微少量炭素年代測定法の開発とその応用
－琵琶湖の淡水リザーバー効果の変遷と古環境復元への応用－

Development of trace radiocarbon dating and its application : The radiocarbon age differences caused by shell species, tissues or collected locations and their application for reconstruction of paleoenvironment in Lake Biwa, Japan

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Abstract

Using newly collected data combined with data from previous studies, we compared the measured radiocarbon ages of archaeological samples, which was the pair of the charred seed and molluscan shells, and terrestrial and aquatic animal bones around Lake Biwa, and of pine needles, Phragmites, and molluscan shells, collected in 1966, 1970, 1990 and 2008 at Lake Biwa in Japan, to examine freshwater reservoir effects at Lake Biwa. We also tested for age differences in radiocarbon dating among shell species, tissues and collected locations in the lake, to evaluate the influence for radiocarbon dating of archaeological samples in Lake Biwa. The molluscan shells collected after 1990 were largely unaffected by the nuclear testing that occurred in the 1950s and 1960s, whereas the 1966 and 1970 samples appeared to be affected by it, which make the reservoir ages older than expected. The shells collected after 1990 had radiocarbon ages that were 330–450 ^{14}C years older than those of the coeval atmosphere. The apparent differences in radiocarbon age (about 300 ^{14}C years) for the pair of shell fossils and wood samples, and turtles and terrestrial mammals excavated from the same layer of the submerged Awazu shell midden at Lake Biwa suggest that the freshwater reservoir effect also existed in the middle Holocene (the Middle Jomon period, about 5000 years ago). Because the present-day average residence time of Lake Biwa water is less than a decade, its direct influence on the reservoir effect is small, which suggests that anyway old carbon has been supplied into Lake Biwa. To put it more concretely, there is the high possibility that the system as keeping the value of the freshwater reservoir effect in 300–450 ^{14}C years (steady state) function in Lake Biwa and then the closed Lake Biwa system has been in dynamic equilibrium state from 1950's up to the present, correspondingly enormous ^{14}C input by atmospheric nuclear testing and its gradually decreasing.

Based on the observe radiocarbon age difference between, for example of C. sandai at South Lake, the shell and meat of a shellfish, the people living in Awazu submerged archeological site were thought to uptake the meat of C. sandai which were 75 ± 25 ^{14}C years younger than the hard shells and be, actually, 360 ± 25 ^{14}C years older than coeval atmosphere. When we try to reconstruct the paleodiets and paleoenvironments to use the radiocarbon dating in detail, it is very important to evaluate the radiocarbon age differences caused by shell species, tissues or collected locations and to be clear their influence for radiocarbon dating of archaeological samples.

Keywords: Radiocarbon dating; Reservoir effect; Lake Biwa; Apparent age difference ; Reconstruction of paleoenvirnment
キーワード：炭素年代測定；淡水リザーバー効果；琵琶湖；見かけ上の年代差；古環境復元

1. Introduction

The marine and freshwater reservoir effect of archaeological remains are very likely to reflect the diets or habitats of the organisms whose remains are studied (paleodiets), and knowledge of their diets and habitats might allow the reconstruction of marine and freshwater environments when the archaeological site was inhabited (paleoenvironments). To estimate the influence of reservoir effects, we use the hard tissues such as shell, human and animal bones excavated from the archaeological sites, because of no existence of soft tissues actually eaten by human and animals such as shellfish and meats. However, if there is the radiocarbon age differences caused by shell species (bivalves vs. snails), tissues (soft and hard tissues) or collected locations (north vs. south Lake), the premise to evaluate the reservoir effects by the use of the radiocarbon data of the hard tissues from archaeological sites is not so well-grounded. The simple solution of positivism is to estimate the ^{14}C content of the past soft tissue taken up by living organisms, in comparison of the past and modern carbon cycle and by checking modern biological samples in terms of radiocarbon age differences.

The ^{14}C content of the phytoplankton as primary producer in the sea surface which located in the basement of food chain in marine environment is likely to dominate the ^{14}C content of living organisms included in the whole water mass. Thus, it is not so often that there is difference in radiocarbon ages between the hard shells (,which is composed of dissolved calcium and inorganic carbon (DIC) in the lake water) and their meats (, which made by the intake of particulate organic carbon) in the same living organisms.

