

¹⁴C ANOMALY OF FRESHWATER ALGAE IN ANTARCTIC COASTAL PONDS AND LAKES

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Abstract: In order to clarify the credibility of ¹⁴C dating of Antarctic freshwater algae, $\delta^{13}\text{C}$ values and ¹⁴C concentrations of algae collected from some lakes and ponds in Antarctic coastal areas were analyzed. ¹⁴C concentration was measured by Tandemron Accelerator Mass Spectrometry. The $\delta^{13}\text{C}$ values of algae from Antarctica are relatively higher than global values. The reason for the relatively high $\delta^{13}\text{C}$ values of Antarctic algae may be sought in the limited CO₂ (aq) supply for algae in lake water. ¹⁴C concentrations of algae from ponds in the First Crater and Crater Hill near McMurdo Station on Ross Island, where glacial meltwater does not flow into the ponds, are close to the global level in the same year. On the other hand, the algae from Richardson Lake in the Mt. Riiser-Larsen area in Enderby Land, where glacial meltwater flows into the lake, apparently have low ¹⁴C concentration, *ca.* 90% of the global level. These facts lead us to the conclusion that the ¹⁴C anomaly is attributable to a DIC of relatively low ¹⁴C concentration derived from glacial meltwater with older carbon. If such samples are used for ¹⁴C dating, the age determination will be erroneous.

key words: AMS ¹⁴C measurement, Antarctic algae, ¹⁴C anomaly, reservoir effect

1. Introduction

Radiocarbon (¹⁴C) dating is a very useful technique for paleo-environment studies. In Antarctica, however, dissolved inorganic carbon (DIC) of relatively low ¹⁴C concentration is supplied by upwelling of oceanic deep water, and causes ¹⁴C anomalies in Antarctic organic materials known as the reservoir effect (BROECKER, 1963). This reservoir effect invalidates the initial ratio assumption, which is one of the most important assumptions of ¹⁴C dating, and produces an erroneous age. On the other hand, DIC in meltwater of ice sheets or glaciers is derived from air bubbles trapped there for a long time (*e.g.*, DORAN *et al.*, 1999). The ¹⁴C-depleted DIC has been supplied to organic materials, and also causes a ¹⁴C anomaly (*e.g.*, BIRD *et al.*, 1991; MELLES *et al.*, 1994; GORE, 1997). The effect on dating of carbonaceous materials caused by the reservoir of relict carbon varies considerably depending upon location and sample type. Although the

reservoir effect of Antarctic marine organisms has been discussed by many authors (*e.g.*, OMOTO, 1983; STUIVER *et al.*, 1986; BARD, 1988; UJIE *et al.*, 1996), there has been little discussion of the reservoir effect of Antarctic freshwater organisms in coastal lakes and ponds.

In this study, we compare the $\delta^{13}\text{C}$ values and ^{14}C concentrations of freshwater algae collected from Richardson Lake, Lake Canopus and small ponds of Ross Island. Richardson Lake in Enderby Land has an inflow of the glacial meltwater, whereas Lake Canopus of Wright Valley and small ponds on Ross Island in south Victoria Land do not. We investigate the effect of glacial meltwater on the ^{14}C anomaly and the credibility of ^{14}C dating of Antarctic samples.

2. Sampling Sites and Samples

Five Antarctic algae samples were available for the stable and radio carbon isotopic analysis. These were collected from Richardson Lake in the Mt. Riiser-Larsen area of Enderby Land, ponds in the First Crater and the Crater Hill near McMurdo Station on Ross Island, and Lake Canopus in the Wright Valley in south Victoria Land (Fig. 1). Table 1 gives brief descriptions of all samples.

One sample of algae floating on the water surface in Richardson Lake was collected in January, 1997, and designated AARB (Fig. 1b). The lake surface in the northern part of Richardson Lake was perennially covered with thick ice of *ca.* 4 m. Open water, however, often appears in the southwestern part of the lake during the austral summer (Fig. 1b). The sample was collected in open water. Meltwater from the ice sheet, situated at the northwest edge of the lake, flows into the lake in summer. The lake water is mainly derived from the meltwater, not sea water (ZWARTZ *et al.*, 1998).

