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COMPOUND-SPECIFIC RADIOCARBON ANALYSIS OF ORGANIC COMPOUNDS FROM MOUNT FUJI PROXIMAL LAKE (LAKE KAWAGUCHI) SEDIMENT, CENTRAL JAPAN

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ABSTRACT. Differential sources of sedimentary organic compounds in a volcanic region were revealed by determining radiocarbon content ($\Delta^{14}C$) of organic compounds in surface sediments from Lake Kawaguchi, at the northern foot of Mount Fuji, central Japan. The $\Delta^{14}C$ values of C_{16} fatty acid (−124‰) and chlorophyll *a* (Chl *a*) (−133‰) were similar to the $\Delta^{14}C$ of dissolved inorganic carbon (DIC) in surface water (−117‰), suggesting that a significant portion of these compounds originated from modern primary producers with a reservoir age of ~1000 years. On the other hand, a large offset between the $\Delta^{14}C$ values of Chl *a* (−133‰) and those of 13^2, 17^3-cyclopheophorbide-*a*-enol (−169‰) and pheophytin *a* (−179‰) suggested contributions from older pigments. In addition, the $\Delta^{14}C$ of long-chain (C_{24}, C_{26}, and C_{28}) fatty acids (−183 to −75‰) showed a large offset from that of a plant leaf remain (0‰) within sediments, demonstrating that the long-chain fatty acids were affected by substantial contributions from pre-aged terrestrial materials. Overall, the sedimentary organic compounds gave ^{14}C ages older than the plant leaf fragment within sediments; however, the similarity between $\Delta^{14}C$ of the C_{16} fatty acid and DIC implies potential for applying compound-specific radiocarbon analysis as a dating tool in volcanic lake environments.

KEYWORDS: cores, lipid analysis, radiocarbon AMS dating.

INTRODUCTION

Lake sediments in volcanic regions record valuable information on past eruptions (Koshimizu et al. 2007; Van Daele et al. 2014; Obrochta et al. 2018) and their environmental consequences (Yamamoto et al. 2018). Terrestrial plant remains are generally considered ideal ^{14}C-dating materials in lake sediments because they contain carbon derived directly from atmospheric CO_2 (Bertrand et al. 2012) and are rapidly delivered to sediment (Gierga et al. 2016); however, terrestrial plant remains are rarely found in volcanic region sediment as volcanisms can severely restrict vegetation cover. Total organic carbon (TOC) may be used as an alternative but it often contains uncertainties arising from the reservoir effect (Fontes et al. 1996), source organic matter heterogeneity (Uchida et al. 2005), and contribution of redeposited aged organic matter (Naeher et al. 2016).

Mount Fuji is the largest active volcano in Japan and its activity began ca. 100,000 yr BP (Takada et al. 2016). To date, several studies have attempted to reconstruct its eruptive history using sediments from proximal volcanic-dammed lakes (Lakes Motosu, Shoji, Sai, Kawaguchi, and Yamanaka), namely the Fuji Five Lake (Taba et al. 1990; Koshimizu et al. 2007). These lakes are distributed from the northeast to northwestern flank of the mountain and contain a large number of tephra layers within sediments that originated from Mount Fuji volcanism. However, most studies have been limited owing to the lack of fossil leaves, except for Lake Motosu where a high-fidelity age model was recently published based on high-density radiocarbon dating of terrestrial macrofossil and bulk organic matter (Obrochta et al. 2018).

The development of compound-specific radiocarbon analysis (CSRA) (Eglinton et al. 1996) has enabled ^{14}C measurement of source-specific organic compounds (biomarkers) to

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become a promising tool for determining depositional ages in settings where traditional dating methods are impractical. For example, Uchikawa et al. (2008) measured the radiocarbon in plant wax *n*-alkanes that were retrieved from lake sediments in Hawaii and found that they were in good agreement with the ^{14}C ages of terrestrial macrofossils in nearby horizons. Furthermore, Hou et al. (2010) also demonstrated that lignin phenols in late Quaternary lake sediments had ^{14}C ages that are compatible with varve-counted and macrofossil-dated sediment horizons. In contrast, substantial contributions of pre-aged plant waxes in lake sediments from tropical lakes in Mexico and Lake Soppensee in Switzerland (Douglas et al. 2014; Gierga et al. 2016; Douglas et al. 2018) highlights the limitation when using terrestrial higher plant biomarkers as a dating tool in the environments, wherein significant amount of pre-aged materials have been transported from the catchment.

