*Limnol. Oceanogr.*, 26(5), 1981, 907–924

# Chemistry of a 7.5-m sediment core from Lake Valencia, Venezuela[1]

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*Abstract*

A 7.5-m core from the middle of Lake Valencia, Venezuela, was analyzed chemically and mineralogically. This information is interpreted with assistance from studies of the modern lake and other supplementary paleolimnological information. The basin appears to have been dry between 13,000 and 10,500 B.P. At about 10,000 B.P., a very saline lake formed. Saline but less extreme conditions prevailed until about 9000 B.P., as indicated by precipitated aragonite, high Mg:Ca ratios in the carbonates, and other indicators; salinity had been considerably reduced by 8000 B.P., when the lake almost certainly discharged water. Indicators including allogenic loading, Mg:Ca ratios, carbonate precipitation, shallow-water cores, and microfossils suggest two subsequent returns to higher salinity, the latest of which began about 2500 B.P., causing the lake to become endorheic in A.D. 1727. The general sequence of events in the lake over the last 13,000 years is strikingly similar to sequences documented from the African lowland tropics. The chemical conditions of Lake Valencia have varied in a major way over the recent geologic past.

Lake Valencia is a large natural lake occupying a graben in the north-central region of Venezuela, 15 km south of the Caribbean Sea (Fig. 1). The coastal range, running east and west at elevations up to 1,800 m, separates the lake's watershed from the Caribbean on the north; the interior range bounds it to the south, but is not so high (900 m). The La Victoria fault runs east and west through the elongate trough (Aragua Valley) between the mountains (Bell 1971).

Von Humboldt (1820) noted substantial decline in the level of Lake Valencia from an outlet sill at 427 m. He attributed the desiccation of the lake to deforestation and agriculture. Decline in water level has continued since von Humboldt's time at an average rate of 10–15 $cm \cdot yr^{-1}$, but with an acceleration in the last few decades (Jelambi 1972; Schubert 1979). Principally from anecdotal information, Bockh (1956) fixed the last date of discharge over the outlet sill at A.D. 1727. Evidence shows that the lake must have been full or nearly so before the 18th century (Schubert 1979).

The lake currently has an area of 350 $km^2$, about a third its maximum area (Berry 1939; Schubert 1979), and a watershed of 3,000 $km^2$; maximum lake depth is currently 39 m. The modern vegetation around the lake in undisturbed areas is tropical deciduous forest at lower elevations and evergreen moist forest or cloud forest at higher elevations, but the watershed has been mostly deforested. The Aragua Valley is an agricultural center, principally for sugar cane but also for other row crops. A large portion of the watershed is covered by a fire climax of tough grasses and small fire-resistant woody plants that are maintained by repeated burning during the dry season, which extends over about 100 days from December through March. The water yield of the unforested portions of the watershed to the lake is negligible except for a short period during the rainy season. Of the streams indicated in Fig. 1, only

[1] This work was supported by National Science Foundation grants DEB 7604300 and DEB 7805324, and the Limnology Laboratories of the Universidad Central de Venezuela and the University of Colorado.

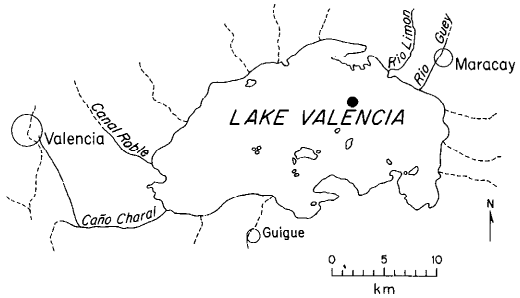


Fig. 1. Map of Lake Valencia; ●—deep-water core (36.5 m depth, 10°12′30″N, 67°64′00″W).

the Rio Limon, which drains a forested area, flows all year. Further details of the status of the lake are given by Lewis and Weibezahn (1976).

Interest in the lake as a major site for the study of paleoclimate and paleolimnology has continued since von Humboldt's visit, but has not resulted in comprehensive studies until recently, when a joint Venezuelan-North American effort resulted in coring the lake in 1977. Schubert (1979) gave the best overview of earlier studies and of speculations on the lake's past, most of which deal with desiccation. One school of thought, represented by von Humboldt, and by Cruxent and Rouse (1958) who made deductions from archeological data, argues that the decline in lake level is a direct result of human activity. In contrast, Tamers and Thielen (1966), who estimated groundwater flow rates from $^{14}C$ dates of water in aquifers, presented a case for long term climatic change, buffered by large groundwater reservoirs, as the agent of modern desiccation. Unquestionably the recent use of the watershed and its aquifers has exacerbated desiccation by increasing water loss to the atmosphere and drawing down groundwater sources, but the possible origin of this trend in a climatic change remains unclear.

Peeters (1968, 1970, 1971) studied the sediments above the present lake levels, using mainly undated stratigraphy, and has concluded that the present desiccation was preceded by at least one and probably several earlier desiccation episodes. Past stabilization of the lake at intermediate levels below the outlet sill is unquestionable, given the presence of prominent benches and nick points on islands within the lake (*see* Schubert 1979).

Lake Valencia contains an extensive sediment record. The complete length of this record is not known, but detailed acoustic studies of the sediment (Schubert and Laredo 1979; Schubert 1980) have demonstrated the presence of 100 m of lacustrine sediment without reaching the rock basin. The acoustic studies show clear evidence of three separate sediment layers over the entire lake basin. These have thicknesses of about 8 m (upper), 15 m (middle), and 35 m (lower). These three layers are underlain by still another layer of indeterminate thickness. The studies also show old delta deposits of coarse clastics well below present waterline.

