

# **<sup>14</sup>C anomaly of algae in inland ponds and lakes, Antarctica**

Hiroshi A. TAKAHASHI<sup>1</sup>, Hideki WADA<sup>2</sup>, Toshio NAKAMURA<sup>3</sup> and Hideki MIURA<sup>4</sup>

<sup>1</sup> Earth and Planetary Sciences, Graduate School of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602

<sup>2</sup> Biology and Geosciences, Faculty of Science, Shizuoka University, 836, Oya, Shizuoka 422-8529

<sup>3</sup> Dating and Materials Research Center, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602

<sup>4</sup> National Institute of Polar Research, 9-10, Kaga 1-chome, Itabashi-ku, Tokyo 173-8515

## **Abstract**

In order to clarify the credibility of <sup>14</sup>C dating using Antarctic samples, <sup>14</sup>C concentrations of fresh water algae collected from some coastal lakes in Antarctica were analyzed by Tandem Accelerator Mass Spectrometry. Samples were collected from Lake Richardson near the Mt. Riiser-Larsen in Enderby Land, the First Crater and Crater Hill near McMurdo Station in Ross Island, and Lake Canopus at Wright Valley in Victoria Land, Antarctica. In the dry valleys and the McMurdo areas around the McMurdo Sound, lakes and ponds are located at glacier free terrain, whereas an inland glacier is close to the Lake Richardson.

The <sup>14</sup>C activities of algae from the dry valleys and McMurdo areas record almost same as those of global level in collecting year. These kinds of samples can be used for <sup>14</sup>C dating. On the other hand, modern algae from the Lake Richardson, which has melt water inflow from the terminal glacier, has slightly low activity of <sup>14</sup>C, *ca.* 90 % of the global one. The algae of Lake Richardson might have used "old" carbon supplied by melt water of glacier. If such samples are used for <sup>14</sup>C dating, the age determination will be erroneous.

key words: AMS <sup>14</sup>C measurement, Antarctic algae, <sup>14</sup>C anomaly, reservoir effect

## **1. Introduction**

Radiocarbon (<sup>14</sup>C) dating, which is useful to paleo-environments studies, needs two assumptions in order to obtain a proper age. The first is "the closed system assumption" which is justified on the basis that the complex organic materials can not exchange carbon with environment

after death. It is possible that contamination with external organic materials can occur. To exclude such contamination, rigorous sample preparation procedures have been developed. An Acid-Alkali-Acid treatment (the AAA treatment) has been found to be effective (Olsson, 1980). The second is "the initial ratio assumption", which implies the atmospheric CO<sub>2</sub> has been and a constant <sup>14</sup>C activity through time as a result of equilibrium between production rate and decay rate. The problem of constant <sup>14</sup>C activity can be corrected using the calibration curve from tree rings (*e.g.* Stuiver and Pearson, 1993), the varved clay in the lake sediments (Kitagawa and van der Plicht, 1998) or the other radio isotopic dating methods (*e.g.* Bard *et al.*, 1990). On the other hand, we must check the effect of <sup>14</sup>C heterogeneity in global scale to <sup>14</sup>C dating. In Antarctica, dissolved inorganic carbon (DIC) of relatively low <sup>14</sup>C concentration is supplied by upwelling from deep sea and melt water of glacier, and causes <sup>14</sup>C anomaly (reservoir effect) in the organic materials (Bard, 1988; Ujiie *et al.*, 1996).

Dry valleys area in south Victoria Land is the largest oasis, *ca.* 4000 km<sup>2</sup>, in Antarctica, and their arid environment might not be changed during past millions of years. The melt water from mountain glacier results in many lakes and ponds in dry valleys area. On the shore of Lake Vanda in Wright Valley, we can see the horizontal old strandlines which are observed up to about 50 m higher from the present lake water level. These old strandlines would be remnants of shoreline orientation of pebbles and sands covered with algae that lived in Lake Vanda, and show the lake level changes in the past. When we use these algae samples for <sup>14</sup>C dating, we must examine the influence of reservoir effects in <sup>14</sup>C anomaly from surrounding glacier. In this study, we analyzed fresh water algae collected from some coastal lakes and ponds in Antarctica using Tandemron Accelerator Mass Spectrometry in order to clarify such reservoir effects.

