Molecular Dynamics Simulation for Cs Sorption Behavior under Various Kinds of Conditions

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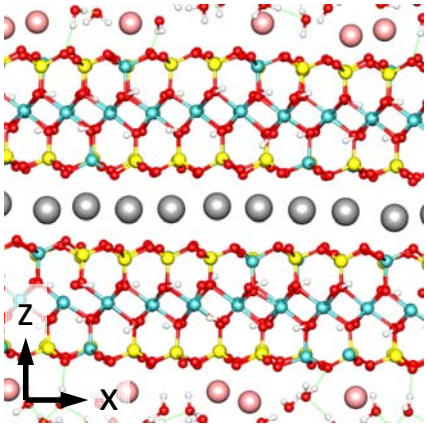
Purpose

1. Typical structural models of some selected clay minerals (illite, vermiculite) are constructed so that first principles MD is applicable at reasonable computational cost.
2. By comparing structural data obtained by our simulations and XAFS experiments using X-rays of SPring-8, possible candidates of sorption sites of Cs^+ are picked up.
3. By examining closely structural and electronic properties of particular sites where desorption of Cs^+ hardly occurs, a set of parameters controlling the stability of Cs^+ sorbed in clay minerals are identified.
4. Accumulated knowledge is hopefully applied to develop efficient methods for desorbing radiocaesium from clay minerals.