Our study deals with the upper 7.5 m of sediment taken from the middle of Lake Valencia in 37 m of water (Fig. 1). Other cores were taken from shallower water but are harder to interpret because of the physical perturbation associated with past changes in lake level. The midlake core provides a record, undamaged by physical perturbation, of changes in the lake and its watershed over about 13,000 years.

Much credit for this work is due to S. Rogstad, J. P. Bradbury, S. H. Bowen, and J. F. Saunders. The manuscript benefited from comments by E. S. Deevey, D. A. Livingstone, and D. Runnells. We thank M. Salgado-Laboriau, C. Schubert, B. Leyden, M. Binford, D. G. Frey, and D. Whitehead for sharing unpublished data.

## *Methods*

The midlake core was taken with two piston corers of the Livingstone type, one specially designed for the upper 1 m of sediment and the other for deeper sediments. A coring platform was secured in midlake. To minimize the disturbance of the surface–water interface and facilitate the subsampling of unconsolidated sediments at the top of the core, we took the

upper 134-cm portion of the sediment with a transparent plastic tube (5-cm diam) equipped with an internal piston as is the standard Livingstone sampler. The piston was positioned 15 cm over the sediment–water interface and the tube pushed over the piston into the sediment far enough to penetrate thoroughly into consolidated material. The corer was raised to the deck where the piston was removed through the top end of the sampler. The overlying 15 cm of water in the core was then siphoned off. The space above the sediment–water interface was flushed with nitrogen during the siphoning to ensure that the upper sediments would not become oxygenated. After removal of the water, the first 5.5 cm of mud was siphoned off into a polyethylene bottle which had been thoroughly cleaned and flushed with nitrogen and the bottle sealed and not reopened except under nitrogen atmosphere. This procedure was repeated for the next 3-cm segment of the core (depth range 5.5–9.0 cm). Below 9 cm, the sediment was consolidated enough to be extruded with the piston.

The extrusion process for the first section of the core (taken with a surface corer) and for all subsequent core sections (taken with a standard 5-cm Livingstone corer) was specially designed to prevent oxygenation of the samples. Sealed, clean plastic bags just large enough to fit the corer were flushed with nitrogen and the sediments immediately extruded inside these bags, which were then sealed. The sediments were subsampled the same day under a nitrogen atmosphere. Subsamples intended for chemistry were mechanically homogenized and stored in bottles that had been flushed with nitrogen so that the samples were not exposed to oxygen before analysis. Similar precautions were taken in the laboratory to prevent oxygenation of the samples during the analytical procedures, except when it would be irrelevant to the outcome.

The arrangement of the 43 subsamples along the core is indicated in Fig. 2, which shows all of the core except the upper 9-cm portion that was removed with the siphon. Figure 3 shows the analytical scheme by which the sediment samples were processed. Methods for the most part follow Dean and Gorham (1976) or Brunskill et al. (1971). Analytical methods for solids were checked against standard USGS rock samples.

A portion of each sample was centrifuged at 7,500 rpm for 30 min under a nitrogen atmosphere to separate interstitial water from the rest of the sediment and the supernatant drawn off with a pipet, measured, and stored in a screwcap bottle under nitrogen. From this point forward, analysis of this interstitial water diverged from the analysis of the rest of the sediment.

The pH of the insterstitial water samples was measured, and all samples were then diluted to 500 ml with deionized-distilled water. The absorbance at 360 and 300 nm was measured with a spectrophotometer at 2-nm bandpass on a 10-cm cell, from which the dissolved organic carbon was estimated (Lewis and Canfield 1977). This method was not cross-checked with $CO_2$ analysis for these specific samples, so the values are of interest only for major trends. The conductance of the sample was measured with a sensitive conductivity bridge and corrected to 25°C. Metals were determined by atomic absorption. Total primary amines dissolved in the interstitial water were determined with fluorescamine (North 1975); glycine was used to construct the calibration curve.

Eh was measured in whole sediments with a platinum electrode and corrected to pH 7 with the equation of Langmuir (1971). Corrected Eh is traditional with paleolimnologists, but some geochemists oppose its use because the underlying assumptions lack validity (D. Runnells pers. comm.). The correction makes little difference to the Eh profile, as the pH values differ little through our core, so we report corrected Eh.

A portion of the sediment from which the interstitial water had been removed was dried at 105°C to constant weight for an estimate of noninterstitial water. Part of the dry sediment was ground to a fine

