



The Coprecipitation of Hydrated Cd(II) on Stepped Calcite Surfaces: an Ab Initio Study

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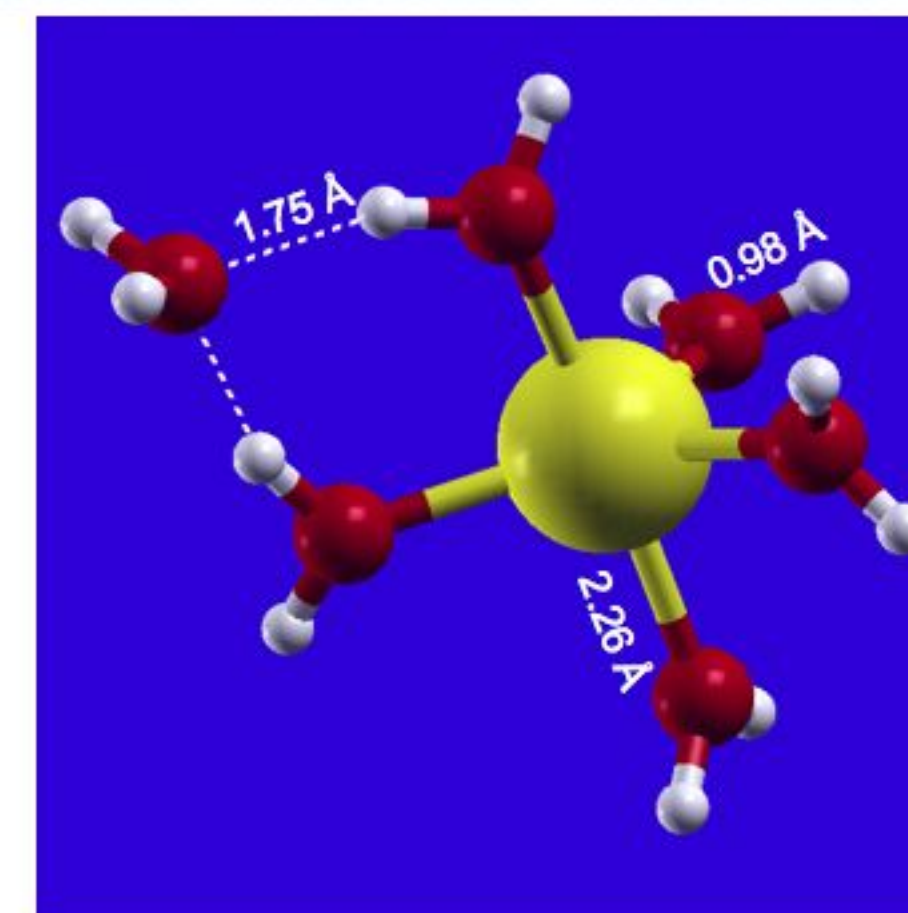
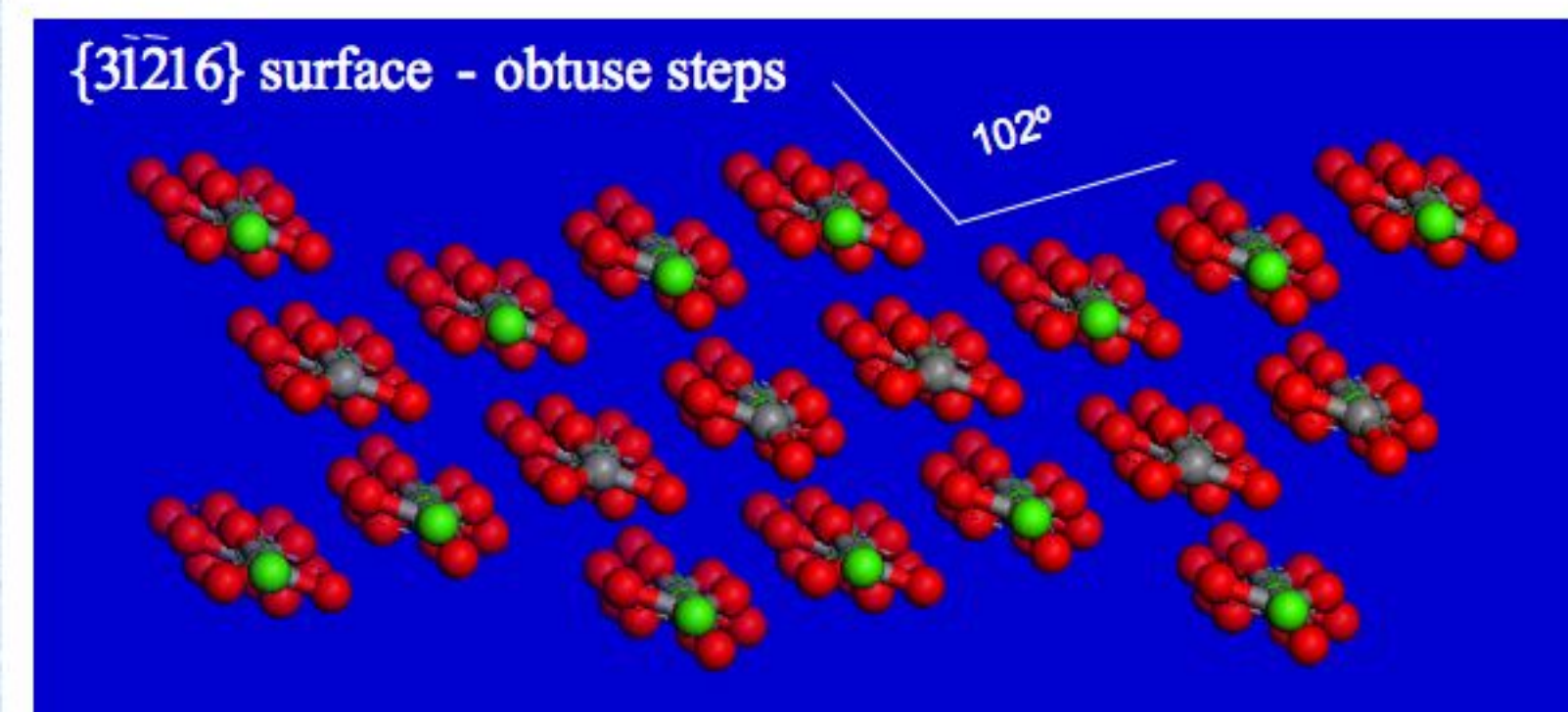
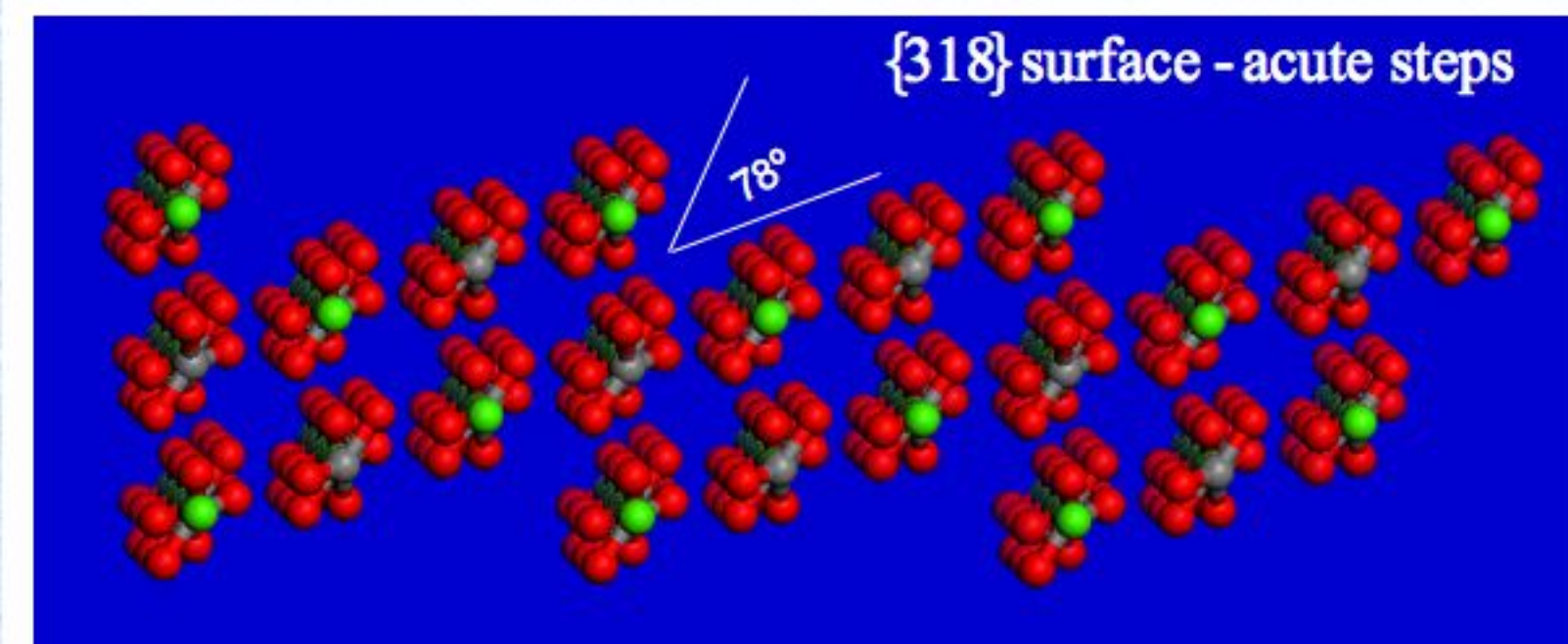
MOTIVATION

