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炭酸カルシウム表面/クラスターにおける2価陽イオンの安定性に関する理論的考察
Theoretical analysis on the stability of divalent cations in the surface sites and clusters of calcium carbonate

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Formation process of calcium carbonate polymorphs, calcite, aragonite and vaterite has been extensively investigated, and impurity effect has been proposed as controlling phenomena in order to account for the formation of a particular polymorph. For example, it has been reported that an addition of Mg^{2+} in a solution inhibits calcite formation and promotes aragonite formation, however incorporation mechanism of this kind of impurities is poorly understood.

In general, smaller divalent cations than Ca^{2+}, like Mg^{2+}, cannot form solid solution with aragonite. However, the structure of a crystal surface or small cluster forming at an initial stage of crystal growth can be different from the bulk crystal because of its flexibility, and it can act as the site for incorporation of ions which is unstable in the bulk structure. In the present study, the stability of divalent cations, especially Mg^{2+}, (1) on hydrated aragonite surface and (2) in the cluster forming in an early stage of nucleation was investigated by quantum-chemical calculations, and the impurity effects on the formation of polymorphs were discussed.

The calculation results show that Mg^{2+} is easier to be incorporated into a small cluster, while the hydration energy of Mg^{2+} is higher than that of other divalent cations. This indicates that Mg^{2+} is difficult to be released from hydration shell, however, once released, it is easy to incorporate into the cluster. Atomic arrangement of these clusters including Mg^{2+} is different from that of additive-free $CaCO_3$ clusters. Furthermore, Mg^{2+} on the aragonite surface considerably affects the surface structure and has an influence on the stability of aragonite. Thus, incorporation of Mg^{2+} into the clusters and surfaces sites should play an important role on the formation of the crystalline nuclei and the consequent crystal growth.

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