## 2. Samples

Five algae samples were used in this study. These were collected from Lake Richardson near the Mt. Riiser-Larsen in Enderby Land, the First Crater and Crater Hill near the McMurdo Station in Ross Island, and Lake Canopus at Wright Valley in south Victoria Land (Fig. 1). Table 1 shows brief descriptions of all samples used in this study.

One of the living algae samples designated as AARB was floated on the lake surface and collected from Lake Richardson in January, 1997 (Fig. 1b). At Lake Richardson, main lake surface was covered with thick ice, *ca.* 4 m, all round the year. However, during the austral summer season, the open surface water normally can be found around the west of the Lake Richardson, and the locality where the sample collected is often melted completely (asterisk in Fig. 1b). Inland glacier was attached at the northern west of the lake and the melt water from the glacier which was located along the cost of Lake Richardson flowed into the lake in the summer season.

Four algae samples were collected from lakes and ponds in south Victoria Land (Fig. 1c). One

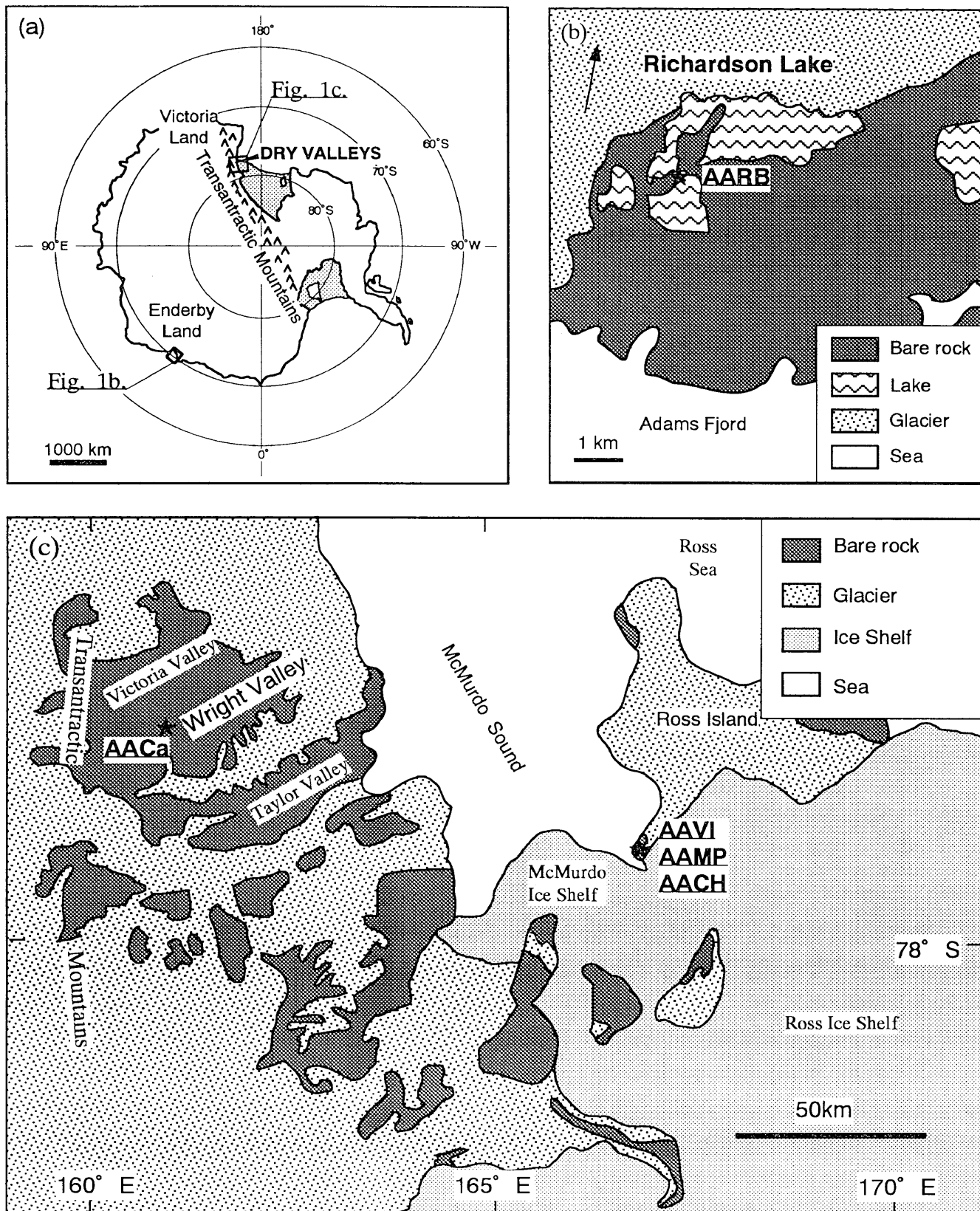


Fig. 1 Sampling points of the Antarctic alga.

Table 1 The list of algae samples.

Samples	Sampling Points	Sampling Date	Remarks
AARB	66° 42' S 50° 40' E	Jan. 1, 1997	water surface, L. Richardson in Enderby Land
AACa	77° 34' S 166° 00' E	Jan. 7, 1987	water surface, L. Canopus in dry valleys area
AAMP	77° 50' S 166° 39' E	Dec. 12, 1986	water surface, 1st Crater McMurdo area, Ross I.
AAVI	77° 50' S 166° 39' E	Dec. 12, 1986	in ice, 1st Crater McMurdo area, Ross I.
AACH	77° 50' S 166° 43' E	Dec. 19, 1986	water surface, Crater Hill McMurdo area, Ross I.

was collected from Lake Canopus in the Wright Valley in January, 1987 and designated as AACa. Lake Canopus is a circular shape and small lake which radius is about fifty meters, and located to the south of Lake Vanda in glacier free area. This lake is normally surrounded by open surface of melt water during the summer season, and the central part of the lake is always