Therefore, if there is such radiocarbon age difference, then it is reasonable to infer that such phenomenon is easy to occur not in the marine environment, but to some extent closed freshwater environment such as the lake and pond, where the older aged organic matter accumulates in the bottom and the organic matter often resolves and is possible to supply the older radiocarbon aged dissolved inorganic carbon. In this study, we select Lake Biwa as target, which is biggest lake in Japan and shows simple structure that all the inflow rivers are about 120 in only North Lake, whereas the outflow river is only Seta River from South Lake as shown in Fig.1.

2. Method

The samples which used for the research were the hard shells of bivalves (*Corbicula sandai* and *Cristaria plicata*) and snails (*Heterogen longispira* and *Semisulcospira nipponica*). Andmore, *Corbicula sandai* from the North and South Lake collected from April to May, 2008 were gathered, together with pine leaves and Phragmites as comparison samples of ^{14}C content in atmosphere. The sampling points (alphabetic numbered) around Lake Biwa were shown in Fig.1.

Sample preparation was carried out at the Radiocarbon Dating Materials Laboratory, NMJH (National Museum of Japanese History) and at CCR (Nagoya university) is summarized as follows. The hard shells were washed with an ultrasonic washer using Milli Q water and acetone, repeatedly. Then, the bit of the shell, as much as possible, was sharpened, which were leached with HCl and the surface contamination of the shell were removed. On the other hand, soft tissues of the shells were freeze-dried. The bone samples were repeatedly ultrasonicated in distilled water followed by 0.2 M NaOH treatment, and rinsed with distilled water, then the samples were lyophilized and pulverized. The sample was treated with different concentrations of HCl solutions in a cellulose tube in a beaker or directly in a beaker for 24 h at 4 ℃. The decalcified bone sample, which is acid-insoluble, was separated by centrifugation, rinsed with distilled water, and lyophilized. The decalcified bone was treated with acidic hot water to extract gelatin collagen from the humic acid residue. More, Phragmites and pine leaves were washed with an ultrasonic washer using acetone. The samples, then, were prepared by the conventional acid–alkali–acid (AAA) treatment. Each sample was reacted 2 or 3 times with 1 N HCl, 1–2 times with 0.1 N NaOH, 4–5 times with 1 N NaOH, and 2 times with 1 N HCl for 1 h at 80 °C. The purified sample was then neutralized, washed with pure H_2O, filtered, and dried.

The cleaned samples, such as hard shell, their soft tissues, Phragmites and pine leaves, were then sent to Paleo Labo Inc., Ltd., Gifu, Japan, where the hard shells, part of the samples, were decomposed with H_3PO_4 in an evacuated bottle to produce CO_2 gas, which was then purified in liquid N_2 and EtOH-Liquid N_2 traps and their soft tissue, Phragmites and pine leaves were combusted with CuO at 850 °C for 3 h in a sealed quartz glass tube to produce CO_2 gas, which was then purified in liquid N_2 and EtOH-Liquid N_2 traps. The all purified CO_2 gas was reduced to graphite with an iron powder catalyst. The graphite (plus iron powder) was then pressed into targets and analyzed at the Compact AMS facility of Paleo Labo Inc., Ltd., Gunma, Japan. For only extracted bone collagens, the organic fractions were combusted at 850°C in a sealed glass tube together with CuO, Cu and Ag wires to produce CO_2 gas, which was then purified cryogenically and reduced to graphite in the same way described above. The bone sample was analyzed at the Tandem AMS of CCR, Nagoya University, Japan.

3. Result and discussion

Figure 2 shows the results of radiocarbon dating of hard shells sampled from Lake Biwa in 1966 compared with the ^{14}C content in the atmosphere. The ^{14}C content of the shells of bivalves was clearly lower than that of the contemporary atmosphere (Figure 2). The differences in ^{14}C content between the shells from Lake Biwa and atmosphere may have been caused by the freshwater reservoir effect. The detailed explanation of the results is discussed in section 3.1.

