# D-1.2.1 Research on Long-term Change of Element Cycles in Ocean based on Chemical Components

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### Abstract

Sediment core (GC1002) taken in the Enderby Land in Antarctic ocean was used. Planktonic foraminifers were isolated under microscope and age determination by <sup>14</sup>C was conducted using by Tandetron accelerator Mass-spectrometer. It was found that age of core in 10 - 12cm depth was 20,000 ±610 years. Also it was found from the correlation analysis of Ca and Al measured by neutron activation method that biogenic sedimentation flux was composed of calcium carbonate rather than opal.

Key Words

Element cycle, Trace metals, Antarctic Ocean, Sediment core, Foraminifera

#### 1. Introduction

Sediment in the ocean contains minerals transported from land and atmosphere, microfossils such as foraminifers or diatoms and organic matter. In addition various kinds of marine pollutants since industrial revolution are accumulated. It is necessary to clarify the causative mechanism of long-term change of element cycle in ocean by analyzing these microfossils, trance metals, organic matter and anthropogenic chemical pollutants in sediment core, in order to predict the future of global environment.

Sediment in the ocean does not reflect directly marine productivity in the surface of the ocean because of the decomposition of organic matter during sinking process and decomposition on the surface of sediment. Therefore it has been difficult to estimate the marine productivity and element cycle in the past from sediment core analysis. The method for estimating element cycle in the past will be developed by evaluating the composition of organic matter, trace metals, calcium carbonae and foraminifera, in the sediment.

Measurement methods of marine pollutants, trace metals, organic matter, oxygen carbon stable isotope ratios in the sediment core sampled around Antarctica will be also developed.

## 2. Material and Method

a) Sediment core sampling

Sediment core (GC1002) was taken from the Enderby Basin (1989. Dec.

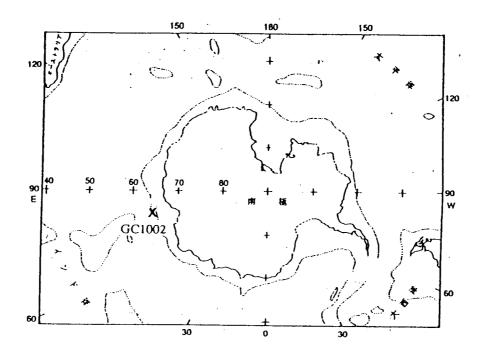


Fig. 1 Sampling location of GC1002 in Antarctic Ocean

23; 63°48'30"S, 78°53'27"E; Depth 3658m, Fig. 1) and the length of the core was 3.96m. Core sample was kept at 5°C until analysis.

## b) Isolation of planktonic foraminifer

Samples (ca. 10g in wet weight) were dried in  $60^{\circ}$ C for 3 days and dry weight was measured. After adding boiled water, samples were washed through  $63\,\mu$  m mesh and dried. Planktonic foraminifers were isolated under microscope.

## c) Age determination by <sup>14</sup>C method

Isolated planktonic foraminifers were treated with Hcl to remove about 10% of the sample surface and washed with distilled water. Samples were treated (Kitagawa et al., 1993) and age of the samples were determined by using TAND TRON (Nagoya Univ.)

### d) Neutron activation analysis

Sediment layers of 2cm in length were sampled at 10cm intervals in the core of GC1002. These subsamples were freeze-dried and subjected to the following non-destructive neutron activation analysis.

Determination of long-and medium-lived nuclides (Rb, Cs, Ba, Fe, Co, Cr, As, Sb, Br, Sc, La, Ce, Nd, Sm, Eu, Yb, Lu, U, Th, Hf and Ta): Each dried sample of ca. 100mg was heat-sealed in double polyethylene bags. Fifteen wrapped samples were packed in an irradiation capsule along with a spectrum monitor of Co  $(50\,\mu\,\mathrm{g})$  impregnated in a sheet of Millipore filter (HAWP, 25mm i.d.). Irradiation was carried out for 50 min. in a pneumatic tube (Pn-2,  $\phi$  tn = 2.75 X  $10^{13}$  n/cm².s) of Kyoto University Reactor (KUR). After the irradiated samples were allowed to stand for 7-10 days and stripped off the outer polyethylene bag,  $\gamma$ -ray spectra were determined using a Ge (Li)-diode detector coupled to a 4K-channel pulse height analyzer, and tape-recorded. The program based upon a comparator method (Koyama and Matsushita, 1980) was used to analyze the  $\gamma$ -ray spectra and

finally calculate concentrations of the above 21 elements.