covered with ice. Lake water is supplied by ground water which is derived from the melting of Sykes Glacier of the Asgaard Range. Algal mats are observed in the shorelines and formed films coated pebble and floating objects. Greenish and brownish colored algal deposits are observed in the algal mat. Probably these algae may have piled up by wind flow. Other three samples were collected from First Crater (2 samples) and Crater Hill near the McMurdo Station in the Ross Island in December, 1986. They denoted as AAMP (water surface), AAVI (in ice) and AACH (water surface), respectively. Greenish algae sample (AAMP) was observed in the open surface water with several centimeters in depth. During the summer seasons, ice covered partly the surface of these ponds. These small ponds are located in a crater of the Crater Hill and the First Crater, and far away from the glacier and glacial tongue.

### 3. Methods

Samples are treated using the AAA treatment sequence of HCl (1.2N), NaOH solution (1.2 N), HCl (1.2N), to remove any possible carbon contamination. The treated samples, containing carbon of *ca.* 2 mg, was combusted to CO<sub>2</sub> at 850 °C for 2 hours in a vacuum sealed Vycor® tube with CuO, and cryogenically purified in vacuum glass line. The CO<sub>2</sub> gas was reduced into graphite with

hydrogen gas (Kitagawa *et al.*, 1993). The graphite targets prepared from sample and standard of NBS oxalic acid (RM-49), were used for  $^{14}\text{C}$  analysis with a Tandemtron accelerator mass spectrometer at the Dating and Materials Research Center in Nagoya University. The  $^{14}\text{C}$  concentration is expressed in pM (percent modern, %) which is  $^{14}\text{C}$  concentration percentage of samples relative to the atmospheric  $\text{CO}_2$  in 1950. The isotopic fractionation was corrected using the sample  $\delta^{13}\text{C}$  value in evaluation of the  $^{14}\text{C}$  concentration. The  $\delta^{13}\text{C}$  values was measured with isotope-ratio mass spectrometers (Finnigan MAT<sup>TM</sup> 252 in the same laboratory).

