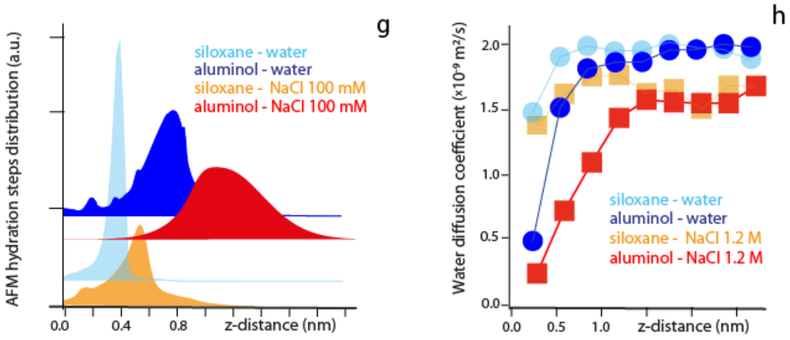
Comparing decay lengths: hydration steps distribution in better agreement with simulated water diffusion

Soft cantilever can probe water molecules diffusion at the solid surface rather than density of hydration layers

VI. The effect of salt



Adding ions enhances structuring of water molecules.
At high concentration (~1 M), multiple overlapping layers



Ions: higher probability of AFM tip to break, further away from solid surface, through a solid-like hydration layer