On the other hand, CSRA of short-chain (i.e., C_{14}, C_{16}, and C_{18}) fatty acids derived from various eukaryotes and eubacteria and that of chlorophyll *a* degradation product (e.g., cyclopheophorbide-*a*-enol) has been applied to reconstruct chronologies in settings where significant contribution from relict organic carbon leads to anomalously old ^{14}C ages (Ohkouchi et al. 2003; Yamane et al. 2014). These compounds in surface sediments have Δ^{14}C values that are consistent with those of dissolved inorganic carbon (DIC) in surface water (Uchida et al. 2001; Ohkouchi and Eglinton 2008; Kusch et al. 2010a), suggesting that they likely represent a time when sediments were deposited without contribution from relict materials. To date, several studies have reported the ^{14}C ages of the short-chain fatty acids in both marine and lacustrine environments (e.g., Uchida et al. 2005; Camuera et al. 2018); however, their application may be limited, especially in lacustrine settings due to large discrepancies (>4000 yr BP) in ages with those from autochthonous emergent plants (C_{24} fatty acid; Camuera et al. 2018).

In this study, we performed CSRA of organic compounds in surface sediments obtained from Lake Kawaguchi, central Japan. We compared radiocarbon contents (Δ^{14}C) of short- (C_{16}) and long-chain (C_{24}, C_{26}, and C_{28}) fatty acids, chlorophyll *a* (Chl *a*) and its derivatives [13^2, 17^3-cyclopheophorbide-*a*-enol (CPhe *a*) and pheophytin *a* (Phe *a*)] with those of TOC, terrestrial plant remains (leaf and wood fragments), and DIC in surface water to reveal differential sources of organic compounds in the sediments, which could provide insight into their potential as a dating tool in volcanic lake environments.

MATERIALS AND METHODS

Study Site and Sampling

Lake Kawaguchi (35°31′N, 138°45′E; Figure 1) lies 830.5 m above sea level with a surface area of 5.7 km^2 and a maximum depth of 14.6 m. The lake basin has a west-to-east orientation and is divided into three basins by the ridge of the Neogene basement rock. Lake Kawaguchi has no year-round, sustained river input except for the Terakawa and Okukawa rivers (Figure 1); instead, the lake is mainly fed by groundwater and seasonal surface runoff from its catchment, which is mainly caused by typhoons during the fall season, (area = 103.5 km^2; Horiuchi et al. 1992). The groundwater primarily enters the lake from the north and permeates into the underground valley approximately 5 km south of the lake (Kanno et al. 1986). Contribution of volcanic CO_2 to the lake water is unlikely because the volcanic activity of Mount Fuji has been dormant for more than 300 years without any marked CO_2 outgassing around the mountain. There is no natural outlet; however, a small amount of water (0.485 m^3/s: Jan.–Dec. 2016 average; unpublished data from Yamanashi Prefecture)