#### 4. Results and Discussions

The  $^{14}\text{C}$  concentration,  $\delta^{13}\text{C}$  values and C/N ratios of Antarctic algae measured here are shown in Table 2. The  $\delta^{13}\text{C}$  values are ranged from -6.1 ‰ to -17.0 ‰. Commonly, the  $\delta^{13}\text{C}$  value of  $\text{C}_3$  plants lies around -25 ‰, but the present algae show higher values. Many studies reported the  $\delta^{13}\text{C}$  value of algae or Particulate organic matter (POM) to be around -24 ‰ (POM, tropical lake in Brazil, Wada and Yoshioka, 1996), -30 ‰ (algae and POM, arctic lake in Alaska, Kling *et al.*, 1992) and -20 to -30 ‰ (plankton, southern ocean, Rau *et al.*, 1982). The pH and alkalinity of these Antarctic lake water suggest that quaintly low DIC concentration. Torii *et al.* (1994) compiled geochemical data in the dry valleys area and Ross Island. The pH and alkalinity of water in the Lake Canopus on Jan. 7 in 1987 are 9.57 and 0.4 meq/l, respectively. In these condition,  $\text{CO}_2(\text{aq})$  in lake water might be not enough for photosynthetic activities during the algal growing season. The  $\delta^{13}\text{C}$  values of supplied carbon for algae must be high in lake water, since  $\text{CO}_2(\text{aq})$  would extremely deplete under carbon assimilation activity and high pH value of lake water. Therefore, the algae of Antarctic lake would assimilate the  $^{13}\text{C}$  enriched carbon in lake water. Wada and Yoshioka (1996) reported the  $\delta^{13}\text{C}$  of POM in the Lake Suwa, central Japan, is increased in the summer to -21 ‰ (May) to -17 ‰ (August), and suggested photosynthetic carbon assimilation was largely limited by  $\text{CO}_2(\text{aq})$  and/or  $\text{HCO}_3^-$  supply in eutrophic lake in the summer.  $^{13}\text{C}$  enriched values of such Antarctic algae in comparison with the isotopic data of the lake algae should be strongly derived from the limited carbon.

Figure 2 shows the  $^{14}\text{C}$  concentration Antarctic algae studied here and a comparison with other materials, atmospheric  $\text{CO}_2$ , tree rings, moss and leaves (Nakamura *et al.*, 1990; Levin *et al.*, 1993; Manning *et al.*, 1994; Shore and Cook, 1995; Takahashi *et al.*, 1998). The  $^{14}\text{C}$  concentration of several kinds of materials from global scale shows the world-wide homogenization for  $^{14}\text{C}$ . These global  $^{14}\text{C}$  concentration show the highest value in 1960s corresponding to the nuclear testing in the atmosphere and the decreasing trend because of dilution by ocean reservoir and release of the anthropogenic  $\text{CO}_2$  from fossil fuel burning as well as radioactive decay of  $^{14}\text{C}$ . With regards to the

Table 2 Results of  $^{14}\text{C}$  concentration,  $\delta^{13}\text{C}$  and C/N ratio in algae samples.

