American Mineralogist, Volume 101, pages 289–296, 2016

MINERALS IN THE HUMAN BODY

Growth dynamics of vaterite in relation to the physico-chemical properties of its precursor, amorphous calcium carbonate, in the $Ca\text{-}CO_3\text{-}PO_4$ system

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Abstract

Vaterite is one of three non-hydrate calcium carbonate crystalline polymorphs and is formed as an initial phase under pseudo-biological conditions. However, biological hard tissues that use vaterite are rare; the reason for vaterite rarely appearing in vivo is still unclear. There is consensus that, in phosphate-containing solutions, vaterite barely forms and amorphous calcium carbonate (ACC), the precursor of crystalline calcium carbonate and considered as aggregation of growth unit of vaterite, is stabilized. In this study, to clarify the biomineralization process, we investigated how phosphate acts as an inhibitor of vaterite growth. We measured vaterite growth rates in situ and estimated the essential crystal growth parameter, edge free energy, in the $Ca\text{-}CO_3\text{-}PO_4$ system in relation to the physico-chemical properties of ACC. The effects of PO_4 on the ACC structure and dynamics were also observed.

Co-existed PO_4 reduced the growth rate of vaterite even when it was added in μM-scale concentrations. The surface free energy of vaterite increased with increasing PO_4 concentration and was 10× higher in a 10 μM PO_4-containing solution than in a PO_4-free solution. Spectroscopic analyses showed that the chemical bonds in ACC particles were drastically changed by the addition of μM-scale PO_4, and the particles could no longer transform into vaterite. We conclude that PO_4 inhibits vaterite growth and changed the ACC structure. And the original growth units of vaterite were also modified to the other structures. Thus, vaterite crystals could not grow by association of these growth units, which resulted in an increase in the apparent surface free energy of vaterite.

Keywords: Vaterite, crystal growth, intermediate phase, biomineralization