Four algae samples were collected from a lake and ponds in south Victoria Land (Fig. 1c). One was collected from Lake Canopus in Wright Valley in January, 1987, and designated AACa. Lake Canopus is circular, of radius about 50 m, 500 m south of Lake Vanda in an ice-free area (Fig. 1d). This lake had open water along the coast and the central part of the lake surface was frozen at the sampling time (Fig. 2). Lake Canopus has no permanent river and the lake water is mainly supplied by ground water derived from the Sykes Glacier of the Asgard Range (Fig. 1c). AACa is part of the accumulated

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 near McMurdo Station, Ross I.
AAVI	77°50'S 166°39'E	Dec. 12, 1986	In ice, 1st Crater near McMurdo Station, Ross I.
AACH	77°50'S 166°43'E	Dec. 19, 1986	Water surface, Crater Hill near McMurdo Station, Ross I.

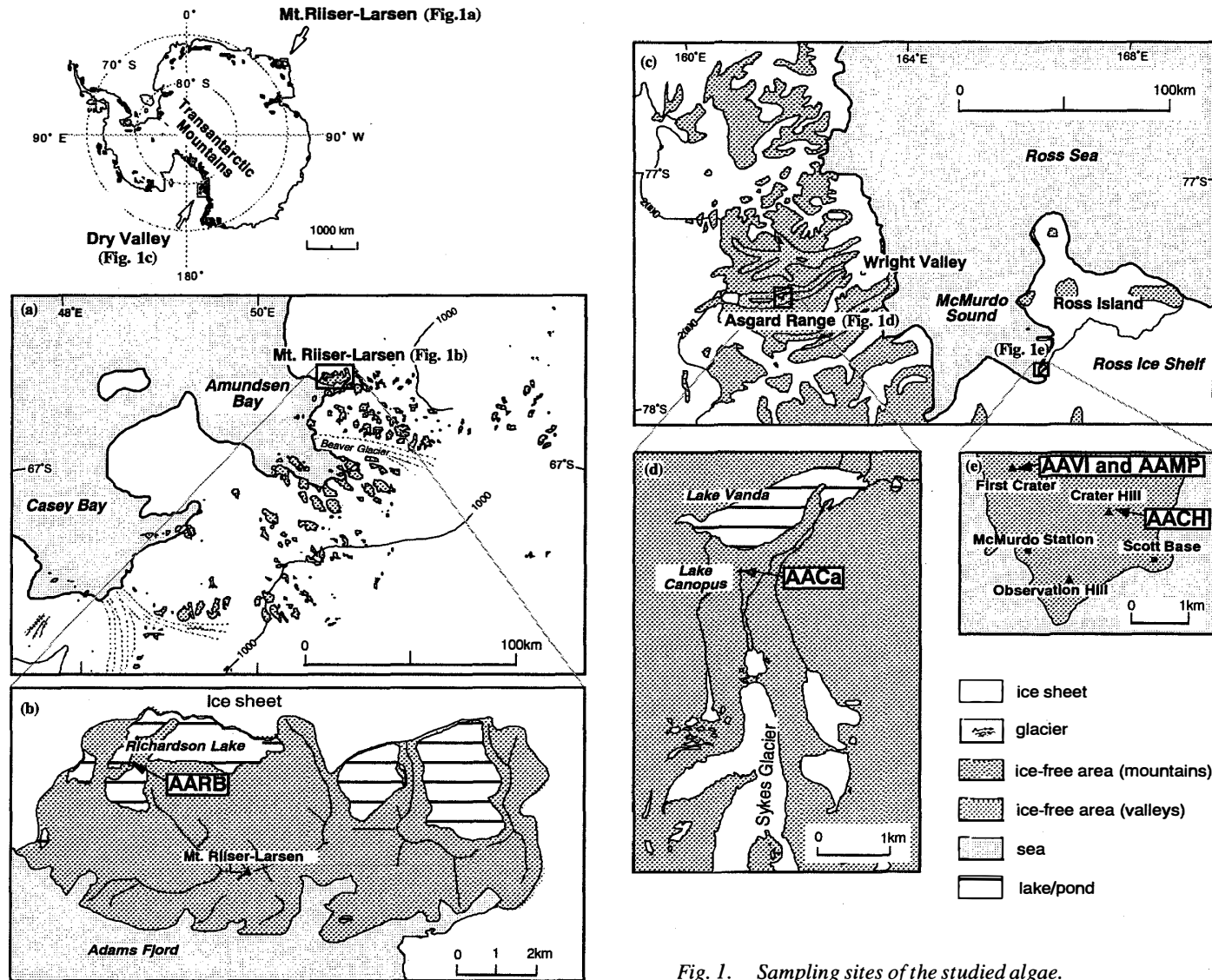


Fig. 1. Sampling sites of the studied algae.



Fig. 2. Lake Canopus located 500 m south of Lake Vanda in the Wright Valley.



Fig. 3. The First Crater on the Ross Island.

algal mat, because it is composed of mixed greenish and brownish colored deposits on the lake shore. Three other samples were collected from ponds in the First Crater (2 samples) and Crater Hill (1 sample) near McMurdo Station on Ross Island in December 1986. The pond in the First Crater is located on a volcanic peak, which is no longer active. One of two samples from the pond in the First Crater was collected several centimeters below the open water surface, and designated AAMP. The other was trapped in the lake ice, and designated AAVI. Another sample, floating on the water surface in the pond near Crater Hill, was designated AACH. These small ponds are located in a crater of Crater Hill and the First Crater (Figs. 1e and 3), where glacial meltwater never flows.

3. Methods and Results

