

## The Role of Water Molecules in Stabilizing Amorphous Calcium Carbonate: A Computer Simulation Study

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### Session 18b. Nucleation, Growth, and Dissolution in Aqueous Environments: Elementary Processes and Atomistic Models

Amorphous calcium carbonate (ACC) is a critical transient phase in the inorganic precipitation of  $\text{CaCO}_3$  and in bio- and biomimetic mineralization. Proteins known to be responsible for the biomineralization of, for instance, bird egg shells, bind to ACC nanoparticles and lower or remove the energy barrier to crystallization. The mechanisms of these processes are related to the structures of hydrous and anhydrous ACCs, but the details are poorly known. To advance fundamental molecular-level understanding of the bulk hydrous and anhydrous ACC, we studied these systems using both classical and quantum mechanical simulation methods. Car-Parrinello molecular dynamics (CPMD) simulations of calcium carbonate solvated in a bath of water molecules have been performed at a temperature of 300K to elucidate the microscopic structure, dynamics, and electronic properties of water molecules in the first two solvation shells of calcium carbonate. The reorientational dynamics of near-neighbor water molecules around  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  ions are investigated through first- and second-order time correlation functions, and are in good agreement with nuclear magnetic resonance experiments. The intramolecular vibrations of  $\text{CO}_3^{2-}$  ion have also been examined through an analysis of the velocity autocorrelation function of the atoms and are compared with that of isolated  $\text{CaCO}_3$  and existing vibrational spectra of calcium carbonate. In addition, classical molecular dynamics simulations of pre-nucleated ACC are carried out to understand the role of water molecules in stabilizing these clusters. Starting from a hydrous ACC model with a  $\text{CaCO}_3/\text{H}_2\text{O}$  ratio of 1/1, we gradually reduced the water concentration of the system to completely dehydrated ACC. Simulation results using the DL\_POLY software on the structure and dynamics of the constituent molecules due to drying will be presented.

### Acknowledgements

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[1] Goodwin, A. L.; Michel, F. M.; Phillips, B. L.; Keen, D. A.; Dove, M. T.; Reeder, R. J. (2010) *Chemistry of Materials* **22**, 3197.

## New U-Pb ages for gabbro sills within the Ramah Group, northern Labrador: implications for Paleoproterozoic extension in Nain craton, and metallogeny

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Archean gneisses of the North Atlantic craton (NAC) in northern Labrador are unconformably overlain by three principal Paleoproterozoic supracrustal remnants – the mostly clastic Snyder/Falls Brook Group, the dominantly volcanic Mugford Group, and, furthest north, the chiefly sedimentary Ramah Group.

Ramah Group is an ~1700m thick cover sequence of lowermost siliciclastic quartz sandstone capped by a distinct supratidal dolomite horizon, together defining a west-facing shallow shelf sequence, overlain by euxinic, pyritic shales and mudstones and pyrite-chert associations (Nullataktok Formation). Upwards, this unit passes through a mixture of carbonate debris flow breccias, and then into voluminous turbiditic sandstones. Sills of diabase or gabbro extensively intrude the upper sedimentary units. The sills typically exhibit chilled margins, and are clearly transgressive to their host sediments. Sills reach up to ~100 m in thickness, though many are only a few meters thick, in many places with preserved primary layering. The entire sequence of sedimentary rocks and sills was deformed and (locally) metamorphosed to amphibolite facies, as part of an east-verging fold-and thrust belt on the east margin of the 1.78 Ga Torngat Orogen. The depositional age of the Ramah Group has only been bracketed only between its late Archean (ca. 2.5 Ga), Nain craton-derived detrital zircons, and Torngat deformation.

We have dated both gabbroic and ultramafic compositional variants of Ramah sills, from samples collected from thick sheets intruding the Nullataktok Formation. ID-TIMS U-Pb baddeleyite analyses yield identical ages of emplacement at  $1888 \pm 5$  and  $1887 \pm 4$  Ma. These represent the first precise U-Pb dates for extension-related mafic magmatism of this age in the NAC in Labrador, and provide a new minimum age for the host Ramah Group sediments. Mafic magmatism of this age is unknown in the Greenland portion of the craton, but is well represented in the Circum-Superior belt, including the ca. 1883 Ma Molson dyke swarm and Fox River sill of Manitoba (Molson Igneous Events), the 1890-1870 Ma Raglan-Expo-Katiniq sills of the Cape Smith belt, Ungava, and the 1884-1874 Ma mafic-ultramafic magmatism of the Labrador Trough.

By analogy with contemporaneous Circum-Superior sediment-sill complexes (Thompson, Birchtree, Raglan-Expo), Ramah Group may have potential for magmatic Ni-Cu-PGE sulfide deposits.