CHLOROPHYLL DERIVATIVES, SULPHUR, AND CARBON IN SEDIMENT CORES FROM TWO ENGLISH LAKES¹

EVILLE GORHAM

Abstract

Chlorophyll derivatives, sulphur, and carbon exhibit similar trends in each of two sediment cores, one from the fertile Esthwaite Water and the other from the unproductive Ennerdale Water. In Esthwaite Water maximum levels of all three constituents were reached early in the course of lake development, while in Ennerdale Water maxima were attained much later, and, in the case of chlorophyll derivatives and sulphur, were much lower than in Esthwaite. Relatively high optical densities of acetone extracts between 400 and 500 $m\mu$ suggest the presence of carotenoids in surface muds from Esthwaite Water. Much lower optical densities were recorded for this wave-length range in extracts of deeper sediments from Esthwaite and all sediments from Ennerdale. Low ratios of optical density at 410 $m\mu$ to density at 350 $m\mu$ are characteristic of surface sediments from infertile lakes such as Ennerdale Water, and of woodland soils. However, higher ratios near to those observed throughout the Esthwaite core were found in the deeper Ennerdale sediments, with the exception of the deepest sample.

Ratios of chlorophyll derivatives to carbon and of sulphur to carbon were higher in the more fertile Esthwaite Water, although relatively low ratios during the earliest stages of development indicate that this lake may have been less fertile then. In Ennerdale Water the ratio of chlorophyll derivatives to carbon exhibited a much slower rise to maximum values than in Esthwaite, and these maxima were much the same as the early Esthwaite minima. The ratio of sulphur to carbon was also consistently lower in Ennerdale Water.

Introduction

Chlorophyll derivatives, sulphur, and carbon show marked intercorrelations in surface muds from five lakes in the English Lake District, and rise in concentration with increasing lake fertility (2). The present study examines these constituents in sediment cores from two of the above lakes, one shallow and fertile (Esthwaite Water) and the other deep and unproductive (Ennerdale Water). Some physical and chemical properties of these lakes are given in an earlier paper (2). In Esthwaite Water the bottom waters become anaerobic in summer, while in Ennerdale Water oxygen concentrations remain high (5).

Methods

Sediment cores down to the glacial deposits were taken from the deepest parts of the lakes with the Mackereth core sampler (3), and stored in a cold room. Fresh samples taken at irregular intervals down the core were analyzed for chlorophyll derivatives within a few days. Dried samples were stored for carbon and sulphur measurements. The analytical methods have been described (2). Relative concentrations of chlorophyll derivatives were estimated from the light absorption peak of 90% acetone extracts at about 667 $m\mu$, and are reported in arbitrary units. One unit is equivalent to an optical density of

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Contribution from the Department of Botany, University of Toronto, Toronto, Ontario.

0.1 in a 1-cm cell when dissolved in 100 ml of solvent (cf. 8), after subtracting an approximate correction obtained by drawing a freehand baseline to the absorption curve between 550 and 750 $m\mu$ (cf. 6).

Results

Analytical results for the lake muds are presented in Fig. 1, on a dry weight basis. The first point to remark is the similarity of carbon concentrations in the upper muds of both lakes. Other cores from Esthwaite Water have shown up to twice the carbon concentrations of the present core, and Esthwaite surface muds are usually much richer in carbon than those of Ennerdale. Unfortunately it was not possible to analyze other cores before the author's departure from England, but the similarity of carbon values in these two cores accentuates the differences in their contents of sulphur and chlorophyll derivatives.

While carbon, sulphur, and chlorophyll derivatives follow similar trends, the two lakes exhibit marked dissimilarities in profile distribution of these three constituents. In Esthwaite Water all show a rapid rise to maximum levels rather deep in the mud column, especially in the case of carbon. The maximum for carbon is 9.5% dry weight at 340 and 380 cm depth, for sulphur 0.59% at 340 cm, and for chlorophyll derivatives 114 units per 100 g dry weight at 310 cm. In subsequent deposits a slight decline is evident in concentrations of all three constituents. In contrast to Esthwaite, maximum concentrations

FIG. 1. The distribution of carbon, chlorophyll derivatives, and sulphur in cores from Esthwaite Water (ES) and Ennerdale Water (EN).

are reached much more slowly in Ennerdale and occur in the upper half of the mud column. In this case the maximum for carbon is 11.6% dry weight at only 70 cm depth, for sulphur it is 0.32% at 250 cm, and for chlorophyll derivatives 38 units per 100 g dry weight at 178 cm.

