Geochemical indicators in lake sediment of upland erosion caused by Indian and European farming, Awenda Provincial Park, Ontario

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Neutron-activation analysis, loss on ignition (LOI), and X-ray diffraction of eight cores collected in Second and Gignac lakes are correlated with historic and palynologic records to identify elements linked to erosion from deforestation and farming.

Forest disturbance and farming are identified in cores of organic detritus sediment (gyttja) by decreased LOI and increased Na, Mg, Ba, Al, Ti, and Dy. LOI is not suitable for identifying forest disturbances in carbonate sediments. From neutron-activation analysis of carbonate mud only Na, Al, and Dy indicate erosion.

Elements linked to the quantity of organic matter in sediments include U, V, and Cl, whereas Mn and I in surface sediments presumably correspond with variations in the oxidation potential and plant productivity, respectively.

Sedimentation patterns relate to basin morphology. In Gignac Lake the basin is steep sided and relatively deep. Clastic detritus entering the lake is carried over the shallow, nearshore carbonate bank into deeper water. In Second Lake the basin is shallow and gently sloping. Minerals eroded from onshore are more equally distributed in this basin. In Second Lake the most rapid sedimentation is nearshore where submerged aquatic macrophytes produce and trap carbonate mud. In Gignac Lake the top of the shallow carbonate bank has few aquatic macrophytes; lime mud formed on the bank is washed into deep water offshore, where it dissolves.

Les résultats de l'analyse par activation neutronique, de la perte au feu (PAF) et de la diffraction des rayons-X de huit carottes prélevées dans les lacs Second et Gignac sont mis en corrélation avec les registres historiques et palynologiques dans le but d'identifier les éléments impliqués dans l'érosion provoquée par la déforestation et la mise en culture. La déforestation et la pratique de l'agriculture se traduisent dans les carottes de sédiments de détritus organique (gyttja) par une diminution de la PAF et une augmentation du Na, Mg, Ba, Al, Ti et Dy. La PAF de sédiments calcaires ne permet pas de dépister les abattements forestiers. Dans l'analyse par activation neutronique de boues calcaires, seuls le Na, Al et Dy peuvent indiquer un événement d'érosion.

Les éléments liés à la quantité de matière organique dans les sédiments incluent U, V et Cl, tandis que Mn et I des sédiments de surface correspondent possiblement aux variations du potentiel d'oxydation et à la productivité des plantes, respectivement.

Les motifs de la sédimentation sont en relation avec la morphologie du bassin. Le bassin du lac Gignac est profond et présente des côtés abrupts. Le détritus clastique entrait dans les lac est transporté par-dessus le banc calcaire de faible profondeur près de la rive dans une zone d'eau plus profonde. Dans le lac Second le bassin est peu profond et les parois ont une faible pente. Les minéraux libérés par l'érosion des terrains en bordure du lac sont distribués de manière plus homogène dans ce bassin. Dans le lac Second le taux de sédimentation est plus élevé près de la rive du lac où des macrophytes aquatiques submergés produisent et piègent de la boue calcaire. Dans le lac Gignac le sommet du banc calcaire sous une mince lame d'eau ne possède que très peu de macrophytes aquatiques; la boue calcaire formée sur le banc est lavée et transportée en eau profond où elle est dissoute.

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Introduction

Deforestation, whether by natural or artificial means, increases the erosion of minerals and nutrients to rivers and lakes (Baker and Krumer 1973; Bormann *et al.* 1974; Davis 1976; Likens *et al.* 1977; Brugham 1978*a,b*; Mathewes and D'Auria 1982; Engstrom and Wright 1984). Evidence of erosion depends upon the intensity and duration of deforestation and the preservation potential of the eroded material.

Lakes collect material eroded from the upland areas. Minerals and nutrients wash into lakes and settle to the bottom where a stratigraphic record is preserved. Ancient vegetation disturbances that produced increased influx of detrital minerals should be easily recognized in the sediment. However, in practice, deforestations are difficult to identify from lake sediment. Little is known about the natural evolution of lakes, sediment diagenesis, and the effects of upland vegetation disturbance on sedimentation.

Our purpose is to examine the geochemistry of lake sediments using neutron-activation analysis (NAA), X-ray diffraction analysis (XRD), and loss on ignition (LOI) to identify elements and minerals linked to deforestation and erosion. Sediment cores from Second and Gignac lakes (Fig. 1) are examined for systematic stratigraphic changes that correlate with historic accounts and palynologic evidence of deforestation. These lakes are suited for examining sediment variations related to deforestation. From about A.D. 1450 to 1650, Huron Indians cleared land around these lakes for fields of corn, beans, and squash. Later, between 1870 and 1950, Europeans cleared the forest that had grown since the Indians abandoned the area and farmed the land around Second Lake for grain and other crops. By identifying vegetation disturbances from the palynologic record, variations in elements, minerals,

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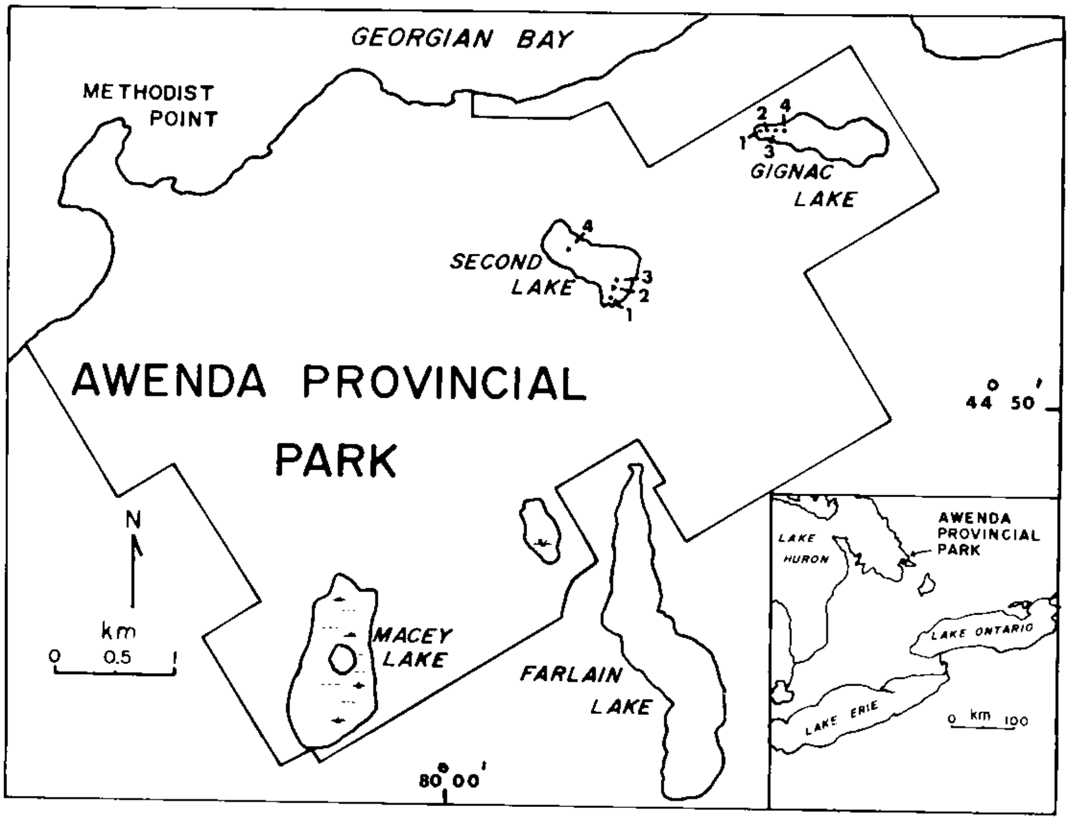

FIG. 1. Location map of Awenda Provincial Park showing coring sites in Second and Gignac lakes.

and LOI linked to deforestation are identified. By recognizing events related to human activity, changes to lakes from fires and other natural phenomena may be more easily identified and upland and lacustrine response patterns established.

