

## Supplementary Information: Reactive Force Fields for Aqueous and Interfacial Magnesium Carbonate Formation

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**Supplementary Note 1: Magnesium charge screening in ReaxFF:** ReaxFF, in general, implements an approach similar to electronegativity equalization method (EEM) to equilibrate atomic charges<sup>1</sup>. However, the functional form of the electrostatic energy is a bit different from the EEM approach. Based on equation (5) in the main text the total electrostatic energy is defined as:

$$E_{es}(q_1 \dots q_N, x_1 \dots x_N) = \sum_i (E_{i0} + \chi_i q_i + \frac{1}{2} J_i q_i^2) + \sum_i \sum_{j < i} q_i q_j J_{ij} \quad (1)$$

In this equation,  $J_{ij}$  describes the interaction between one unit charge on atom  $i$  and one unit charge on atom  $j$ . The choice of a proper functional for  $J_{ij}$  is a bit subtle due to the following reasons. First, it should approach  $1/r_{ij}$  at long distances, where  $r_{ij}$  is the interatomic distance, because the two charges act like point charges at very long distances. Also, at very short distances where  $r_{ij}$  approaches zero, the electronic clouds of the two atoms overlap. The value of  $J_{ij}$  at  $r_{ij}=0$  should be equal to a finite value, denoted as  $\gamma_{ij}$  in ReaxFF. In ReaxFF, the functional form for  $J_{ij}$  is:

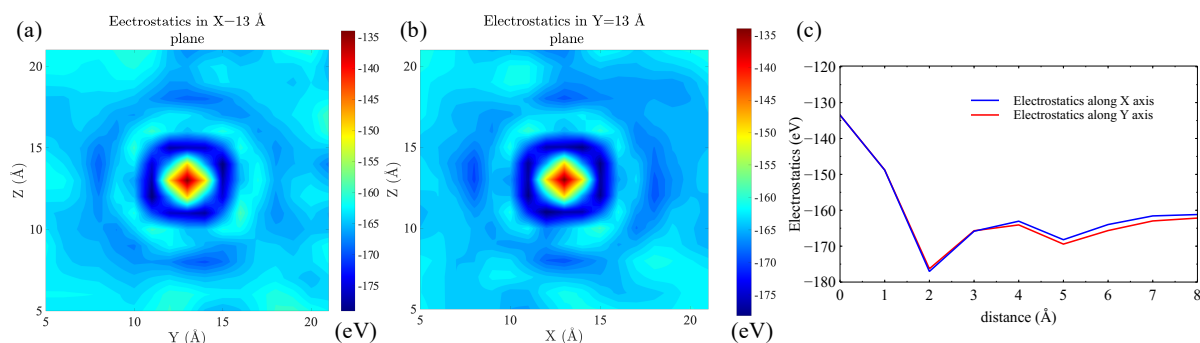
$$E_{coulomb} = Tap.C. \frac{q_i q_j}{[r_{ij}^3 + (1/\gamma_{ij})^3]^{1/3}} \quad (2)$$

Compared to the exact value of the electrostatic potential<sup>2</sup>, this type of functional satisfies the two criteria mentioned above.

Although the charge of magnesium is fixed in our forcefields, it is obvious that at short distances the electrostatic potential approaches the value of the screening parameter,  $\gamma_{ij}$ , defined as  $\sqrt{\gamma_i \gamma_j}$ . In our forcefield,  $\gamma_{Mg}$  is iteratively fitted to a set of crystals as well as magnesium-water clusters.

To further investigate the screening of the magnesium charge resulted from our forcefield, we construct a 25Åx25Åx25Å box of water with a magnesium charge fixed at the center. To neutralize the cell, we place two hydroxyl groups at least 12Å away from the magnesium cation at the center and fix them so they do not diffuse in the shell. To avoid structural diffusion, we fix two Zundel-like groups (O<sub>2</sub>H<sub>3</sub><sup>-</sup>). We run the simulation in NVT ensemble for 2 ns to allow the system to relax and the water shells around magnesium to have enough exchanges. We output the configurations every 500 steps with timestep of 0.25fs.

Then, we average the potential energy in a grid with 17x17x17 points in the X, Y and Z directions respectively that is centered on the position of magnesium ion. The results are shown in **Supplementary Fig. 1**. The two electrostatics contours that are shown in **Supplementary Fig. 1. a** and **Supplementary Fig. 1. b** are taken from a plane that passes through the magnesium atom in the X and Y directions, respectively. As can be seen in both of these two figures, the center has the highest electrostatics potential of about -134 eV. As we move away from the center, we reach

