111. Chloroform Extractable Substances in a 1400 m Core Sample of Lake Biwa. I

Chlorophyll-like Substances and Total Extractable Carbon—A Preliminary Study

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Introduction. The relationships between fossil pigments and primary production or paleoclimates have been described by Wetzel (1970), Sanger and Gorham (1972), Gillan and Johns (1980), Handa (1975, 1984), Guilizzoni *et al.* (1983) and others. In this study, paleoclimates and paleoproductivities of Lake Biwa are estimated from chloroform extractable substances and chlorophyll-like pigments in a 1400 m long core sample of Lake Biwa taken from Northern Basin of the lake in 1982 by S. Horie and others (Kyoto University).

Handa (1975) determined chlorophyll derivatives by relative fluorescence intensity and carotenoids by spectrophotometer at 450 nm in a 200 m core sample of Lake Biwa collected in 1971 and described the importance of those pigments and ratios of three major organic compounds carbon (carbohydrates + proteins + lipids carbon) to total organic carbon for paleoproductivities and paleoenvironments. Contrary to the homogeneous clayey 200 m core sample, the 1400 m core sample is composed of clays, silts, sands, gravels and basement rocks.

Analysis. Samples were taken from a composite 20 cm layer at 6 m intervals selecting finer samples from the upper to about 820 m in depth. Organic substances in wet sediment samples (about 3 g in dry weight) stored under -10°C and dark before analyses, were extracted with 30 ml chloroform/methanol (2/1) ultrasonically and the solvent mixtures were separated by filtrating using Whatman GF/C from solid materials. The chloroform extractable (CHL-E) substances were obtained by washing the mixtures with 25 ml redistilled water and chloroform is added to the separated chloroform layer by centrifugation to a volume of 25 ml.

Total CHL-E carbon was determined by using a thin-chromatograph with FID detector (IATROSCAN TH-10 TLC/FID Analyser). The aliquote of the CHL-E was concentrated to be 250–2500 ppm in carbon. Five microliters of the concentrated was spotted on around a chromarod SII (silicagel rod) and the total carbon was determined using cholesterol in acetone as a standard. An investigation was undertaken to determine the reproducibility, limit of detection, standard substances and method of spotting. Details will be described elsewhere (unpublished).

The portion of the CHL-E solution was concentrated until just before dry-up and redissolved in 90% acetone. Chlorophyll-like pigments was determined by a Hitachi 200A spectrophotometer (measuring wavelength: 480, 510, 630, 645, 665, 750 nm) using the Lorenzen equation (Lorenzen, 1967) for the measurement of chlorophyll *a* and pheophytin in water.

Results and discussion. The lithofacies of upper 910 m of the 1400 m core

sample of Lake Biwa (Fig. 1) shows 5 major sections. T Bed (Biwako Clay) is mostly comprised of clays. S Bed is constructed with the alternation of gravels, sands and silts. R Bed is composed of clays and sands. Q Bed is composed of gravels, sands and silts. P Bed is composed of gravels (Yokoyama and Takemura, 1983).

Fig. 1

Fig. 2

Fig. 1. Lithofacies, and variations of total organic carbon (TOC) and C/N with depth in a 1400 m core sample of Lake Biwa. TOC and C/N: determined by N. Nakai. Lithofacies: determined by T. Yokoyama, Y. Nakagawa and K. Takemura. T Bed, clays; S Bed, alternations of sands and silts with gravels; R Bed, clays and sands; Q Bed, gravels, sands, and silts; P Bed, gravels.

Fig. 2. Variations of chloroform extractable (CHL-E) carbon and chlorophyll-like pigments with depth in a 1400 m core sample of Lake Biwa ($\mu\text{g/g}$, in dry weight of sediment).

Total organic carbon and C/N (after N. Nakai) in Fig. 1 are consistent with the lithofacies. Significant amount of organic substances in T Bed may be derived from aquatic organisms, while that of S Bed may be derived from terrestrial substances rather than aquatic biota, according to C/N and grain size.