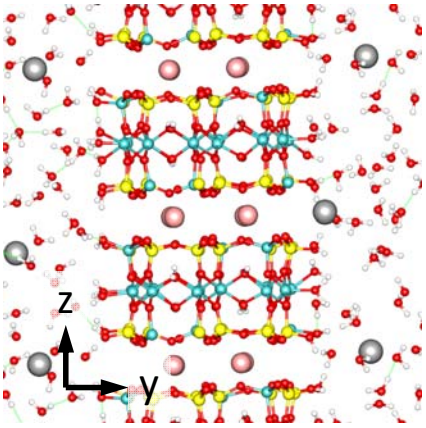
Structural models adopted

(001) surface



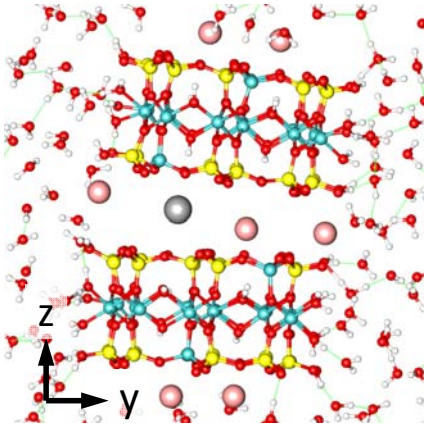
Diffusion of cations within interlayers

(010) surface



Initial sorption of Cs^+

(010)+(001) surface



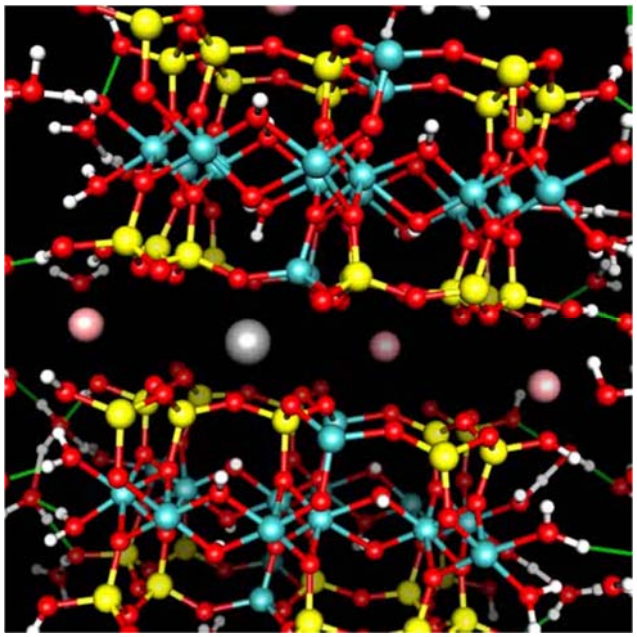
Sorption of Cs^+ & relaxation of layers

Computational details

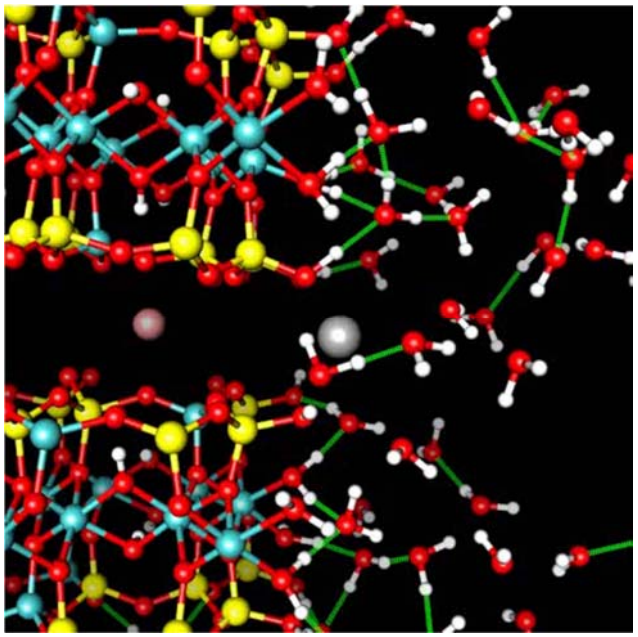
- Car-Parrinello molecular dynamics (CPMD) approach based on density functional theory (DFT) within Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation combined with Grimme's semiempirical van der Waals corrections (DFT-D2) as implemented in CPMD code
- Norm conserving Troullier-Martins pseudopotentials (PP) for O, Al, Si, K, analytical Car-von Barth PP for H, and Goedecker PP for Cs generated based on the full relativistic electronic structure calculations of a single atom
- Typical system size: 748 atoms contained in monoclinic supercell of a=10.4042 Å, b=30.0 Å, c=33.0 Å, β=101.57°
- Plane wave basis set with E_{cut}=80 Ry
- Brillouin zone sampling: Γ point only
- Small fictitious mass and time step: μ=340 a.u., Δt =3.0 a.u.

