

Interfacial Energy Evolution of Heterogeneous CaCO₃ Nucleation in the Presence of Sulfate

YAGUANG ZHU AND YOUNG-SHIN JUN

Washington University in St. Louis

Presenting Author: ysjun@wustl.edu

A better understanding of the effects of sulfate on the formation of calcium carbonate (CaCO₃) is essential to enhancing carbon dioxide removal (CDR) via metal carbonation and to understanding the formation mechanisms of biominerals. As an environmentally abundant anion, sulfate can affect the formation of CaCO₃ and control its morphologies and properties. However, it has been experimentally challenging to elucidate CaCO₃ formation in its explicit first step: nucleation. Here, to observe the heterogeneous formation of CaCO₃, we utilized synchrotron-based *in situ* grazing incidence X-ray techniques and examined a series of processes (*i.e.*, nucleation, growth, and Ostwald ripening) in CaCO₃ formation in the presence of sulfate (Zhu et al., 2022; Zhu et al., 2021). The results showed that sulfate incorporation into CaCO₃ nuclei resulted in a nearly 90% decrease in the CaCO₃ nucleation rate and inhibited phase transformation from vaterite to calcite. Quantitatively, sulfate concentrations showed a non-linear relationship with the effective interfacial energies of CaCO₃. Furthermore, in the nucleation process, in the presence of sulfate, the revised interfacial energy and bulk energy cooperatively increased the nucleation barrier, decreasing nucleation rates. In the growth process, sulfate ions reduced the electrostatic repulsion in the experimental systems, facilitating CaCO₃ growth. Moreover, sulfate adsorption on newly formed CaCO₃ nanoparticles inactivated the CaCO₃ surface, inhibiting Ostwald ripening. The findings of this study can be readily extended to studies of other impurities in metal carbonation systems that seek to obtain quantitative relationships between additive concentrations and CaCO₃ interfacial energies. The improved understanding will critically advance our ability to predict controlled metal carbonation in CDR and natural and engineered environmental systems.

References

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