Samples excepted AARB were kept in plastic bags after the dried until the start of sample preparation. All samples were treated using an Acid-Alkali-Acid treatment sequence consisting of HCl (1.2N), NaOH solution (1.2N), HCl (1.2N), to remove any possible contamination with external organic materials. The treated samples containing *ca.* 2 mg of carbon were combusted to CO₂ at 850°C for 2 hours in a vacuum sealed Vycor tube with CuO. The cryogenically purified CO₂ gas was reduced to graphite with hydrogen gas (KITAGAWA *et al.*, 1993). The graphite targets prepared from a sample and a standard of NBS oxalic acid (RM-49) were used for ¹⁴C analysis with a Tandemron Accelerator Mass Spectrometer at the Dating and Materials Research Center of Nagoya University (NAKAMURA *et al.*, 1985).

The ¹⁴C concentration is expressed in pM (percent modern, %) which is the percentage of sample ¹⁴C concentration relative to the atmospheric CO₂ in 1950. The carbon isotopic composition of the sample resulted from isotopic fractionation during photosynthesis and/or carbon exchange between DIC and atmospheric CO₂. We must correct for the isotopic fractionation effect on ¹⁴C concentration. The differential uptake referred to as fractionation was corrected using the sample $\delta^{13}\text{C}$ value in evaluation of the ¹⁴C concentration. The $\delta^{13}\text{C}$ value was measured using an isotope-ratio mass spectrometer (Finnigan MAT 252 in the same laboratory).

The raw ¹⁴C concentration, $\delta^{13}\text{C}$ values and ¹⁴C concentration with $\delta^{13}\text{C}$ correction of Antarctic algae measured in this study are shown in Table 2. The $\delta^{13}\text{C}$ values and ¹⁴C concentration of the Antarctic algae range from -17.0‰ to -6.1‰ and 99.2 pM to 128.6 pM, respectively. Although ¹⁴C concentration or date without isotopic correction has not been commonly reported in recent studies using ¹⁴C analysis, this study shows both non-corrected and corrected values, since $\delta^{13}\text{C}$ values of algae in this study is higher than those of regular C₃ plants.