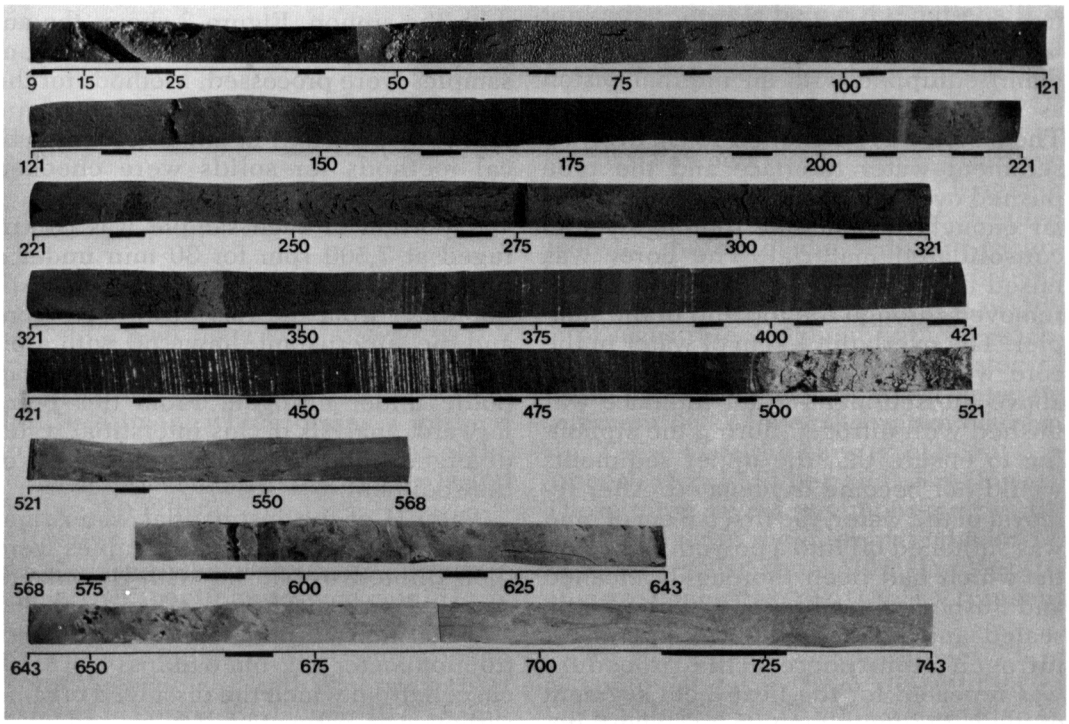


Fig. 2. Photograph of sliced 7.5-m core from midlake. Dark bars indicate position of subsamples. Upper 9 cm were sampled by siphon as indicated in text. Scale is marked in centimeters (photo by W. M. Lewis, Jr.).

powder. About 500 mg was weighed, placed in a crucible (precombusted at 550°C), combusted at 550°C for 1 h, and reweighed. About half of the remaining material was weighed, combusted at 1,000°C, and then reweighed. The weight loss between 105° and 550°C was attributed to combustion of the organic matter. The weight loss between 550° and 1,000°C was attributed to loss of $CO_2$ from calcium carbonate (rationale given by Dean and Gorham 1976). Weight loss multiplied by 2.27 provides the estimate of carbonates originally present in terms of $CaCO_3$ (even though some is $MgCO_3$).

A subsample of the material which had been combusted at 550°C was digested with a mixture of $HF$-$HNO_3$-$H_2SO_4$ (2:1:1 by volume). The digestion was carried out at <200°C and the mixture heated to dryness repeatedly (5–15 times) until the residue consisted of pure white crystals. This digest was dissolved in 1 N HCl, diluted to 100 ml, and stored in a plastic bottle.

Portions of the dried sample were combusted in a CHN analyzer. The carbon thus measured is a combination of carbonate and organic matter; these were later separated by calculations based on the amount of carbonate in the samples as determined by the differential combustion process.

Another portion of the dried sample was digested with heat in concentrated $H_2SO_4$ and Se in a Kjeldahl apparatus for an estimate of total phosphorus by the method of Murphy and Riley (1962). Still another portion was extracted in 1 N ammonium acetate at pH 5.2 and diluted to 100 ml; this treatment dissolves calcite and aragonite but not dolomite (Wangersky and Joensuu 1967; Dean and Gorham 1976). A portion was also digested in concentrated sodium hydroxide with heat to dissolve the silica (Shapiro and Brannock

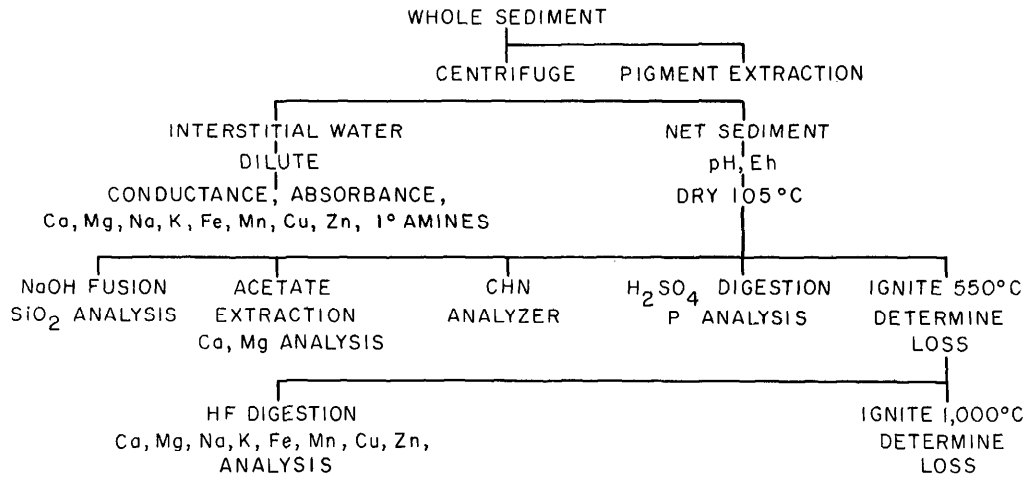


Fig. 3. Analytical scheme for processing sediment samples.

1956), measured by the molybdate method (Armstrong and Butler 1962).

Pigments were extracted and quantified by the methods of Sanger and Gorham (1972). Sedimentary chlorophyll was estimated from the corrected absorbance peak near 667 nm, carotenoids from the absorbance peak near 450 nm, and bacteriochlorophyll from the absorbance peak near 750 nm. Exact locations of the peak absorbances were determined empirically in each sample. Baseline correction (Sanger and Gorham 1972) was used in all cases. The results are expressed as pigment units per gram of organic matter (Vallentyne 1955). One pigment unit is defined here as the amount of pigment needed to give an absorbance of 1.0 in a 1-cm spectrophotometer cell when the solvent volume is 100 ml. Reference to specific pigment classes is always assumed to include optically active degradation products of those classes.