While carbon concentrations are generally similar in the upper parts of the two cores, that from the more fertile Esthwaite Water is much richer in both chlorophyll derivatives and sulphur. High levels of both these constituents, and high ratios to carbon, are associated with strongly reducing conditions (2), which are more likely to occur in the surface sediments and bottom waters of productive lakes such as Esthwaite Water than in those of infertile lakes like Ennerdale Water (5).

Examination of the absorption spectra of 90% acetone extracts, from which amounts of chlorophyll derivatives were estimated, presents interesting problems. In Fig. 2 are shown spectra for a surface sample (0-5 cm) from Esthwaite Water, a core sample from 570 cm in the same lake, a surface sample (0-5 cm) from Ennerdale Water, and another core sample from 550 cm in the latter lake. All have been adjusted to give equal optical densities for the red peak between 665 and 670 m μ . The first spectrum is similar to others from samples taken at 0-1, 6-7, and 9-10 cm in Esthwaite Water, while the second is much the same as spectra from Esthwaite core samples at 250 and 380 cm. The surface Ennerdale sample provides a spectrum only slightly different from those at 0-1 and 10-11 cm, while the spectrum of the deep sample closely resembles that of another sample at 300 cm, and yet another at only 16 cm depth. The points of resemblance between these spectra and that of pheophytin *a* have been described in the earlier study of surface muds (2, cf. also 6).

It is apparent that the surface Esthwaite spectrum shows much greater optical density in the region of 400-500 m μ than does the deeper spectrum.

FIG. 2. Absorption spectra of 90% acetone extracts of muds from different depths in Esthwaite Water and Ennerdale Water.

If the values for the deep core are subtracted from those of the surface mud (cf. 8), the difference curve exhibits a distinct maximum optical density at 450 $m\mu$, and a shoulder at 470–480 $m\mu$, suggesting (cf. 7) that carotenoid pigments may be present in the surface deposit to a much greater degree than below. If so, it is impossible at present to state whether or not they were initially high in the sample at 570 cm depth, and destroyed during diagenesis; but the problem deserves further investigation. Neither surface nor deep Ennerdale samples show such high optical densities at 450–480 $m\mu$ as does the Esthwaite surface sample. Surface muds in Ennerdale are much better aerated than those of Esthwaite (5), so that carotenoids might be more liable to oxidative destruction in the former lake.

Work on surface muds (2) suggested that the ratio of optical density at 410 $m\mu$ to that at 350 $m\mu$ rises with increasing lake fertility. However, while surface samples from 0–1, 5–6, and 0–5 cm depth in Ennerdale yielded low ratios of 1.1, 0.8, and 0.9 respectively, the 18 samples from 16 cm downward in the Ennerdale core gave ratios ranging from 1.2 to 1.5, except for the deepest sample, which yielded a ratio of only 0.8. Esthwaite core ratios of 1.4, 1.4, 1.6, 1.6, and 1.4 were recorded from 140-, 250-, 380-, 460-, and 570-cm depths respectively. The subsurface Ennerdale core ratios are therefore only slightly lower than those of Esthwaite, and they also fail to show any correlation with either carbon content or the amounts of chlorophyll derivatives in the mud. Possibly the high optical densities shown by extracts of Ennerdale surface mud at 350 $m\mu$ are due to substances produced by oxidation in the relatively aerobic uppermost deposits in this lake; and these substances might subsequently be reduced when further sedimentation has led to development of anaerobic conditions in the former surface layer. Spectra from extracts of aerobic woodland soils resemble those from surface Ennerdale muds in exhibiting high optical densities at 350 $m\mu$, but are even more extreme in this respect (1).