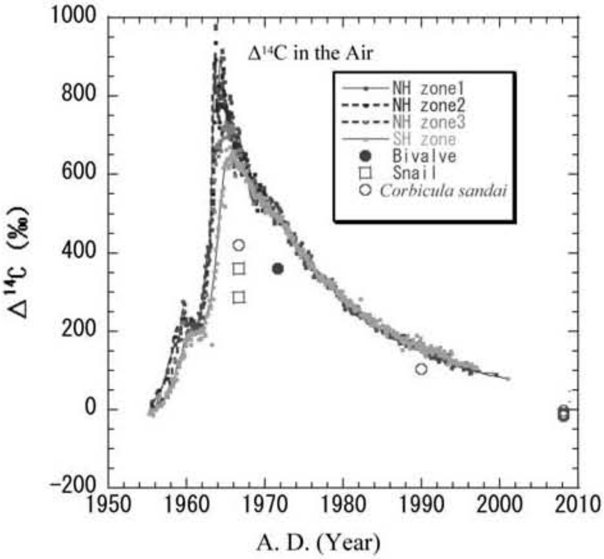

Fig. 2. Δ14C of biological samples (hard shells) from Lake Biwa and Δ14C atmospheric data since 1955 (Hua and Barbetti, 2004). NH: northern hemisphere; SH: southern hemisphere. NH zone 1 is the area from ~ 40°N to the North Pole; zone 2 is not accurately determined, but in Asia, it extends from the summer maximum position of the summer ITCZ to ~ 40°N; and zone 3 is from the equator to the position of the summer ITCZ. Bivalve indicates *C. plicata*. This figure was modified after Miyata et al. (submitted).

3.1 Bivalves vs. snails

At first, we paid attention to the observed age differences in radiocarbon dating between the hard shells of bivalve (C. sandai) and snails (H. longispira and S. nipponica) collected in 1966 at Lake Biwa (Fig. 2). Because of the influence of atmospheric n

uclear testing from the 1950s, the ^{14}C content in the atmosphere increased suddenly from 1962 to 1965. If the ^{14}C content in Lake Biwa water increased in the state that synchronized for the input from the sudden atmospheric increase, a difference in radiocarbon age among the three types of shells would indicate a difference in the response to the sudden rise.

On the other hand, if a difference in response is not the case, the difference in

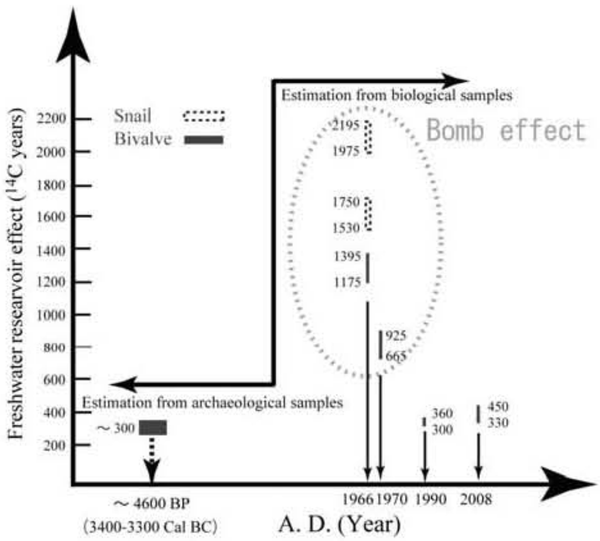

Fig. 3. Fluctuation of the freshwater reservoir effect at Lake Biwa, as estimated using archaeological and biological samples. This figure was based on Miyata et al. (submitted).

radiocarbon age is likely to be caused by the different locations where the bivalve and snails were collected. The snails were collected at western South Lake, whereas the bivalve was collected at eastern South Lake as shown in Figure 1. If eastern South Lake was more affected by the younger carbon originating from the bomb test than western South Lake, the differences in ^{14}C content between the bivalve and snails may have been due to the difference in sampling locations.