Geological and limnological setting

Second and Gignac lakes are two elongate, east–west-trending kettle lakes in a boulder till dominated by mixed calcareous sand and crystalline rock, here partly modified by glacial streams and proglacial and postglacial lakes. Shoreline terraces of glacial Lake Algonquin surround each lake, and a prominent postglacial Lake Nipissing bluff separates these small lakes from Georgian Bay to the north. Dunes and sand and boulder beaches cover much of the original till and outwash surface around each lake.

Water flow into these lakes is controlled by surface runoff, small springs, seepage, and precipitation. Second lake is drained by a small stream at the northeast end of the lake. The drainage from Gignac Lake is by groundwater seepage because there is no outlet.

Limnological data for these lakes are scant. The bottom of Second Lake slopes gently away from the shore into a shallow basin 4.5 m deep. Uniform profiles of temperature (15°C), oxygen (8 mg L^{-1}), carbon dioxide (10 mg L^{-1}), pH (6.6), and alkalinity (130 mg L^{-1}) were measured from the deepest part of the lake in May 1968 (Odom and Wildsmith 1968). In this part of southern Ontario, lakes over 3.5 m deep begin to stratify in late May through early June; lakes less than 3.5 m deep are unstratified (R. Toth, personal communication, 1984). A poorly developed hypolimnion 1 m thick probably occupies the centre of the lake basin in the summer months.

The bathymetry and morphometry of Gignac Lake are only known from the western end of the lake where coring in 1975 and a SCUBA dive in 1976 were done. Here a nearly level carbonate bank in water about 1 m deep extends from the western shore about 200 m into the lake. The bank edge slopes between 30 and 45° into a basin approximately 9 m deep. Although no measurements were collected on the dive, the deeper water was noticeably colder than the surface water. A well developed hypolimnion up to 5 m thick is probably present in this basin during the summer months.

Around the shore of Second Lake there are marshes with sedges and rushes growing among recently drowned trees. Offshore, the bottom of Second Lake supports a dense mat of *Chara* and *Najas*. At Gignac Lake the forest extends to the shoreline (Burden 1978). Aquatic plants include *Chara* on the carbonate bank and a dense *Chara* bed at the break in slope below the carbonate bank.

Methods

The collection and sampling of cores for analysis are outlined in Burden *et al.* (1986).

Samples for water content and LOI (3–5 cm^3) were collected from each level with a syringe (see Fletcher and Chapman 1974) and dried and ashed (Dean 1974).

A Phillips X-ray diffractometer was used to determine the mineralogy of surface sediments from Gignac Lake. Surface samples of the four cores were dried at 105°C for 6–8 h and powdered for analysis. Diffractograms made with Fe-filtered radiation at 40 kV and 15 mA were scanned at 1° 2θ/min with a 1° divergence slit and a 1° receiving slit. Radiation was detected with a focusing monochrometer and sealed proportional counter. For mineral identification, diffractograms were compared with mineral standards in Berry (1972).

Before detrital minerals were successfully detected in these surface sediments, carbonate was removed by dissolving with 10% HCl and organic matter ashing at 500° for 1 h.

A quantitative estimate of element stratigraphy was determined by instrumental NAA. Elements were selected from the major and detrital minerals identified by XRD and the measurable elements chemically associated with organic matter. The important nutrient elements P, N, and C were not examined here because their nuclear properties were not suited to the irradiation technique.

The University of Toronto SLOWPOKE-II nuclear reactor was used to irradiate samples. Sample preparation for irradiation followed Cwynar (1978) In addition, each 250 mg sample was powdered and homogenized before being transferred to a 1 cm^3 polyethylene vial.

All samples were irradiated individually at position 1 in the reactor for 3 min at 2 kW with a flux of 1×10^{11} neutrons cm^{-2} s^{-1}. Irradiated samples were set aside for 12 min to allow isotopes to decay to countable levels. They were then positioned adjacent to the vertical face of a Canberra Ge(Li) detector coupled through a 452 Ortec spectroscopy amplifier to a Canberra 8100 series, 4096 channel analyser. Gamma ray emissions were counted for 5 min; total emission and background radiation levels produced by the elements were measured. The kinds of elements counted varied with the sediment composition and the detection limits possible with the irradiation formula.

An outline of the limits to precision of analysis and accuracy of determination achieved for elements examined is listed in Table 1. Further details on National Bureau of Standards (NBS) standards and multiple analyses of sediment samples have been given in Burden (1978).

Influx calculations

To determine variations in element influx into these lake sediments, the sedimentation rates were estimated from the palynologic record of local historic events (Fig. 2). Three palynologic horizons were linked with historic events (Burden *et al.* 1986) to determine sedimentation rates (Fig. 3).

Only offshore cores, collected from deeper water, were analysed for influx. Shallow-water cores were unsuitable for calculating influx. In Second Lake core 1 a high sedimentation rate and a good stratigraphic record were expected, but bioturbation and sediment drag from roots during coring caused contamination of critical horizons. In Gignac Lake the shallow-water cores 1 and 2 have very slow sedimentation rates; pollen analyses indicate that this condensed stratigraphy is blended (Burden *et al.* 1986). The deeper water cores from both lakes contain a continuous stratigraphic record.

The most straightforward method for calculating sedimentation rate is to assume constant sedimentation between dated stratigraphic intervals. For long cores of uniform sediment composition this method is probably accurate to the limits of the dated intervals. However, for short cores, where more precise dating is required, constant sedimentation rates are probably not realistic. Compaction with dehydration and variations in sediment composition can cause large, albeit short-term, variations in the real sedimentation rate. Davis (1976) showed that if the pollen influx to surface sediments is considered constant, the variations in pollen concentration at depth reflects differences in sedimentation rates. This method is most useful if the vegetation producing the pollen is undisturbed, a requirement not met here. Two cycles of deforestation and regeneration have occurred during the last 530 years (Burden *et al.* 1986).

More complex models for determining sedimentation rates are not easily derived. Useful models must consider both the compaction rate and fossil material as variables. For our study, a curve is empirically fitted to the marker horizons in each core (Fig. 3). For cores of uniform composition (i.e., Gignac Lake 4) this probably reflects the real sedimentation rate. However, for cores of variable sediment composition only total compaction and dehydration are considered; differential compaction of the various lithologies is not measured.

TABLE 1. Analytical precision and accuracy of element analyses

Element	Analytical precision (%)	Accuracy (%)
Ca	5	10
V	5	15
U	12	10
Cl	9	10
Br	10	25
I	2	Unknown
Na	15	20
Mg	7	20
Mn	2	5
Ba	15	25
Al	4	10
Ti	12	25
Dy	26	Unknown

NOTES: Precision and accuracy are calculated from multiple analyses of NBS standard cements (SRM 1011, 1015, and 1016), a limestone (SRM 16), a coal (SRM 1632), a standard sewage sludge (CCIW "D"), and carbonate mud and gyttja from both lakes. (See Burden 1978.) Elements with poor or unknown precision or accuracy are used for determining general distribution trends only.

Element influx into lake sediment was determined by relating the concentration of an element (micrograms or milligrams per gram) in a measured sediment sample with the rate of sedimentation. The equation used to determine the influx is

$$\text{element influx (g cm}^{-2}\text{ year}^{-1}) = \frac{\text{dry wt. sample (g)} \times \text{element concentration (g)}}{\text{wet sample (cm}^{3}) \times \text{deposition time (years cm}^{-1})}$$

Recurring element groups

Correlation coefficients of geochemical data, corrected for differences in the number of samples analyzed with a *t* test for probability of significance, were calculated from Kirch (1973).

Recurring groups of elements were calculated from element pairs correlated above 0.99 probability (Fager 1957). By identifying relationships among elements in cores, recurring groups of elements and elements associated with recurring groups but not forming part of a group were determined. Statistically significant recurring element groups were compared with sediment mineralogy, the history of sedimentation, and other more comprehensive studies of lake sediment chemistry to illustrate elements linked to erosion and other environment variations.

