

## Aragonite-calcite phase transition of pelagic surface sediment revealed by XAFS technique

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### Introduction

Aragonite, which originated in biogenic matters, has been alternated calcite by authigenic effect in deep-sea sediment. As compared with calcite, crystal structure of aragonite is due to be unstable slightly. However, the detailed *in situ* process of calcite-aragonite phase transition in sediments, especially required reaction time for transition has not been clarified. In this study in order to elucidate crystal structure transition of calcium carbonate by high time resolution, XAFS measurements of calcium in pelagic sediment with detailed sedimentation age were performed.

### Experimental

Surface sediment core was collected from Chatum islands (New Zealand) offshore located 39°59.57'S., 169°59.85'W. in 2005 by JAMSTEC and Ocean research institute, the university of Tokyo, and recovery core length was *ca.* 30cm where it was equivalent to 201kyr (201,000 year) sedimentation age. U-Th dating method was applied to sediment samples.

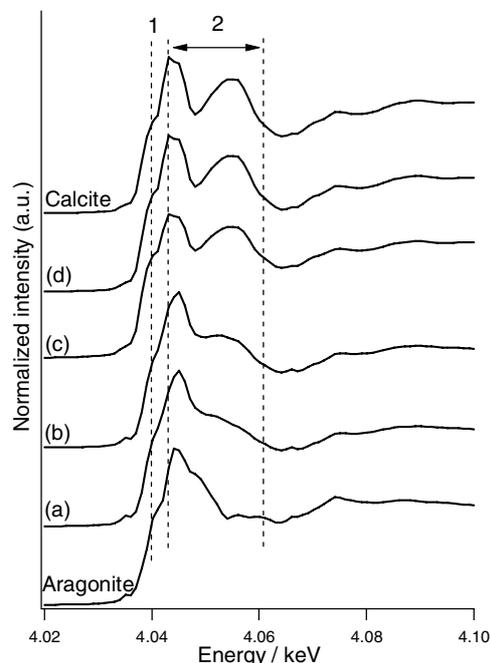
XAFS spectra were measured using a synchrotron radiation ring at the BL-9A, 9C and 12C facilities of the Photon Factory. A Si (111) double crystal was used to monochromate X-ray. All samples were cut by 1.0cm (*ca.* 150mg) for each immediately, and were kept at 4 °C until the measurements. Each sample was sealed with prolene film. Ca K-edge XAFS spectra were obtained in fluorescence mode using a Lytle-type detector at room temperature under atmospheric pressure. EXAFS spectra of samples were analyzed with FEFF 8.4 assuming the scattering path of Ca-O bond.

### Results and discussion

All carbonates for measurement were low-Mg calcite judging from the results of elemental and XRD analyses; therefore, crystal structures of carbonate in this sediment were calcite or aragonite. Figure indicates Ca K-edge XANES spectra of pelagic sediments of various sedimentation ages. The feature of spectrum of sediment whose sedimentation age was 1.6kyr (depth: 1.5cm) had a strong resemblance to that of aragonite. Observed shoulder on K-edge around 4.04keV was small (marked line 1), and at higher energy region than K-edge, spectrum had the same feature as that of aragonite

(marked region 2). Spectrum of 4.1kyr sediment (depth: 7.5cm) was composed of that of aragonite and calcite by 1:1 ratio, and spectrum of 128kyr sediment (depth 19.5cm) had the almost same feature as that of calcite. This tendency continued to the core bottom (201kyr, depth: 29.5cm), and transition from spectrum of 1.6kyr sediment to that of 128kyr sediment was continuously.

Since the water depth of the sampling station (>4500m) was beyond the Calcite Compensation Depth boundary, only aragonite may have leached into sea or interstitial water. However, the possibility was very low because of the results of elemental analysis and XRD spectrum of this sediment. Therefore, the sequential spectra variation resulted from authigenic effect of aragonite-calcite phase transition, and crystal structure transition from aragonite to calcite in high time resolution was clarified by this measurement.



**Figure** Ca K-edge XANES spectra of pelagic sediments of various sedimentation ages. (a): 1.6kyr (depth: 1.5cm), (b):4.1kyr (7.5cm), (c):128kyr (19.5cm), (d):201kyr (29.5cm). Line 1 indicated shoulder on edge at *ca.* 4.04keV. Spectra had specific variation in region 2.

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