

# Sorption of trace metals on synthetic calcite

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## 1. INTRODUCTION

Calcite, CaCO<sub>3</sub>, is one of the most abundant carbonate minerals in nature and its significance in controlling the concentrations of dissolved trace metal ions and their mobility in natural systems have been noted by many researchers (Zachara et al., 1991; Davis et al., 1987; Zhong and Mucci, 1995).

Until relatively lately, sorption processes at solid-water interfaces were studied mostly by macroscopic methods, such as the measurement of adsorbate uptake and adsorbent surface charge as functions of solution pH, dissolved species concentration, complexing ligand concentration, and ionic strength (Schindler and Stumm, 1987; Zachara et al., 1991). However, most of experimental sorption and coprecipitation studies have been carried without taking into account the crystal surface structure factors (Davis et al., 1987; Zachara et al., 1991; Comans and Middelburg, 1987).

The present study aims to examine the effect of surface morphology on the trace metals partitioning behavior on synthetic calcite surface. The growing of micro-calcite crystals by spontaneous nucleation method was adopted. The partitioning behavior of common trace metals such as Sr<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, and Mg<sup>2+</sup> on three different types of synthetic micro-calcite crystals has been examined by sorption experiment.

## 2. EXPERIMENTAL METHODS

### Micro-calcite growth by spontaneous nucleation

Powder sized (< 10 $\mu$ m) pure micro-calcite crystals were prepared from spontaneous nucleation method. The 0.02M, 0.2M and 0.4M CaCl<sub>2</sub>·2H<sub>2</sub>O supersaturated solutions were prepared in 1000ml beakers with corresponding NH<sub>4</sub>Cl concentrations. The concentrated solution of ammonium carbonate was added to each reaction vessel to yield desired final compositions. As soon as the ammonium carbonate solution was introduced into the reaction vessel, it starts to nucleate powder sized calcite crystals almost instantaneously. This reaction lasts few minutes. After 5 to 10 minutes, the whole system was well cleaned, and the powder-sized calcite crystals were centrifuged for further adsorption experiments.

### Adsorption experiments of Sr<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, and Mg<sup>2+</sup> on pure calcite

The adsorption experiments were conducted for powder-sized pure calcite crystals. The adsorption behaviors of Sr<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, and Mg<sup>2+</sup> on synthetic calcite were measured for each type of calcite in the 10<sup>-8</sup>M metal concentrations at fixed pH conditions without any supporting electrolyte. The calcite crystals grown from spontaneous nucleation method were fairly uniform in size (> 10 $\mu$ m), and they were directly used for sorption experiment.

The adsorption experiments were performed in the acid-cleaned 20ml polypropylene bottles. The solution mass was recorded gravimetrically and the weighed synthetic calcite crystals were then added to the reaction vessel for separate measurements. After the calcite suspensions were prepared in each experiment, the exact volume of known concentration of mixed or separate metal chloride stock solutions of Sr<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, and Mg<sup>2+</sup> (~ 10<sup>-8</sup> M) were added to the suspension. The metal concentration of the solution was kept well below the saturation with respect to any of metal carbonate minerals. After the calcite suspensions were again prepared, then they were gently shaken for 2 hrs and tightly closed to

prevent it from reacting with the atmospheric CO<sub>2</sub>. Total of 20ml suspensions were filtered at each sampling time and the metal ion concentrations of filtrate were analyzed using ICP-AES (JY 138 Ultrace) at the Korea Basic Science Institute.

#### **Characterization of Synthetic CaCO<sub>3</sub> Crystals**

Calcite crystals were characterized by XRD and SEM observations and the surface area was measured by BET method using Quantachrome Monosorb MS-18 at the Mineralogical Lab. of Department of Geological Sciences, Seoul National University.