Movies

Inside of interlayer

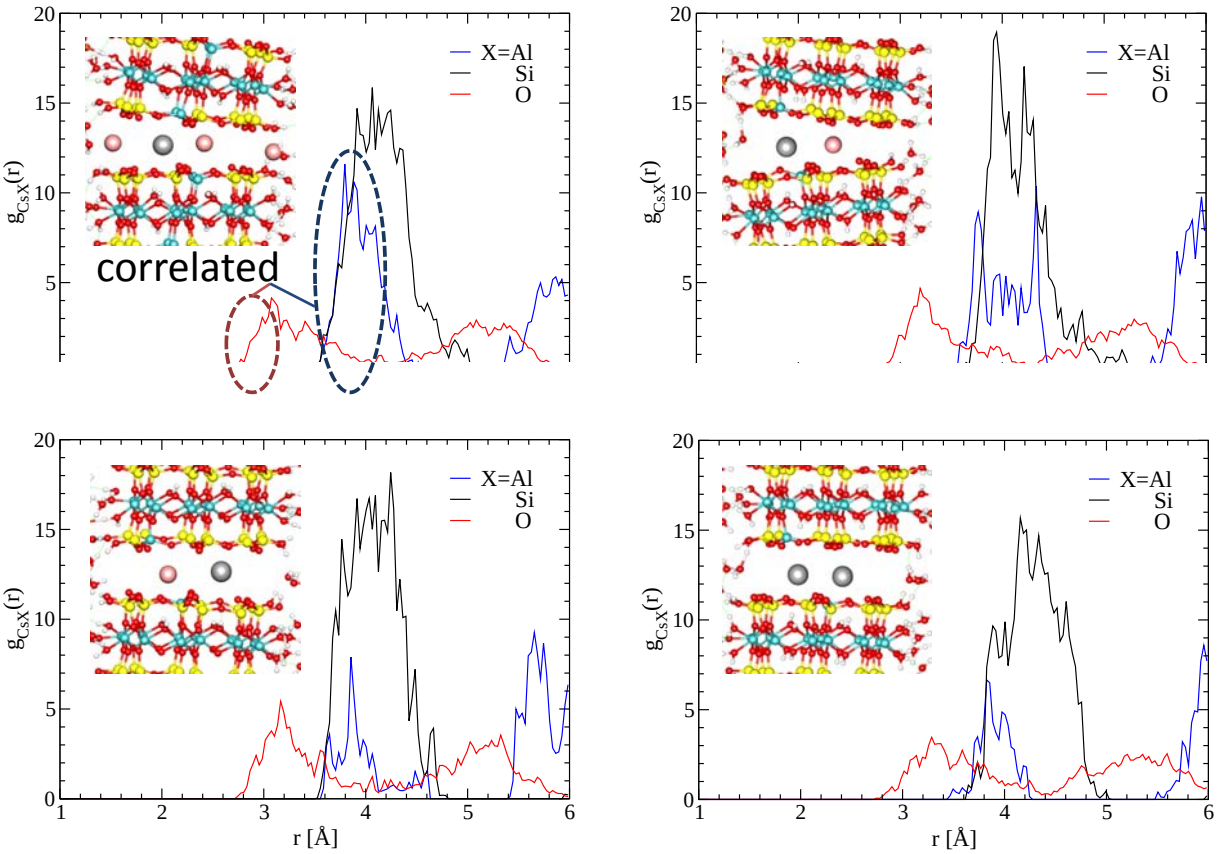


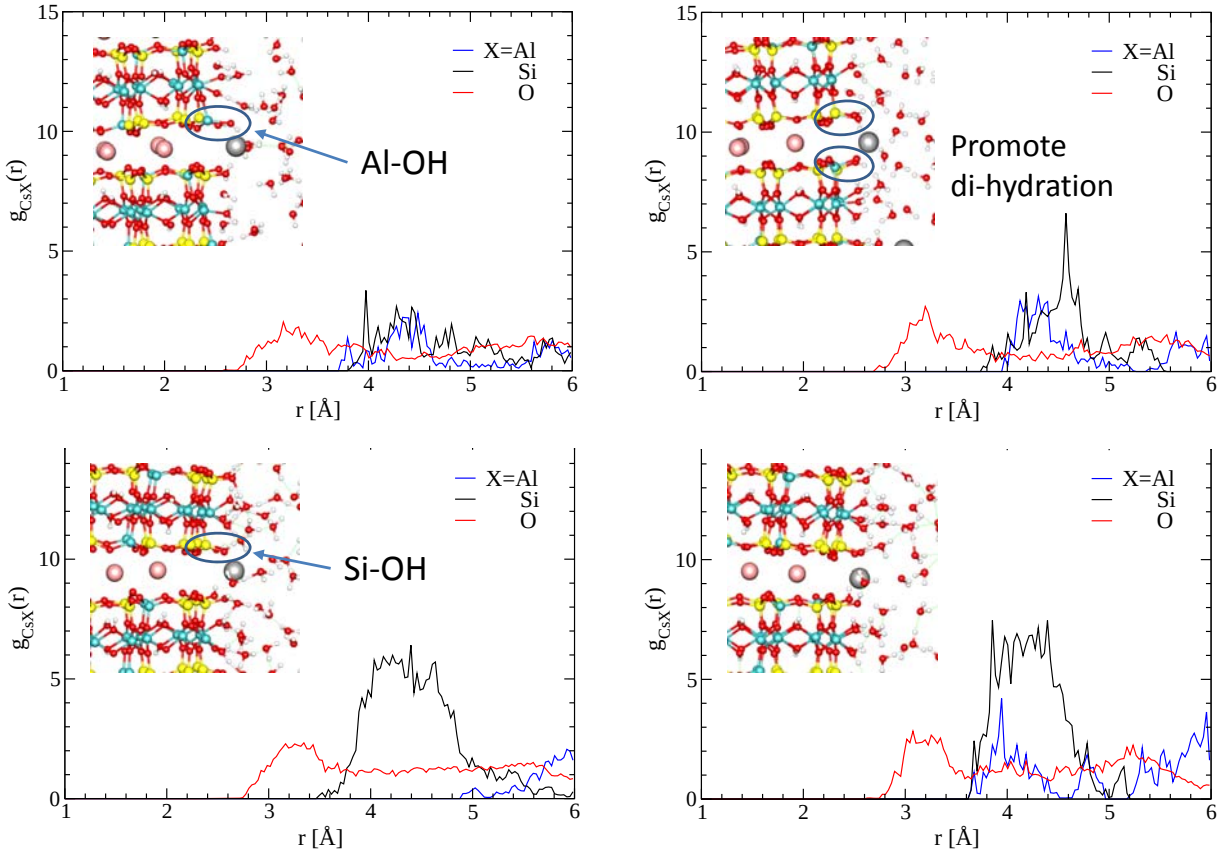
Edge



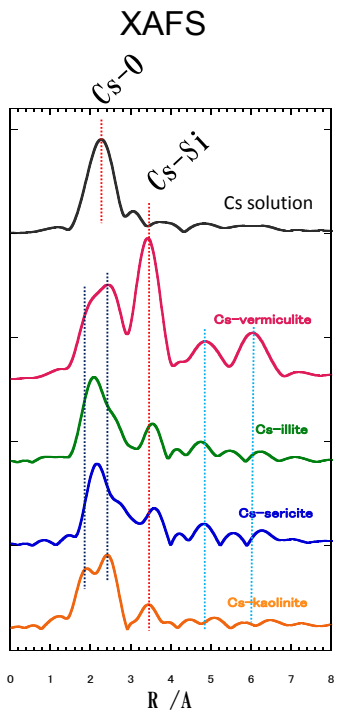
- The stability of Cs^+ appears to depend on various factors.
- Desorption of Cs^+ is rather difficult even if it is partially hydrated.

