Nucleation of crystalline $CaCO_3$ phases from amorphous calcium carbonate: Computational molecular dynamics modeling

MOUMITA SAHARAY,[1] AND R. JAMES KIRKPATRICK*[2]

[1]Department of Chemistry, Michigan State University, East Lansing, MI 48824 USA, saharaym@chemistry.msu.edu
[2]College of Natural Science, Michigan State University, East Lansing MI 8824, USA, rjkirk@msu.edu

Amorphous calcium carbonate (ACC) is a precursor to the crystalline $CaCO_3$ phases (vaterite, calcite, aragonite) in biogenic and inorganic processes, and its dehydration is thought to be an essential step in its transformation. Classical molecular dynamics simulation studies of the dehydration of hydrated ACC shows that although its average structure is not well described by the structures of any of the crystalline $CaCO_3$ phases, the local structural environments of those Ca^{2+} sites that are 6-coordinate by oxygen (as in all the crystalline phases) are quite similar to those in vaterite but not those in calcite or aragonite. Crystal-like volumes are present at all hydration levels, and the abundance of vaterite-like volumes is greater than for calcite- and aragonite-like volumes. The results, thus, suggest that nucleation of vaterite can occur by internal reorganization of ACC nano-particles, whereas calcite and aragonite are more likely to nucleate externally. This conclusion is consistent with the highly disordered structure of vaterite and suggests that the nucleation of other disordered oxysalt phases can occur in the same way. It is also consistent with experimental results that show the formation of ordered regions of colloidal particles by internal reorganization of amorphous clusters (Zhang and Liu, 2007). Our 3-dimensional analysis of the local structures around Ca^{2+} ions is done using a bond orientational order parameter that incorporates the distance-related angular orientation of the carbonate groups.

[1] Zhang, T.H., and Liu, X.Y., 2007, *J. Am. Chem. Soc.,* **129**, 13520