Figure 4 shows the $^{14}C$ dates for the core (some dates are by USGS, some by DICARB). Carbonates were liberated before dating. The dates do not all fall on the same line, so references to specific dates in the manuscript are taken from the line segments shown in Fig. 4, which also shows the sedimentation rates as determined from the $^{14}C$ dates. The $^{14}C$ dates might be questioned because of the possible influence of reworked carbon within the lake-watershed system, despite the exclusion of carbonates from dating (Krisnaswami and Lal 1978; Deevey et al. 1954; E. S. Deevey pers. comm.). They do seem to imply reasonable sedimentation rates, however, and over most of the core the sediments represent a continuously flushing system likely to give reliable dates. The laminated area of the core is most subject to question. How-

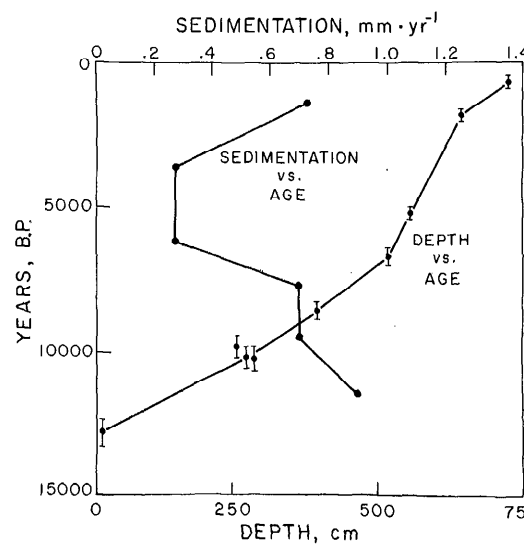


Fig. 4. Carbon-14 dates, standard deviations, and computed sediment rates.

ever, we will assume that the dates are valid.

*Gross stratigraphy of the core*

The gross stratigraphy of the core is evident in Fig. 2. For purposes of discussion, we recognize four general zones from top to bottom: unlaminated lacustrine muds, sparsely laminated transition zone, intensely laminated zone, and clay layer.

The laminae consist principally of crystals which have been shown by X-ray crystallography to be aragonite (Bradbury and Lewis unpubl.). In general, annual banding in hard-water lakes is associated with either seasonal photosynthetic or temperature changes (Kelts and Hsu 1978). The bands in the Lake Valencia sediments do not seem numerous enough to be annual, however, and therefore probably result from supra-annual events, such as changes in lake volume with variations in annual precipitation. Instances of supra-annual banding in saline lakes are known (Eugster and Hardie 1978).

Below just about the 500-cm mark there is an abrupt change from banded organic sediments to a thin crustose layer, followed by an extremely fine and compact clay of high textural purity which extends to the bottom of the core at 743 cm. The clay layer is almost certainly identical with the boundary between the upper two major sediment members revealed by the acoustic studies and is thus a lakewide feature.

The fine structure of the core from top to bottom suggests undisturbed accumulation of sediments. Disruption of the layering by burrowing organisms is unlikely in the central basin of the lake because for much of the year the sediment surface is anoxic. Benthic insect populations do not extend to midlake.

*Present sediment and lake water chemistry*

Table 1 compares average chemical characteristics of the deeper water near the site of the core with those of sediment from the upper 10 cm of the core. The recent trend toward desiccation of the lake accounts for the relatively high ion concentrations in the water. The approximate position of the system on an equilibrium diagram for calcite can be determined from the pH (8.9), pCa (3.4), and $pHCO_3^-$ (2.13) at a given temperature (25°C: Lake Valencia bottom temperatures are always within 1.5° of 25°C). On the diagram of Stumm and Morgan (1970: fig. 8-7), the 25–30-m zone of Lake Valencia would occupy a position similar to that of groundwater in contact with dolomite and would be supersaturated with $CaCO_3$. However acidification of particulate material collected on filters results in very little weight loss (<2%), indicating limited carbonate precipitation. Titration of the water with standard acid to the carbonate inflection point leads to similar conclusions. Supersaturation is of course quite common for natural waters and is not always accompanied by significant precipitation (Kelts and Hsu 1978).

The absence of significant carbonate in the water seems to conflict with the presence of considerable carbonate in the upper sediments (0–10 cm: 13.1% of dry weight is carbonate as $CaCO_3$). The rapid increase in salinity over the past 100 years has caused depletion of calcium by precipitation; however, this has been reduced recently because of the inhibition

Table 1. Comparison between chemical characteristics of lower water column of Lake Valencia and surface sediments in deep water (36.5 m). CNP data are averages for weekly analyses over 52 weeks beginning in January 1977; other data are averages for weekly analysis over 35 weeks beginning in January 1977.

| | Water column 25–30 m | Sediment 0–10 cm |
|---|---|---|
| pH | 8.9 | 7.8 |
| Conductance ($\mu$mho·cm$^{-1}$) | 2,017 | 2,830* |
| Particulates, %C (total) | 26.0 | 10.8† |
| Particulates, %N | 5.03 | 0.87 |
| Particulates, %P | 2.06 | 0.12 |
| Organic C:N | 5.17 | 10.5 |
| Organic C:P | 12.6 | 76.6 |
| Ca (mg·liter$^{-1}$) | 18.7 | 22.3* |
| Mg (mg·liter$^{-1}$) | 67.8 | 93.0* |
| Na (mg·liter$^{-1}$) | 217 | 237* |
| K (mg·liter$^{-1}$) | 45.1 | 41.0* |

* For interstitial water.
† 9.2% is organic carbon, 1.6% is carbonate carbon.