Samples	$^{14}\text{C}$ concentration (pM)	Lab. Nos. (NUTA)	$\delta^{13}\text{C}$ PDB (‰)	C/N
AARB	$99.1 \pm 0.9$	5453	-6.1	7.2
AACa	$129.6 \pm 1.0$	5454	-9.6	10.0
AAMP	$113.3 \pm 1.6$	5461	-10.0	7.7
AAVI	$118.6 \pm 3.5$	5463	-9.7	9.9
AACH	$119.7 \pm 1.4$	5460	-17.0	6.7

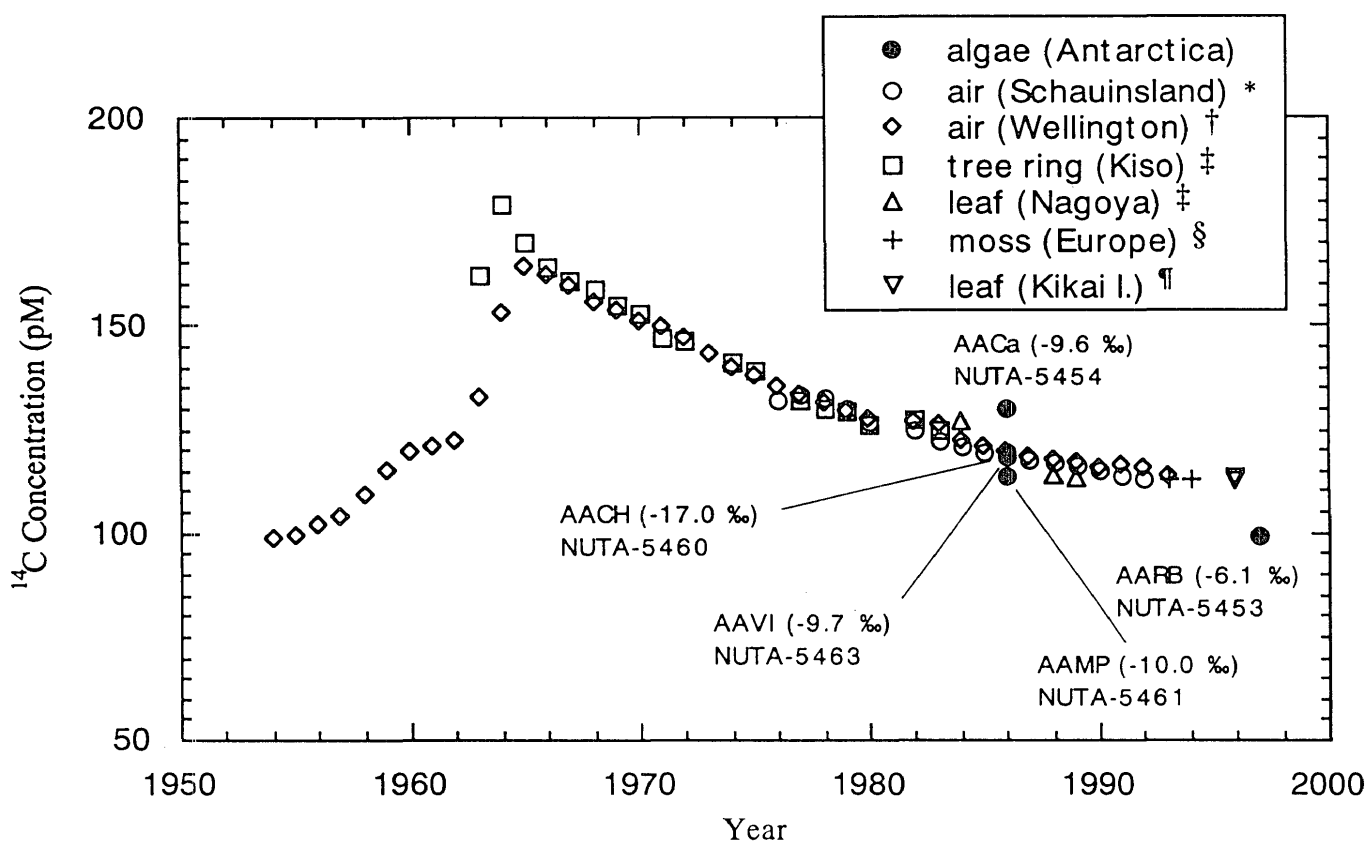


Fig. 2 The  $^{14}\text{C}$  concentration of Antarctic algae with  $\delta^{13}\text{C}$  value in parentheses and other materials (\* Levin *et al.*, 1993; † Manning *et al.*, 1994; ‡ Nakamura, 1990; § Shore and Cook, 1995; ¶ Takahashi *et al.*, 1998).

