# Spontaneously Induced Reduction of Trivalent Ytterbium in Synthesized Crystal of Calcite

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XANES spectra showed the occurrence of divalent ytterbium in the synthetic calcite ($CaCO_3$). Approximately 15% ytterbium ion existed as divalent in calcite, although ytterbium ion was trivalent in the starting solutions.

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Trace amount of rare earth elements (REEs) induces significant effects on the crystal growth and dissolution of calcium carbonate. The substantial increase in the solubility of $CaCO_3$, the stabilization of the vaterite (labile phase of $CaCO_3$) and the inhibition of calcite growth were caused by the addition of trace amount of lanthanum into the aqueous system.[1–4] Furthermore, enrichment of REEs into calcium carbonate was shown by several studies.[5,6] It was unclear that the uptake mechanism and chemical state of REEs incorporated into calcium carbonate. X-ray absorption fine structure (XAFS) is practically the only method for the structural characterization of trace elements in the solid materials.[7] XAFS in a fluorescence mode offers the advantage of element-discrimination and potentially high sensitivity to trace elements. In the present work, we investigated the chemical species of ytterbium incorporated in calcite using X-ray absorption near edge structure (XANES) technique.

Yb-doped calcium carbonate was prepared from a mixture of calcium chloride and sodium hydrogen carbonate solutions (30 mmol kg$^{-1}$, respectively) containing a given amount (5 µmol kg$^{-1}$) of ytterbium chloride. In general, $Yb^{2+}$ can be formed by electronic reduction, but it is extremely unstable and readily oxidized to $Yb^{3+}$ by water in aqueous medium.[8] Thermodynamic calculation indicates that $[Yb^{2+}]/[Yb^{3+}]$ ratio in the starting solution is smaller than $10^{-31}$.[9] The experiments were conducted in a closed system in a surface-silanized glass vessel at 30 °C. The pH of solution changed from 7.8 at the beginning of reaction to 6.4 at the end of reaction. After standing for 1 day, the precipitate was filtered with a membrane filter with a pore size of 0.45 µm (Millipore® HAWP 024 00), rinsed with milli-Q water and dried at 110 °C. Powder X-ray diffraction pattern indicated that the sample obtained was composed of calcite exclusively. The concentrations of ytterbium in the precipitates were determined by an inductively coupled plasma atomic emission spectrometer (ICPS-7000, Shimadzu Inc.). $Yb(OH)_3$, $NaYb(CO_3)_2\cdot n(H_2O)$, $Yb_2O_3$, $Yb_2(CO_3)_3\cdot n(H_2O)$ and 5 mmol kg$^{-1}$ $YbCl_3$ solution were used as standard materials of XANES measurements.

The XANES spectra were collected in the fluorescence mode at the beamline BL12C of the Photon Factory, High Energy Accelerator Research Organization (KEK-PF) in Tsukuba, Japan.[10] A Si(111) double-crystal monochromator was used and the beam was smaller than 1 square mm. The Yb $L_{III}$ (8947 eV) absorptions of samples were measured by the fluorescence yield (Yb L$\alpha$1: 7415.6 eV) using a 19 elements pure Ge solid-state detector with energy resolution sufficient to separate Yb signals from Compton scattering and fluorescence of other elements.[11,12] The energy region around Yb fluorescence was selected by single-channel analyzers (SCA). The monochromator was calibrated at 8947 eV (Yb $L_{III}$ absorption edge) using ytterbium oxide powder. XANES spectra of solid samples were measured at approximately 20 K. The incident X-ray intensity ($I_0$) was monitored by an ion chamber which was filled with nitrogen gas. The X-ray absorption ($\mu$) is expressed as $\mu = I_f/I_0$, where $I_f$ is the intensity of fluorescence X-ray and $\mu$ is plotted against incident X-ray energy. Multiple scans (typically 3–5 times) were carried out and then averaged for each sample.

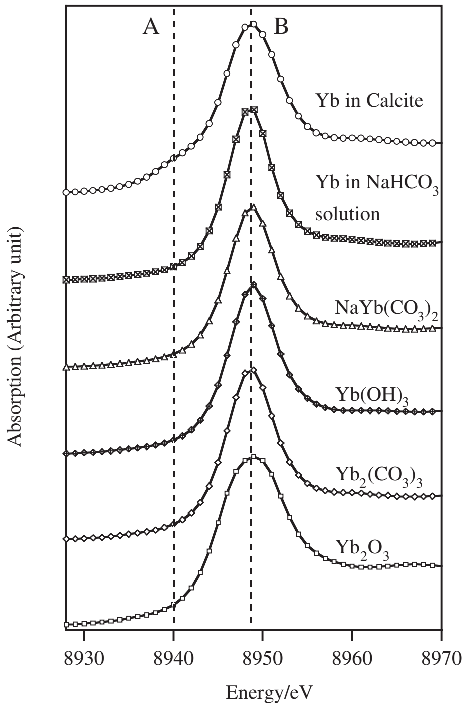

**Figure 1.** Yb $L_{III}$ edge normarized XANES spectra of Yb-bearing in synthesized calcite and Yb of various standard materials, $Yb_2O_3$, $Yb_2(CO_3)_3$, $Yb(OH)_3$, $NaYb(CO_3)_3$ and Yb (5 mmol kg$^{-1}$) in $NaHCO_3$ (15 mmol kg$^{-1}$)-NaCl (45 mmol kg$^{-1}$) solution.