Sediment stratigraphy

Second Lake

Five beds of lime mud and gyttja with up to eight light and dark coloured interbeds have been identified in Second Lake (Fig. 4), although only core 4 contains all five beds. Sedimentation rates in core 4 are apparently slower, and older strata were penetrated. The nearshore cores have only two or three beds in a similar length of sediment. Rapid sedimentation in the nearshore cores provides greater stratigraphic resolution

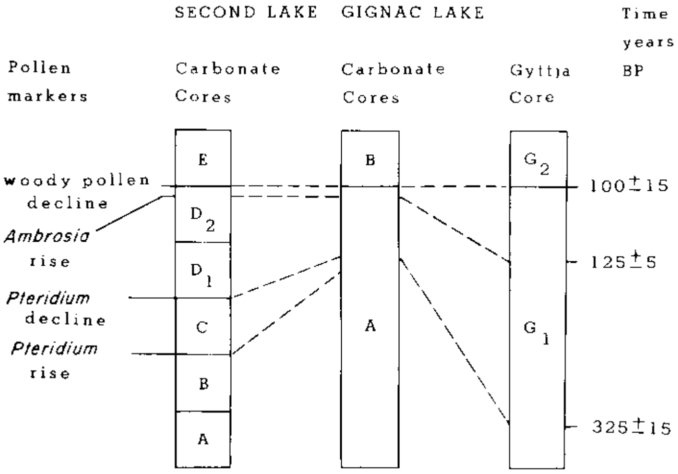

FIG. 2. Correlation of palynological horizons of historical events in Second Lake and Gignac Lake cores and their approximate age. Letters identify strata in each lake.

and are useful for separating near-recent geochemical and palynoflora changes.

Beds can be traced across the Second Lake basin. Environment fluctuations reflected in the biostratigraphy (Fig. 4) correspond with stratigraphic horizons. From the correlation of cores in Second Lake it is clear that the pattern of sedimentation is not uniform; sedimentation rates apparently increase in shallow littoral area; beds D_2 and E increase from 30 cm thickness in core 4 to 94 cm in core 1.

Gignac Lake

Three beds of lime mud and gyttja have been recognized (Fig. 5). Beds A and B occur in the carbonate bank, whereas bed G is found in the deep water off the edge of the bank. A facies change between the shallow-water carbonate in cores 1, 2, and 3 and the deep-water gyttja of core 4 precludes a correlation based on lithology, but palynology provides correlation of the shallow- and deep-water cores.

In October 1976 the shallow-water top of the bank had an almost level surface of grey–brown mud with small, scattered *Chara* (Fig. 6). Surface sediments were loose, and shell debris with leaves and twigs was scattered on the surface; yellow–brown patches of algae-bound sediments were present. Linear gouges, exposing light grey to white sediment, were attributed to motor boat activity. The bank edge had a 30 and 45° slope, but there was no evidence of slumping. At the base of the slope the contact between the carbonate and gyttja is sharp. The surface of the basin was a mottled brown, loose, and easily disturbed gyttja; macrophytes were absent.

Sediment mineralogy

There are three types of sediment: carbonate mud, carbonate mud with organic detritus, and gyttja. The carbonate is light grey–brown, and gastropod and bivalve shells and the cortication tubules of *Chara* are abundant. As the organic detritus in the carbonate increases, it becomes dark brown, with fewer shells, cortication tubules, small twigs, and leaf fragments.

The gyttja is dark brown to grey–brown organic detritus with complete and fragmented tree leaves, twigs, and *Chara* oogonia. It lacks shells, cortication tubules, and sand-size minerals.

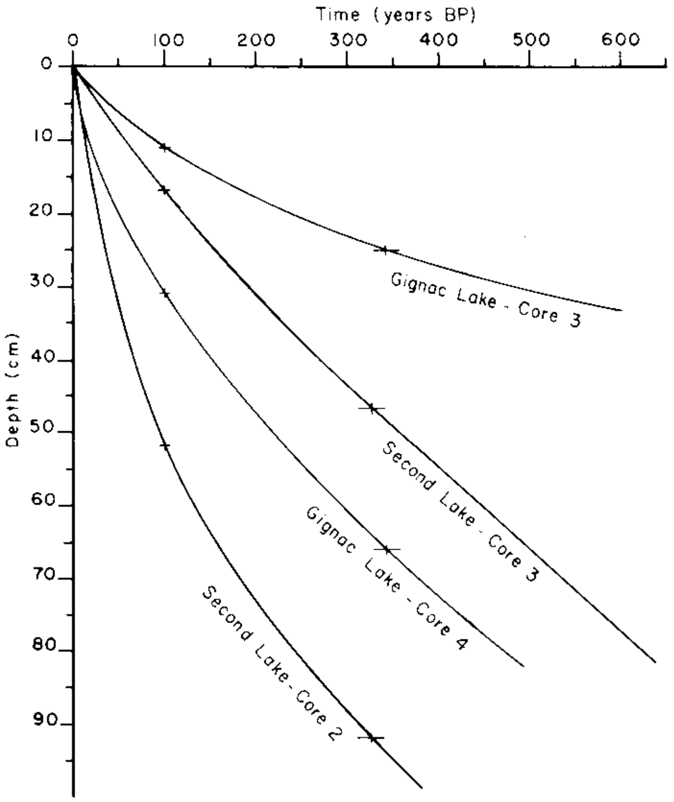

FIG. 3. Graph of sedimentation rates for Second Lake cores 2 and 3 and Gignac Lake cores 3 and 4. Time-stratigraphic horizons are for early logging and farming 100 ± 5 years BP (1875) and the initiation of forest recovery following the dispersal of the Huron 325 years BP (1650).

During examination of palynomorph residues, silt-size silicate mineral grains were identified from both the gyttja and lime mud (Table 2).

Formal identification of the minerals was by XRD (Table 2). Acid leaching of the carbonate and ashing of the organic material were used to concentrate identifiable quantities of detrital silicate minerals. A by-product of the ashing of organic sediment is anhydrite.

Sediment geochemistry

Second Lake

Water content, LOI (organic matter content), and NAA element determinations for four short cores are given with palynologic correlations in Fig. 7. The elements selected occur in the minerals identified by XRD (Ca, Na, Mg, Ba, Al, Ti, Dy), provide information concerning the redox potential of the sediments (Mn), and form organic complexes (V, U, and the halogens). Beds A, B, D_1, and E have relatively high water content and organic matter; beds C and D_2 have more ash and Ca with less water and organic matter.

Recurring element groups in cores 2 and 3 (Fig. 8) indicate geochemical and sediment relationships that perhaps correlate with historic and palynologic records. These cores are from different parts of the lake basin, but both sedimentological and palynological analyses show deposition in similar lacustrine environments.

Two groups of elements, informally called the lime mud association (CaA) and the lime and organic detritus association (CaODA), are identified by recurrent group analysis. These

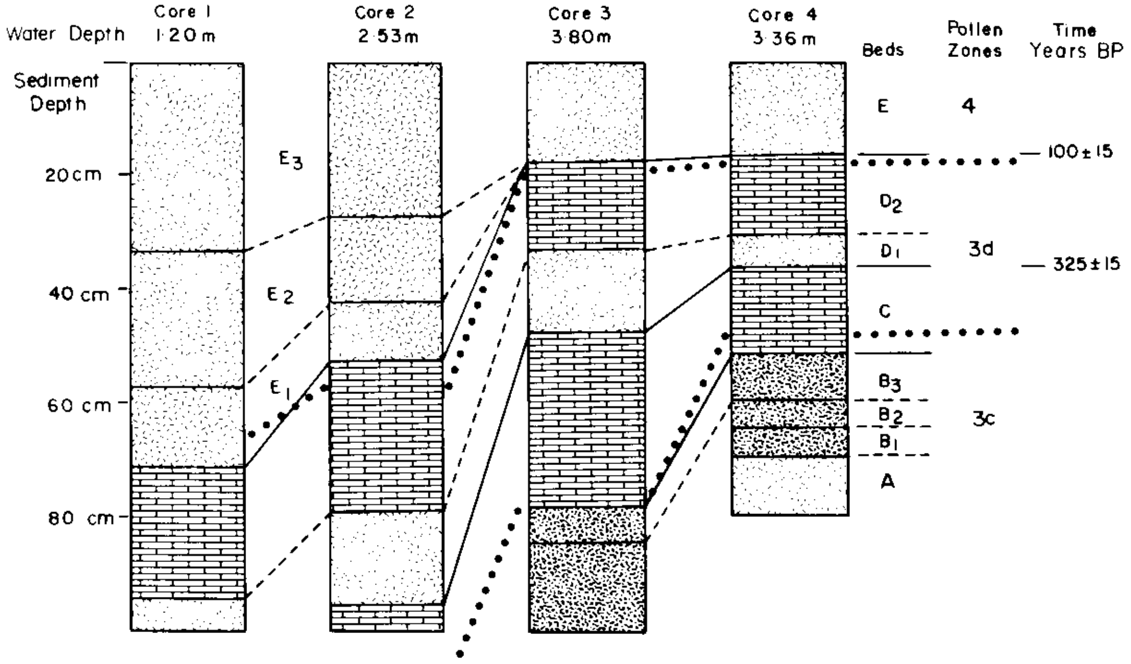

FIG. 4. Lithology and correlation of Second Lake cores. For legend see Fig. 5.