### **3. RESULTS AND DISCUSSION**

#### **Pure calcite crystal**

Three different micro-calcite crystals which were prepared from supersaturated solutions with 0.02, 0.2, and 0.4M CaCl<sub>2</sub>·2H<sub>2</sub>O, respectively, are designated as a-, b-, and c-type calcite, respectively. The prepared micro-calcite crystal show characteristic surface morphology (as the calcite crystals grown from free-drift method) and have almost same size of ~10μm in diameter (Fig. 1). It is interesting that they have almost uniform in crystal size for all three type of micro-calcite. The calcite grown from the lowest Ca<sup>2+</sup> solution concentration (0.02M) exhibits single crystals with distinct rhombohedral cleavage. On the contrary, the calcite crystals grown from moderate (0.2M) to high supersaturation (0.4M) exhibit twin crystals or small crystal aggregates under SEM as in the crystals prepared from free-drift method. Growth surfaces of the b- and c-type micro-calcite are generally more complicated and have many overlapped small and short terraces of a few μm in width. The measured surface area of the a-, b-, and c-type micro-calcite are 1.0306, 1.5695, and 0.9244 m<sup>2</sup>/g, respectively.

Calcite crystals characterized by XRD show no indication of aragonite and other form of CaCO<sub>3</sub> polymorphs such as vaterite.

#### **Adsorption of Sr<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, and Mg<sup>2+</sup> on calcite**

The sorption experiments were conducted for the powder-sized micro-calcite crystals and the results are shown in Figures 2 and 3.

The rate of Me<sup>2+</sup> sorption on calcite in this study varies considerably with time. The rapid uptake in the initial stage decreased progressively with time until after approximately 100hrs. About 20 to 40% of the Mn<sup>2+</sup> in solution was sorbed within the first 1 hr, and 30 to 60% after roughly 24hrs. About 10 to 30% of the Co<sup>2+</sup> was sorbed within the first 1hr and 20 to 40% after 24hrs.

The sorptions of trace metal ions on three types of micro-calcite crystals show different behaviors to one another. According to the calculated moles of sorbed Me<sup>2+</sup>/m<sup>2</sup> the highest partitioning of Mn<sup>2+</sup> and Co<sup>2+</sup> is observed on the c-type micro-calcite, the second highest partitioning on the b-type micro-calcite, and the lowest surface partitioning on the a-type micro-calcite .

The sorption behaviors of trace metal ions on these three different synthetic micro-calcites clearly show that the metal ion sorption is controlled by the crystal surface properties. The partitioning affinity of trace metals on the a-, b-, and c-type micro-calcite crystals varies in the order; Mn<sup>2+</sup> > Co<sup>2+</sup> > Sr<sup>2+</sup> > Mg<sup>2+</sup> for same sorption reaction time.

### **4. CONCLUSION**

The partitioning behaviors of trace metal ions such as Sr<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, and Mg<sup>2+</sup> on calcites have been examined for three types of synthetic micro-calcite crystals prepared by the spontaneous nucleation method.

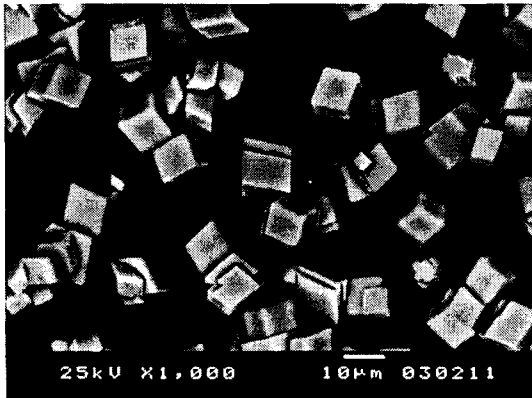
The sorption experiments show that calcites show characteristic preferred sorption affinities for trace metal ions. The partitioning affinity of trace metals on the a-, b-, and c-type micro-calcite crystals is in the orders; Mn<sup>2+</sup> > Co<sup>2+</sup> > Sr<sup>2+</sup> > Mg<sup>2+</sup>. The sorption behaviors of three types of micro-calcite show that the

metal ions on calcite surface is controlled by crystal surface properties. The sorption experiments of metal ions on calcite crystals show that sorption behavior on the rhombohedral cleavage is different from that on the many twinned and complicated surface morphology.