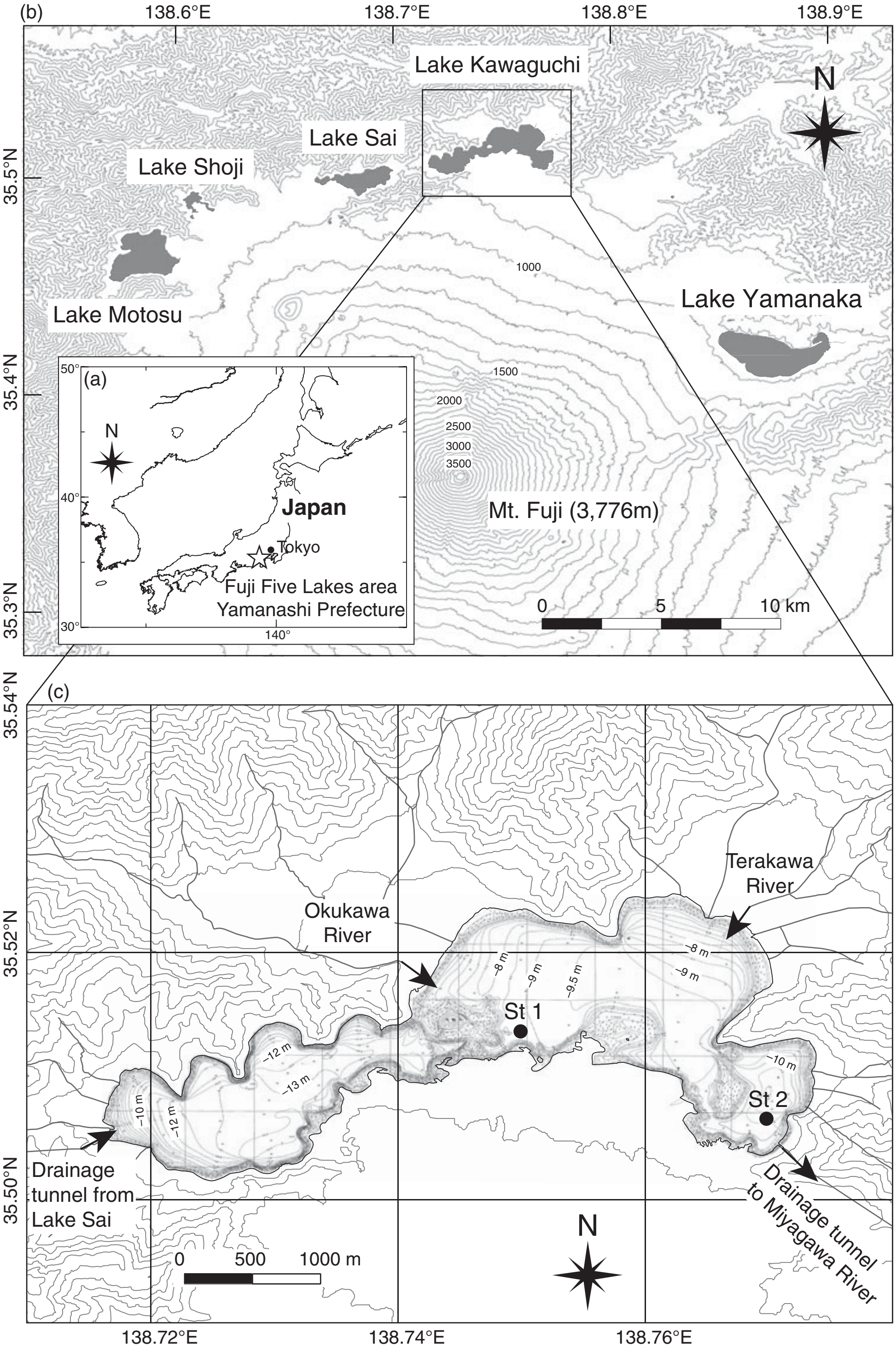

Figure 1 Map showing the location of (a) the Fuji Five Lakes area, Yamanashi Prefecture, Japan, and (b) Lake Kawaguchi, and (c) a bathymetric map of Lake Kawaguchi with major inlet rivers and artificial drainage tunnels (solid arrows). Solid circles indicate sampling locations. These sites were selected because the sedimentation rate has been estimated based on the ^{210}Pb and ^{137}Cs dating in the adjacent cores.

continuously discharges through artificial drainage tunnels that were constructed in 1917 for flood control, irrigation, and power generation (Figure 1). The phytoplankton in Lake Kawaguchi is typically characterized by diatoms (*Asterionella* and *Melosira*) with an occasional dominance of cyanobacteria (*Microcystis*) during summer (Tanaka 1992; Yoshizawa et al. 2005).

Surface sediment (upper ca. 10 cm layer) was collected on August 1, 2016 (St 1; 35°30′49.30″N, 138°44′59.70″E, water depth = 8.5 m) and on March 19, 2017 (St 2; 35°30′23.91″N, 138°46′10.65″E, water depth = 10.4 m) using an Ekman–Birge grab sampler. Lake water was collected at St 2 on June 9, 2017 using a Van Dorn water sampler. Sampling locations are indicated by solid circles in Figure 1c. The water sample was obtained from the depth of 1.5–2 m below the surface to avoid precipitation influence and was immediately spiked with $HgCl_2$ to inhibit microbial activity. Sediment and lake water samples were stored in a refrigerator (4°C) until they were analyzed.

Extraction and Separation of Organic Compounds

Fatty Acid Methyl Esters

Total lipids were ultrasonically extracted from the homogenized dried sediments (50–70 g) using dichloromethane (DCM)/methanol (MeOH) (95:5, v/v). Then, the extracts were combined and concentrated using a rotary evaporator under vacuum and blown with N_2 gas to near dryness. Neutral fractions of the extracts were removed with *n*-hexane/DCM (10:1) after saponification with 1.0 M KOH in MeOH, and the remaining solution was then acidified with 6 M HCl and carboxylic acids were extracted using DCM. The acidic fraction was further treated with 5% HCl/MeOH to convert acids into their methyl esters. Fatty acid methyl esters (FAMEs) were then obtained using column chromatography with a silica gel (deactivated with 1% H_2O) column and elution with *n*-hexane/DCM (1:2). Concentration of the methyl esters was determined using an Agilent 6890 gas chromatograph equipped with an on-column injector, DB-5 fused silica column (30 m × 0.32 mm i.d., 0.25-μm film thickness), and a flame ionization detector (GC-FID).