4. Discussion

4.1. The cause of the high $\delta^{13}\text{C}$ value of Antarctic algae

As shown in Table 2, the $\delta^{13}\text{C}$ values of the Antarctic algae range from -17.0‰ to -6.1‰. In general, the $\delta^{13}\text{C}$ values of terrestrial C₃ plants range from -32‰ to -22‰ (O'LEARY, 1995), and those of marine plankton range from -30‰ to -17‰ and show

the lowest value at the southernmost localities, 80°S in the Pacific Ocean (RAU *et al.*, 1982). Besides, the $\delta^{13}\text{C}$ values of algae or particulate organic matter (POM) have been reported to be around -24‰ (POM, tropical lakes in Brazil, WADA and YOSHIOKA, 1996) and -30‰ (algae and POM, arctic lakes in Alaska, KLING *et al.*, 1992). Compared with these values, the Antarctic algae represented here show relatively higher $\delta^{13}\text{C}$ values. Why are the $\delta^{13}\text{C}$ values of Antarctic algae high?

In growing plants, there will be a tendency for the lightest isotope ^{12}C to be preferentially taken up, and ^{13}C will be taken up in preference to ^{14}C (FARQUHAR *et al.*, 1982). Plants are therefore expected to have a lower ^{14}C level than the atmosphere. However, the photosynthesis of algae leads to a deficiency of CO_2 (aq) in lake water and therefore $\delta^{13}\text{C}$ in lake water will be relatively high. Generally, under high pH conditions, even if alkalinity is high, there is little CO_2 (aq) which plants in water utilize. According to TORII *et al.* (1994), the pH and alkalinity of water in Lake Canopus on January 7, 1987 were 9.57 and 0.4 meq/l, respectively. Under such conditions, total DIC and CO_2 (aq) in lake water are calculated to be 0.3 mM and 0.06 μM , and the $\delta^{13}\text{C}$ values of algae and CO_2 (aq) will be continuously high for photosynthetic activity, since the exploited carbon in lake water cannot be replaced by new carbon. With the progress of photosynthesis, $\delta^{13}\text{C}$ values of algae will become higher and higher.

TAKAHASHI *et al.* (1990) also reported the equivalent shift in $\delta^{13}\text{C}$ of phytoplankton in Lake Suwa, central Japan, while the corresponding $\delta^{13}\text{C}$ of DIC decreased in summer, and phytoplankton kept enough photosynthetic activity. They suggested that the reason for this equivalent shift is that photosynthesis of phytoplankton assimilated CO_2 under limitation of substrate supply due to low DIC concentration is only 0.2 mM (normal DIC concentration: 0.8 mM) and high pH to be *ca.* 10 (normal pH: *ca.* 8.5). The lower $\delta^{13}\text{C}$ value of AACH than that of other algae suggests that the CO_2 (aq) concentration on Crater Hill is a bit high. This is because the pH and alkalinity of pond water on Crater Hill on December 19, 1984 were 8.84 and 2.52 meq/l, respectively (TORII *et al.*, 1994). These values give higher CO_2 (aq) concentration (5.14 μM) than Lake Canopus. Although we do not have pH and alkalinity data for Richardson Lake and the pond of the First Crater, the $\delta^{13}\text{C}$ values of AARB, AAMP and AAVI suggest that CO_2 (aq) concentrations in Richardson Lake and the pond of the First Crater are also lower than Lake Canopus and almost same as Lake Canopus, respectively.

On the other hand, it is well known that the benthic algal mats usually show high $\delta^{13}\text{C}$ values (*e.g.*, DESCOLAS-GROS and FONTUGNE, 1990), since carbon supply is limited by the diffusion fence of upper algal layers. This benthic effect also has the potential to explain the higher $\delta^{13}\text{C}$ values of algae samples studied here, since all Antarctic algae are benthon.

4.2. Radiocarbon concentration of freshwater algae

The ^{14}C concentration of Antarctic algae are shown in Table 2. Figure 4 shows the time-series variation of ^{14}C concentration of atmospheric CO_2 , tree rings and present Antarctic algae collected after 1984 (NAKAMURA *et al.*, 1990; LEVIN *et al.*, 1993; MANNING and MELHUISH, 1994; LEVIN and KROMER, 1997). The ^{14}C concentrations of several kinds of materials on the global scale indicates worldwide homogenization of ^{14}C . The global ^{14}C concentration shows the highest value in the 1960s corresponding to the

Table 2. Results of the raw ^{14}C concentration, $\delta^{13}\text{C}$ values and ^{14}C concentration with $\delta^{13}\text{C}$ correction of Antarctic algae.