Radial distribution functions g_{CsX} for bulk





Comparison with XAFS experiments



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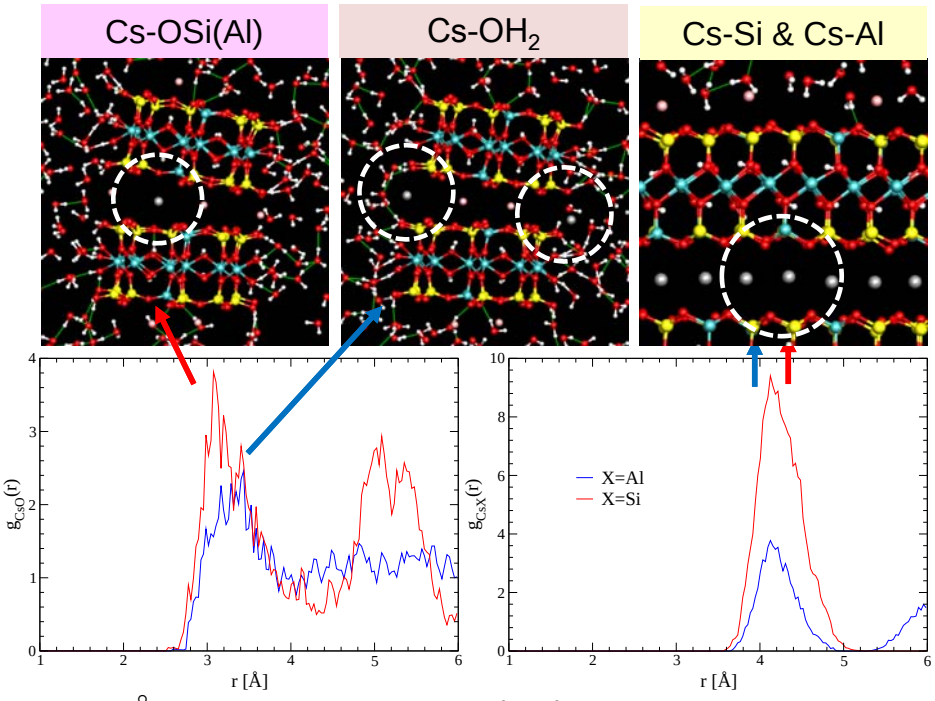
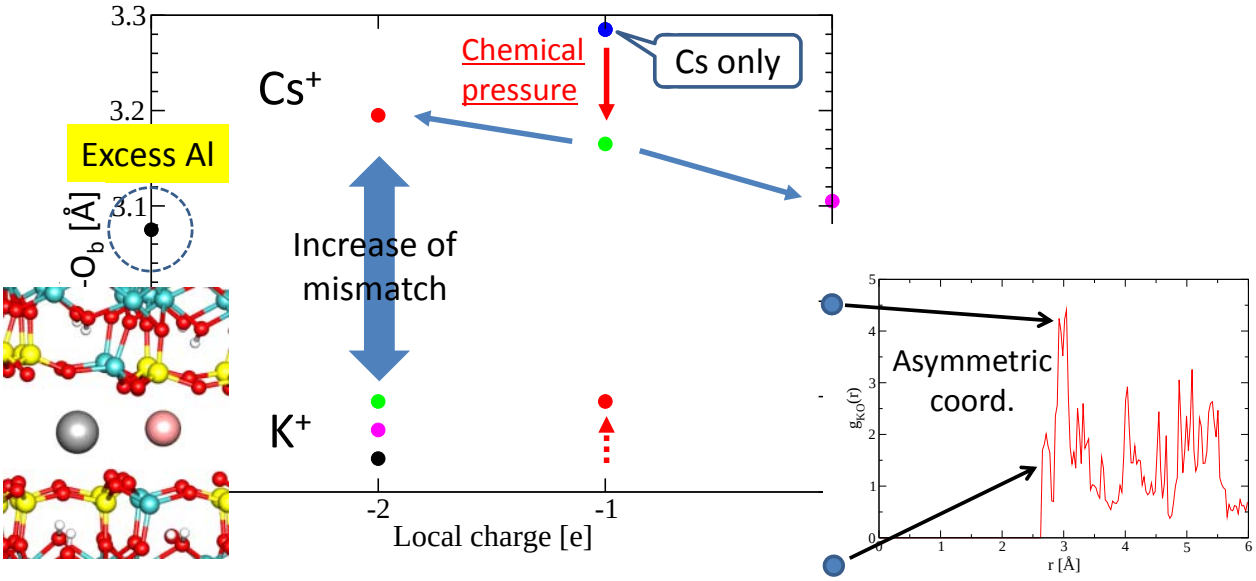


- ~3 Å : Cs^+-basal oxygen (O_b) & water oxygen
- ~4 Å : Cs^+-Si (Al) of tetrahedral sheet
- ~5 Å : Cs^+-apical oxygen(O_a)