Industrial activity has often a major drawback: soil and water pollution. Very expensive investments are needed to remove contamination and, according to the technology, create sludge disposal issues.

Heavy metals incorporation into calcareous materials can be a convenient and cheap solution for the decontamination of polluted environments, specifically waters. Calcite is an ubiquitous biomineral and has sorbent capabilities with respect to a number of metal cations [1], among which Cd²⁺.

The mechanism of hydrated Cd²⁺ entrapment into the {318} and the {31216} calcite surfaces, called coprecipitation, must still be clarified. This work is an ab-initio study that aims to contribute to shed light on this topic at an atomic level.

CALCITE SURFACES AND Cd²⁺ AQUA-ION



Cd²⁺ aqua-ion cluster with its first hydration shell, as resulted from calculations: 5 water molecules bonded to the cation, one bridging two H₂O's in the inner sphere shell.

Acute steps supercell dimensions: (12.8x9.5x35.7) Å
Obtuse steps supercell dimensions: (12.8x11.9x34.8) Å
21Å vacuum along c

COMPUTATIONAL DETAILS

Statics:

Density Functional Theory (DFT-D) in the Generalized Gradient Approximation (GGA-PBE) and ultrasoft pseudopotentials are considered. van der Waals dispersion forces are accounted for.

Plane waves kinetic energy cutoff: 32 Ry and 256 Ry;
k-sampling limited to the Γ -point of the Brillouin zone;

Dynamics: Car Parrinello MD (AIMD)

1 ps equilibration run.