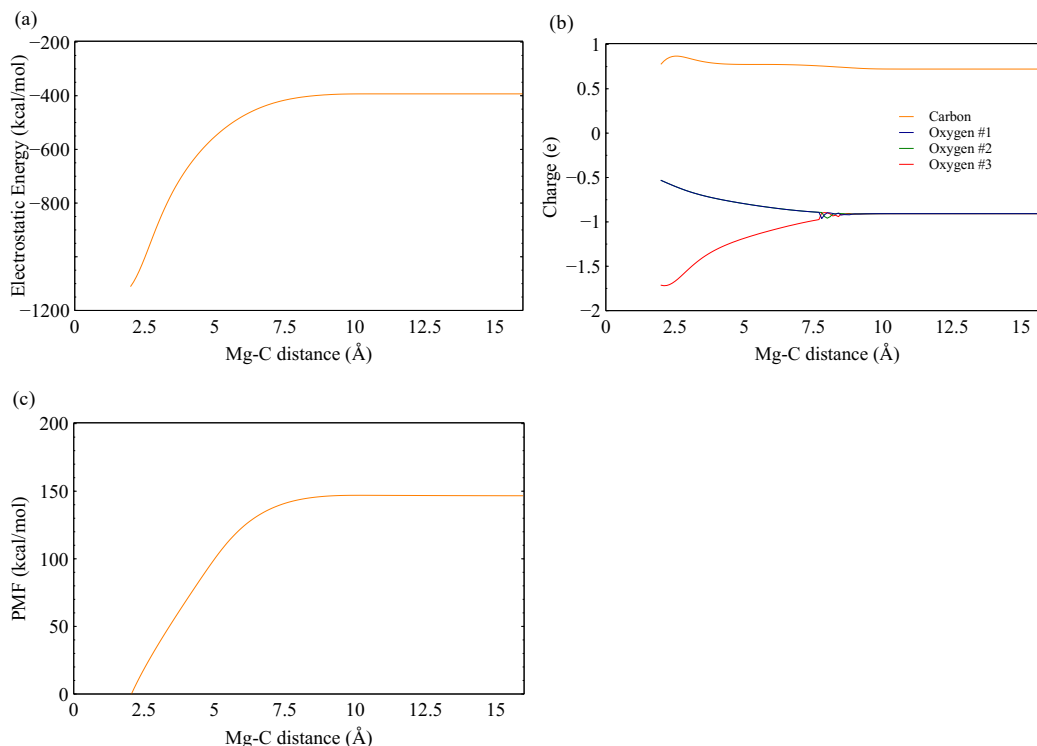


**Supplementary Figure 1.** The ReaxFF electrostatics potential in water centered around magnesium cation (a) Electrostatics at different distances between magnesium and carbonate. (b) Average charges of the carbonate group at different distances between magnesium and carbonate. (c) The potential-of-mean-force (PMF) based on the electrostatics between a magnesium atom and carbonate group.

to the first shell of water oxygens that are shown to have the lowest electrostatics potential on the grid. We of course expect this, since the water oxygen atoms have negative charge. If we move from the center for about 5 Å, we can see another dip in the potential that corresponds to the second shell of water oxygens.

The two minima described above could be better seen in the one-dimensional electrostatics plotted in **Supplementary Fig. 1. c**. Moving further away, the electrostatics potential is almost constant, see **Supplementary Fig. 1. c**. This shows that, although the charge of magnesium is fixed in our ReaxFF forcefield, the electrostatics potential is effectively screened in water in the range of 7 Å - 8 Å. We should note that, this screening is not only brought about from the charge transfer through water molecule, but also from the change of geometry in the hydrogen bond network across the liquid.

**Supplementary Note 2: Validation of the taper function for electrostatics:** To ensure that there is no discontinuity in the electrostatics potential between magnesium and other species, we perform two calculations: 1) The free energy based on the distance between magnesium and carbonate in vacuum. 2) The electrostatics potential between magnesium and carbonate at different distances. To do the free energy calculation, we construct an empty cubic box with dimensions 25 Å\*25 Å\*25 Å. Then, we place the magnesium and carbonate atom inside the box, and perform molecular dynamics in NVT ensemble using Langevin thermostat that relaxes the temperature over 50 fs. We also make the carbonate ion rigid to avoid unnecessary degrees of freedom, and turn off the vDW interactions between magnesium and the rest of the system. We change the distance between magnesium and carbonate in the range 2 Å-16 Å in 140 windows using the distance between the center of masses as the collective variable. The biased force constant of 5000 kcal/molÅ<sup>-2</sup> is chosen. After ensuring that the distribution of distances in all windows sufficiently overlap, we use the weighted histogram analysis method (WHAM) to calculate the free energy difference as shown in **Supplementary Fig. 2**. We also average the electrostatics potential in each window along with the species charges in **Supplementary Fig. 2**.



**Response Figure 2.** The electrostatics of the pairing of the magnesium-carbonate (a) Electrostatics at different distances between magnesium and carbonate. (b) Average charges of the carbonate group at different distances between magnesium and carbonate. (c) Potential of Mean Force (PMF) based on the electrostatics between magnesium and carbonate.

## Reference:

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