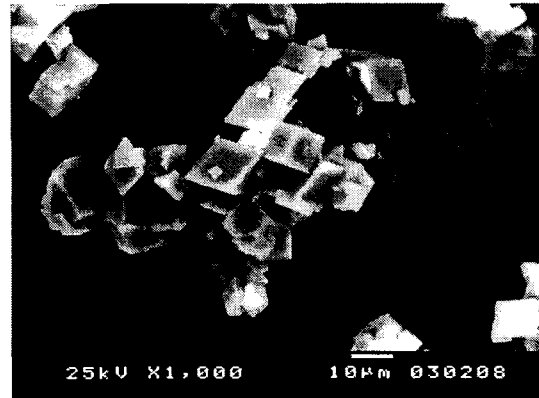
Although the simplest way to explaining the preferred adsorption behavior is the ionic size, we observed many exceptions during this study and from others. Thus, the detailed study with different experimental settings for adsorption experiments with trace metal ions might require in near future.

## 5. REFERENCE

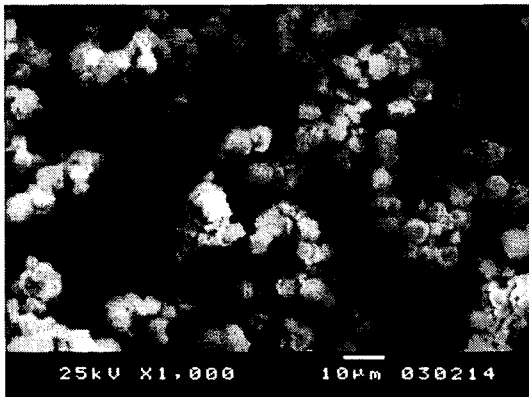
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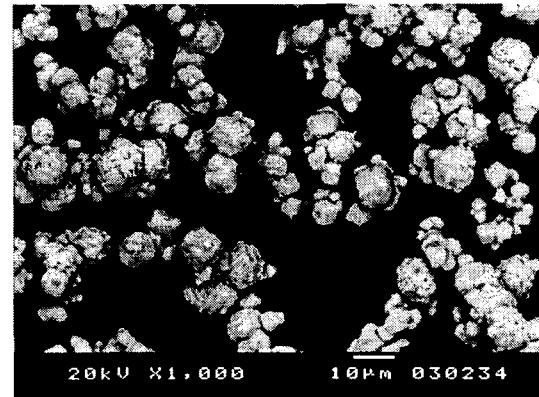
(1) a-type micro-calcite



(2) JT-Bakers calcite



(3) b-type micro-calcite



(4) c-type micro-calcite

Figure 1. SEM photographs of micro-calcite crystals grown by spontaneous nucleation method. (1) a-type calcite from 0.02M  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , (2) J.T. Baker, reagent grade calcite Lot# 1294-01, (3) b-type calcite from 0.2M  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , and (4) c-type calcite from 0.4M  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , and.