NVT ensemble. $\Delta t = 0.14$ fs; T=400 K; 4 layer slabs

{318}: 26 CaCO₃ units (8 on surface) 19 ps simulation time

{31216}: 30 CaCO₃ units (8 on surface) 17 ps simulation time

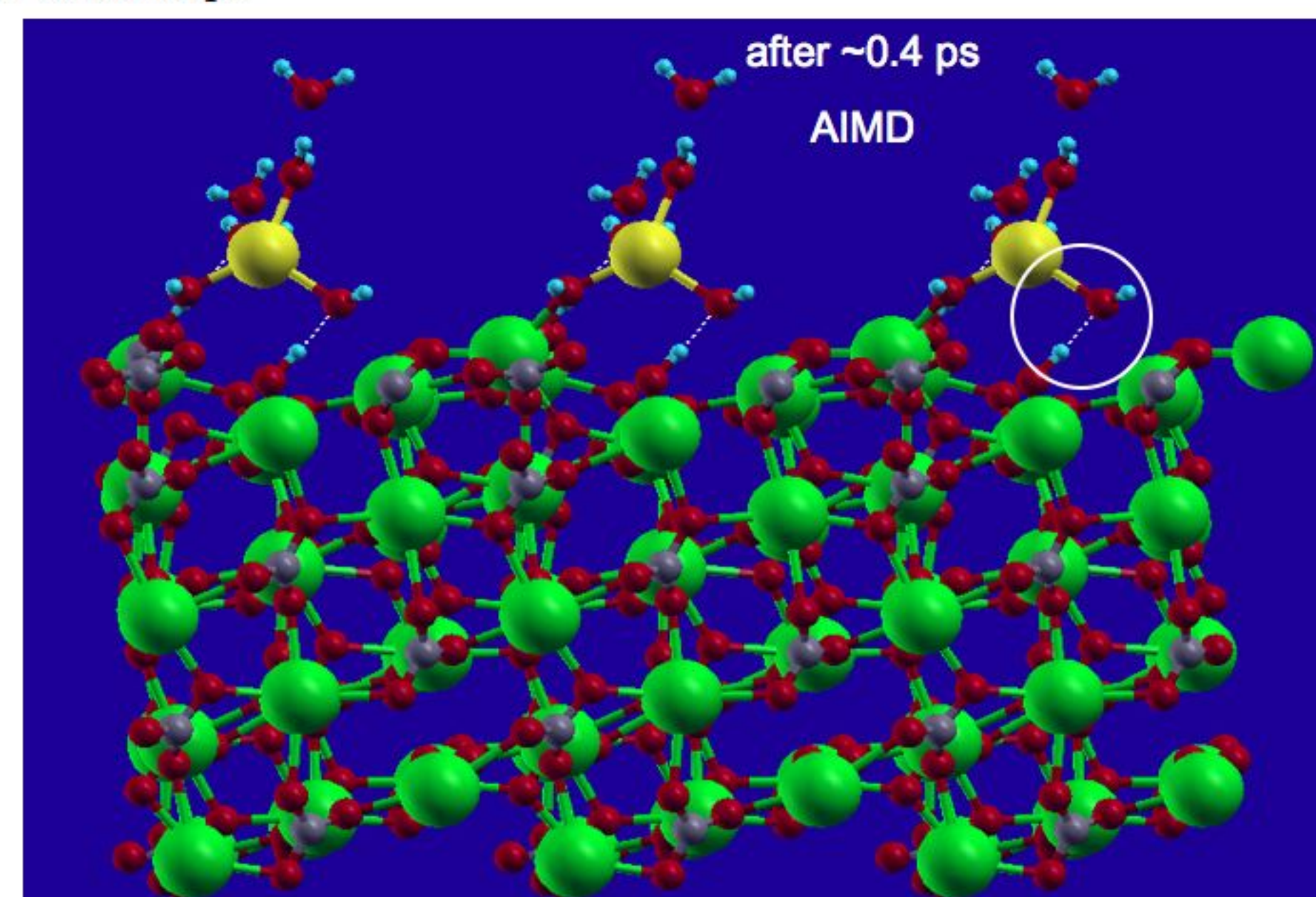
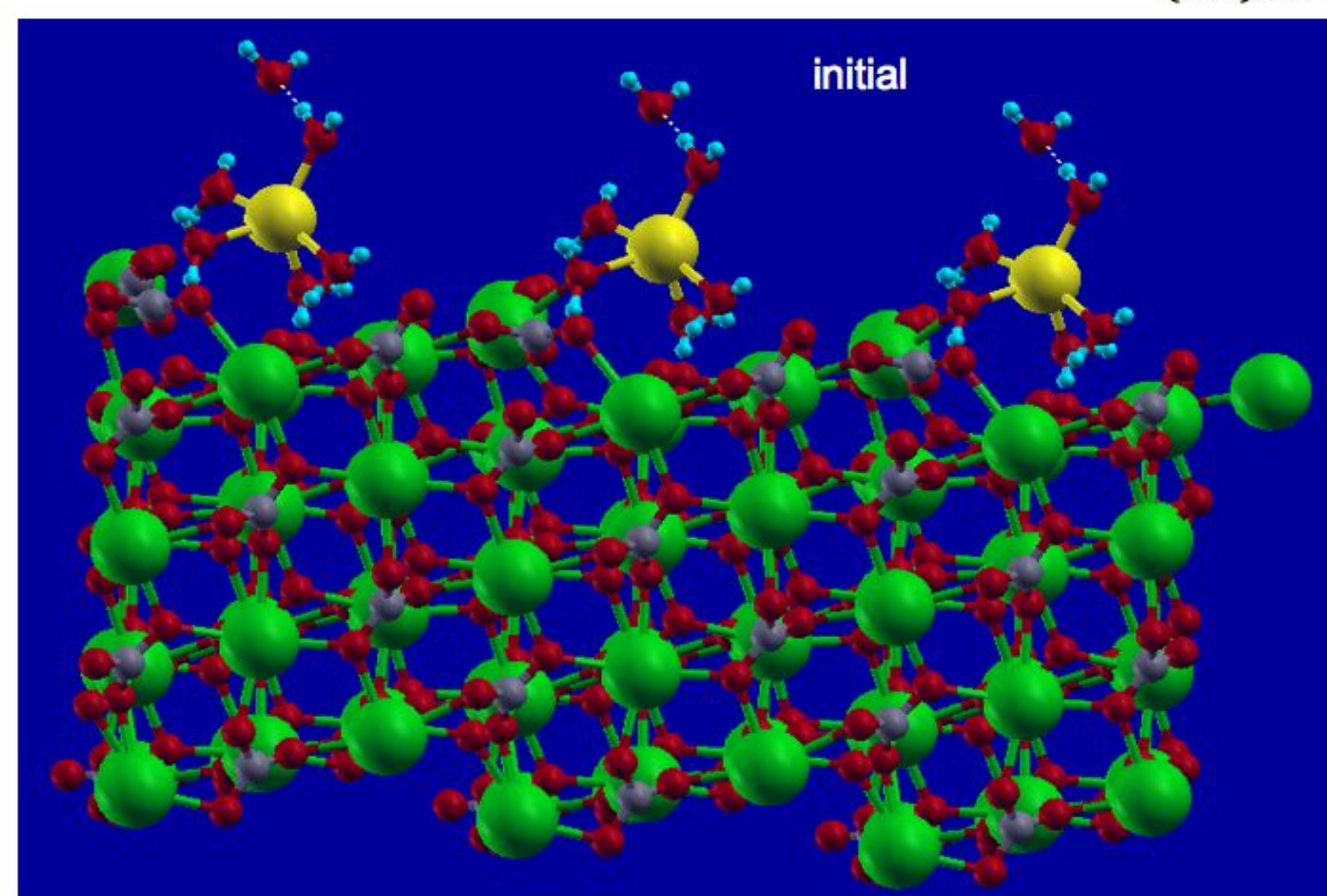
Nudged Elastic Band (NEB) method was used to calculate the diffusion barriers.

