Water dynamics in the calcite-water interface

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Elucidation of water dynamics around Calcium

Importance

- Carbonate rocks: important hydrocarbon reservoirs and basins for CO_2 sequestration.
- Aim of project: study calcite ($CaCO_3$) dissolution and growth on atomic scale, pore scale and field scale.
- Via Molecular Dynamics we obtain key information on how fast water moves near the surface sites where it all happens. How fast water moves determines how fast reactions can occur and therefore key information for rate equations.

Method

- Classical Molecular Dynamics (MD) Simulations of aqueous (solvated) calcium ion and calcite surfaces.
- From the output, we calculate the **Mean Residence Time (MRT)** of water coordinated to calcium using two different methods:
1. The "direct method", measures each exchange and obtains the MRT from the inverse of the exchange frequency (results not shown here).
2. The Impey survival function measures the time a water molecule stays in the first shell (e.g. **Graph 1, 2**).
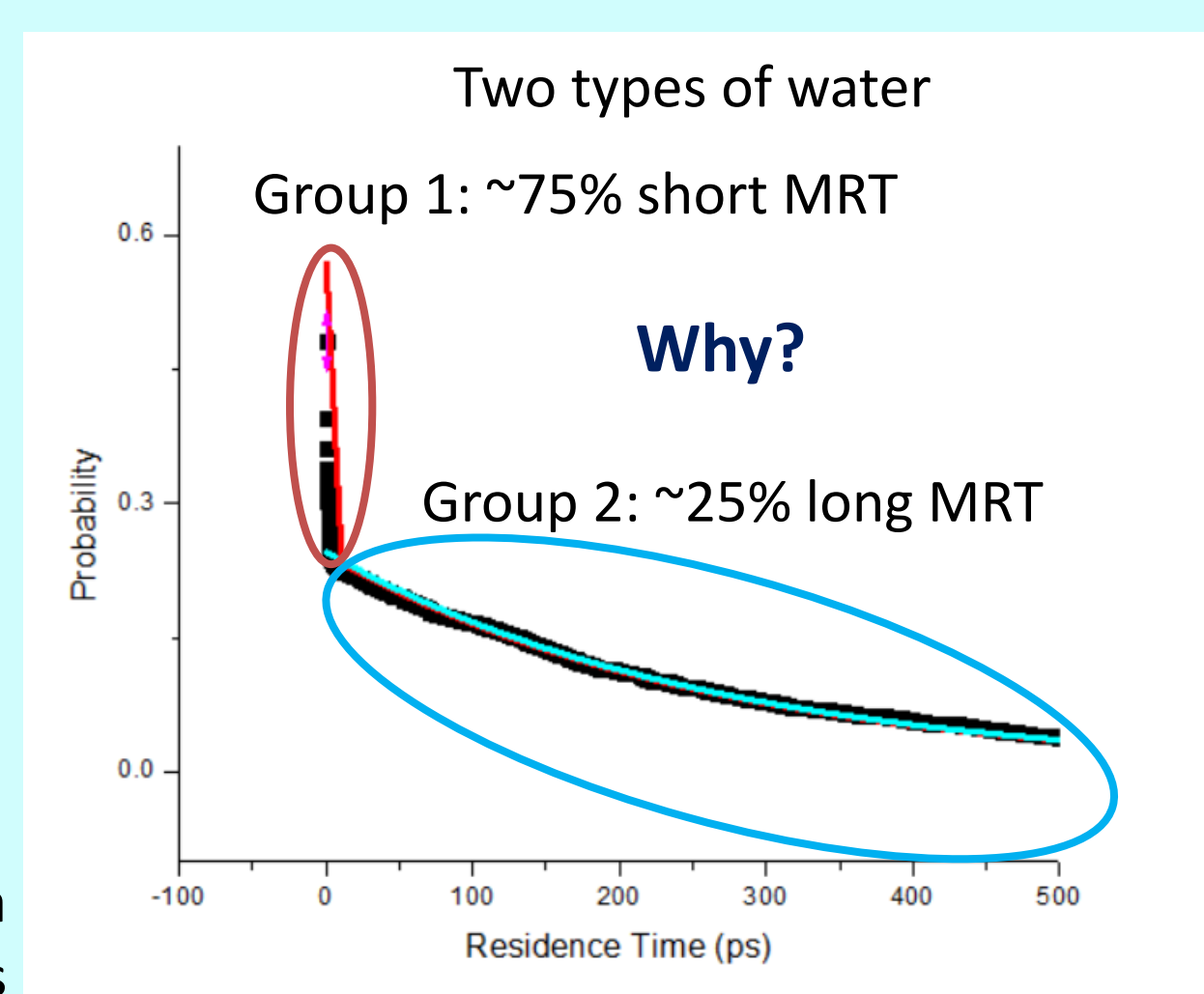
The advantage of the second method is that it is the same method used in experiments.

