Supporting Information

Dehydration-induced Amorphous Phases of Calcium Carbonate: A Molecular Dynamics Study

Moumita Saharay[1,*], A. Ozgur Yazaydin[2], R. James Kirkpatrick[3]

[1] Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, USA

[2] Department of Chemical Engineering, University of Surrey, Guildford, GU2 7XH, United Kingdom

[3] College of Natural Science, Michigan State University, East Lansing, Michigan 48824, USA

*To whom correspondence should be addressed. E-mail: saharaym@msu.edu; Tel.: +1 (517) 355-9715 ext 336. Fax: +1 (517) 432-1054

Modeling of a second ACC with a $H_2O/CaCO_3$ ratio of 1.0 begun with a different initial configuration.

To test the convergence of our S1.0 model to an equilibrium structure, we undertook a second simulation of ACC with a $H_2O/CaCO_3$ ratio of 1.0 but with a very different starting configuration. The steps involved in generating this system (R1.0) were the following,

- A cluster consisting of one formula unit of $CaCO_3$ and one water molecule was gemetry optimized using the Gaussian03 [1] package with B3LYP exchange correlation.

- This optimized cluster was then repeated 1620 times in an orthorohmbic box of 65.0×55.4×73.0 $Å^3$ to have the similar composition to S1.0 (Supplementary Figure 1a)

- This system was then modeled with NPT molecular dynamics simulations at 300K for 2 ns. The snapshot of the equilibrated system shown in Supplementary Figure 1b visually illustrates the disordering of the system that occured during the simulation.

- The final equilibrium box dimension was 50.0×43.0×56.1 $Å^3$.

The Ca-O_C and Ca-Ca radial distribution functions shown in Supplementary Figure 2 demonstrate that the structures beginning from the Singer *et al.* [2] model (S1.0) and R1.0 are essentially identical.

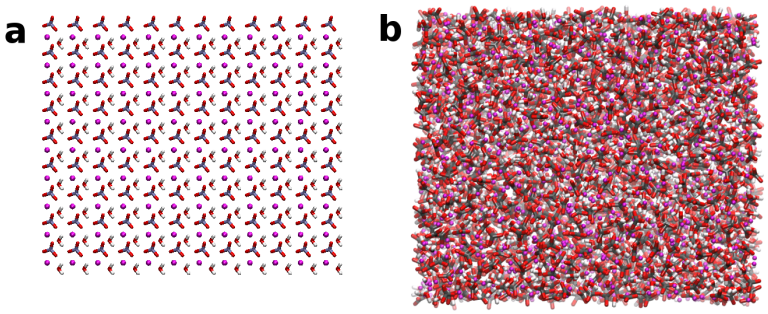

Figure S1: (a) Initial configuration of a simulation cell of ACC with $H_2O/CaCO_3$ =1.0. (b) Final amorphous structure of this configuration after 5ns of MD simulation. Color scheme: Oxygen in red, Carbon in gray, Calcium in magenta, Hydrogen in white.

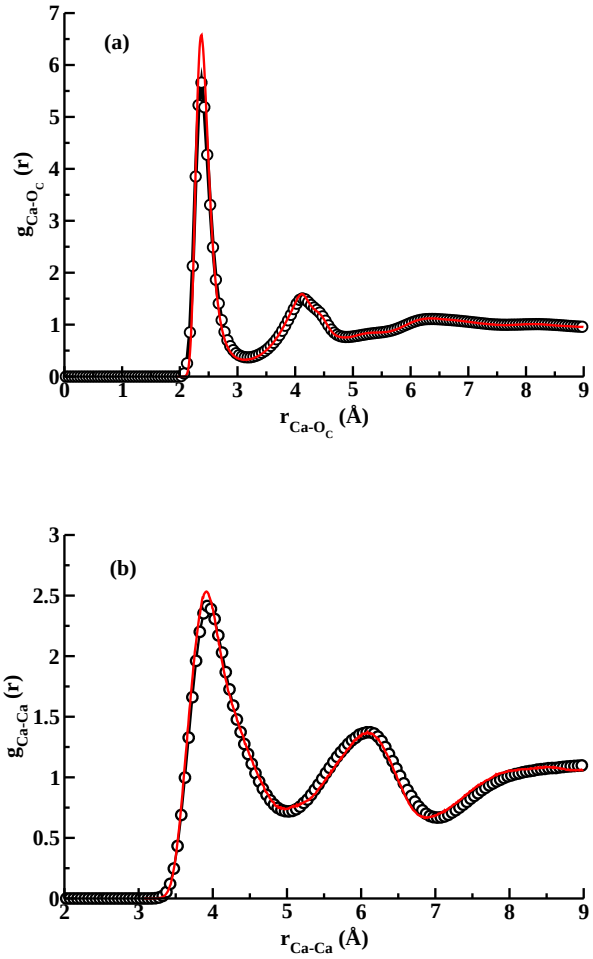

Figure S2: Intermolecular radial distribution functions between (a) Ca-O_C, and (b) Ca-Ca in R1.0 (black open circle), and S1.0 (red).

References

[1] Frisch, M. J. *et al.* Gaussian 03, Revision C.02. Gaussian, Inc., Wallingford, CT, 2004.

[2] Singer, J. W.; Yazaydin, A. O.; Kirkpatrick, R. J.; Bowers, G. Structure and Transformation of Amorphous Calcium Carbonate: a Solid-State ^{43}Ca NMR and Computational Molecular Dynamics Investigation. *Chem. Mater.* **2012**, *24*, 1828-1836.