All calculations are performed using Quantum-ESPRESSO code

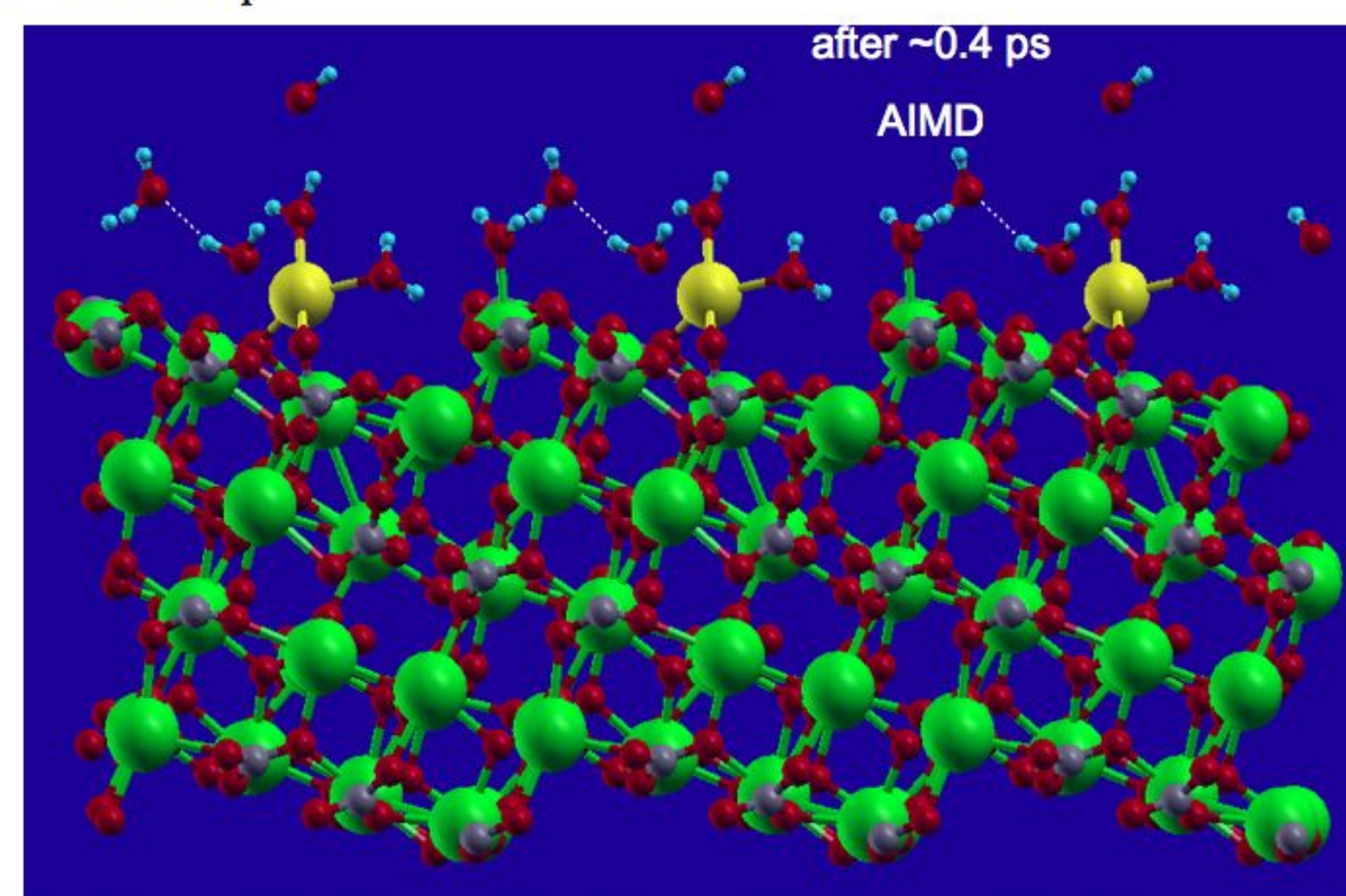
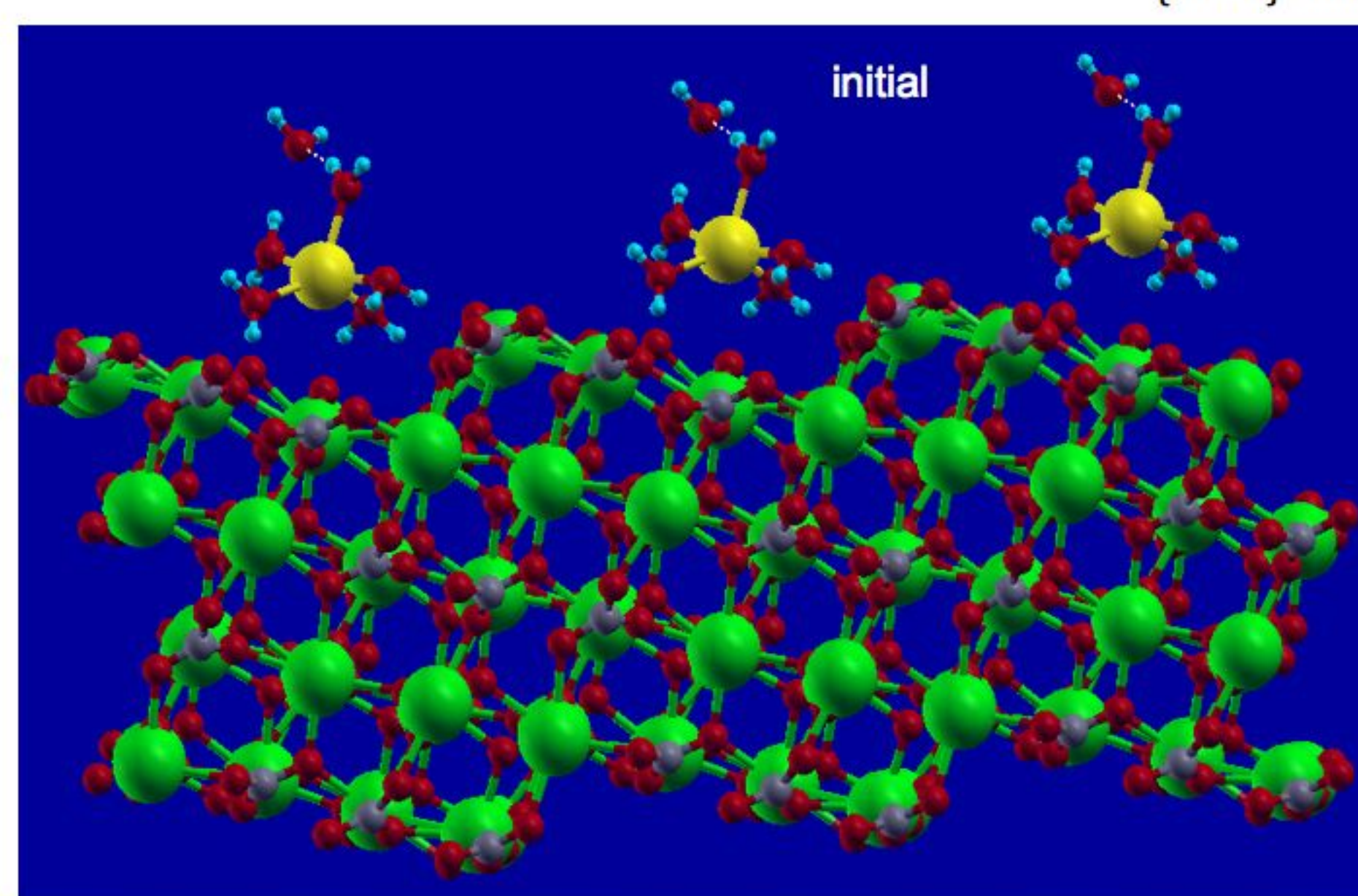
(<http://www.quantum-espresso.org>)