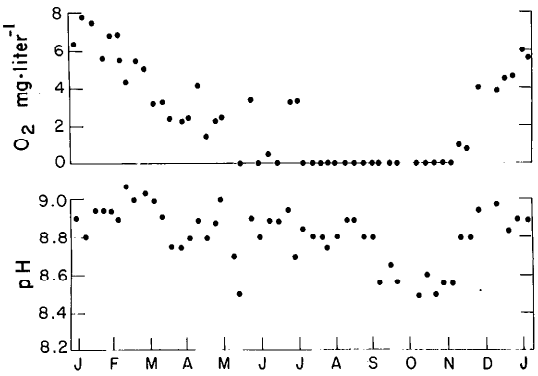


Fig. 5. Oxygen concentration and pH at 25–30-m depth during 1977.

of carbonate precipitation by magnesium ions (Kelts and Hsu 1978).

The pH of the water is affected by seasonal changes in the depth of mixing (Fig. 5). The pH of the sediments is slightly lower than that of the water. The data in Table 1 on specific conductance and cation concentrations indicate that ionic strength and composition of the interstitial water in the upper sediment layer are similar to but slightly higher (ca. 30%) than that of the overlying water. Presumably the baseline conductance is determined by lake water and the increase beyond this by decomposition or solution of precipitated minerals. The monovalent cations in the interstitial water are in close equilibrium with those of the overlying water, whereas the divalent cations tend to be significantly more concentrated in the interstitial water: this suggests significant solution of carbonates in the sediments.

The chemistry of particulate materials differs greatly between the deep water and the sediment. Particulate materials taken from the lower water column are about a quarter carbon by weight; since this is not significantly reduced when they are treated with acid, the particulate carbon in the water column must be essentially all associated with organic compounds. In the sediments, 10.8% of the dry weight (0–10 cm) is carbon, and a small portion of this (14.9%) is carbonate carbon.

Anoxia develops in the deep water during stratification (April–October) and the redox potentials get low enough to permit the reduction of sulfate to sulfide. A cool season (November–March) with greater average wind strength (Lewis 1981) ensures an extended complete circulation once a year, and the deep water is reoxygenated (Fig. 5). At the same time, fine particulate matter is brought to the center of the lake from the lake bottom below shallower water; this was observed in weekly counts of particles over a 2-year period (unpubl.). Large particles (>50 m) are not transported in observable amounts even during circulation.

The ratios of organic C to N are not as drastically different between sediment and the lower water column as one might expect, although the sediments evidently lose some nitrogen in the course of decomposition, either by leaching of inorganic nitrogen or by denitrification (Table 1). The sediments are in a relative sense (C:P ratio) much lower in phosphorus than the particulate materials of the water. Coprecipitation of phosphorus with iron or with calcium carbonate could be expected under present conditions in the lake (Mackereth 1966; Otsuki and Wetzel 1972), but Table 1 offers no evidence that the sediments are significantly enriched by these mechanisms.

### *Major mineral elements and interstitial water chemistry*

The total mineral content of the sediment is relatively high (usually 60–90%) throughout the core, indicating efficient oxidation of organic matter near the bottom during the period shown in Fig. 6. The highest sustained percentages of minerals are associated with the clay layer. A high and steady percentage of minerals is also typical of the top 150 cm with the possible exception of the uppermost sediments, where diagenesis may still be occurring. The mineral content in the midsection of the core is quite variable but shows one extended region of high values (210–270 cm).