Isolation of the C_{16}, C_{24}, C_{26}, and C_{28} FAMEs were conducted using the method described in Yamane et al. (2014) with some additional modifications. Briefly, FAMEs were introduced into a reversed-phase high performance liquid chromatography system (HPLC; Agilent 1100 series) equipped with two series-connected columns (Develosil C30-UG-5, 4.6 × 250 mm, 5 μm particle size, Nomura Chemical) with guard column (Develosil C30-UG, 4 × 10 mm, 5 μm particle size, Nomura Chemical), a Corona charged aerosol detector (CAD; Dionex) and each target compound is separately collected by a fraction collector. Two types of mobile phase [Acetonitrile/MeOH (1:2, v/v) with 0.5% pyridine (eluent A) and ethyl acetate with 0.5% pyridine (eluent B)] were used for isolation. The compounds were eluted isocratically with 100% eluent A for 25 min, followed by adding eluent B with a linear gradient up to 15% for 50 min, and then held isocratically until reaching 110 min. The remaining FAMEs ($>C_{28}$) were flushed out with 100% eluent B until 126 min. Oven temperature was kept constant at 15°C from 0 to 25 min, increased at 2°C/min up to 50°C, and then held isothermally until reaching 126 min. The flow rate of the mobile phase was 1 mL/min. All the isolated fractions were subjected to silica gel column to remove any impurities derived from HPLC process. The purity of each compound was confirmed using GC-FID and GC-MS [Agilent 7890A/5975C GC-MSD with a VF-5ms fused silica column (30 m × 0.25 mm i.d., 0.1-μm film thickness)].

Chlorophyll *a* and Its Derivatives

Pigments were extracted and separated using the method described in Kusch et al. (2010a) with some additional modifications. Freeze-dried sediment was ultrasonicated in acetone at 0°C for 15 min followed by liquid–liquid separation (water:*n*-hexane = 3:1, v/v). The *n*-hexane layer was then dried under argon, and precipitated pigments were dissolved in dimethylformamide (DMF). The pigments were then isolated using an HPLC system (Agilent 1100 series) equipped with an Agilent Eclipse XDB-C18 column (250 × 4.6 mm; 5 μm) connected to an Agilent XDB-C18 guard column (12.5 × 4.6 mm; 5 μm), photodiode array detector (DAD), and fraction collector. Acetonitrile with 0.5% pyridine (eluent A) and ethyl acetate with 0.5% pyridine (eluent B) were used as mobile phases for isolation. The pigments were eluted isocratically with 75% eluent A for 5 min and then increased the ratio of eluent B with a linear gradient up to 50% for 50 min at a flow rate of 1.0 mL/min. The oven was kept constant at 30°C.

Purification of the isolated pigments was achieved using an Agilent Eclipse PAH column (250 × 4.6 mm; 5 μm) with a guard column (12.5 × 4.6 mm; 5 μm). The eluents used for this purification step is the same as for the first separation. Pigments were eluted isocratically using 20% eluent B for 5 min, followed by increasing of the ratio of eluent B with a linear gradient of up to 60% for 30 min and then up to 100% for 13 min at 1.0 mL/min. The oven temperature was kept at 15°C and 30°C for Phe *a* and CPhe *a*, respectively. The purified pigments were washed again with DCM/*n*-hexane and NaCl solution, and the DCM/*n*-hexane layer was then dried under argon. The C/N ratios of the extracted pigments were measured using a FlashEA1112 automatic elemental analyzer connected to a Thermo Finnigan Delta plus XP (Ogawa et al. 2010) to confirm high purities of the isolated compounds.

Δ^{14}C Measurements

For the ^{14}C measurements, purified compounds were transferred to quartz tubes and recovered as CO_2 by combustion with CuO. Plant remains, i.e., a single piece of plant leaf debris and a wood fragment, were handpicked from sieved (>150 μm) sediment residues under microscope, which were then converted to CO_2 in quartz tubes after acid–alkali–acid pretreatment (Miyairi et al. 2004). DIC samples (250 mL) were acidified with 3 mL of 85% H_3PO_4 and purged with 0.8 atm of He gas to collect CO_2 gas in glass tubes. Then, the evolved CO_2 was purified cryogenically and reduced to graphite using the method described in Yokoyama et al. (2010). The Δ^{14}C values were measured using a single-stage accelerator mass spectrometer (AMS) at the Atmosphere and Ocean Research Institute, the University of Tokyo (Yokoyama et al. 2019). The Δ^{14}C values are defined as follows (Stuiver and Polach 1977):

$$\Delta^{14}C = \delta^{14}C - 2(\delta^{13}C + 25)(1 + \delta^{14}C/1000) \qquad (1)$$

The Δ^{14}C values of FAMEs were corrected for the contribution of methyl carbon obtained from MeOH ($\Delta^{14}C = -991‰$; Yamane et al. 2014) during the esterification using isotope mass balance. The HPLC procedural blank was measured for each compound using a sensitivity improved on-line system of FlashEA1112 automatic elemental analyzer connected to a Thermo Finnigan Delta plus XP (Ogawa et al. 2010), which was confirmed to be smaller than 0.10 μgC. The ^{14}C dates were calibrated using Oxcal v4.2 calibration software (Bronk Ramsey 2009) with the IntCal13 dataset (Reimer et al. 2013).