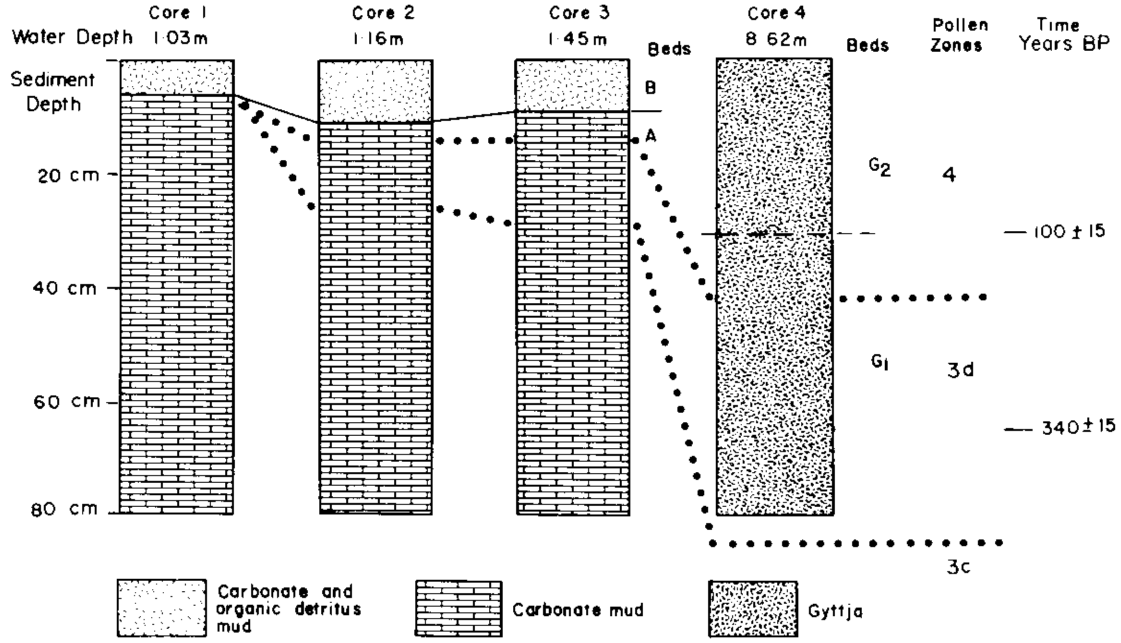

FIG. 5. Lithology and correlation of Gignac Lake cores.

groups of elements relate to lacustrine conditions in beds either at the time of sedimentation or during an ensuing diagenetic change.

In cores 2 and 3 the CaA elements are Ca and ash and Ca, Mg, and ash, respectively (Fig. 8), whereas the CaODA elements consist of U, V, Mn, Na, Dy, Al, I, H_2O, and LOI in core 2 and U, V, Cl, Na, Al, H_2O, and LOI in core 3. In core 3 Dy was not examined, and the element I had too many unreliable analyses to warrant inclusion here.

Within the CaODA element set there are subsets presumably related to the development of organic complexes (V and U in core 2 and V, U, and Cl in core 3) and subsets associated with wet, lime, and organic detritus surface sediments containing clastic mineral detritus (Dy, Al, I, H_2O, and LOI in core 2 and Na, Al, and LOI in core 3). The elements Cl, Ba, and Mg in core 2 and Ba and Mn in core 3 are not statistically associated with recurring element groups at 0.99 probability. At lower probability levels, Mg in core 2 and Mn in core 3 link with the subset of lime and organic detritus surface sediments.

Gignac Lake

For each core the water content, LOI, and element determinations are shown with palynologic correlations in Fig. 9.

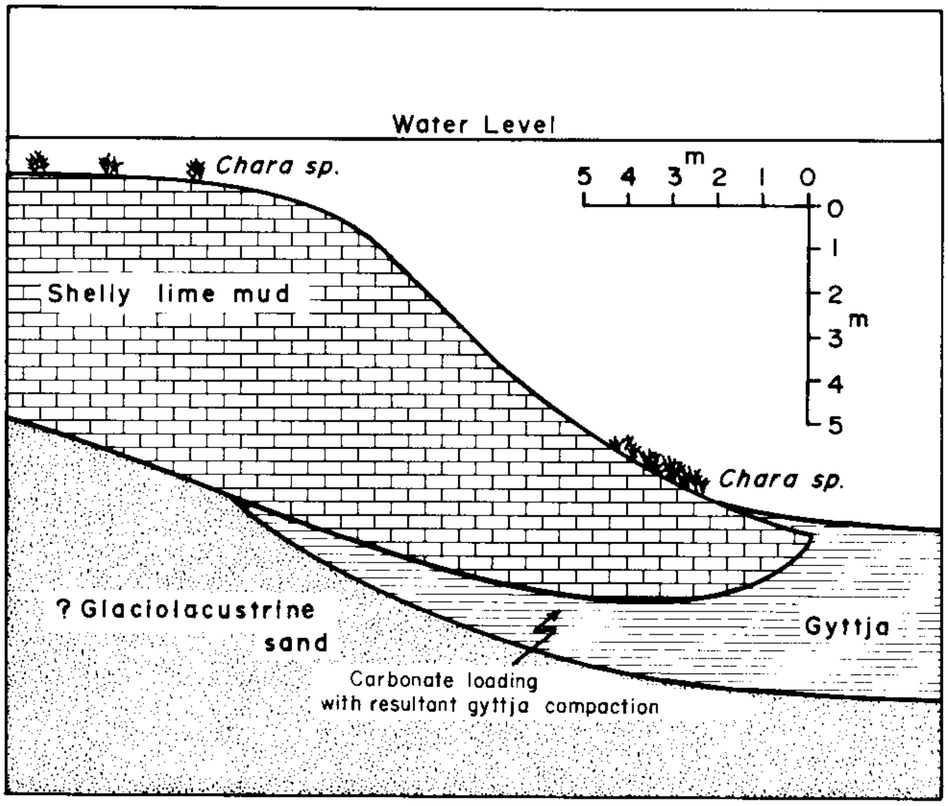

FIG. 6. Schematic carbonate bank to basin transition in Gignac Lake.

TABLE 2. Lithology and mineral identifications determined from field and laboratory studies

		Laboratory examination	
	Field examination	Microfossil residues	X-ray diffraction
Lithology and major minerals	Lime mud Lime and organic detritus mud Gyttja		Calcite
Detrital minerals		Quartz Feldspar Amphibole Pyrite Garnet	Quartz Plagioclase Amphibole Illite

The reasons for selecting these elements is the same as for the Second Lake cores. The gyttja of core 4 is enriched over the carbonate in all the elements measured except for Ba, Mg, Mn, and Ca. Only Ca and Mn occur in significantly greater concentrations in the lime muds. Water content in core 4 decreases slightly from 99% at 1 cm to 97% at 80 cm. In contrast, in the lime mud the water content drops from 99% at the surface to 60–75% at 50–70 cm depth. A pronounced decrease in water content occurs either at or immediately below the A–B contact. The LOI in the gyttja is 60–80%. This is much higher than that in the carbonate cores, where LOI is 10–25%. Detailed comparisons between the carbonate and gyttja are not practical because both the collection sites and sediment lithologies indicate different lacustrine environments.