The profiles for Si, Na, and K are similar to each other in most respects. All

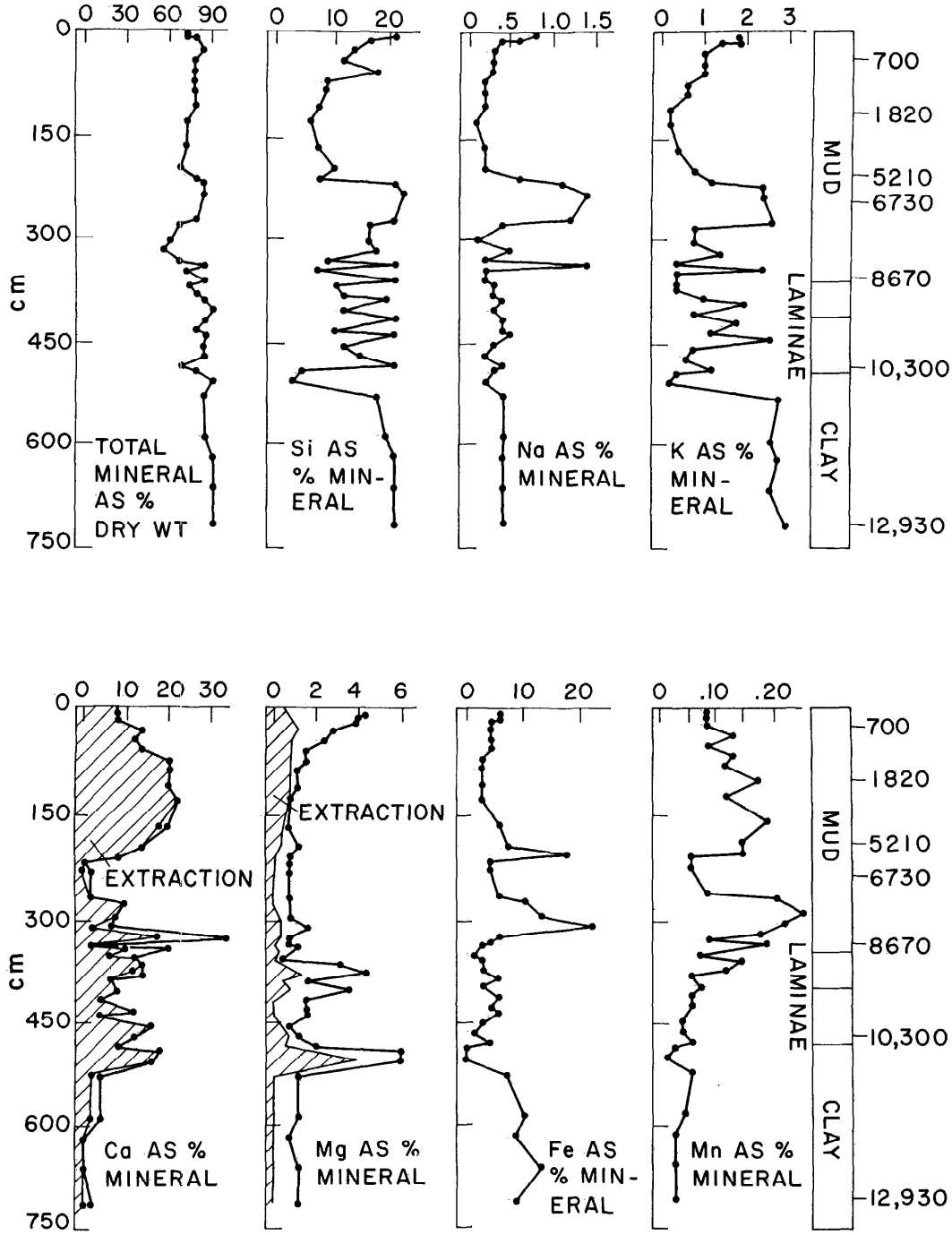


Fig. 6. Total mineral content and elemental composition of inorganic fraction (as percent dry inorganic weight) in 7.5-m core.

three decrease in relative abundance from the surface down to about 130 cm and then increase from 130 to about 210 cm. There is a marked Si peak at 55 cm (1200 B.P.) which does not appear in the Na and K curves; this peak corresponds to a period of intense diatom frustule deposition (Bradbury in press). The upper 210 cm is followed by a plateau of maximum abundance for all three elements (210–270 cm). The X-ray diffraction data show that this plateau corresponds to large amounts of quartz and plagioclase feldspar plus substantial relative abundances of illite and kaolinite, indicating strong allogenic sources for it (Jones and Bowser 1978). From the plateau to a point just above the clay layer (490 cm), all three elements show irregular profiles.

Extractable Ca and Mg parallel closely the profiles for total Ca and Mg. At all depths, extractable Ca and Mg predominate over nonextractable, suggesting that calcite and aragonite are much more important than dolomite. X-ray diffraction analysis shows independently that the laminae appearing in the core are primarily composed of aragonite and that calcite (but not dolomite) is a major mineral in the core.

Through much of the core the Ca profile is the mirror image of the Si-Na-K profiles, suggesting an inverse relation between clastic loading and authigenic carbonate loading of the sediments. The Mg profile does not match the Ca profile closely, and the percentage of Mg is often substantial.

The Ca profile in relation to Mg and to the mainly allogenic indicators (Si-Na-K) provides some insight about lake salinity and watershed moisture. Under dry conditions, calcium supply to the lake is reduced, causing an increase in the Mg:Ca ratio of the water because the calcium is removed by precipitation. There follows a significant suppression of calcium carbonate precipitation, as in the present-day lake. High Mg:Ca ratios will be evident directly from the precipitated carbonates and from the formation of aragonite, which requires Mg:Ca ratios >12 (Muller et al. 1972). Thus high Mg:Ca ratios in authigenic minerals and interstitial water, and aragonite, will be taken as evidence of early brine evolution (Eugster and Hardie 1978). More intense calcium precipitation is possible under moister conditions, because Ca is supplied in greater quantities and Mg inhibition is not as important. Larger amounts of $CaCO_3$ should thus follow from a moister watershed and lower salinities.

Clastic materials will be more prominent with a drier watershed having lower water levels, more sporadic and energetic transport, and lower vegetative impediment to mineral movement (Sly 1976). If we thus take clastics as an indicator of dryness, we have an independent check on the proposed interpretation of carbonate and Mg:Ca ratios. These two indicators prove valid for the two points in the profile where conditions are known: the modern lake, which is drying, and the clay zone, which is devoid of lacustrine fossils and thus represents a dry era. At other points in the core these two indicators typically provide the same interpretation. Salinity decreases upward from the clay layer, at first with great variation, reflecting the sensitivity of an endorheic lake to slight moisture changes, and peaks at about 8000 B.P. The clastic plateau of 7400–6000 B.P. is a return to drier conditions, followed by wetter conditions up to about 2800 B.P. and a final reversal that extends to the present. Other indicators also support this interpretation.

Both Fe and Mn are probably mainly of authigenic origin; they are not associated in the profiles with other allogenically derived elements, and none of the allogenic minerals detected in quantity are likely to contain much iron. Iron-organic matter associations are of course likely if allogenic iron is minimal, and Fe and Mn peak during periods when total mineral content is low and total organic matter content is high. These conditions coincide with moisture transitions. Maximum moisture leads to high authigenic mineral loading ($CaCO_3$) and minimum

moisture boosts allogenic mineral loading; so organic accumulation, and thus Fe and Mn accumulation, reaches maximum relative levels under intermediate conditions.