Results

- We observe two two different types of behaviour of water: "fast" and "slower" exchanging water (**Graph 1 and 2**) *Why?*
- Graph 2 reveals that the distance plays an important role in the MRT.
- There is a characteristic number of water molecules around the calcium ion, for our MD water model, CN is 7.
- When we compare the CN for both water types 1 and 2 we two groups of Ca-O distances, see **Figure 1**.
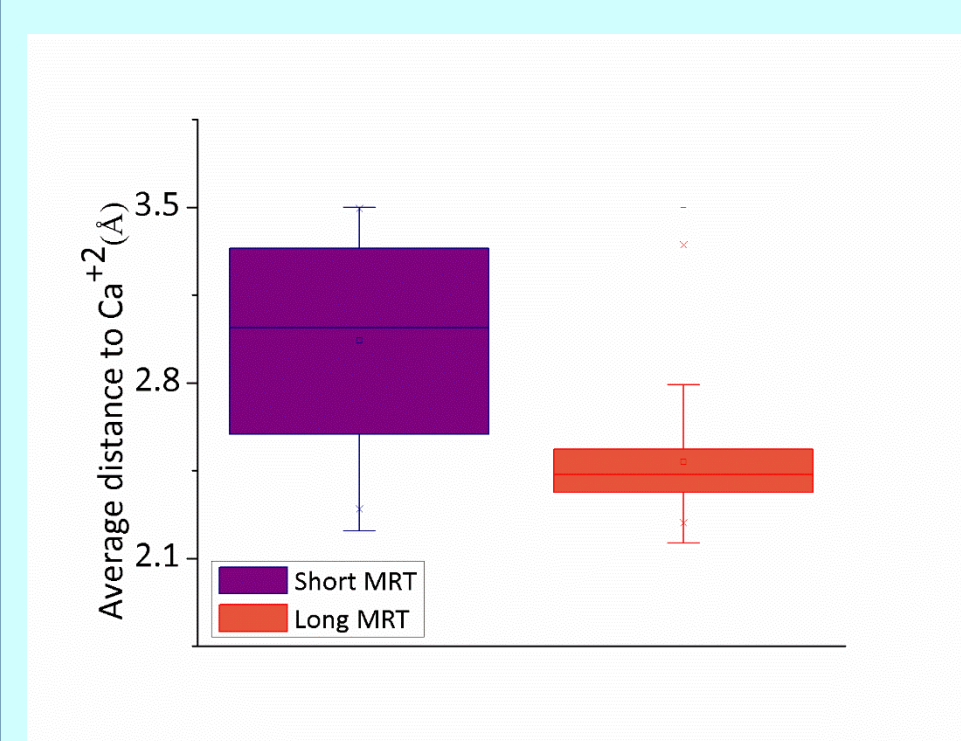

Graph 2 The boxplots show the distance between the water and the calcium for the first 20 picoseconds of the residence time (RT).

Figure 1 Shows a snapshot configuration of the simulation of the waterbox with a Calcium ion. The waters in the first shell are collored and grouped according to their distance. To its left an ideal sketch of the same configuration