Discussion

Calculation of the amounts of chlorophyll derivatives and of sulphur per unit of carbon reveals some points of interest, as shown in Fig. 3. Not only is the Esthwaite core richer than the Ennerdale core in absolute terms, but the ratios of both constituents to carbon (and therefore to total organic matter) are also higher in the more fertile Esthwaite Water. This is in accord with results from surface muds (2).

For Ennerdale, Fig. 3 shows a gradual increase in the ratio of chlorophyll derivatives to carbon from the bottom of the core upward, to levels varying between about 3 and 5 units per g of carbon in the upper half of the core. If results from surface deposits in the five lakes previously studied (2) are any guide, this suggests a gradual increase in lake productivity. The ratio of sulphur to carbon is more constant, with sulphur ranging between 2.4 and 4.1% of carbon. The percentage is rather high toward the bottom of the core, and perhaps in these relatively inorganic sediments there may be a greater contribution from pulverized rock flour than in the upper and more organic muds. The minimum percentage of sulphur is found at 400 cm depth, above which levels tend to increase toward the surface. There is, however, a low value

FIG. 3. Chlorophyll derivatives and sulphur calculated per unit of carbon in cores from Esthwaite Water (ES) and Ennerdale Water (EN). Interrupted lines join thin sediment bands to continuous mud column.

(2.7%) at 70 cm, where organic carbon is maximal; and at this depth the content of chlorophyll derivatives in the organic matter also shows a marked drop (to 2.8 units per g carbon).

In Esthwaite Water the content of chlorophyll derivatives per unit organic matter is lower in the two organic bands at the bottom of the core, and in the bottom sample from the continuous mud column, than in the muds above. However, the levels toward the bottom of the core are about the same as the maximum levels attained in Ennerdale Water, ranging from 4.6 to 5.6 units per g of carbon. This suggests that Esthwaite at its least productive may have been as fertile as Ennerdale at its best. A sharp rise occurs in subsequent Esthwaite deposits, to levels of about 10–13 units of chlorophyll derivatives per g of carbon throughout the top 3 m of the core. These values are similar to those obtained from six surface samples of distinctly higher organic content, whose carbon concentrations ranged from 11 to 13% dry weight.

The lower concentrations of chlorophyll derivatives in the organic matter of the earliest deposits indicate that Esthwaite Water may have been less productive in its early than in its later stages of development. Even where carbon concentration reached 9.3% dry weight, at 420 cm, there were only 5.5 units of chlorophyll derivatives per g of carbon. According to Mackereth (4), the exceptionally high levels of manganese toward the bottom of Esthwaite mud cores suggest that these early deposits did not become reduced right to the surface during summer, as they do at the present day; and this supports the view that the lake was less productive then. Further evidence comes from the deepest horizons of the continuous mud column, where sulphur also is low, being 4.3% of carbon at 420 cm depth, and 3.4% at 380 cm, in contrast with levels above 6% in the immediately succeeding deposits. A slight decline in sulphur concentrations occurred as sedimentation proceeded, to levels of about 5–6% of carbon in the uppermost muds.

It may be noted that the thin organic bands in the glacial deposits of Esthwaite Water are relatively rich in sulphur, especially the upper one. While much of the sulphur in the mud column above is no doubt of organic origin, presumably a good deal of the sulphur in the thin mud bands has

migrated in along a negative redox gradient from the pulverized rock flour above and below. In the case of Esthwaite Water this rock flour must be largely derived from the sedimentary rocks of the drainage basin; Ennerdale Water, on the other hand, drains mainly igneous strata. In this connection, too, the upper material of the glacial deposit between the two organic bands is probably much less weathered than the lower, since the former effervesces with hydrochloric acid and therefore retains much of its original calcium carbonate (Mackereth, oral communication). Such an unweathered sedimentary rock flour might well contain appreciable amounts of sulphur, as suggested by the high concentrations recorded from the mud band in it.

Concluding Remarks

From the foregoing results, taken together with those from surface deposits (2), it would seem reasonable to conclude that high ratios of chlorophyll derivatives to carbon may indicate productive phases in the history of a lake, while low ratios reflect periods of relative infertility. If so, it is noteworthy that the more fertile lake, Esthwaite Water, developed rapidly toward a more or less steady level of high productivity, while the relative sterility of Ennerdale Water entailed a much slower development to its present low level of productivity.

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