Figure 7 summarizes the chemical data for the interstitial water; the sediment carbonate profile is also included to provide continuity with Fig. 6. The amount of interstitial water in the sediments is rather variable but is probably not subject to meaningful interpretation because of the many influences on it (sediment texture, amount of organic material, degree of compaction by sediments above, etc.). The changes in noninterstitial water content (Fig. 7) are a rough mirror image of the total mineral content (Fig. 6), which implies that organic matter holds most of this water. The clay layer of course has much less water than the overlying mud.

The conductance of interstitial water is a complex function of the conductance set by the lake water when the sediment is deposited, subsequent ionic loading by solution and decomposition of sediment, and ion migration. The uppermost sediments show a slight increase toward the present in interstitial salinity, which is compatible with the postulated increase in water column salinity beginning about 2800 B.P. Interstitial salinities are uninterpretable in the middle of the core due to rapid shifts and to the lack of data for sediments with essentially no interstitial water. The salinity of the interstitial water generally decreases upward from 490 cm through the laminated zone to about 300 cm. This parallels the hypothesized general decrease in lake salinity from 10,500 B.P. to about 8000 B.P. A straightforward interpretation of the major trends in the interstitial conductance profile, while subject to many caveats, is thus compatible with the interpretation based on mineral element profiles.

Interstitial Ca and Mg show reciprocal trends, indicating Ca depletion at high salinities (linear correlation coefficient is $r = -0.31$, $P < 0.05$). The two together generally account for 50–60% of the cations except in the uppermost sediments. This high composite percentage probably represents significant enrichment of divalent cations with respect to lake water, due to interstitial solution, throughout most of the history of the lake. There are many indications that the salinities of the lake have often been sufficiently high over the past 10,000 years to produce a predominance of monovalent cations in the water column, as at present. The Mg:Ca ratios are consistent with the interpretations of salinity changes that have already been given.

The dissolved organic carbon and primary amines in the interstitial water have an enormous range of variation, but tend to parallel each other (Fig. 8). The marked peak in the vicinity of 250 cm coincides with the high allogenic mineral plateau, where carbonate content of the sediments is minimal. This maximum in DOC is probably explained by the absence of carbonates, which would tend to adsorb and aggregate organic matter (Chave and Suess 1970; Otsuki and Wetzel 1973). If this is true, then we should also expect to see reduced DOC in the interstitial water of the very recent sediments where conditions will be similar to those of the plateau when diagenesis and compaction are complete. The sediments are as yet immature, so this cannot be verified. There is also a pronounced DOC peak toward the top of the core in the vicinity of 50 cm (1200 B.P.) which corresponds to the distinctive diatom silica peak shown in Fig. 6.

### *Variables of direct biological significance*

Figure 9 summarizes those characteristics of the core which can be expected to have the closest direct relationship to the biological characteristics of the lake. The first of these is the redox potential, expressed as Eh adjusted to pH 7. Reliable measurements of redox potential are difficult, but drift was minimal and we could obtain repeatable readings. The sediments thus showed evidence of being well poised, typical of alkaline sediments and ideal for Eh determination (Langmuir 1971).