Graph 1 The survival function, fitted with a sum of two exponential decays

Two types of water
Group 1: ~75% short MRT
Why?
Group 2: ~25% long MRT
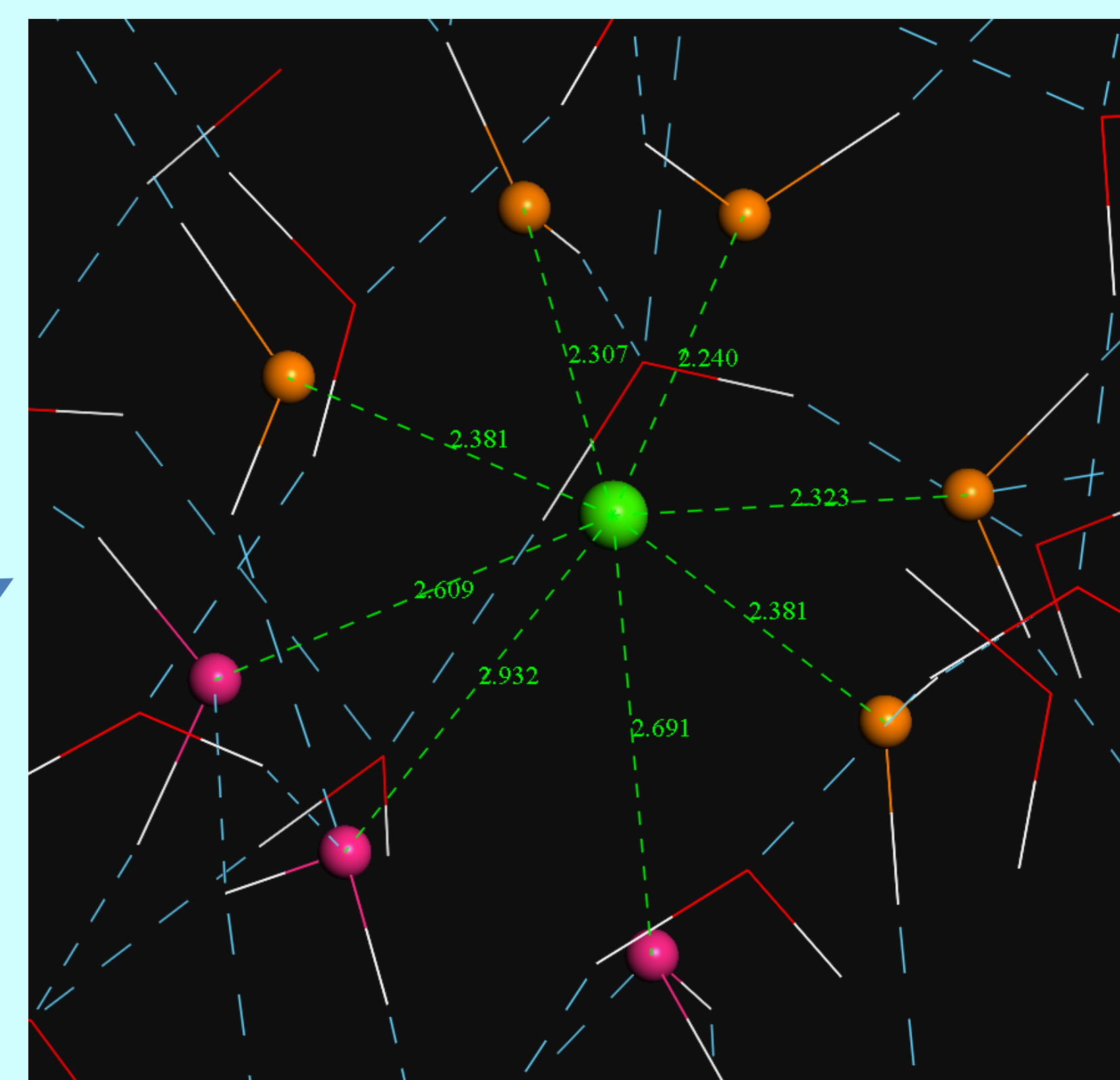
Conclusion

- Using the Impey survival function, two classes of water molecules are captured, depending on their distance to the coordinating Ca ion.
- 75% of the water molecules entering the 3.5 radial distance from the ion are of type 1 (pink oxygens in Figure 1, at longer distance from Ca).
- Only 25% are of type 2 (orange oxygens in Fig. 1, shorter distance to Ca).
- In the direct method this distinction cannot be made.
- Both methods can be used study the relative reactivities of sites, but to measure the correct MRT, and compare to experimental data, the survival method is recommended.

