

## Comparative study on the inhibiting effects of rare earth elements on the dissolution of calcium carbonate polymorphs

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### Introduction

Precipitation and dissolution of calcium carbonate are fundamental processes for understanding of the global cycling of carbon on the earth. There were numerous reports about the nucleation and growth of calcite. However, systematic study on the dissolution of calcium carbonate was limited. Particularly, the dissolution of calcium carbonate seems to be a key process to understand supersaturation state for calcium carbonate in the ocean. Calcium carbonate has three polymorphs; calcite, aragonite and vaterite in order of the thermodynamic stability at atmospheric pressure and temperature. In this study, we report a comparison of reactivity for rare earth elements among the polymorphs at the dissolution for calcium carbonate.

### Experimental

Single crystals of calcite were cleavage fragments of mineral species from Brazil and those of aragonite were fragments from Fukuoka, Japan. Analytical-grade chemical reagent (Wako) was also used for a powder sample of calcite. Pure vaterite powder was synthesized from the mixture of 15mM sodium hydrogen carbonate and 15mM calcium chloride solutions. Excess amount of calcium carbonate exceeding the solubility was added into milli-Q water or 5microM lanthanum chloride solution in PFA vessel at 30 degrees with stirring. Increase of pH with release of hydroxide ion was observed using a pH meter. The single-crystal experiments were performed in a closed vessel not to introduce atmospheric carbon dioxide into the reaction solution.

In-situ observation of the dissolution process for calcite was carried out with an atomic force microscope (AFM) in order to observe surface processes of the dissolution on a monoatomic scale. AFM images of 1 micrometer x 1 micrometer area were observed with a contact mode and a scanning frequency of 3Hz. AFM observation was carried out for a single crystal of calcite which was placed on the center of a fluid cell, followed by filling with milli-Q water, to which the additive lanthanum ion was dropped.

### Results

The addition of lanthanum ion (5microM) caused decrease of dissolution rate as compared with lanthanum-free water. This phenomena was commonly observed for calcites of single crystal and powder. However, the decrease of dissolution rate was not observed for aragonite and vaterite of powder crystal. The addition of lanthanum ion with higher concentration (500microM) caused decrease of dissolution rate of aragonite like the observation for calcite. In-situ AFM images of calcite showed micro-precipitates on the step site of surface crystal with lanthanum ion, and the step immigration was not observed in contrast to the lanthanum-free case. Therefore, these results suggest that the inhibition of dissolution for calcite was caused by the precipitates covering the step site, where crystal dissolution occurs actively in case of absence of lanthanum ion.

According to our chemical equilibrium calculation, lanthanum carbonate is most likely to precipitate at the step site. However, lanthanum carbonate is also likely to appear at the dissolution process of aragonite with lanthanum ion of 5microM for the calculation. It is suggested that the difference of surface reactivity with rare earth element exists among three polymorphs of calcium carbonate.