

Surface structures, stabilities, and growth of magnesian calcites: A computational investigation from the perspective of dolomite formation

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ABSTRACT

Atomistic computer modeling methods are used to investigate the surface structures and stabilities of magnesite MgCO_3 and dolomite $\text{MgCa}(\text{CO}_3)_2$ in comparison with calcite, CaCO_3 . The surfaces are generally more stable than magnesite, but less so than calcite. Upon hydration, the magnesite $\{10\bar{1}4\}$ surface becomes more stable than either calcite or dolomite, due to the less favorable interactions between dolomite surface ions and adsorbing water molecules. The high affinity of the surface magnesium ions for adsorbing water molecules, shown by the large average hydration energy over all surfaces for magnesite (134 kJ/mol), is negated in the case of dolomite by the inaccessibility of the surface magnesium ions, due to surface relaxations and rotation of the carbonate groups. In addition, the larger lattice spacing of dolomite compared to magnesite disrupts the extensive network of hydrogen bonding between the adsorbed water molecules that are present on the latter, leading to similar average hydration energies for calcite, dolomite, and magnesian calcite surfaces (80–101 kJ/mol). Not only are the dolomite planes under aqueous conditions less stable than their calcite counterparts, dolomite-like surfaces of disordered magnesian calcites are calculated to be more stable than either pure calcite or dolomite surfaces. Extensive molecular dynamics simulations of the growth of CaCO_3 and MgCO_3 at two experimentally observed calcite steps show that, on thermodynamic grounds, Mg is easily incorporated into a growing calcite crystal, but will then inhibit incorporation of further Ca. Furthermore, although the calculations suggest a small energetic advantage (~ 10 kJ/mol) to ordering of the Ca and Mg ions on the obtuse growth step, a disordered arrangement is favored at the acute growth step and incorporation of Mg is always energetically more favorable than Ca, in accord with the occurrence of highly magnesian calcites in nature.