Implications for crystal growth rate

The rate-determining integration step consists of two simultaneous phenomena:

a) Dehydration of the cation (figure 2&3 illustrate where the dehydration in the surface takes place)
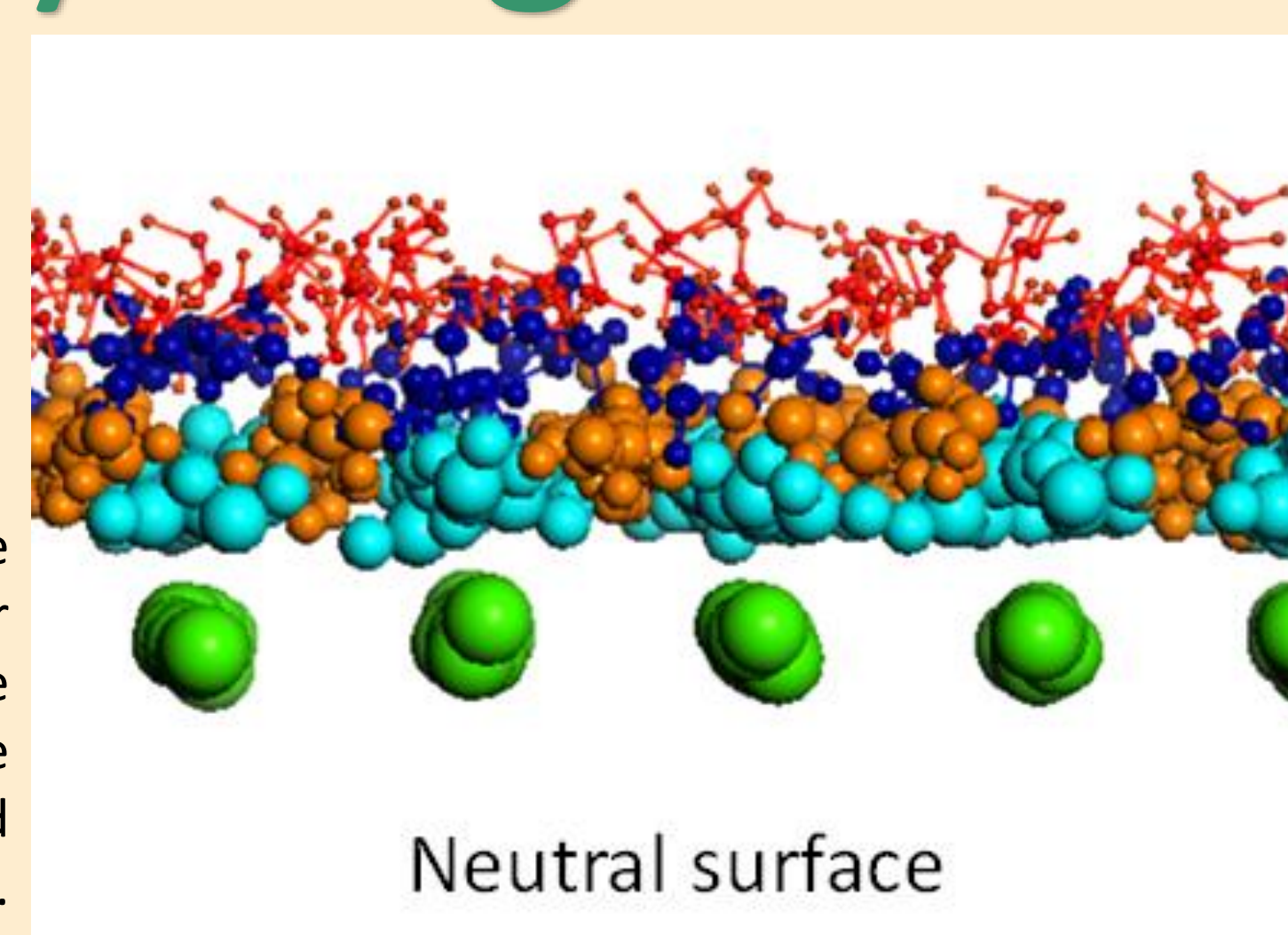b) Diffusion of the cation into the lattice site from a neighbouring position.

