Controlled bio-inspired synthesis of composites: a close simulation of biomineralization process

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Many structural biomaterials, biopolymers as well as biominerals, derive their mechanical properties from a complex hierarchical fibrillar organization. An intriguing example is the Stomatopod Dactyl club that consists of an impact resistant calcium phosphate-chitin composite structure. The chitin matrix has a highly expanded helicoidal organization.

In nature, biominerals often grow at controlled reacting conditions, such certain pH value, temperature, concentrations of reactants and also reaction rate. However, most bio-inspired mineralization studies cannot control those parameters during the reaction.

In this study, we investigated self-assembly and reaction process of chitosan and calcium phosphate in water solution, control the reaction parameters, and obtain ordered composite structures in a controlled biomimetic way. In addition, we investigated the interaction rules between biopolymers and minerals during assembly and mineralization process on the molecular level, which will be very helpful for biomineralization research and biomaterials synthesis. A controlled reaction system assisted by a titration setup was built up. The assembly process of chitosan, the nucleation and growth of calcium phosphate, and the formation process of chitosan/calcium phosphate biocomposites were investigated by the cryo-transmission electron microscopy (cryoTEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) etc.

A theoretical approach of isotope fractionation mechanism for thermal diffusion processes

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Under thermal gradients, not only chemical compositions of a homogeneous system will be significantly changed between high temperature and low temperature ends, but also its isotopic compositions will be tremendously changed (e.g., Richter *et al*.. 2008, 2009; Huang *et al*.. 2010). However, the isotope fractionation mechanism of such thermal diffusion processes is still under debating. Dominguez *et al*.. (2011) used transition-state theory (TST) model to explain stable isotope fractionations in high-temperature silicate melts. They mainly considered the zero-point vibrational energy (ZPE) of diffusing species with different isotopes. Other kinetic energies were completely ignored even they are important under high temperatures. They also did not consider kinetic energies (ZPE, translational, rotational energies, etc.) for the activated complex at transition state. Their treatment resulted in an unusually large ZPE difference for different isotopologues, which was questioned by Lacks *et al*.. (2012a) for the unusually large wavenumber of a vibration. Lacks *et al*.. (2012b) proposed a new model based on Chapman-Enskog theory to treat the thermal diffusion processes and used a specially designed classical molecular dynamics (MD) method to treat temperature gradients. They concluded that the classical mechanical collisions maybe the essence reason of isotope fractionation, but not the quantum effect suggested by Dominguez *et al*.. (2011). They also found that heavier isotope systems (i.e. Fe, Ca, Mg) can be fractionated to larger extents than those of network formers but lighter isotope systems (i.e., Si, O). Until now, all theoretical studies are focused on high temperature conditions, there is no theoretical framework for systems with temperature gradients at low or medium temperatures.

Here, we propose a new theoretical model for dealing with isotope fractionation by thermal diffusion. We used a newly developed thermodynamic law which directly relates Soret coefficient to entropy (Duhr and Braun, 2006a; Duhr and Braun, 2006b). We have developed its counterpart for isotope fractionation treatment. By following this approach, we provide a unified equation for the calculation of isotope fractionation under thermal gradients for any temperature condition. Using high temperature silicate melts as examples, we test our equation and find out the relationship between isotope fractionation and temperature gradients.

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