CALCITE SURFACE WITH Cd²⁺ AQUA-ION

{318} surface - acute steps



{31216} surface - obtuse steps



Adsorption energies are calculated with the formula:

$$E_{ads}^q = E_{surf+molec}^q - [E_{surf}^0 + E_{molec}^0] + q\mu_e$$

where:

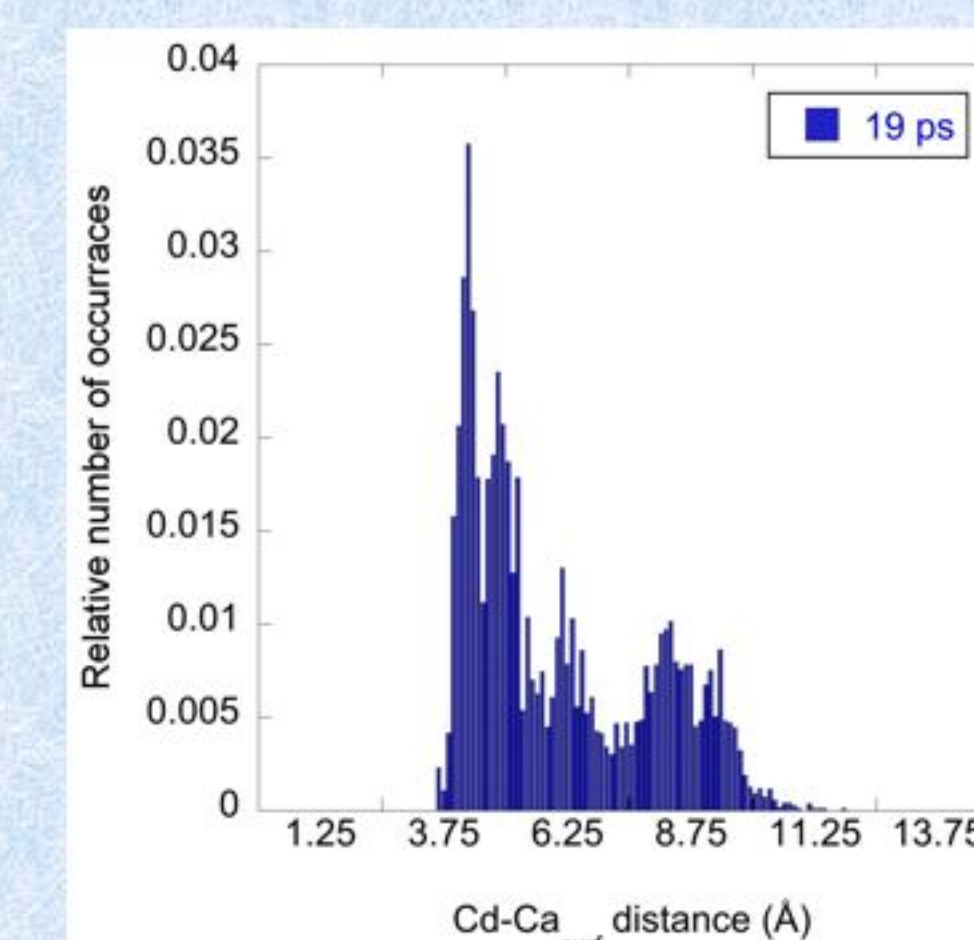
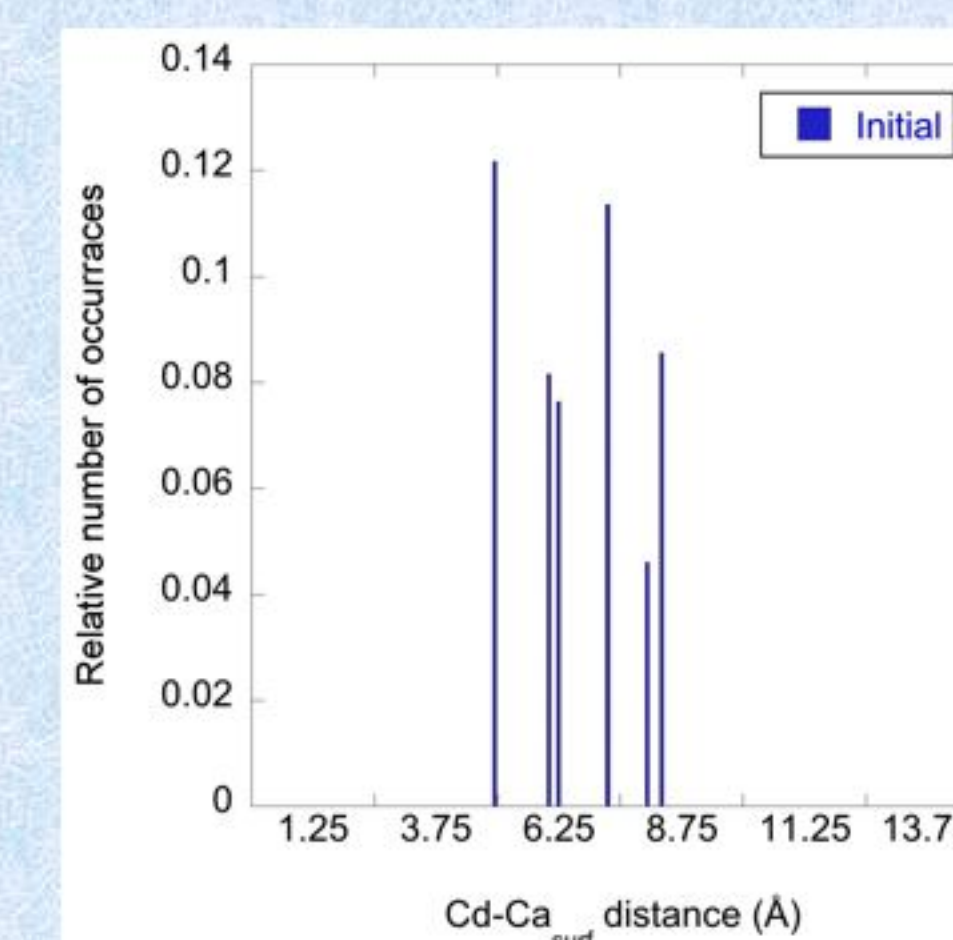
the E_{surf}^0 and E_{molec}^0 are the total energies of the neutral ($q=0$) surface and the aqua-ion, respectively; $E_{surf+molec}^q$ is the total energy of the charged surface+aqua-ion, $q=+2$ is the charge. μ_e is the chemical potential.

$$E_{ads_acute}^{2+} = -326.81 \text{ kJ/mol} + 2\mu_e$$
$$0.0 \leq \mu_e \leq 377.26 \text{ kJ/mol (3.91eV)}$$