Figure 3 A zoom in of the calcite water interface. (For clarity, the carbonates are removed in the images). The exchange of coordinated water (cyan) is process 'a'.
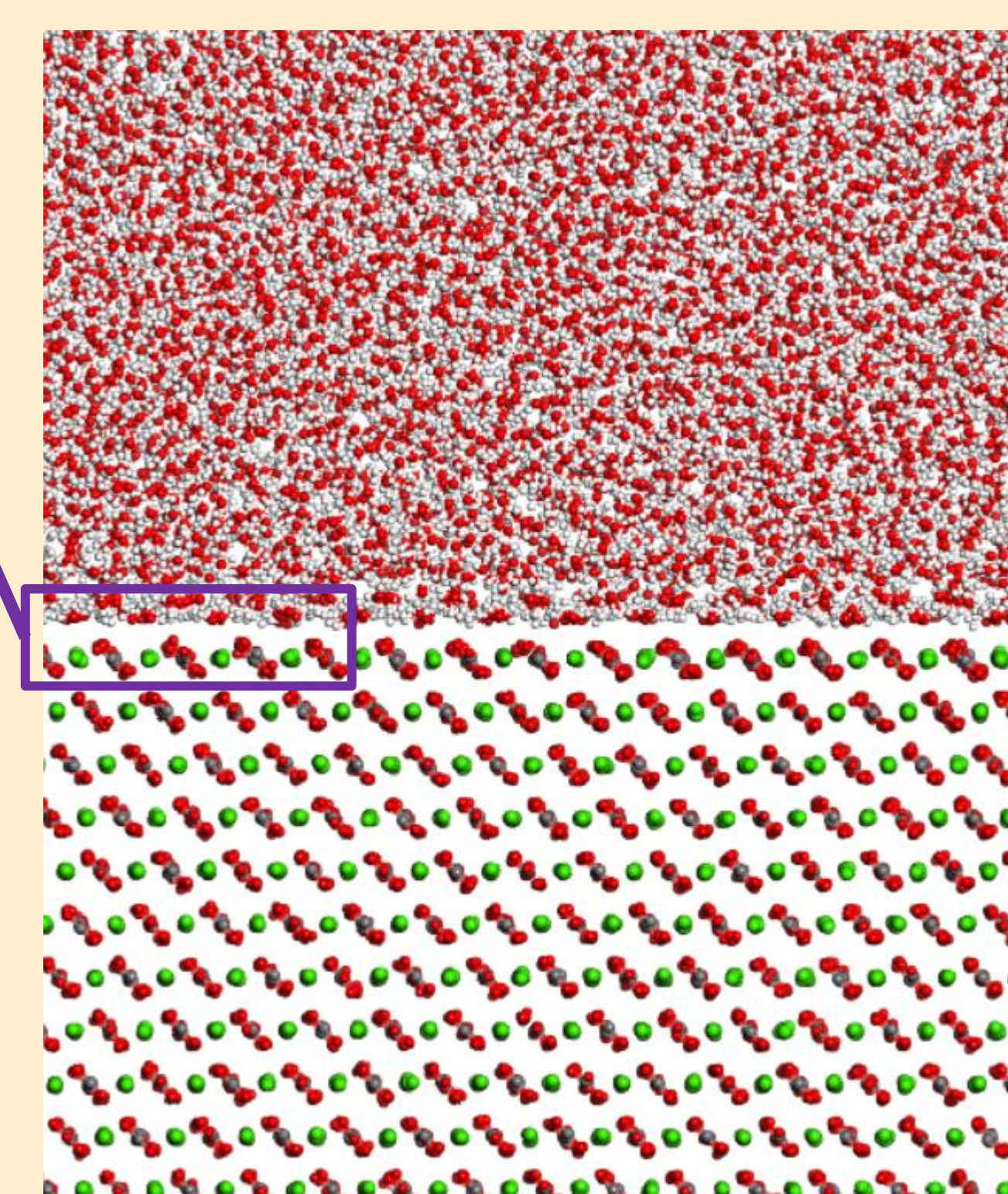
Neutral surface

Figure 2 Shows a snapshot configuration of the simulation of a 10$\bar{1}$4 calcite (ordered lower half of the Figure) crystal surface exposed to water (red-grey top half of the Figure).

Current status in the field:

Based on the experimental values of Eigen, the dehydration of the cation is the slowest process. (Phenomenon 'a' is 100x slower than process 'b')

This study (Classical and ab initio MD):

The dehydration of Calcium = 10^{-2} times Eigen's value
In agreement with neutron scattering (IQUENS) experiments.