Relationship between local charge and M^+-O_b distance



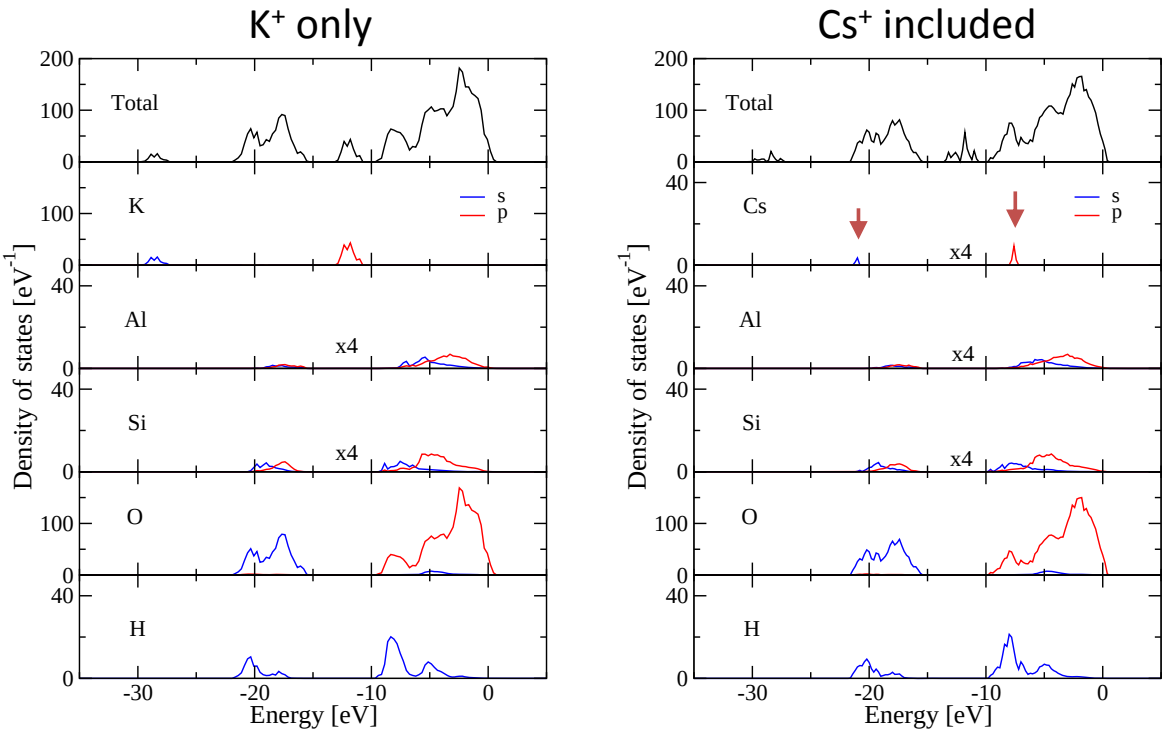
<u>Cs^+-O_b distance:</u>

- Local charge ↑ → Cs-O_b distance ↑
- Cs & K mixed → Cs-O_b distance ↓
- Excess Al → Cs-O_b distance ↓↓

⇒ irreversibility ?

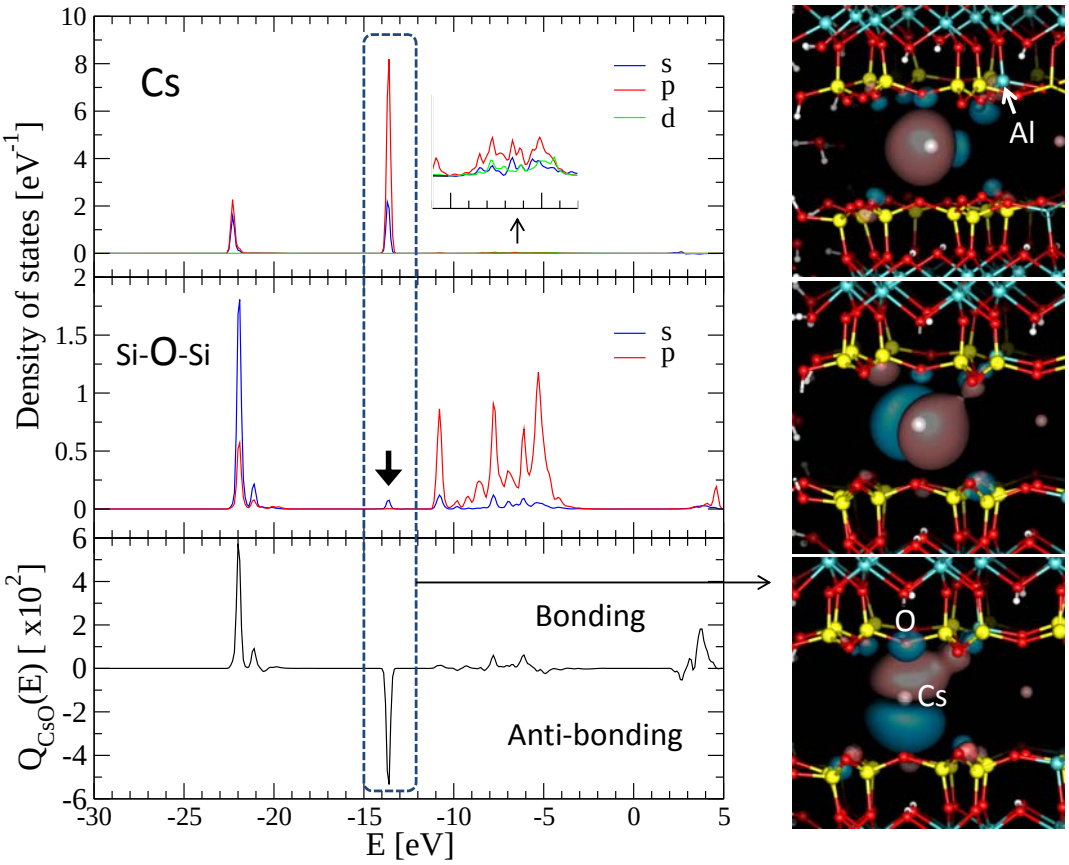
⇒ strong adhesion?