Recurring groups of elements are calculated for Gignac Lake cores 3 and 4 (Fig. 10). These cores come from two distinctive lacustrine environments; core 3 is a carbonate mud from a shallow-water bank, whereas core 4 is a gyttja from a deep-water basin. Both cores exhibit distinctive recurrent element groups. Those of core 3 groups (Fig. 10) are nearly identical to the CaA and CaODA clusters from the Second Lake cores. However, in Gignac Lake core 4 the element groups are distinctly different from those found in carbonate muds. Here four recurring groups, a hydrophile association (HA), a lithophile association (LA), an organic association (OA), and a lithophile–organic bridge (LOB), are identified (Fig. 10). Each group is tied to another by correlations among elements from different recurring groups. Thus, for HA and LA, Mn has linkages with H_2O and I, whereas Ba has linkages with I. For LA and LOB, Dy and Ca are associated, whereas for groups LOB and OA, U, and V are associated. There are no correlations between HA and LOB, HA and OA, and LA and OA.

Element influx

Influx using variable sedimentation rates is calculated for Gignac Lake 4 and Second Lake 2 and 3 (Fig. 11). These cores provide well preserved stratigraphic sections representing the two lakes and two distinct sedimentary environments.

For Second Lake, element influx is consistently higher in core 2; values range from 2 to 10 times that of core 3. Most differences are attributed to the higher sedimentation rate of core 2; but for I the very high influx is perhaps plant material.

Influx to bed B in Second Lake is calculated from only one analysis. Comparison with overlying carbonate mud is weak; element influx for this organic sediment closely matches data for Gignac Lake core 4, bed G_1.

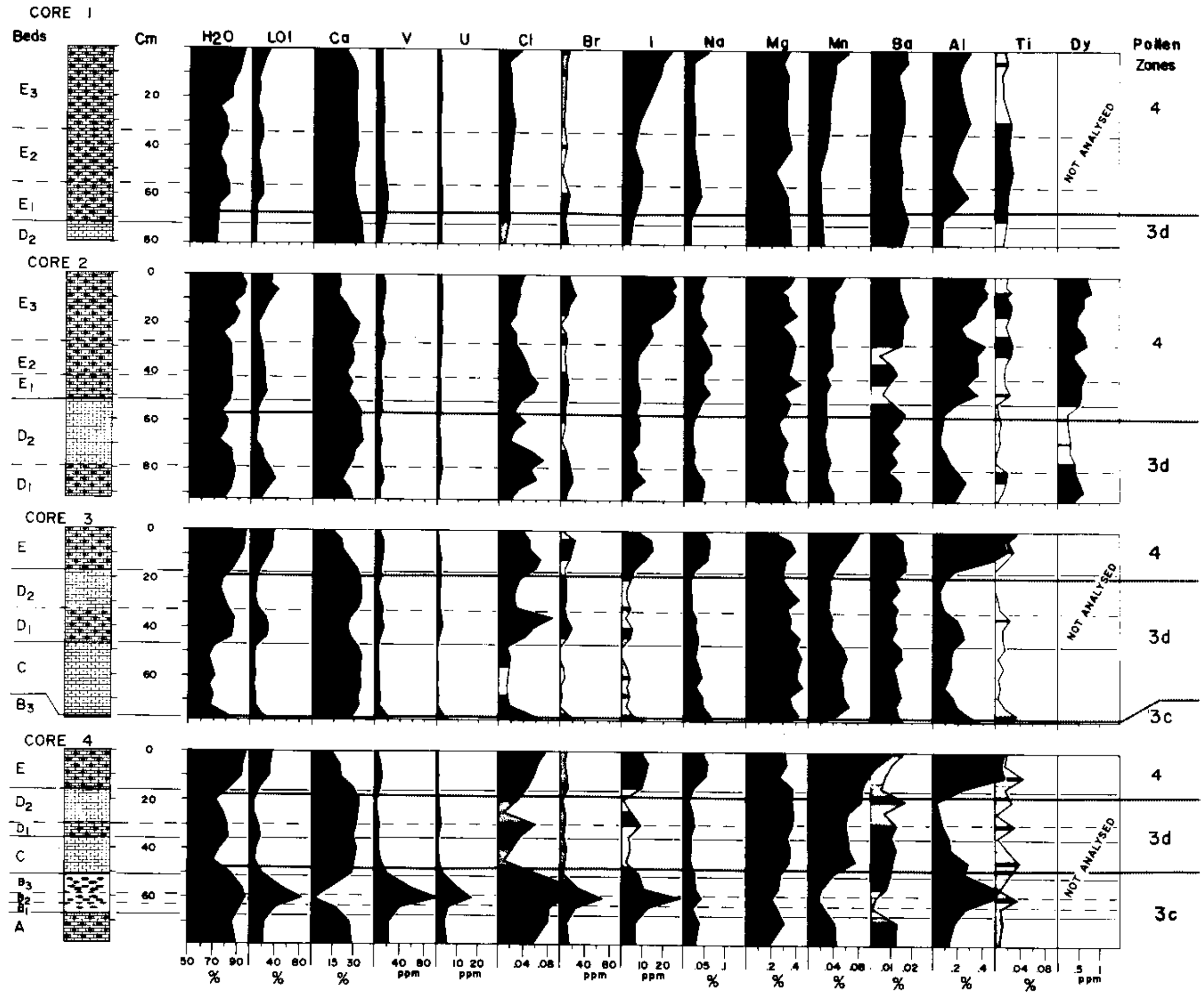

FIG. 7. Sediment geochemistry of Second Lake. Elements with unreliable analyses are unshaded.

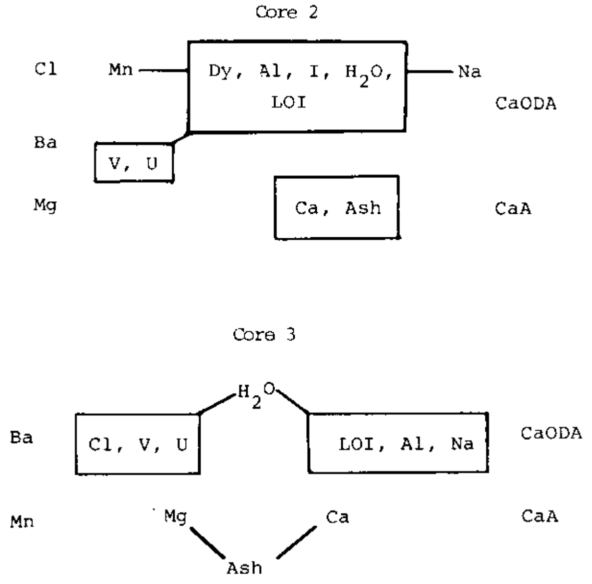

FIG. 8. Recurring element groups in Second Lake cores 2 and 3. The elements Cl, Ba, and Mg in core 2 and Mn in core 3 do not link with recurrent groups at 0.99 probability.

In bed C of Second Lake core 3, the influx of Ca, Na, Mg, Mn, Ba, and Al increase, whereas the halogens, U, V, and Ti, decrease.

Bed D_1 in cores 2 and 3 shows a reduction in the influx of Ca, Na, Mg, Mn, Ba, Al, and Dy; Cl and U increase slightly. The distribution of elements in bed D_2 is similar to bed C; Ca, Mg, Mn, and Ba are of higher influx than bed D_1. In contrast to the case for bed C, the influx of Cl, Br, and U is high, whereas the influx of Na and Al is unchanged or slightly reduced from values encountered in bed D_1.