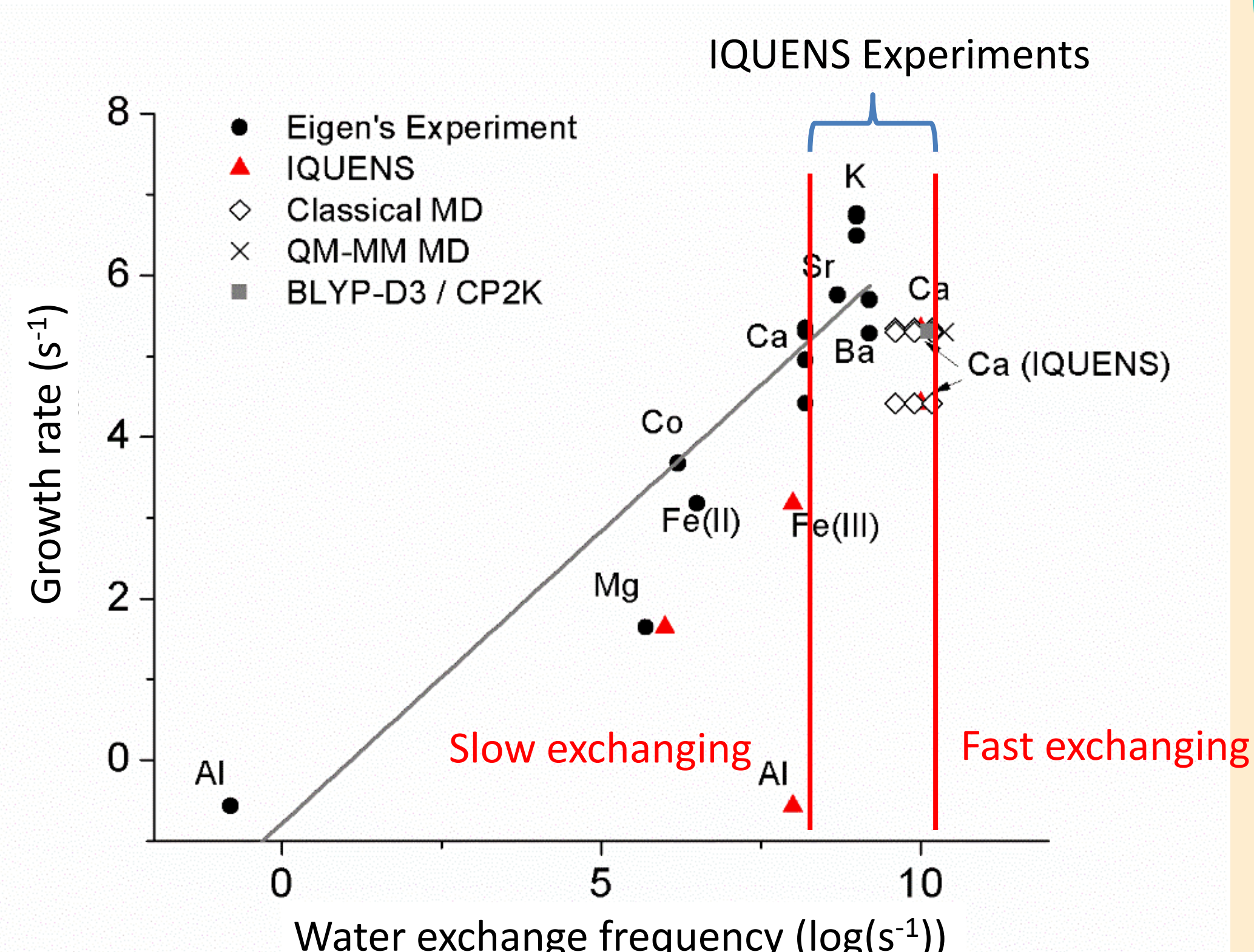Calcium is a fast water exchanging ion

Figure 4 Correlation between the dehydration of the cation and the integration step. IQUENS experiments revealed three classes of fast, intermediate and slow water exchanging ions. The results of MD for calcium are all in the fast water exchanging class.

Conclusion:

Based on the two processes in the growth reaction the rate limiting step is diffusion of the cation into the lattice site from a neighbouring position.