The XANES spectra were analyzed with a PC program (REX2000, Rigaku Co.).

The concentrations of Yb in the synthesized calcite samples were about $1.1 \times 10^{-3}$ in Yb/Ca molar ratio. Figure 1 shows the Yb $L_{III}$ XANES spectra of the calcite and Yb-bearing standard materials. Every spectrum had a significant white line around 8948 eV (see Figure 1, the dotted line B), which was assigned to electron transition 2p → 5d6s of $Yb^{3+}$.[13,14] The XANES spectra of Yb in calcite shows a discernible shoulder in the lower energy side of the main white line (around 8940 eV, dotted line A, in Figure 1). We attempted to fit the main peak at 8948 eV and the shoulder by a couple of a Lorentzian function for white line and an arctangent function for continuum absorption, respectively. Fitted variables were peak position, peak height and FWHM of Lorentzian curve, and an offset from the position of Lorentzian curve and height of arctangent curve. The initial conditions of peak position were set at 8948 eV for the main peak and at 8940 eV for the shoulder, respectively. Figure 2 shows the deconvoluted XANES spectrum of Yb in calcite. A small peak (Peak A in Figure 2) was resolved from the spectra of calcite. Resultant peak position, peak height and FWHM of Lorentzian curve for Peak A are 8940.2 eV, 0.14 a.u. (arbitrary unit) and 6.1 eV, and those for Peak B are 8948.6 eV, 0.88 a.u. and 6.1 eV. The position of Peak A was in lower energy by 8 eV than that of Peak B and is close to that of the absorption of $Yb^{2+}$.[13–16] Thus, we attributed peak A to $Yb^{2+}$. We duplicated the synthesis and measurements, and the relative intensity of Peak A was reproduced. These results indicate that significant proportion of ytterbium existed as divalent ions in the calcite structure. Tanaka et al. (1993) suggested that the ratio of areas of peak A and B indicates directly the relative amounts of $Yb^{2+}$ and $Yb^{3+}$.[14] Based on the report, we calculated that the 14–17% of Yb exist as $Yb^{2+}$ in calcite. In the starting solutions and Yb-doped sodium hydrogen carbonate solution, trivalent ytterbium was predominant and divalent ion was negligible ($[Yb^{2+}]/[Yb^{3+}] = <10^{-31}$, and also see Fig. 1). This suggests that a part of Yb was reduced at some stage of calcium carbonate formation. In general, $Yb^{3+}$ substitutes in the six-fold coordination for the $Ca^{2+}$ site in calcite.[17] The ionic radii of $Ca^{2+}$, $Yb^{3+}$ and $Yb^{2+}$ in the sixfold coordination are 100, 86.8 and 102 pm, respectively.[18] The ionic radius of $Yb^{2+}$ is quite close to that of $Ca^{2+}$. It is expected that $Yb^{2+}$ can substitute at the calcium site of calcite with higher stability (affinity) than $Yb^{3+}$ without significant mismatches in ionic radius as well as the ionic valence. To explain the occurrence of $Yb^{2+}$ in the crystal, there could be three possible reduction stages: 1) reduction of $Yb^{3+}$ to $Yb^{2+}$ in the solution followed by selective uptake of $Yb^{2+}$; 2) reduction at the interface during the crystal growth; 3) reduction after the incorporation in the crystal or in the course of the aging of the crystal. The first possibility can be ruled out, because the absolute number of $Yb^{2+}$ in the starting solution is smaller than $10^{-13}$ and the presence of $Yb^{2+}$ in the initial condition is unlikely. For the stabilization of $Yb^{2+}$ in the calcite structure, it is possible that some defects such as oxygen vacancy in the crystal structure of calcite can compensate the formation of $Yb^{2+}$ in the oxidative condition.

In conclusion, XANES spectra of Yb incorporated in calcite indicated that approximately 15% of ytterbium ion existed as divalent in calcite, although the calculated molar ratio of $[Yb^{2+}]/[Yb^{3+}]$ was smaller than $10^{-31}$ in the starting solutions. This finding might provide a new knowledge for behavior of trace elements not only in synthetic materials but also in natural materials for environmental interests. It is worthwhile to survey various natural carbonate minerals for trace divalent Yb ion using XANES.

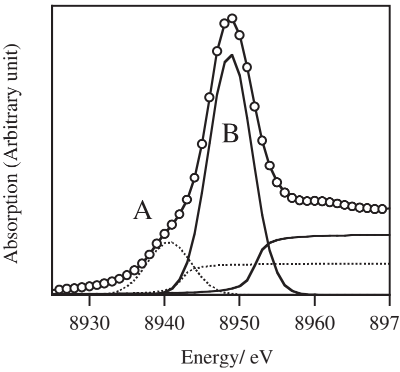

**Figure 2.** Yb $L_{III}$-edge normalized XANES and the deconvoluted spectra of Yb incorporated in calcite. A: $Yb^{2+}$, B: $Yb^{3+}$.

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9 The equilibrium coefficient was calculated from Nernst equation at the pH scale of starting solution as 7.8. The following reactions were considered; $Yb^{3+} + e^- = Yb^{2+}$ ($E^0 = -1.15$ V), $O_2 + 4H^+ + 4e^- = 2H_2O$ ($E^0 = 1.23$ V).
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