Aragonite – calcite seas and the evolution of biocalcification

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The influence of aragonite-calcite sea conditions on the evolution of biocalcification remain poorly understood. While selection for the polymorph favored by the aragonite-calcite sea status is relatively strong for organisms that evolved shells for the first time [1], there is no statistically significant correlation between shifts in the aragonitic/calcitic proportions in calcareous skeletons through time and sea chemistry [2]. However, case studies suggest that changes in aragonite/calcite sea conditions can influence the mineralogy of individual calcifying lineages [3].

A particularly intriguing group in this context is trimerellids, the only known group of aragonitic brachiopods [4]. With shells up to 20cm wide, trimerellids were also the most prolific calcifiers amongst brachiopods of the Ordovician/Silurian calcite seas. The success of trimerellids as measured by their large shell size and cosmopolitan distribution in the Ordovician/Silurian palaeo-tropics suggests that the innovation of aragonite during a calcite sea interval was advantageous for this group.

This success is best explained by considering the role of temperature on $CaCO_3$ polymorph formation. While the switch between aragonite and calcite sea conditions is commonly attributed to the ratio of Mg/Ca or pCO_2 [5, 6], it is often ignored that Mg/Ca controls the formation of aragonite and calcite as a function of temperature [7], with warmer temperatures favoring aragonite. When combining the values of marine Mg/Ca through time [5] with the Mg/Ca – temperature curve that separates aragonite from calcite precipitation fields [7] it becomes apparent that aragonite was the favored polymorph in warm tropical surface waters even during calcite sea intervals (Fig. 1).

Based on the available data [5, 7], water temperatures above 25° C favored the formation of aragonite even during calcite sea intervals (Fig. 1). The conventional view of aragonite/calcite sea conditions as a globally homogenous model needs to be reconsidered in the light of latitudinal surface water temperature differences.
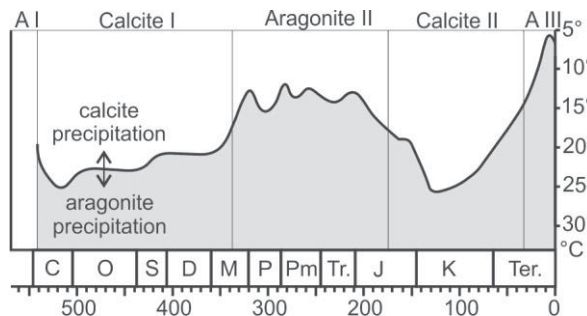

Figure 1: temperature separating the marine aragonite/calcite precipitation fields through time (from [4]; based on [5] and [7]).

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A transferable classical polarizable model for the water molecule

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The model

We developed a new model for the water molecule, which contains only three Gaussian charges. Using the gas-phase geometry, the dipole moment of the molecule matches, the quadrupole moment closely approximates the experimental values. Two positive charges are on the hydrogen atoms, while the negative charge is connected by a harmonic spring to its gas-phase position. This position is on the main axis of the molecule between the oxygen and the hydrogen atoms. The polarized state is established by the equality of the electrostatic forces and the spring force of the negative charge. In each time step the position of the massless negative charge is determined by iteration. Using the technique of Ewald summation, we derived expression for the energy, the forces, and the pressure for Gaussian charges. The dispersion interactions were fitted [1].

Tests of the new model

The model was tested and provided good results for the properties of gas-phase clusters up to 6 molecules, ambient water and hexagonal ice [1]. We calculated the properties of ice polymorphs under high pressure as well. In moderately dense phases the closest O-O distances are very close to the same distances in hexagonal ice. In compressed phases, however, the number of neighboring molecules in the second shell is larger than in hexagonal ice. To use a repulsion suitable for hexagonal ice gives low density for the compressed ice phases. We calculated the "compressing force" for each particle and connected a variable "size" to this force. With this approach we obtained agreement from water clusters to ice VII up to 25 GPa [2]. Relying on earlier studies, we devised a reasonable form for an electric field dependent polarizability of the molecules. At low fields the polarizability starts from the experimental gas-phase value towards a treshold at high fields. The decline of this function was determined by the calculated dielectric constant of ambient water [3]. The model was tested for liquid-vapor behavior. The surface structure of the model was analysed. Its surface tension provides superior estimates of the experimental value than nonpolarizable models [4]. The algorithm of the program code is given for the model. Due to different numerical speeding up methods, it is only 2.6 times slower than the code of the well-known TIP4P nonpolarizable model [5].

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