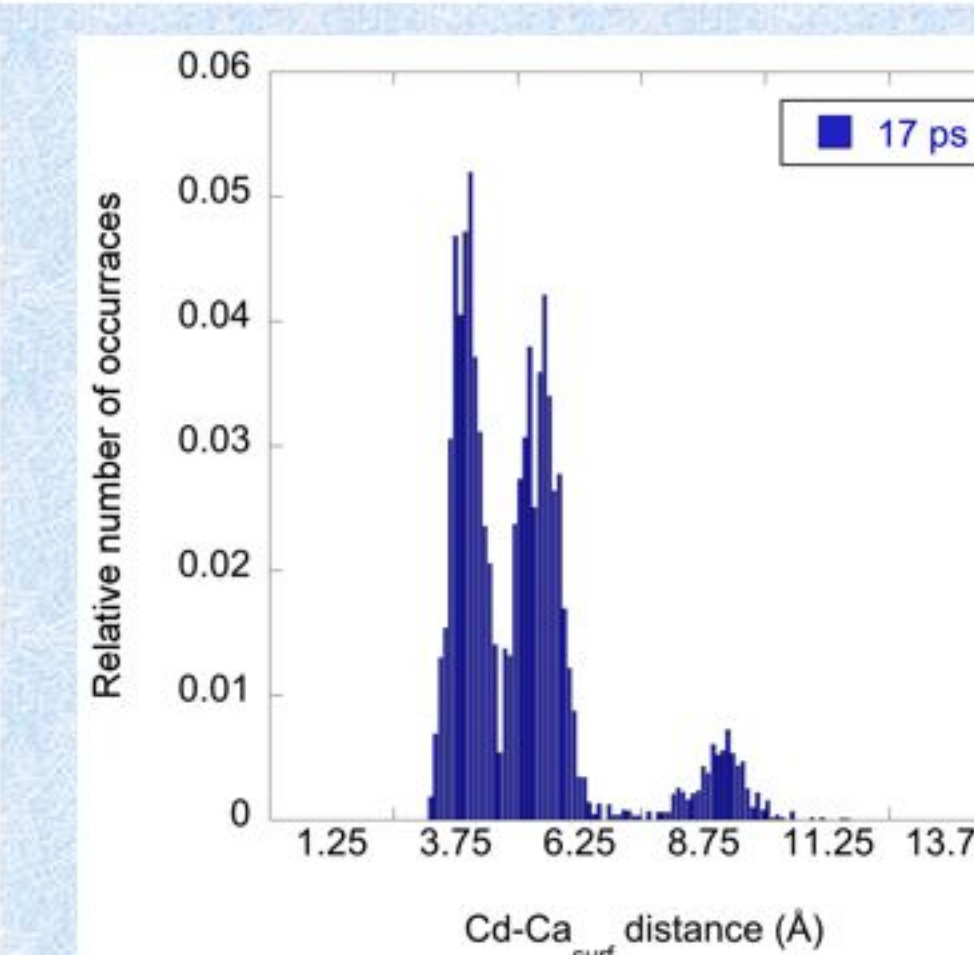
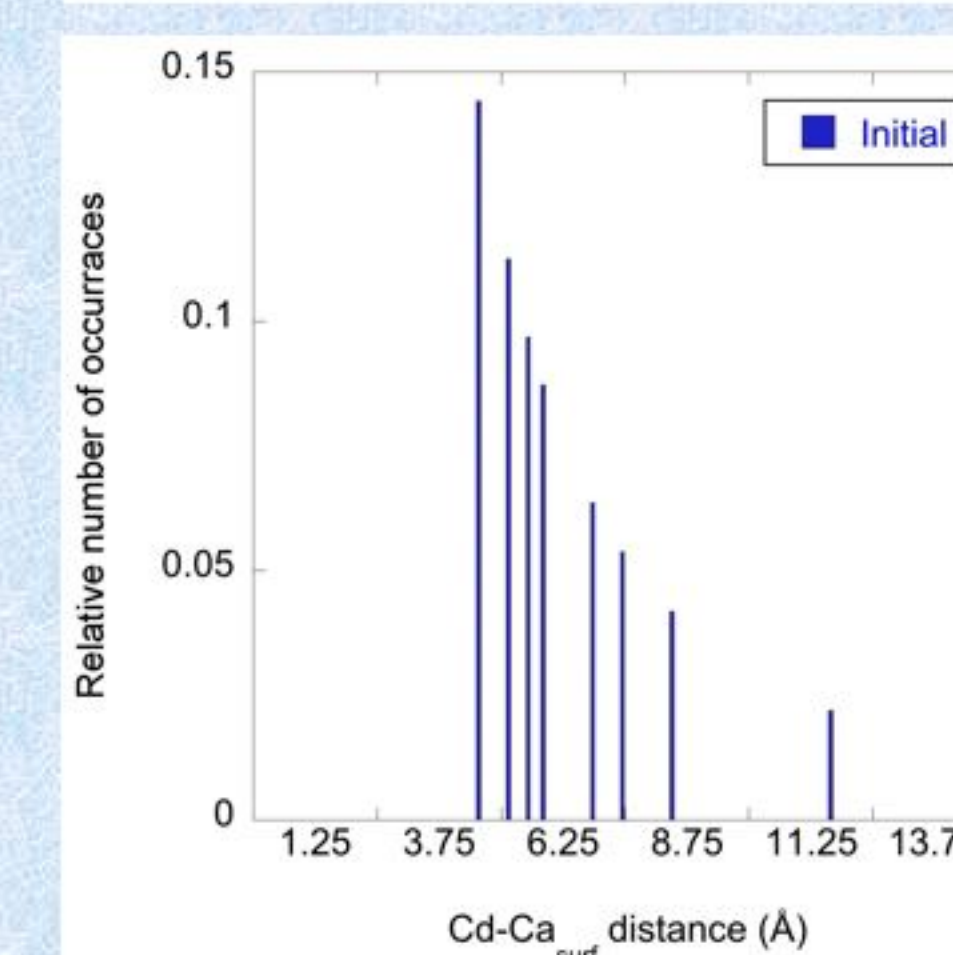
$$E_{ads_obtuse}^{2+} = -371.15 \text{ kJ/mol} + 2\mu_e$$
$$0.0 \leq \mu_e \leq 394.62 \text{ kJ/mol (4.09eV)}$$

The second adsorption site seems to be preferred by the aqua-ion.

