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# Energetics and kinetics of carbonate orientational ordering in vaterite calcium carbonate

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## ABSTRACT

Vaterite is a less stable anhydrous crystalline calcium carbonate than calcite or aragonite and, thus, a rare mineral in geologic settings. However, vaterite is commonly found in biological environments. The mechanisms of crystal nucleation, transformation, and stabilization of vaterite in host materials remain unresolved. Understanding these issues may lead to answer some fundamental questions such as carbonate formation in geological systems and the intriguing occurrence of vaterite in biological systems. This requires an accurate knowledge of the crystal structure of vaterite and its order-disorder transformation. This study employs molecular-dynamics simulations to understand the thermodynamic stability of vaterite and kinetics of the orientational ordering of the carbonate ions. The results show that the potential energy change from disordered to ordered vaterite is about –11 kJ/mol, which significantly changes the relative stabilities of vaterite with respect to other anhydrous calcium carbonate polymorphs, including amorphous calcium carbonate. The heat capacity of vaterite is estimated to be 102.1 ± 0.4 J/(K·mol), comparable to an experimental result of 91.5 ± 3.8 J/(K·mol). The molecular-dynamics simulations also show similar energies for vaterite with different stacking structures, suggesting possible stacking disordering along the [001] axis. Cyclic high-temperature simulated-annealing molecular-dynamics simulations show that the $CO_3$ orientational disorder-order transition is thermally activated. The calculated activation energy for the transition is 94 ± 10 kJ/mol with a pre-exponential factor of ~$1.6 \times 10^{13}$ $s^{-1}$. A good linear fit of the logarithmic transition rate to inverse temperature (the Arrhenius plot) indicates that the transition is controlled by a single activation process that is related to a cooperative rotational motion of $CO_3$ groups in vaterite.

**Keywords:** Molecular simulation, vaterite, ordering, energetics, kinetics, calcium carbonate