The influx of elements into shallow and deeper water sediments of Second Lake varies in bed E. Sedimentation rates and influx calculations for slowly accumulating sediments in core 3 do not provide the same resolution as for core 2. In core 3 the influx of all elements decreases, except Na and Al. Here Na remains relatively constant, whereas Al increases to approximately the same level as bed C. Sedimentation is rapid enough in core 2 to allow differentiation of the subtle changes in element influx in bed E. For bed E_1 the influx of Al, Na, Dy, and Cl increases, Ca and Ba decrease slightly, and U, Mg, and Mn remain constant. Bed E_2 has a continued increase in the influx of Al, Na, and Dy. Likewise, Ca, U, Mn, and Mg increase slightly, whereas Cl and Ba are reduced. In bed E_3 the influx

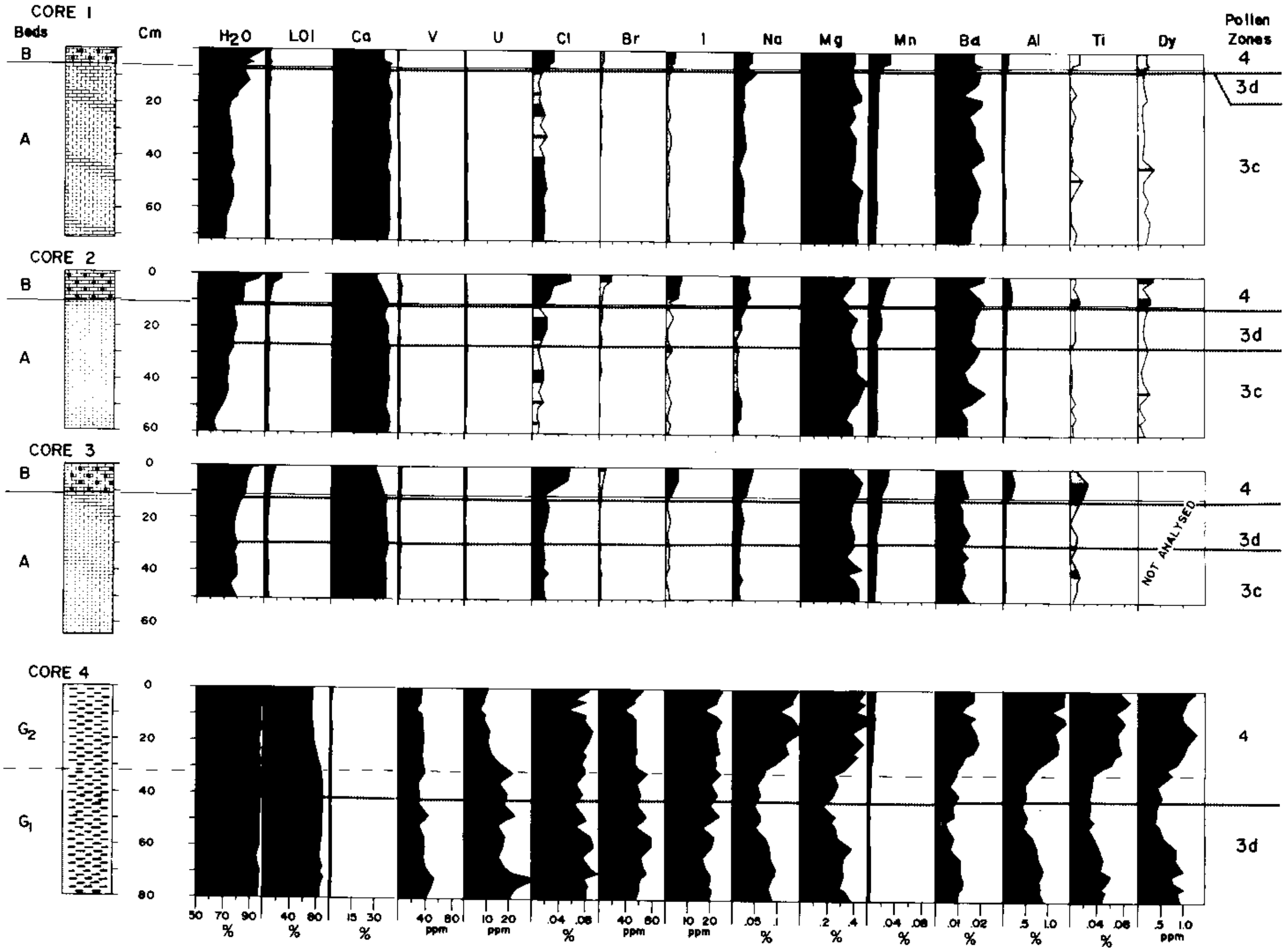

FIG. 9. Sediment geochemistry of Gignac Lake. Elements with unreliable analyses are unshaded.

for all elements decreases, except for I, which increases in these shallow-water sediments

Changes in element influx to Gignac Lake core 4 correspond with those of interbeds G_1 and G_2. For G_1 the overall influx of elements is low when compared with G_2. There is, however, a slight increase in element influx between 60 and 80 cm of bed G_1 (Fig. 11). Only U influx remains constant throughout this core.

In bed G_2, the deposition rate for elements in Gignac Lake increases. Almost every element measured increases from two to four times the influx for G_1.

The sedimentation rates for Gignac Lake core 4 and Second Lake core 2 are almost equal (Fig. 3), but element influx differs. In general, Second Lake has a much higher influx of Ca, Mg, and Mn than that in Gignac Lake core 4. Other elements have up to five times greater influx than that for Gignac Lake.

Discussion

The variations in the sediment chemistry of these lakes are not random. Physical and chemical processes, both natural and manmade, preferentially enrich different parts of these lakes with mineral and organic material. No one part of either lake contains a complete record of changes to the local environment; to achieve this end, a detailed paleolimnological study is required. From our reconnaissance study and the correlation of lake sediment chemistry and mineralogy with historic and palynologic accounts of deforestation and agriculture, it is possible to identify some of the elements linked to erosion and the production of carbonate and organic muds and to monitor element dispersal in lake basins.

Anthropogenic variations in lake sediment chemistry

Before the development of agriculture by Indians in the park (ca. 1450) the land surrounding Second Lake and Gignac Lake was predominantly deciduous forest (Burden *et al.* 1986). During this predisturbance interval gyttja was deposited in the deeper parts of Second Lake and probably also Gignac Lake. The influx of lithophile elements (recurring group LA) was low.

After 1450 Indians cleared land around Second Lake and probably also Gignac Lake for farm fields. Changes in the composition of the lake sediment correlate with the palynologic record of farming. There is increased Ca, Na, Mg, Ba, Al, Ti, and Dy in both lakes. In Second Lake much of the Ca precipitated as calcite. In Gignac Lake, and likely Second Lake, Ca and some of the other lithophile elements entered the sediment in detrital minerals. Plagioclase, amphibole, and illite identified in lake sediments contain trace to major quantities of the elements measured with NAA. Furthermore, recurrent group analysis links increased ash (detrital minerals) to

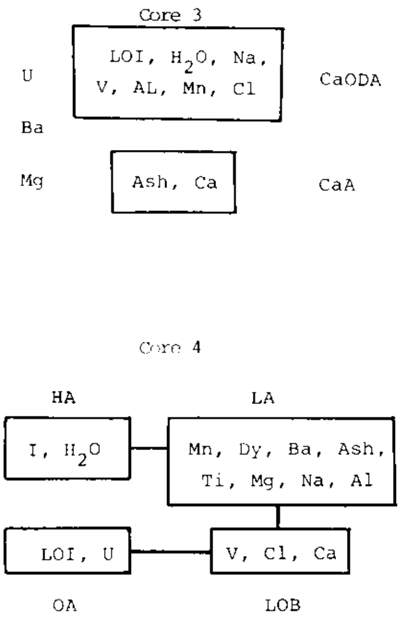

FIG. 10. Recurring element groups in Gignac Lake cores 3 and 4. The elements U, Ba, and Mg in core 3 do not link with recurrent groups at 0.99 probability.

the lithophile elements (Mn, Dy, Ba, Ti, Mg, Na, and Al) in Gignac Lake 4. Thus, with forest clearance and agriculture, increases in the influx of trace quantities of clastic detritus can be readily detected with NAA.

In 1650, after about 200 years of agriculture, the Indians abandoned this area, and it was reforested. Coincident with the pollen record showing reforestation, the sediments deposited on the bottom of each lake have reduced quantities of elements linked to erosion.

The pattern of element dispersal becomes more complex in bed D_2 of Second Lake, where Mg, Mn, and Ba, elements linked to erosion in Gignac Lake 4, increase. Apparently, other chemical (Kemp and Thomas 1976) and biological (Finlay *et al.* 1983) factors may, at times, control influx of Mg, Mn, and Ba into lake sediment. Consequently, they cannot be used routinely as indicators of erosion.