The adsorbed Cd²⁺ cation interacts with both kinds of calcite surfaces through a water layer (H-bonds). This is removed immediately after the beginning of the AIMD simulation and the metal cation binds to the carbonate groups. Water dissociates and the H⁺ moves onto the acute stepped surface during cluster rearrangement. Continuous water association and dissociation is observed throughout the calculation. This phenomenon seems not to occur on the obtuse stepped surface



Bar plots of Cd-Ca_{surf} distance of the {318} (top) and the {31216} (bottom) planes showing the approach of Cd²⁺ to the surface of the biomineral



NEB

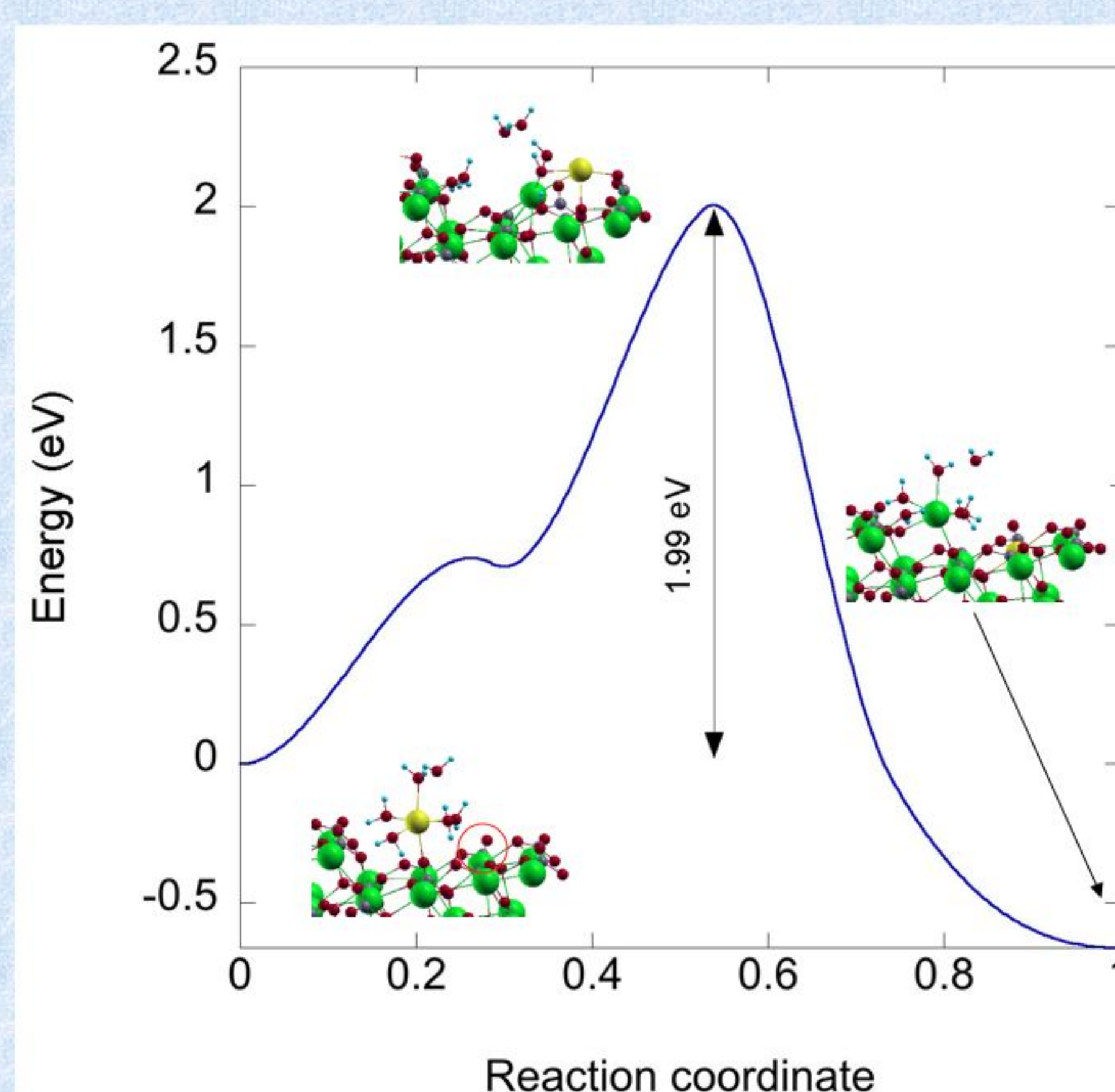
The NEB method allowed us to study a possible mechanism and the energy barrier for the replacement of a Ca²⁺ with a Cd²⁺. Dehydration of Cd²⁺ is the first step in the replacement of a Ca²⁺ on the calcite surface. The heavy metal gets closer to the mineral, a Ca²⁺ ion is gradually released from the surface and hydrates, leaving a hole. The vacancy is then filled by Cd²⁺. Note that CdCO₃ is less soluble than CaCO₃. The whole process is exothermic. Ionic radii of the two cations are similar. Cd²⁺ can easily be embedded in the structure of calcite [2-5]. Activation energies (E_a) computed (preliminary results) are:

$$E_{a_acute} = 1.48 \text{ eV}$$
$$E_{a_obtuse} = 1.99 \text{ eV}$$

Acute: replacement in the step
Obtuse: replacement near the step

We also started to investigate the diffusion of Cd²⁺ in the calcite bulk with the same method for two of the possible paths inside the crystal structure. The E_a s for the two case studies (preliminary results):

$$E_{a1} = 6.93 \text{ eV}$$
$$E_{a2} = 8.49 \text{ eV}$$



CONCLUSIONS

- Calcite adsorbs the hydrated Cd²⁺ ion both on the {318} and the {31216} surfaces
- The water layer between the cation and the mineral is quickly removed and water dissociation is observed on the {318} surface
- No adsorbed species desorbed or diffused during simulation
- The adsorption energy is larger for the obtuse stepped surface, which seems to be a more favorable site for Cd²⁺
- The replacement of a Ca²⁺ ion with a Cd²⁺ process is exothermic, a lower activation energy is computed for the acute stepped surface
- The diffusion of Cd²⁺ in the mineral bulk requires much more energy than the replacement process

REFERENCES

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