3.2 Estimation of freshwater reservoir effects at Lake Biwa from the middle to late Holocene

Using new data collected in this study combined with data from previous studies, we compared not only the radiocarbon ages of archaeological samples, but also the measured radiocarbon ages of molluscan shells, pine needles and Phragmites collected in 1966, 1970, 1990 and 2008 at Lake Biwa to examine the possibility of freshwater reservoir effects at Lake Biwa. Figure 3 exhibits the fluctuation of the freshwater reservoir effect at Lake Biwa by the estimation from these archaeological and biological samples. The radiocarbon ages of samples collected in 1990 and 2008 were 330–450 ^{14}C years older than those of the coeval atmosphere (Fig. 3). As shown in Fig. 2, owing to the influence of atmospheric nuclear testing that began in the 1950s, the ^{14}C content in the atmosphere increased suddenly from 1962 to 1965 and that of DIC in Lake Biwa water correspondingly increased with the sudden atmospheric rise. And then, when the ^{14}C content in the atmosphere decreased monotonously up to the present, that of DIC in Lake Biwa water correspondingly decreased and gradually shrunk the difference with that in the atmosphere. There is the apparent difference in radiocarbon age between the shell fossils and wood samples (290 ± 42 ^{14}C years), and between the terrestrial and aquatic animal bones (318 ± 66 ^{14}C years) excavated from the Awazu submerged shell midden at Lake Biwa, which suggests that the freshwater reservoir effect also existed in the middle Holocene (the Middle Jomon period) at Lake Biwa. Because the present-day average residence time of Lake Biwa water is less than a decade, its direct influence on the reservoir effect is small, which suggests that anyway old carbon has been supplied into Lake Biwa. There are age offsets of radiocarbon dating from both the archaeological and modern biological samples and enormous artificial input of ^{14}C by atmospheric nuclear testing and then the harmonic fluctuation of ^{14}C content of DIC in Lake Biwa water, which strongly indicate that there were freshwater reservoir effects at Lake Biwa from the middle to late Holocene, corresponding to about 5000 years ago to the present, and the high possibility that the system as keeping the value of the freshwater reservoir effect in 300–450 ^{14}C years (steady state) function in Lake Biwa and then the closed Lake Biwa system has been in dynamic equilibrium state from 1950's up to the present, correspondingly enormous ^{14}C input by atmospheric nuclear testing and its gradually decreasing.

A great deal of organic matter has flowed into Lake Biwa, and the degree of freshwater reservoir effects at Lake Biwa may fluctuate, depending on changes in the lake environment, such as inflow into the lake and circulation of the lake water, and changes in the supply of old carbon to the lake.

3.3 Hard shells vs. soft tissues

The ^{14}C content of the four pairs of hard shells (a) and soft tissues (b) collected from the 2008 C. sandai samples (SGMB-K10a -17.2 ± 2.8 ‰, b -6.2 ± 2.9 ‰; K11a -14.5 ± 3.1 ‰, b -7.3 ± 2.9 ‰; K12a -2.8 ± 2.8 ‰, b +1.1 ± 3.0 ‰, b; K13a -11.4 ± 2.8 ‰, b -3.2 ± 2.9 ‰) showed the same tendency—the hard shell was older than the meat in every sample. The hard shells reflect the ^{14}C content of DIC in the lake water, whereas the meat reflects the diet. Therefore, the differences in ^{14}C content between the hard shells and soft tissues may have reflected the difference in carbon source.

Snails likely eat algae, while Corbicula sandai is a filter feeder, but even bivalve diets vary. For example, C. sandai can digest organic matter such as cellulose or lignin, which is normally hard for bivalves to digest. Therefore, if terrigenous organic matter with a lower ^{14}C content is supplied to the lake water and is ingested by C. sandai but not by other species, any radiocarbon age gap in meats between species of shellfish is likely to be caused by differences in diet. By measuring the radiocarbon age of the different species of shell's meats, we may be able to estimate differences in diet and then help to constraint the partly removal process of the carbon in lake and river environment.

3.4 North Lake vs. South Lake

Lake Biwa is divided into two parts, North Lake and South Lake, which have greatly different properties. North Lake occupies more than 90% of the mass of Lake Biwa, and the average water depth is 43 m. In contrast, South Lake is very shallow with an average depth of only 4 m, and sediment is much more likely to be disturbed, for example, by blows or boats. In addition, as shown in Fig.1, about 120 rivers flow into North Lake, whereas the only outflow river (Seta River) flows out of South Lake, which has no inflow

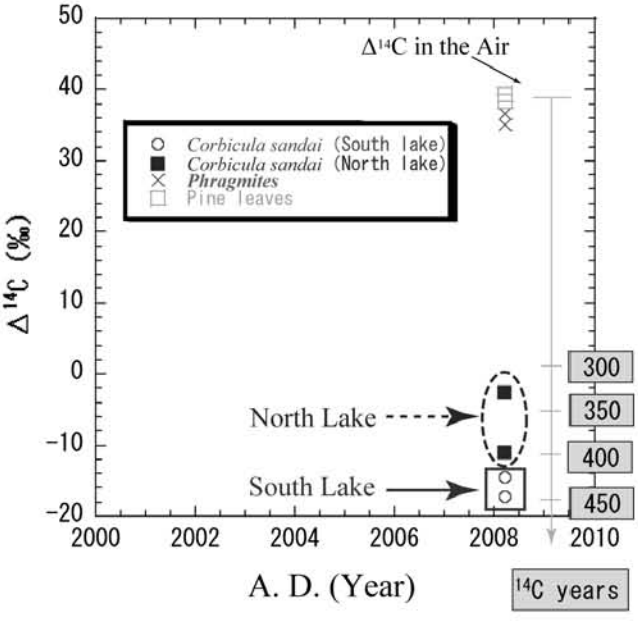

Fig. 4. Radiocarbon age differences of ***Corbicula sandai*** between Lake Biwa's North and South Lakes. This figure was based on Miyata et al. (submitted).