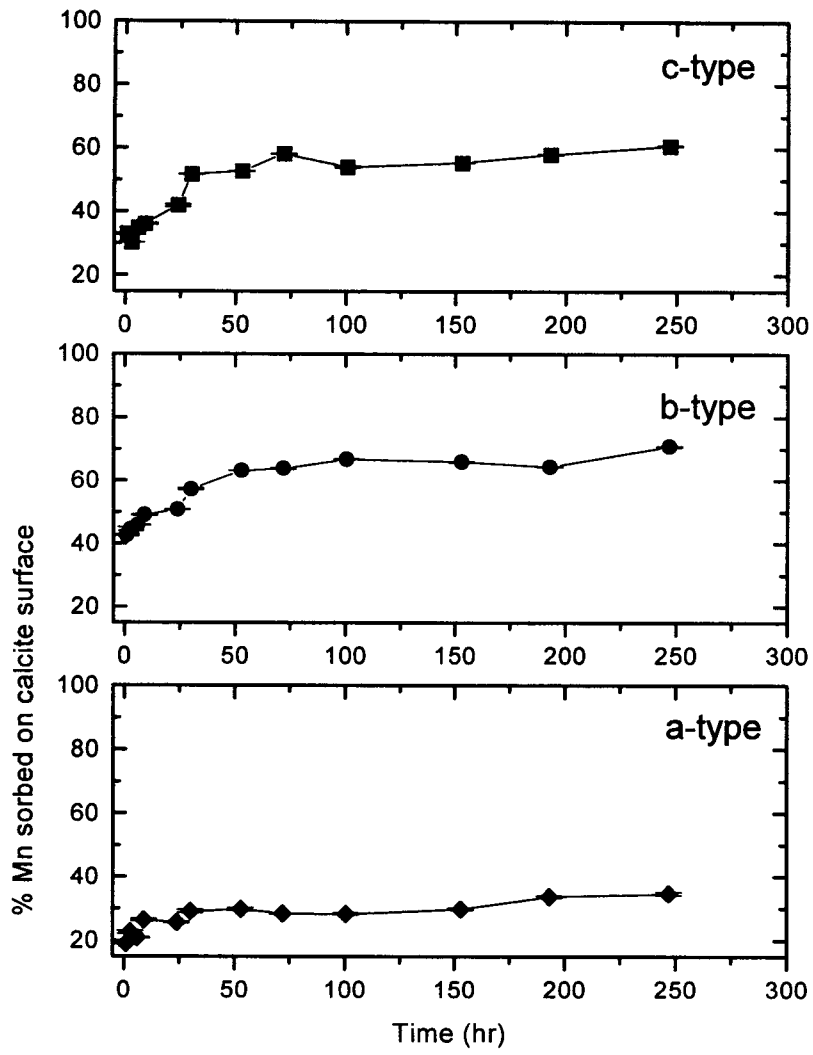


Figure 2. Sorption of  $Mn^{2+}$  on micro-calcites.

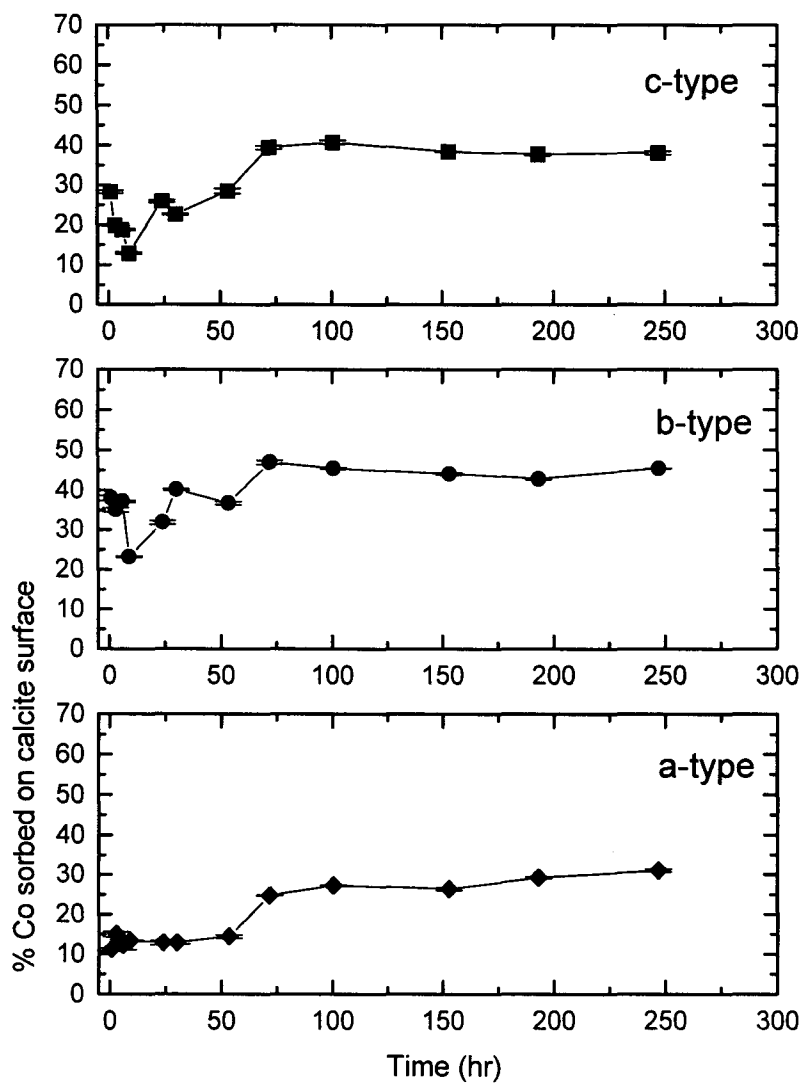


Figure 3. Figure 2. Sorption of  $\text{Co}^{2+}$  on micro-calcites.