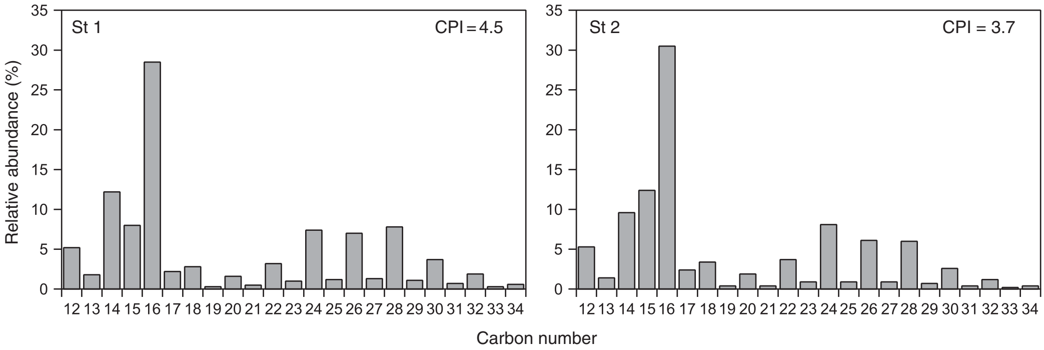

Figure 2 Molecular compositions of *n*-fatty acids in surface sediments from Lake Kawaguchi. St 1 and St 2 indicate sample collection sites.

RESULTS AND DISCUSSION

We detected a homologous series of C_{12}–C_{34} *n*-fatty acids in surface sediments from Lake Kawaguchi. The molecular distribution of *n*-fatty acids showed a strong even/odd carbon number predominance ($\mathrm{CPI} > 3.7$; Figure 2), suggesting their biological origin. The *n*-fatty acids exhibited a bimodal distribution with maxima at C_{16} and C_{28} in St 1 and at C_{16} and C_{24} in St 2. Low molecular weight fatty acids (C_{12}–C_{19}) were generally attributed to various organisms including phytoplankton, bacteria and terrestrial higher plants, whereas high molecular weight fatty acids ($> C_{24}$) originated from terrestrial higher plant waxes (Simoneit 1977; Gagosian et al. 1981) as well as freshwater aquatic macrophytes (Ficken et al. 2000).

The $\Delta^{14}C$ values of plant-derived long-chain (C_{24}, C_{26}, and C_{28}) *n*-fatty acids ranged from −43‰ to −183‰, corresponding to ^{14}C ages of 288–1554 yr BP, respectively (Table 1). In contrast, the $\Delta^{14}C$ of a plant leaf fragment within St 2 sediments exhibited a significantly ^{14}C-enriched value compared to these fatty acids ($\Delta^{14}C = 0‰$; Table 1). Vertical profiles of ^{210}Pb and ^{137}Cs in a core collected near St 2 have revealed a linear sedimentation rate for the upper 20 cm layer (51 mg/cm^2/yr; Sakaguchi et al. 2004), suggesting that our sediments were likely deposited after the late 1940s. Considering the ^{14}C-depleted $\Delta^{14}C$ prior to 1952 via the use of fossil fuel CO_2 (~−23‰; Hua et al. 2013) and a subsequent increases by above ground hydrogen bomb testing (Hua et al. 2013; Hammer and Levin 2017), this plant leaf fragment was likely deposited just after 1955 when the atmospheric $\Delta^{14}C$ began to rise to its maximum in the mid-1960s (Hua et al. 2013). However, we cannot entirely rule out the possibility that plant leaf remains have some decadal-scale resident time due to a lack of its stratigraphic information.

The $\Delta^{14}C$ offset between wood fragment and plant leaf samples can be explained consistently by a longer residence time for wood fragments than plant leaves, as has suggested previously in the late Holocene lake sediment from western Nepal (Nakamura et al. 2012). On the contrary, the ^{14}C-depleted values for the long-chain acids apparently contradict the ages of the sediments. This suggests that the $\Delta^{14}C$ of long-chain acids are likely affected by substantial contributions from pre-aged terrestrial materials in addition to those from contemporary plant leaf waxes with post-bomb $\Delta^{14}C$ signals. Such input of pre-aged materials has been suggested in various marginal marine and lacustrine settings (Smittenberg et al. 2004; Uchida et al. 2005; Kusch et al. 2010b; Feng et al. 2013; Douglas et al. 2014). The depleted

Table 1 Summary of the $\Delta^{14}C$ data for TOC, fatty acids, pigments and plant remains in surface sediment, and surface water DIC from Lake Kawaguchi.