Beginning in 1870, a second cycle of forest clearance and agriculture is recorded in the sediments. In Second Lake the record of rapid sedimentation in core 2 has a sequence of element changes coincident with deforestation and farming. The influx of Na, Al, Dy, and Cl increases in the organic carbonate muds of bed E_1. Increases in Na, Al, and Dy indicate clastic material is entering this lake.

Influx of most elements in Second Lake peaks in the lower part of bed E_3, coincident with maximum European deforestation and farming. Following this some forest recovery is suggested from both the pollen record and the decreased lithophile element influx. A 30–50 year old forest surrounds most of the lake today.

In Gignac Lake core 4 the geochemical signature for forest recovery following late 19th century logging and agriculture is not as clear as that from Second Lake because farming was not practised and erosion from logging was probably low. While the present influx of lithophile elements Na and Al to Gignac Lake is comparable to that of the surface sediments from Second Lake, the influx values from Gignac Lake during the last 100 years suggest increasing soil erosion. Local forest recovery during the last 50 years should have reduced the influx of clastic detritus from the uplands. The explanation may lie in the calculation of sedimentation rates for these very young sediments. Alternatively, other mechanisms may be contributing to the influx of particulate material to these lakes. First, there are cottages on Gignac Lake, and local erosion cannot be discounted. Second, dust and other particulates are introduced to lakes and bogs as atmospheric fallout from automobiles and industry (Shiomi and Kuntz 1973; Erlenkeuser *et al.* 1974; Kemp and Thomas 1976; Oldfield *et al.* 1978; Mathewes and D'Auria 1982). Forest recovery can only eliminate the local influx of elements from erosion; the return of Second Lake to conditions approximating pre-European clearing can be related to modern forest recovery following the cessation of agriculture. With an expanding industrialized society in southern Ontario, atmospheric fallout continues to contribute material to lakes. The small quantities of exotic material found in the surface sediments of Gignac Lake (and probably Second Lake) probably come from outside sources.

Natural variations in lake sediment chemistry

In general, sedimentation in these lakes is related to variations in basin morphology. Sediment focusing models developed by Davis (1973, 1976) and Lehman (1975) agree with the sediment dispersal pattern in Gignac Lake where the lake is a steep sided and relatively deep basin with organic detritus sediments on the bottom. Shallow-water carbonate banks surrounding the lake are areas where sediments accumulate very slowly; carbonate mud and clastic and organic detritus deposited on the banks are washed by wind and currents into the deeper water, where the carbonate dissolves.

Second Lake has a shallow and gently sloping basin with carbonate banks covered with aquatic macrophytes. Carbonate muds may accumulate over the entire basin, as in bed D_2; however, the present situation may be more like that in Gignac Lake, where organic matter is more abundant in the deeper water. The sediment dispersal patterns in Second Lake are unlike those described by Davis (1973, 1976) and Lehman (1975) and unlike those observed in Gignac Lake. The gently sloping margins support a thick plant cover that inhibits the movement of carbonate and eroded clastic detritus into deeper water. Consequently, sedimentation rates are faster near shore.

The distribution of carbonate mud and the clastic detritus is related to physical and biological conditions in each lake. The annual heat budget for lakes is related to lake area, volume, and mean depth (Gorham 1964; Schindler 1971). Small, shallow lakes are more completely heated than areally equivalent deep lakes. Ascending convection cells formed by radiative warming of the bottom water on sunny days promotes heating efficiency (Schindler 1971). Thermal stratification of efficiently heated lakes is weak, and a hypolimnion, if it exists at all, is near the bottom. Second Lake is shallow, whereas Gignac Lake is deep. Thermal stratification and a hypolimnion are thought to exist in Gignac Lake; a weak hypolimnion probably develops below 3.5 m in Second Lake.

In lakes with a hypolimnion, physical and chemical conditions between shallow and deep water differ considerably. During summer months surface waters are very productive; algae use CO_2 in photosynthesis, and the O_2 content is higher (Hutchinson 1957). Lime mud is precipitated by algae in shallow water, where it sinks to the bottom (Brunskill 1969). In many stratified lakes calcium carbonate dissolves before it can reach the bottom (Hutchinson 1957; Gilbert and Leask 1981). Carbonate muds have been accumulating on the bottom

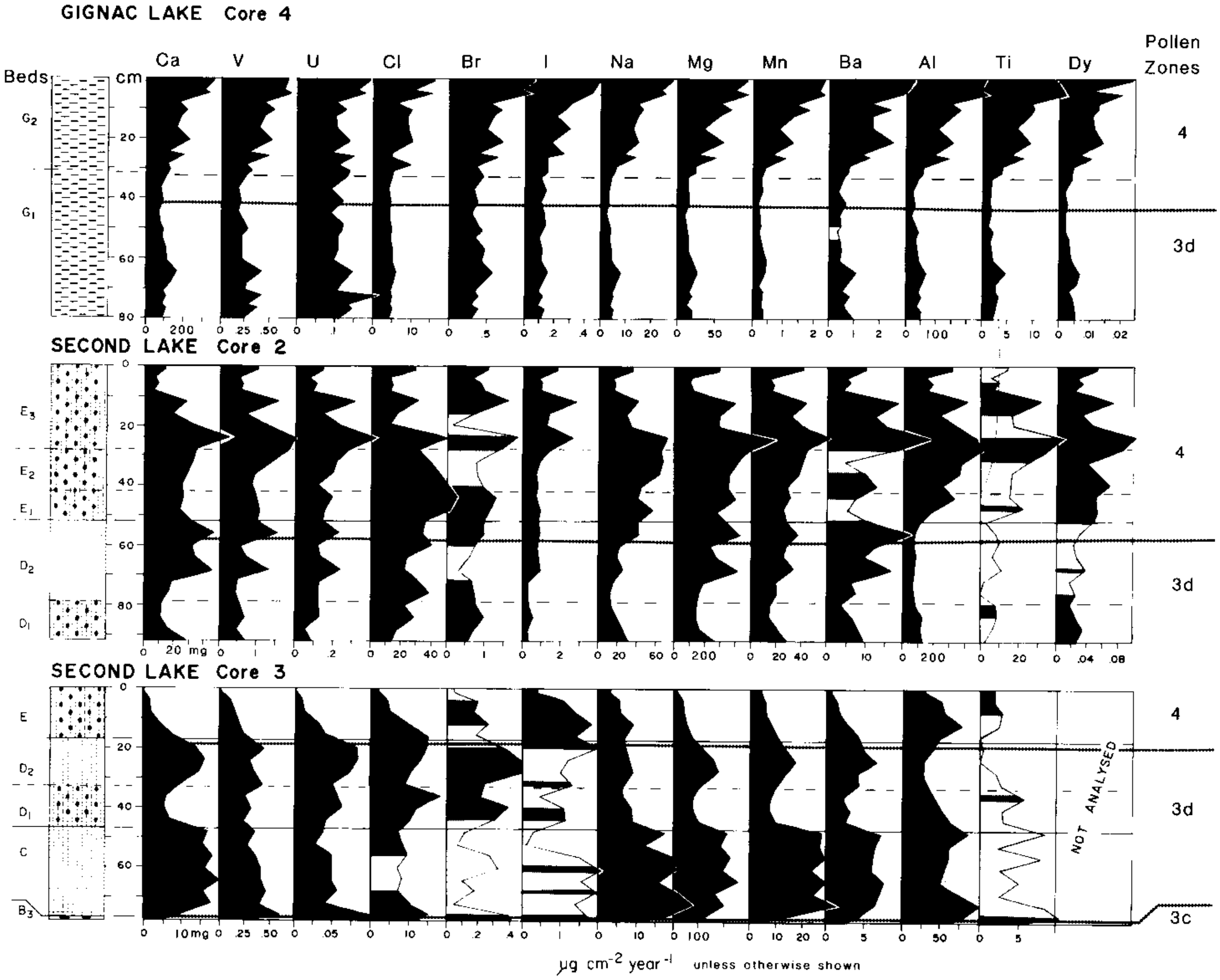

FIG. 11. Element influx to Gignac Lake core 4 and Second Lake cores 2 and 3. Unreliable analyses are unshaded.

of Second Lake for the last 500 years. Before 500 years ago Second Lake was deeper, because the gyttja in bed B indicates a stratified water column similar to that proposed for Gignac Lake.