Electronic structures of illite systems

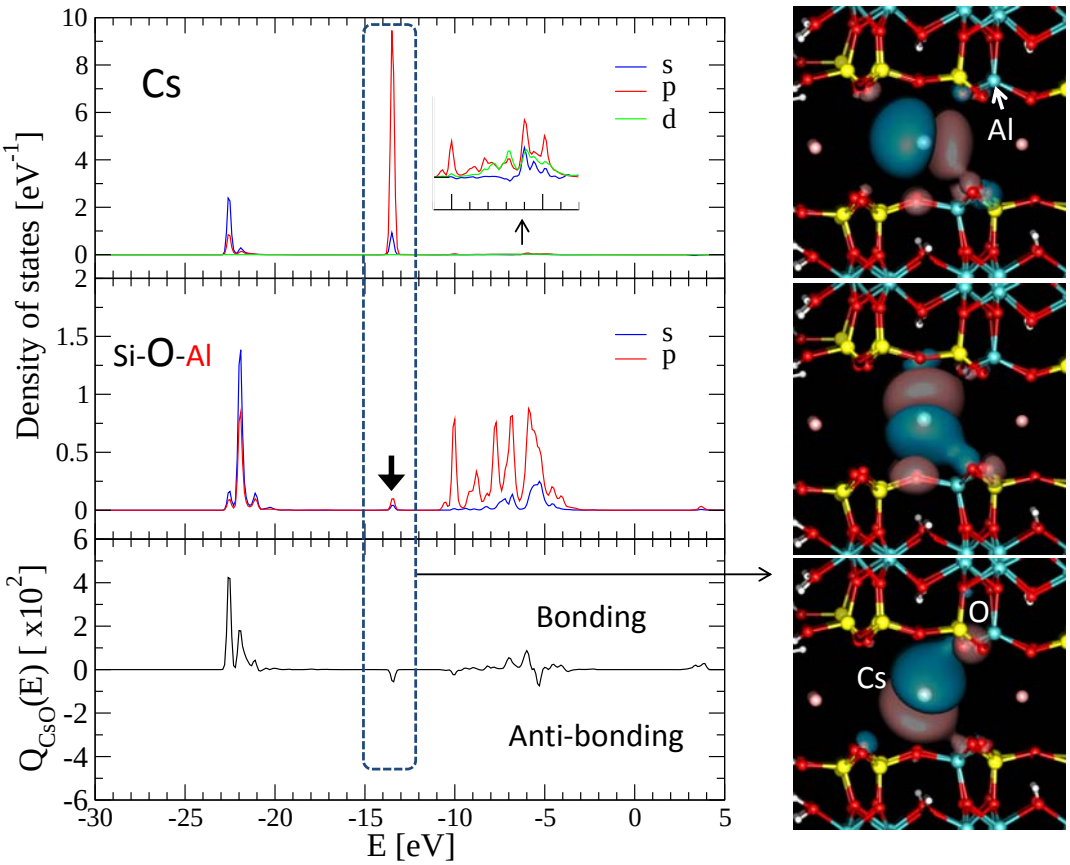


The Cs^+ 5*p* shallow core states overlap in energy with the orbitals of SiO_2 tetrahedral layers.