algae, the  $^{14}\text{C}$  concentration of AACH, AAVI and AAMP are identical with that of other materials, and AACa and AARB were not plotted on the general trend of  $^{14}\text{C}$  level change. This indicates that samples AACH, AAVI and AAMP are not influenced by the reservoir effect. Lakes and ponds in dry valleys and McMurdo areas are located far from the inland glacier. The melt water of the modern alpine glacier inflow to these lakes and ponds such as Lake Canopus. However, DIC in melt water flow might be not so "old" and able to exchange to atmospheric  $\text{CO}_2$ , since it would take a long time to inflow to lake water. As described in previous section, the algae collected from the Lake Canopus was piled up at the coast by strong wind. The high  $^{14}\text{C}$  concentration of the algae carbon was probably derived from the mixture of modern and old (several years back) algae carbons. For small ponds of First Crater and Crater Hill, it might be possible to exchange carbon isotope of lake water with atmospheric  $\text{CO}_2$ , since these lakes and pond are so small and shallow. Therefore, the  $^{14}\text{C}$  concentration of AACH, AAVI and AAMP are consistent  $^{14}\text{C}$  concentration with that of other carbon reservoir in the average  $^{14}\text{C}$  concentration of atmospheric  $\text{CO}_2$ . The  $^{14}\text{C}$  concentration of AACa collected in 1986 is slightly higher than that of other three algae samples collected same summer, and shows the level equivalent to that of 1980. As noticed in previous section, AACa might be a mixture of algae grown in several years before 1986, because we can see that algal deposits in Lake Canopus were mixed with the algal mat. The  $^{14}\text{C}$  concentration of AARB is apparently lower than those of other materials, and shows 88.1 % less than global one. AARB might be assimilated DIC of relative low  $^{14}\text{C}$  concentration with melt water of glacier. The view can be supported by the presence of glacier near by Richardson Lake, sampling site of AARB (Fig. 1b). We estimate the  $^{14}\text{C}$  date difference between AARB and leaves from Kikai Island collected in the previous year (Takahashi *et al.* 1998) to be *ca.* 1000 years.

The twelve  $^{14}\text{C}$  dates of the horizontal laminations on the shore of Lake Vanda were reported by Torii *et al.* (1994) to be ranging of 1280 yr BP to 2920 yr BP. If the algae of Lake Vanda were periodically influenced by reservoir effect, we can not estimate the water level changing of Lake Vanda because of erroneous of  $^{14}\text{C}$  age determination. However, it has been considered that Dry Valley would not change its arid environment as the largest oasis the past million of years. The algae from the dry valleys area and Ross Island dose not show  $^{14}\text{C}$  anomaly in this study. Hence, it would be possible that the lake level changing of Lake Vanda can be estimate from  $^{14}\text{C}$  dates of the horizontal laminations in its shore.

## 5. Conclusion

The  $^{14}\text{C}$  concentration of Antarctic algae is measured using Tandetron Accelerator Mass Spectrometry. The algae from the dry valleys area and Ross Island dose not show  $^{14}\text{C}$  anomaly in this study. These indicate that DIC in lake water is not influenced by the reservoir effect. The  $^{14}\text{C}$  concentration of algae sample from Lake Richardson in Enderby Land is low. This algae is

influenced by the melt water from close by glacier, and has the  $^{14}\text{C}$  age offset around 1000 yr. The geochemical samples from lakes and ponds in stabilized large oasis, like the dry valleys area, shows accurate  $^{14}\text{C}$  age. With regards to the  $\delta^{13}\text{C}$  values, Antarctic freshwater algae measured in this study show relative high  $\delta^{13}\text{C}$  value. The limit of carbon supply for algae caused by the high pH value and low alkalinity of lake water provide the higher  $\delta^{13}\text{C}$  shift of algae.

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## 論文投稿

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