	Sample amount (μgC)[a]	Sample amount (μgC)[b]	$\Delta^{14}C$ (‰)		^{14}C age (yr BP)		Cal age (cal BP)[c]		Lab code
St 1									
C_{26} fatty acid	128.3	162.2	−87	±4	669	±37	620	±40	YAUT-028319
C_{28} fatty acid	135.2	131.0	−43	±5	288	±43	217	±111	YAUT-028316
TOC			−92	±3	712	±25	665	±24	YAUT-029108
St 2									
C_{16} fatty acid	109.9	119.7	−124	±6	996	±53	894	±64	YAUT-037524
C_{24} fatty acid	108.7	88.4	−77	±6	576	±52	590	±39	YAUT-037525
C_{26} fatty acid	95.4	102.8	−183	±6	1554	±55	1451	±59	YAUT-037526
C_{28} fatty acid	81.2	85.9	−75	±7	564	±59	585	±43	YAUT-037528
$13^2,17^3$-cyclopheophorbide-*a*-enol (CPhe *a*)	59.0	61.7	−169	±21	1415	±201	1341	±213	YAUT-044821
Chlorophyll *a* (Chl *a*)	103.0	103.9	−133	±6	1075	±52	998	±59	YAUT-044932
Pheophytin *a* (Phe *a*)	52.0	46.7	−179	±7	1522	±72	1429	±72	YAUT-044822
Surface water DIC			−117	±2	937	±22	854	±37	YAUT-037202
Wood fragment			−82	±4	619	±35	603	±33	YAUT-036537
Plant leaf			0	±2	Modern		Modern		YAUT-036538
TOC			−172	±2	1451	±22	1339	±21	YAUT-036539

[a] Determined by GC-FID for fatty acids and by HPCL-DAD for pigments.

[b] Estimated by CO_2 gas pressure.

[c] Age range with 95.4% probability.

$\Delta^{14}C$ for long-chain acids in St 1 can also be attributed to contribution of pre-aged terrestrial materials because the ^{210}Pb and ^{137}Cs profiles in an adjacent core has revealed linear sedimentation for the upper 10 cm since the late 1980s (123 mg/cm^2/yr; Yamamoto et al. unpublished data).

Previous studies have reported that sedimentary *n*-fatty acids often exhibit a trend becoming older as their chain length increases (Uchida et al. 2001; Ohkouchi et al. 2003; Kusch et al. 2010b; Feng et al. 2013), and such ^{14}C depletion is typically explained by longer-chain homologues having higher resistance to degradation (e.g., Camacho-Ibar et al. 2003). The long-chain fatty acids in our samples had $\Delta^{14}C$ values that showed a large scattering with depletion (44 to 108‰) in C_{26} fatty acid as compared to C_{24} and C_{28} homologues (Figure 3). Similar ^{14}C-depletion for the C_{26} fatty acid has also been noted in surface sediment in the Santa Monica Basin (Pearson et al. 2001) and the shelf of the Washington margin (Feng et al. 2013); the former study suggested potential contamination from the column bleed originating from the thermal degradation of the GC column. Although we cannot completely rule out the possibility that the C_{26} at St 1 could have been affected by extraneous carbon, as suggested by the large difference between the CO_2 pressure- and GC-FID-based estimates on the carbon amount, the high purity of the C_{26} acid is warranted at St 2 based on the good agreement between the amount of samples quantified as CO_2 and via GC-FID (Table 1).

One possible explanation for the ^{14}C-depleted C_{26} fatty acid within the St 2 sediments could be carbon source heterogeneity among long-chain fatty acids. The C_{26} fatty acid has a $\Delta^{14}C$ value that appears to mirror the TOC, whereas the $\Delta^{14}C$ of the C_{24} and C_{28} fatty acids showed a close agreement with that of a wood fragment. This suggests that contribution from sources other than terrestrial plants is not negligibly small for the C_{26} fatty acid unlike the C_{24} and C_{28} acids. Generally, long-chain fatty acids are considered as terrestrial vascular plant biomarkers; however, these acids have been also found in bacteria (Schweizer 1988). Thus, a portion of the C_{26} fatty acid could have derived from heterotrophic microbes that intake TOC at the sediment-water interface. Alternatively, the $\Delta^{14}C$ values of the C_{24} and C_{28} acids could be affected by additional aquatic sources, i.e., aquatic plants and microalgae (Ficken et al. 2000; Feakins et al. 2007; van Bree et al. 2018) with younger age, whereas the C_{26} represents the age of the reworked organic materials within the lake or from the catchment. Moreover, deposition of aeolian dust particles to the sediment could potentially explain the above results because substantially ^{14}C depleted long-chain fatty acids have been reported in aerosols from northern Japan during Asian dust events (~518‰; Matsumoto et al. 2001; Kawamura et al. 2010). Overall the $\Delta^{14}C$ of long-chain fatty acids highlight the potential for large variability in the age and source of these compounds in lake sediments.