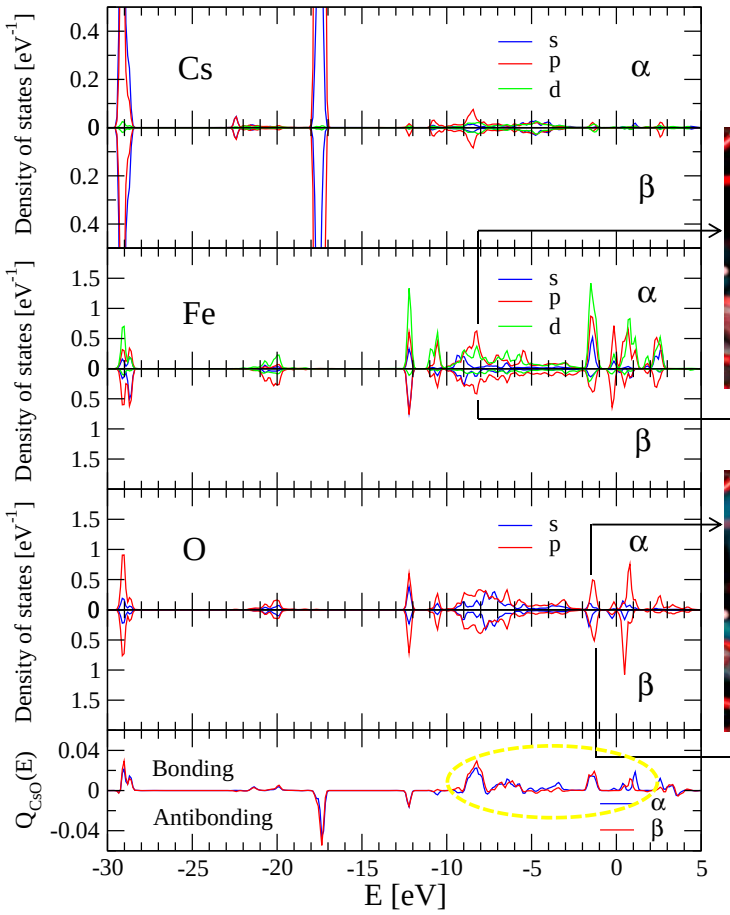
Local density of states & overlap populations

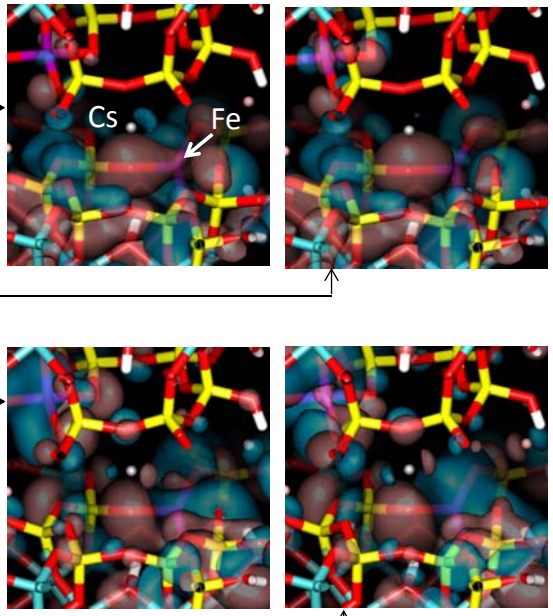


Local density of states & overlap populations (2)



Local density of states & overlap populations for Fe^{3+} included





Summary

- We successfully performed first principle MD simulations by employing typical structural models for selected clay minerals at acceptable computational cost.
- Our theoretical results for structural properties are preferably compared with experimental ones obtained by utilizing X-rays of SPring-8.
- Our simulations suggest that Cs^{+} is strongly sorbed particularly on basal oxygens of tetrahedral layers in close proximity to excess Al^{3+} or Fe^{3+} cations due to the formation of peculiar Cs^{+}-O bonds of non-negligible covalent bond character.