rivers. The lake water has an estimated average residence time of about 10 years. The cycle of lake water in Lake Biwa is strongly prescribed by the flow into and through North Lake, through South Lake, and finally to the Seta River.

Figure 3 shows the radiocarbon ages of the hard shell samples of C. sandai from North and South Lakes. The radiocarbon ages of Phragmites and pine needles collected at the same time are also shown as estimates of modern atmospheric ^{14}C content. The ^{14}C content of the pine needles was –40‰, which is consistent with the ^{14}C content in the atmosphere in 2008. Phragmites had a slightly lower radiocarbon content than the pine needles, possibly because they are affected by old carbon originating from Lake Biwa by a currently unknown mechanism.

The radioactive ages of the hard shells of C. sandai collected in 2008 were 330–450 ^{14}C years older than those of the pine needles. Although there were only 2 samples in each group, the average radiocarbon age of C. sandai in South Lake was 73 ± 23 ^{14}C years older than that in North Lake. This age difference between North and South Lakes is consistent with the flow of water in Lake Biwa. The carbon isotope compositions in lake bottom sediments are lighter going from north to south and sediments in South Lake have been found to have older radiocarbon ages than those in North Lake. Furthermore, the South Lake environment may be more easily affected by mud in lake sediments showing older radiocarbon age because the water depth in South Lake is much shallower than in North Lake. It is therefore likely that the sediment of Lake Biwa itself or the sediment formation process has effects on the radiocarbon age of C. sandai.

4. Summary

Here, we summarize the influence that radiocarbon age differences observed in modern samples give the dating result of the archeological sample in Lake Biwa. There is the freshwater reservoir effect existed at least from the middle to late Holocene at Lake Biwa (from the middle Jomon period to modern). The existence of many submerged archaeological remains at Lake Biwa suggests the diastrophism by a large-scale earthquake repeated in units of a thousand years. Moreover, taking into account the present situation that influence of anthropogenic ^{14}C is smoothed by around 50 years after the nuclear bomb tests, even if the diastrophism by a large-scale earthquake occurred at Lake Biwa several times for this five thousand years and the reservoir age of DIC in the lake water fluctuated in units of a ten years, the value of freshwater reservoir age of the lake water would finally converge to a constant, 300–450 ^{14}C years. To put it more concretely, there is the high possibility that the system as keeping the value of the freshwater reservoir effect in 300–450 ^{14}C years (steady state) function in Lake Biwa and then the closed Lake Biwa system has been in dynamic equilibrium state from 1950's up to the present, correspondingly enormous ^{14}C input by atmospheric nuclear testing and its gradually decreasing. Based on the observe radiocarbon age difference between, for example of C. sandai at South Lake, the shell and meat of a shellfish, the meat of C. sandai which was uptaken by the people and animals lived in near Awazu submerged archeological site would be 73 ± 25 ^{14}C years younger than expected value in DIC (freshwater reservoir effect). The meat of C. sandai, actually, is estimated to be not 435 ± 25 (the hard shell of one), but 362 ± 25 ^{14}C years older than coeval atmosphere. If it is not at South Lake, but at North Lake, it may well be 315 ± 25 ^{14}C years older than coeval atmosphere.

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日本語要旨

本研究では、琵琶湖沿岸の粟津湖底第三貝塚から出土した、貝、獣骨や現生琵琶湖産魚貝試料の見かけ上の炭素年代差を見積もり、琵琶湖水に観察される淡水リザーバー効果の大きさの変遷を推定した。

その結果、縄文時代後期から大正までの琵琶湖水の淡水リザーバー効果の大きさに関する実測データはないが、琵琶湖周辺の石灰岩地帯や琵琶湖岸の泥炭層などに由来する古い炭素の影響によって，完新世後期のおよそ５０００年間、琵琶湖水中の溶存無機炭素中の炭素 14 濃度は、300～450 ^{14}Cyr レベルのリザーバー効果を示す一定の値に保たれていた可能性が高いと推定される。