In deep-water cores, especially in Gignac Lake, organic matter (measured as LOI) forms the bulk of the sediment, since the carbonates are dissolved. Here organic material acts as sites for the adsorption of OA elements and the development of organic complexes, as suggested by Stumm and Morgan (1970) and Golterman (1975). The relationship of V to organic material is in sharp contrast with the findings of Cwynar (1978), who has correlated V and Al and erosion from forest fires. The increased V in Cwynar's study may be a by-product of forest fires. Increases in the influx of burned and partially burned organic detritus may permit greater adsorption of V.

Manganese is one of the more mobile elements in our study. Small negative increases in Eh cause Mn precipitates to dissolve and migrate upward in sediment or water until oxidizing conditions cause reprecipitation (Kemp and Thomas 1976). Surface enrichment with Mn occurs in each core. However, in Gignac Lake 4, where reducing conditions are presumably highest, the influx of Mn is low. In Second Lake core 2, where the water is shallow and oxidized, the influx of Mn is high.

As with Mn, the halogens tend to be more abundant in surface sediments. Unlike Mn, halogens are also enriched in organic sediments for reasons that are not fully understood. Aquatic plants like *Chara* are probably using halogens and keeping the surface sediment concentration high.

Correlation of Na, Al, Ti, and Dy distributions with palynologic assemblages show these elements to be the best indicators of erosion. However, even with historic and palynologic evidence of erosion, care must be taken in the interpretation of influx. The Ti analyses are skirting the detection limits of the NAA irradiation formula used for this study, and the accuracy of Dy analyses is unknown. In addition, Na is an essential element for photosynthesis in *Najas* (Hutchinson 1975); Na may also coprecipitate with aragonite (White 1977). Aluminum found in lakes commonly occurs with mineral and organic complexes that are stable between pH 4 and 8, the normal range for most lake waters (Hutchison 1957). The degree to which biologic activity and diagenesis affects the accumulation of allochthonous minerals containing Al and Na is not known.

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BAKER, D. B., and KRUMER, J. W. 1973. Phosphorous sources and transport in an agricultural river basin of Lake Erie. Proceedings, 16th Conference on Great Lakes Research, International Association of Great Lakes Research, pp. 858–871.

BERRY, L. G., *editor.* 1972. Set 22 of the Powder Diffraction File. Joint Committee on Powder Diffraction Standards. American Society for Testing and Materials, Philadelphia, PA.

BORMANN, F. H., LIKENS, G. E., SICCAMA, T. G., PIERCE, R. S., and EATON, J. S. 1974. The export of nutrients and recovery of stable conditions following deforestation at Hubbard Brook. Ecological Monographs, **44**, pp. 255–277.

BRUGHAM, R. B. 1978*a*. Human disturbance and historical development of Linsley Pond. Ecology, **59**, pp. 19–36.

——— 1978*b*. Pollen indicators of land-use change in southern Connecticut. Quaternary Research, **9**, pp. 349–362.

BRUNSKILL, G. J. 1969. Fayetteville Green Lake, New York II: Precipitation and sedimentation of calcite in a meromictic lake with laminated sediments. Limnology and Oceanography, **14**, pp. 830–847.

BURDEN, E. T. 1978. Pollen and algal assemblages in cored sediments from Gignac Lake and Second Lake (Simcoe Co., Ontario): relationships with lacustrine facies, geochemistry and vegetation. M.Sc. thesis, Department of Geology, The University of Toronto, Toronto, Ont.

BURDEN, E. T., MCANDREWS, J. H., and NORRIS, G. 1986. Palynology of Indian and European forest clearance and farming in lake sediment cores from Awenda Provincial Park, Ontario. Canadian Journal of Earth Sciences, **23**, pp. 43–54.

CWYNAR, L. 1978. Recent history of fire and vegetation from laminated sediments of Greenleaf Lake, Algonquin Park, Ontario. Canadian Journal of Botany, **56**, pp. 10–21.

DAVIS, M. B. 1973. Redeposition of pollen grains in lake sediment. Limnology and Oceanography, **18**, pp. 44–52.

——— 1976. Erosion rates and land use history in southern Michigan. Environmental Conservation, **3**, pp. 139–148.

DEAN, W. E. 1974. Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition: comparison with other methods. Journal of Sedimentary Petrology, **44**, pp. 242–248.

ENGSTROM, D. R., and WRIGHT, H.E., JR. 1984. Chemical stratigraphy of lake sediment as a record of environmental change. *In* Lake sediments and environmental history. *Edited by* E. Y. Haworth and J. W. G. Lund. University of Minnesota Press, Minneapolis, MN, pp. 11–67.

ERLENKEUSER, H., SUESS, E., and WILLKOMM, H. 1974. Industrialization affects heavy metals and carbon isotope concentrations in recent Baltic Sea sediments. Geochimica et cosmochimica acta, **38**, pp. 823–842.

FAGER, E. W. 1957. Determination and analysis of recurrent groups. Ecology, **38**, pp. 586–595.

FINLAY, B. J., HETHERINGTON, N. B., and DAVISON, W. 1983. Active biological participation in lacustrine barium chemistry. Geochimica et cosmochimica acta, **47**, pp. 1325–1329.

FLETCHER, M. R., and CHAPMAN, W. B. 1974. Sediment density and the limits to repeatability of absolute pollen frequency determinations. Geoscience and Man, **9**, pp. 27–32.

GILBERT, R., and LEASK, S. M. 1981. Factors affecting marl deposition in Knolton Lake, southeastern Ontario. Journal of Great Lakes Research, **7**, pp. 286–289.

GOLTERMAN, H. L. 1975. Developments in water science: physical limnology. Elsevier Scientific Publishing Co., New York, NY. 489p.

GORHAM, E. 1964. Morphometric control of annual heat budgets in temperate lakes. Limnology and Oceanography, **9**, pp. 525–529.

HUTCHINSON, G.E. 1957. A treatise on limnology. Vol. 1. Geography, physics and chemistry. John Wiley & Sons, Toronto, Ont., 1015 p.

——— 1975. Treatise on limnology. Vol. III. Limnological botany. John Wiley & Sons, Toronto, Ont., 660 p.

KEMP, A. L., and THOMAS, R. L. 1976. Cultural impact on the geochemistry of the sediments of lakes Ontario, Erie and Huron. Geoscience Canada, **3**, pp. 191–207.

KIRCH, A. 1973. Introduction to statistics with FORTRAN. Holt, Rinehart and Winston, Inc., Toronto, Ont., 458 p.

LEHMAN, J. T. 1975. Reconstructing the rate of accumulation of lake sediment: the effect of sediment focusing. Quaternary Research, **5**, pp. 541–550.

LIKENS, G. E., BORMANN, F. H., PIERCE, R. S., EATON, J. S., and JOHNSON, N. M. 1977. Biogeochemistry of a forested ecosystem. Springer-Verlag, New York, NY.

MATHEWES, R. W., and D'AURIA, J. M. 1982. Historic changes in an urban watershed determined by pollen and geochemical analyses of lake sediment. Canadian Journal of Earth Sciences, **19**, pp. 2114–2125.

ODOM, P., and WILDSMITH, B. 1968. Second Lake: lake survey summary sheet. Ontario Department of Lands and Forests, unpublished report, 3 p.

OLDFIELD, F., THOMPSON, R., and BARBER, K. E. 1978. Changing atmospheric fallout of magnetic particles recorded in recent ombrotrophic peat sections. Science, **199**, pp. 679–680.

SCHINDLER, D. W. 1971. Light, temperature and oxygen regimes of selected lakes in the Experimental Lake area, northwestern Ontario. Journal of the Fisheries Research Board of Canada, **28**, pp. 157–169.

SHIOMI, M. T., and KUNTZ, K. W., 1973. Great Lakes precipitation chemistry: part 1. Lake Ontario basin. Proceedings, 16th Conference on Great Lakes Research, International Association of Great Lakes Research, pp. 581–602.

STUMM, W., and MORGAN, J. J. 1970. Aquatic chemistry. Wiley-Interscience, Toronto, Ont., 538p.

WHITE, A. F. 1977. Sodium and potassium coprecipitation in aragonite. Geochimica et cosmochimica acta, **41**, pp. 613–625.