

Trace metal speciation in aragonite : A first principles density functional theory study

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Trace metals incorporated in biogenic aragonite are widely used to infer the past environmental variables such as temperature and redox conditions. Speciation of some divalent cations in biogenic aragonite, however, remains yet to be determined mainly because synthetic analogues are unavailable to experimentally analyze. We report the structural, thermodynamic, and electronic properties of Mn²⁺-doped aragonite examined by application of the first-principles density functional theory (DFT). In aragonite lattice, Ca²⁺ is in the 9-fold coordination but we found that Mn²⁺ can adopt 5-, 6-, 7- and 9-fold coordination. While the 5-fold Mn²⁺ is a dominant species, the Boltzmann-averaged coordination number (CN) is close to six. The solubility products (K_{sp}) of Mn²⁺-doped aragonite decreased as the CN decreases. We calculated the Mn K-edge emission spectra for each coordination with inclusion of 1s core-hole in its pseudopotential. Our Boltzmann-averaged spectra of Mn²⁺-doped aragonite are consistent with the experimental spectra of biogenic aragonite. These results indicate that Mn²⁺ in biogenic aragonite can exist within the aragonite lattice as mixed species. We also report the K_{sp} and Mg K-edge absorption spectra of Mg²⁺-doped aragonite. These results can guide experimental characterization of trace-metal speciation in biogenic aragonite.