Samples	^{14}C conc. (pM) Non-correction	$\delta^{13}\text{C}$ (‰)	^{14}C conc. (pM) Lab No.
AARB	101.0	-6.1	99.2±0.9 NUTA-5453
AACa	130.6	-9.6	128.6±1.0 NUTA-5454
AAMP	115.7	-10.0	114.0±0.9 NUTA-5461
AAVI	118.5	-9.7	116.7±1.1 NUTA-5463
AACH	120.6	-17.0	119.6±1.1 NUTA-5460

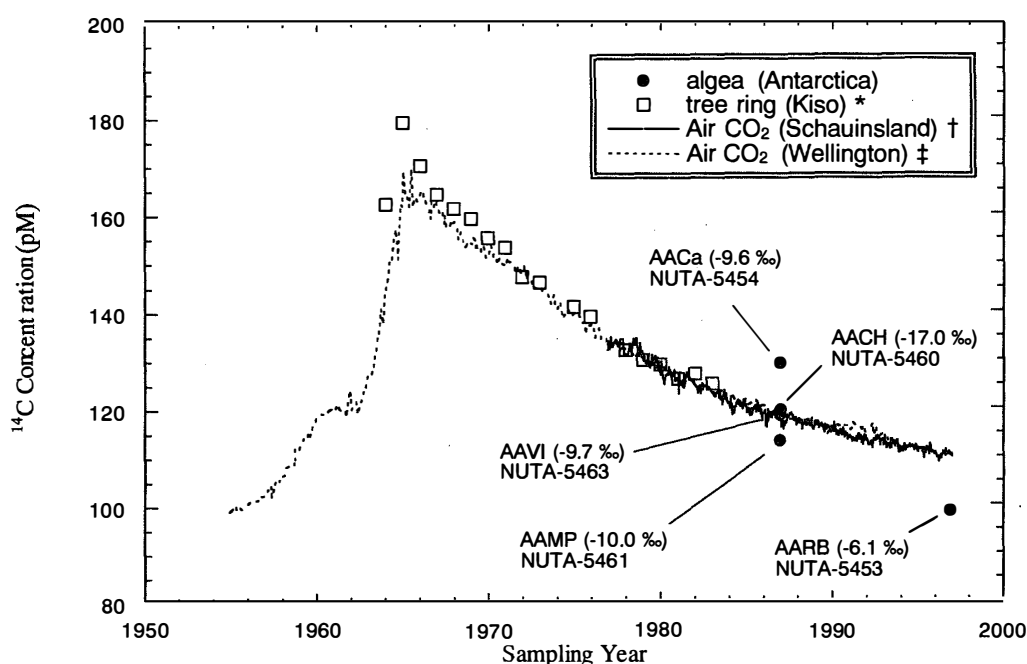


Fig. 4. The ^{14}C concentration of Antarctic algae with $\delta^{13}\text{C}$ value in parentheses and other materials (*NAKAMURA *et al.*, 1990; †LEVIN *et al.*, 1993; LEVIN and KROMER, 1997; ‡MANNING *et al.*, 1994).

nuclear bomb experiments in the atmosphere followed by a decreasing trend because of dilution by the ocean reservoir and release of anthropogenic CO_2 from fossil fuel burning as well as radioactive decay of ^{14}C .

With regard to the Antarctic algae, however, the ^{14}C concentrations of AACH, AAVI and AAMP are approximately consistent with that of atmospheric CO_2 , while those of AACa and AARB deviate considerably from the general trend of ^{14}C concentration. The decrease of the value from the global value, namely the ^{14}C depletion of AARB, may be ascribable to the glacial meltwater effect. Hence, glacial meltwater does not flow into ponds near Crater Hill and the First Crater, where AACH, AAVI, AAMP and AACa were collected, while Richardson Lake has been influenced by meltwater from the nearby ice sheet that has not originated from sea water. Then, AARB might assimilate DIC of relatively low ^{14}C concentration derived from ice sheet meltwater.

