The effect of lanthanum ion on calcite surfaces during dissolution and growth

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Growth and dissolution kinetics of calcium carbonate is one of the central issues of geochemisty involving global carbon cycle, biomineralization, etc. Various trace elements are known to inhibit the kinetics. Recently, it was reported that a trace amount of La (5 μM) induces the stabilization of vaterite, which is the metastable phase of calcium carbonate, in a super saturated solution (Tsuno et al., 2001). The present study is aimed to clarify the effect of lanthanum ion on the dissolution and growth of calcite.

Dissolution rates of calcite and vaterite were investigated by monitoring the increase of pH in the solution using a fluorescence reagent (SNARF-1). This instrument can monitor the kinetics of disolution with a time resolution of 3 msec. As a result, considerable inhibition was observed on calcite in 1 μM $LaCl_3$ solution. By contrast, no inhibition was observed on vaterite.

In situ AFM images of a cleaved surface calcite were observed during dissolution and growth in lanthanum-doped(5 μM) water. Micro-precipitates were observed at the step site of calcite surface. No propagation of steps was observed where the micro-precipitates appeared, whereas the generation and enlargement of etch pits. These results suggest that the micro-precipitates covering the step site cause the inhibition of dissolution for calcite.

On the growth of calcite, step propagations were observed on the super saturated solution (the saturation state is equal to 0.4) before the addition of lanthanum ion. In contrast, the step propagations or reduction in size of etch pits were totally inhibited (see Fig. 1) after the addition of 5 μM lanthanum chloride solution. Lanthanum ion inhibits both growth and dissolution of calcite.

Growth of calcite under the presence of lanthanum ion in various conditions of supersaturated solution will be discussed in detail in the presentation.

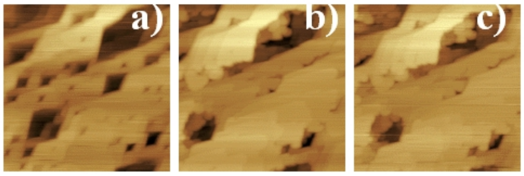

Figure 1: In-situ AFM image of a cleaved surface of calcite taken under the 5 μM lanthanum-doped supersaturate solution (Ω=0.4): (a) immediately after the addition of the lanthanum chloride, (b) 40 minutes later. (c) 160 minutes later. Figure size is 1μm x 1μm.

Distribution of U series nuclides and its implication for U migration in sedimentary rocks in Kanamaru, Japan

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The Kanamaru area is located near the boundary of Yamagata and Niigata Prefectures, and highly radioactive anomalies were discovered in this area half a century ago. In this study, the state of U migration is investigated through the Tertiary sedimentary rocks unconformably overlying the Cretaceous granites. A zone of the radioactive anomalies is recognized at the lower portion of the sedimentary rocks, mainly composed of the arkosic sandstones and conglomerates. The samples were taken downwards from the top of the anomaly zone to the bottom and ^{238}U, ^{234}U, ^{230}Th, ^{214}Pb and ^{210}Pb were determined by using gamma and alpha spectrometers.

The vertical distributions of uranium series nuclides showed two typical peaks; one is at 3.15m below the top and another at 6.3m. The activity of ^{214}Pb (^{226}Ra) at 3.15m is larger than at 6.3m although those of ^{238}U and ^{234}U are larger at 6.3m than at 3.15m. The activity of ^{230}Th at 3.15m is found to be very high comparing with other nuclides. The activity ratios of $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ are plotted in Fig.1. Most of the samples taken from the lower part of the anomaly zone are located around unity, while those of the samples from around 3m below the top largely deviated.

From these results, U is considered to be accumulated in the Tertiary sedimentary rocks and to form a anomaly zone, more than 1 M years ago. It seems that U around 3m below the top of the zone has been suffered both elution and accumulation within 0.3M years at least. X-ray diffraction analysis revealed the presence of chlorite at the U concentrated parts. It is suggested that the chlorite might play the role of U accumulation in this area.

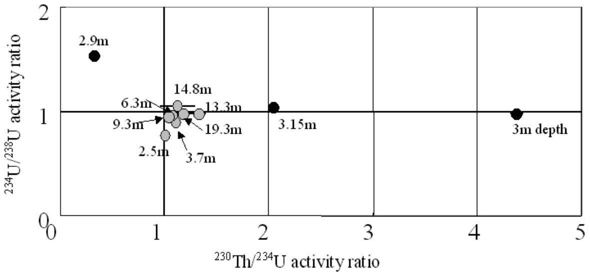

Fig.1 Diagram for $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ activity ratios