On the other hand, the C_{16} fatty acid in St 2 sediments displayed a similar $\Delta^{14}C$ value (−124 ± 6‰) to surface water DIC (−117 ± 2‰), suggesting that this compound is likely derived from primary producers that utilize DIC as carbon sources in photosynthesis. The aquatic origin of the C_{16} acid is also supported by consistent $\Delta^{14}C$ values with chlorophyll *a* within the sediments (−133 ± 6‰; Table 1). However, given that the lake DIC tracks the atmospheric $\Delta^{14}C$ signals and the DIC $\Delta^{14}C$ during the deposition of the St 2 sediments, we expect that the $\Delta^{14}C$ of lake producers should be higher than the modern values reflecting post-bomb ^{14}C signals (~935.5‰ at NH zone 2; Hua et al. 2013). Considering the increasing trends in organic matter along with recent eutrophication in the lake (Hirabayashi et al. 2012) and low resistance of these compounds to microbial oxidation (Kawamura and Ishiwatari 1984; Carpenter et al. 1986), the $\Delta^{14}C$ values for these

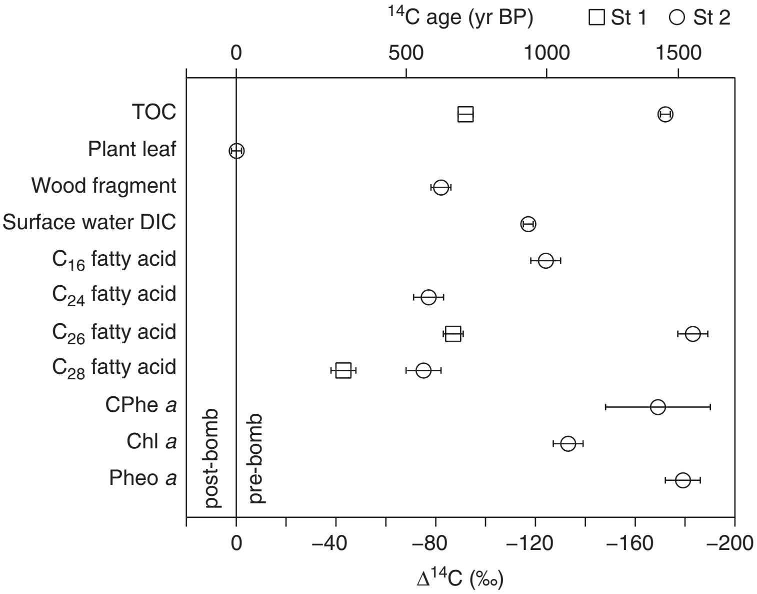

Figure 3 $\Delta^{14}C$ values of individual fatty acids, pigments, terrestrial plant remains (leaf and wood fragments), total organic carbon in the surface sediments, and dissolved inorganic carbon in surface water from Lake Kawaguchi. Sediments from St 1 and St 2 were collected in August 2016 and March 2017, respectively. Lake water was collected in June 2017. CPhe *a*: 13^2, 17^3-cyclopheophorbide-*a*-enol, Chl *a*: chlorophyll *a*, Pheo *a*: pheophytin *a*.

compounds could be biased toward younger ages through post-depositional degradation and enhanced production of those with modern $\Delta^{14}C$ values. Alternatively, the lake reservoir effect could be underestimated due to the paucity in the DIC $\Delta^{14}C$ data, or atmospheric CO_2 contributes minimally to the lake DIC due to the short residence time of the water in Lake Kawaguchi (~0.37 yr; Yamanashi Prefecture 1993). The weak influence of the atmospheric CO_2 to lake DIC has been previously reported in Lake Haruna, Japan, where DIC originated entirely from the decomposition of organic materials (Yamanaka 2017). In general, the age of the lake DIC depends mainly on the input of exogenous old carbon (originated from carbonate rock, degradation of organic matter) and groundwater and on CO_2 exchange between the lake water and atmosphere (Ishikawa et al. 2015; Zhang et al. 2016). The input from carbonate rocks can be discarded in this lake due to their limited exposure in the catchment (Katada 1954). However, the ultimate sources of DIC should be identified by measuring $\delta^{13}C$ in future studies to better understand carbon cycling in Lake Kawaguchi.