The ^{14}C concentration of AARB is 90.2% of the global concentration. We estimate

the ^{14}C date offset of AARB by comparison with atmospheric CO_2 in 1997 (LEVIN and KROMER, 1997) to be 830 years. This value is very similar to the reservoir correction values of marine fossils (*e.g.*, YOSHIDA and MORIWAKI, 1979). DORAN *et al.* (1999) reported that ^{14}C ages of DIC in the surface waters of Lake Bonney are 2080 yr BP. They also assumed that this older age is due to the direct input of large amounts of glacial meltwater with relict DIC. Lake Bonney is glacial meltwater that has flowed directly from the Taylor Glacier, and this is same condition of Richardson Lake. Our result for the ^{14}C age of AARB is *ca.* 800 years in the lake algae; DORAN *et al.* (1999) reported that the ^{14}C age of DIC in surface water is *ca.* 2000 years. This discord might be caused by the age difference of DIC in meltwater of each glacier. Though we did not obtain the ages of an ice sheet snout and its meltwater, nor the carbon isotopic exchange of DIC in flowing meltwater and lake water, we assumed several ^{14}C ages of contaminated carbon and computed the mixing ratio of contaminated old carbon derived from meltwater to total carbon (Table 3). The ^{14}C concentration of AARB of 99.2 pM corresponds to 66 yr BP. Therefore, supposing the age of meltwater to be 66 yr BP, the mixing ratio of contaminated old carbon for algae assimilation is estimated to be 100%, even if we do not take into account a carbon isotopic exchange between lake water and the atmosphere.

Table 3. Mixing ratio of contaminated old carbon derived from meltwater to total carbon.

^{14}C age of contaminated carbon (yr BP)	Mixing ratio of contaminated carbon (%)
66	100.0
100	96.3
200	86.8
500	67.3
750	57.0
1000	49.7
2000	33.6
5000	19.1
10000	13.2
50000	9.8
100000	9.8

On the other hand, the ^{14}C concentration of AACa collected in 1986 is slightly higher than that of the other three samples (AACH, AAVI and AAMP) collected in the same summer. The ^{14}C concentration of AACa shows the level equivalent to that of 1980. As described previously, since we observed that AACa were part of the accumulated algal mat, they probably grew for several years before 1986. Therefore, the elevation of the ^{14}C concentration above the global concentration suggests that the algae grew in the several years before the sampling time and/or accumulated the result of several years. Incidentally, although AAVI and AAMP were collected from the same pond, the ^{14}C concentration of AAVI is slightly higher than that of AAMP. At this stage, we do not know the reason for this difference, but this is possibly ascribable to the different sampling conditions. AAMP floated in the pond water, while AAVI was trapped in the ice. This fact suggests that AAVI had been growing for several years before the sampling. Assuming that this suggestion about growth of AAVI is correct, AAMP and

AAVI are possibly influenced by old carbon.

In conclusion, the algae from the pond on Ross Island without meltwater inflow do not show a ^{14}C anomaly, but the algae from Richardson Lake with inflow of glacial meltwater and resedimented algae have ^{14}C anomaly in this study. Then, if the freshwater algae were periodically influenced by glacial meltwater, we cannot estimate ages because of erroneous ^{14}C age determination.

5. Conclusion

The $\delta^{13}\text{C}$ values and ^{14}C concentration of Antarctic freshwater algae collected from some different lakes and ponds, some where glacial meltwater flows some where it and does not flow into the lake water, were measured by Tandetron Accelerator Mass Spectrometry. The $\delta^{13}\text{C}$ values of Antarctic algae are relatively high. This reason may be sought in the limited CO_2 (aq) supply for algae in lake water under high pH condition.

The algae from the ponds in Ross Island without glacial meltwater flow do not show a ^{14}C anomaly. On the other hand, the algae in Richardson Lake, where glacial meltwater flows, shows an apparent ^{14}C anomaly. These facts suggest that the ^{14}C anomaly is attributed to a DIC of relatively low ^{14}C concentration derived from glacial meltwater. The ^{14}C age offset of AARB is estimated to be around 800 years. Such samples will lead to erroneous ^{14}C age determination.

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