Determination of short-lived nuclides (Na, K, Ti, Mg, Al, Mn and Ca): Three dried samples of ca. 30mg sealed in double polyethylene bags and a monitor of Mn ( $10\,\mu$ g) impregnated in a sheet of Millipore filter were packed together in a capsule and irradiated for 20 sec. in a pneumatic tube (Pn-3,  $\phi$  th = 2.34 X  $10^{13}$  n/cm<sup>2</sup>.s) of KUR. These samples were cooled for ca. 5 min. prior to determination of the  $\gamma$ -ray spectra. Concentrations of the elements were calculated in a way similar to that for long-lived nuclides.

## 3. Results

Sediment core (GC1002) taken in the Enderby Land in Antarctic ocean was analyzed by neutron activation method. Total of 28 elements (Rb, Cs, Ba, Fe, Co, Cr, As, Sb, Br, Sc, La, Ce, Nd, Sm, Eu, Yb, Lu, U, Th, Hf, Ta, Na, K, Ti, Mg, Al, Mu, Ca) were measured at every 10cm for 4m and vertical profiles of each elements were obtained. The vertical profile of Ca showed good agreement with the microscopic counting result of planktonic foraminifer in sediment core of GC1002, and in particular 16% (weight % in dry sample) of Ca was found at the depth of 3.3-4m(Fig. 2). These high concentrations of Ca correspond with abundance of foraminifer. The vertical profile of Fe showed 5% (weight % in dry sample) at the depth of 2.3-3m but showed low concentrations in other depths(Fig. 2).

Age was determined as  $20,000 \pm 610$  years for the core depth of 10-12 cm by using  $^{14}C$  method. Average sedimentation speed is estimated as 0.55

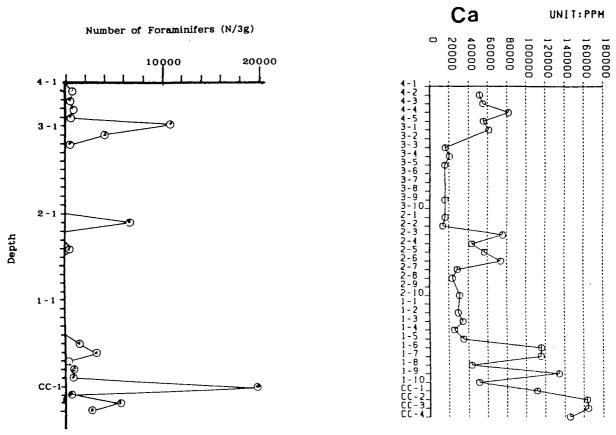


Fig. 2 Vertical profiles of foraminifers and Ca concentration in GC1002

cm/1000 years, which is larger than average sedimentation speed based on the composition of diatoms as 0.32cm/1000 years.

In the core of GC1002, the depth profile of Ca showed inverse correlation to those of many other elements. Fig. 3 showed the relationship between Ca/0.4 and Al/0.08 in the core, in which concentration of the elements was given in % and the numerical factors of 0.4 and 0.08 were abundances of Ca and Al in CaCO3 and the crust, respectively. The inverse correlation of slope ca. -1 (r = 0.873) indicated clearly that the fluctuation in concentration of major elements resulted mainly from dilution of the crustal materials with CaCO3. At the site of GC1002, CaCO3 may have been the dominant fraction of organic sedimentary particles relative to biogenic silica. In addition, Concentration of Hf was high throughout the core of No. GC1002, and reached 32 ppm (ca. 11 times the abundance in the crust) at the depth of 160-162cm. Although this must have been due to deposition of Hf-rich terrestrial materials, further investigation should be conducted to clarify the mechanism.

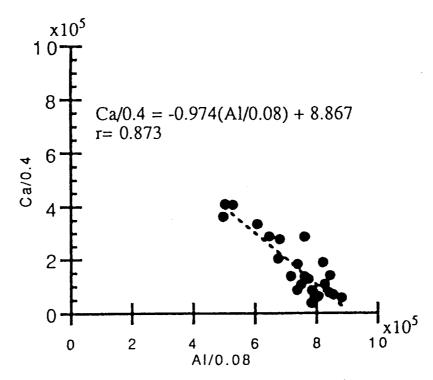


Fig. 3 Correlation between Ca and Al in GC1002

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