Interestingly, we observed a large offset (~46‰) between the $\Delta^{14}C$ values of Chl *a* and those of 13^2, 17^3-cyclopheophorbide-*a*-enol (CPhe *a*) and pheophytin *a* (Phe *a*), which are major degradation products of Chl *a* (Figures 3 and 4). The $\Delta^{14}C$ value of Chl *a* is consistent with the $\Delta^{14}C$ value of DIC in surface water, demonstrating that a significant proportion of Chl *a* is likely derived from contemporary phytoplankton communities. This suggests that ^{14}C-depleted CPhe *a* and Phe *a* in the sediments are most likely explained by contributions from older pheopigments within the lake. In support of this, such contribution has been also suggested by a study on mesotrophic Lake Zurich, Switzerland,

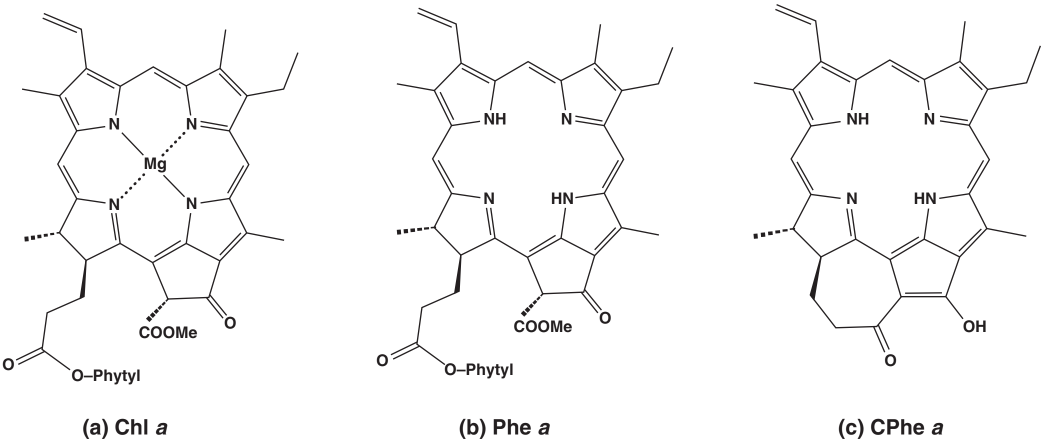

Figure 4 Structures of (a) chlorophyll *a* (Chl *a*) and (b, c) its derivatives [13^2, 17^3-cyclopheophorbide-*a*-enol (CPhe *a*) and pheophytin *a* (Phe *a*)].

wherein degraded Chl *a* derivatives exhibit higher $\delta^{15}N$ than Chl *a* (Naeher et al. 2016). Alternatively, older pigments could be also supplied from soils around the lake as Phe *a* is one of the primary pigments in photosystem II (Kusch et al. 2010a).

It should be noted that large offsets in the TOC $\Delta^{14}C$ values have been observed between the sites, i.e., the $\Delta^{14}C$ of TOC in St 1 (−92 ± 3‰) exhibits more ^{14}C-enriched values than the surface water DIC (−117 ± 2‰), whereas the $\Delta^{14}C$ in St 2 (−172 ± 2‰) is significantly ^{14}C-depleted compared to the DIC value (Figure 3). The averaged TOC concentrations for the upper 10 cm of sediment in the adjacent cores were quite similar between these sites (5.1% for St 1 and 4.8% for St 2; Yamamoto et al., unpublished data). However, St 1 was located at a shallower water depth on the slope of the large alluvial fan of the Okukawa river, and the higher sedimentation rate and more enriched $\Delta^{14}C$ value at St 1 than that at St 2 suggests that the sediments in St 1 likely received more contribution from modern plant (terrestrial/aquatic) sources. On the other hand, the $\Delta^{14}C$ of TOC in St 2 represents significant contribution from reworked/pre-aged organic matter. Anthropogenic input of fossil-fuel-based organic carbon and mobilization of aged carbon associated with anthropogenic land-use change could also affect the TOC $\Delta^{14}C$ values (Griffith et al. 2009; Butman et al. 2015) because the catchment is quite densely populated with many fields and houses, especially in the eastern basin.

In lacustrine sediments, various methods have been proposed for improving chronologies based on TOC ^{14}C dating (e.g., Bertrand et al. 2012; Hou et al. 2012; Obrochta et al. 2018). Bowen et al. (2019) has recently reported a broad similarity in the ^{14}C between simultaneously deposited TOC and algal organic matter in sediments of the Great Salt Lake, Utah, and suggested that TOC is little affected by allochthonous organic matter. However, the application of the TOC may be limited in the Lake Kawaguchi sediments owing to the variable contributions from the ^{14}C-enriched and depleted organic materials between locations. The ^{14}C ages of sedimentary organic compounds in Lake Kawaguchi were overall older than the plant leaf remain, i.e., the most precise age recorder in lacustrine sediments (Nakamura et al. 2012). Nevertheless, the $\Delta^{14}C$ of the C_{16} fatty acid showed similarity to that of DIC, which implies potential for applying CSRA as a dating tool in volcanic lake environments.

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