Concentrations of total CHL-E carbon and chlorophyll-like pigments in dry weight sediment with depth are shown in Fig. 2. The former varies with each depth especially in the S Bed, while a relatively large amount of the pigments is present in the clays (T and R Beds). The relationship between the chlorophyll-like pigments and the CHL-E carbon is very characteristic in the T Bed and others. The CHL-E carbon is abundant in S Bed and it may be derived from terrestrial organic matter or littoral biota such as macrophytes which may supply only a small amount of the chlorophyll-like pigments as suggested by Wetzel (1970) and others. On the contrary, large quantities of chlorophyll-like pigments

are preserved in the sediment of the T Bed in which the water depth is estimated to be about the same as the present lake from Mn concentrations (Koyama *et al.*, 1985) and grain size. Those pigments may be derived from aquatic biota and the CHL-E carbon in the T Bed is the mixture of allochthonous and autochthonous sources.

The significant correlation between the ratios of those total pigments to CHL-E carbon and the percentages of the calculated chlorophyll *a* which is not identified by other methods, in total chlorophyll-like pigments can be obtained in the T Bed ($r=-0.7$, $n=44$). The percentages decrease with increase of the total amount of the pigments and seem to increase again at very high chlorophyll concentrations. Those percentages may reflect the total productivities, climates, species of flora, water depth, geological conditions and others. With respect to the samples in the T Bed those factors can be limited to total productivities and climates. The preservation of the calculated chlorophyll *a* may be good at the ages of extraordinarily large productivities because of large sedimentation rate and low temperatures in the water.

Fig. 3. Variations in the ratios of chlorophyll-like pigments carbon to CHL-E carbon and percentages of calculated chlorophyll *a* to total chlorophyll-like pigments with depth in a 1400 m core sample of Lake Biwa.

Thus variations of the ratios of total chlorophyll-like pigments carbon to CHL-E carbon, determined in this study, may show climatic changes of Lake Biwa in the Pleistocene.

Variations of those ratios and the calculated chlorophyll *a* percentages are shown in Fig. 3. Relatively higher values of chlorophyll-like pigments are obtained at 30–40 m, 70–80 m, 124 m, 136 m, 158 m, 200 m, 230–240 m, 287 m, 457 m, 497 m, 605 m, 668 m, 716 m and 796 m, while relatively higher values of the percentages of the calculated chlorophyll *a* in the total chlorophyll-like pigments

which mean cold climates or rapid input of sands and silts, are obtained at 22 m, 52 m, 104 m, 151 m, 170 m, 222–250 m, 275 m, 336 m, 360 m, 421 m, 473 m, 545 m, 570 m, 665 m and 730 m. Variations of these data in the upper 100 m are similar to those of the relative units of chlorophyll derivatives in the 200 m core sample of Lake Biwa (Handa 1975, 1984), though the variations of the abundance and the depth are not the same. However, there are obviously differences between them in the lower parts. Handa observed relatively higher values in 11–25 m, 59–70 m, 90–99 m, and 140–145 m and described the origins of chlorophyll derivatives partly coming from diatoms at 140–145 m. In this core, Kadota (unpublished) found *pediastrum* at 197.2 m and 638.4 m in which relatively higher contents of chlorophyll pigment are present.

The degradation products of chlorophylls, for instance, phytol, phytane, pristane and substances having porphyrin nuclei such as pheophorbides (Hata *et al.*, 1980) are present in old sediments which are analysed by time-consuming and sophisticated methods. Calculated amounts of chlorophyll pigments with phytol concentrations, determined by gas chromatography in the few samples of the core ranges one to four times of the chlorophyll-like pigments of this study. These differences are due to the various pheo-pigment degradation products absorbing the measuring wave length 665 nm and having different molar extinction coefficients from chlorophyll *a* and pheophytin in the Lorenzen equation. Thus the spectrophotometric analysis is very convenient method for the measurement of paleoproductivities and paleoclimates of core sediments preserved in water.

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