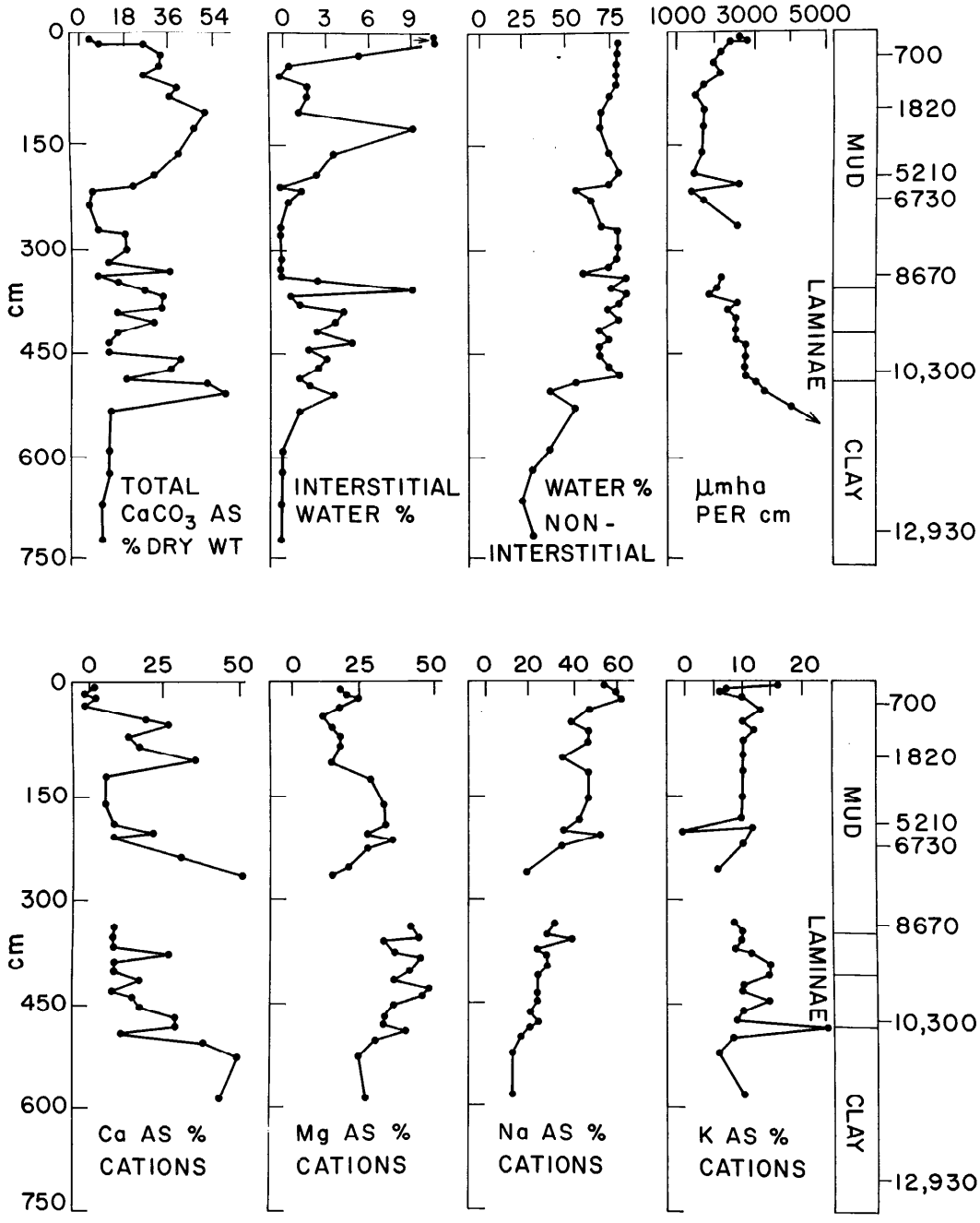


Fig. 7. Profiles of total carbonate (expressed as $CaCO_3$), total interstitial and noninterstitial water (expressed as weight, as a % of total sediment weight), interstitial water conductance ($\mu mho \cdot cm^{-1}$), and relative amounts of four major cations in interstitial water (expressed as % of total cations by weight).

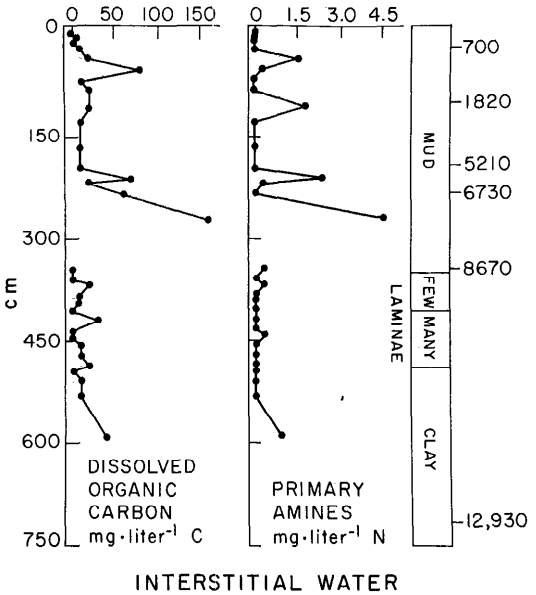


Fig. 8. Amounts of dissolved organic carbon and nitrogen in primary amines.

The most striking characteristic of the redox profile is the relatively high potential throughout the core. A productive lake such as Valencia might be expected to develop considerably lower redox potentials, especially in view of the high temperatures in the sediment and the consequent intensity of decomposition. Mixing seems to offset this tendency. Even when completely full, the lake is only moderately deep, and this essentially guarantees complete mixing for several months each year (Fig. 5). Meromixis or oligomixis is most unlikely (Lewis 1973). The duration of seasonal mixing is greater than in temperate dimictic lakes because of the lack of winter stagnation. Thorough and extended oxidation of the sediment surface can thus be expected annually, but does not rule out the possibility of low redox potentials in the deep water and at the sediment surface during stagnation.

The profiles for total organic matter, total nitrogen, and total phosphorus are similar (Fig. 9). The organic matter profile is obviously of key importance, but is hard to interpret because three major factors affect it. Deposition of authigenic carbonates reduces the percentage of organic matter in sediment. Allogenic minerals have a similar effect but with completely different timing. In addition, the productivity of the lake influences the percentage of organic compounds by controlling the rate of their deposition. The variations in production cannot be specified as confidently as those in mineral deposition, but the chlorophyll *a* profile provides an approximation.

Since authigenic mineral deposition is maximal at low salinities and allogenic deposition is maximal at high salinities, the profile of total organic matter should show some tendency toward maxima at intermediate salinities. Figure 9 shows that this is so. For example, the period between 210 and 270 cm (6000 and 7400 B.P.) has been interpreted as a period of high salinities and low water levels, with a transition above and below to lower salinities. Sediments of these transition areas are high in organic matter.

Phosphorus may be coprecipitated in significant amounts with carbonates (Mackereth 1966; Otsuki and Wetzel 1972), but the percentage of phosphorus reflects the curve for organic matter much more closely than the curve for calcium carbonate. Iron and phosphorus also show similar profiles in the upper half of the core, less so in the bottom half. Iron-phosphorus association is not unusual in saline lakes (e.g. Serruya 1971; Hutchinson and Cowgill 1973), but the oxygen content near the bottom at the time of deposition can affect the strength of the Fe-P association drastically (Williams and Mayer 1972). The associations suggest that most of the phosphorus in the Lake Valencia sediment arrives with organic matter or with iron.

Figure 10 shows more clearly the relationship between carbon, nitrogen, and phosphorus. The organic C:N ratios (wt basis) are relatively low. Few data are available from perennially warm lakes, but our C:N ratios are similar to those from a long core from Lake Huleh (Hutchinson and Cowgill 1973). The C:N ratios of the sediment profile fall for the

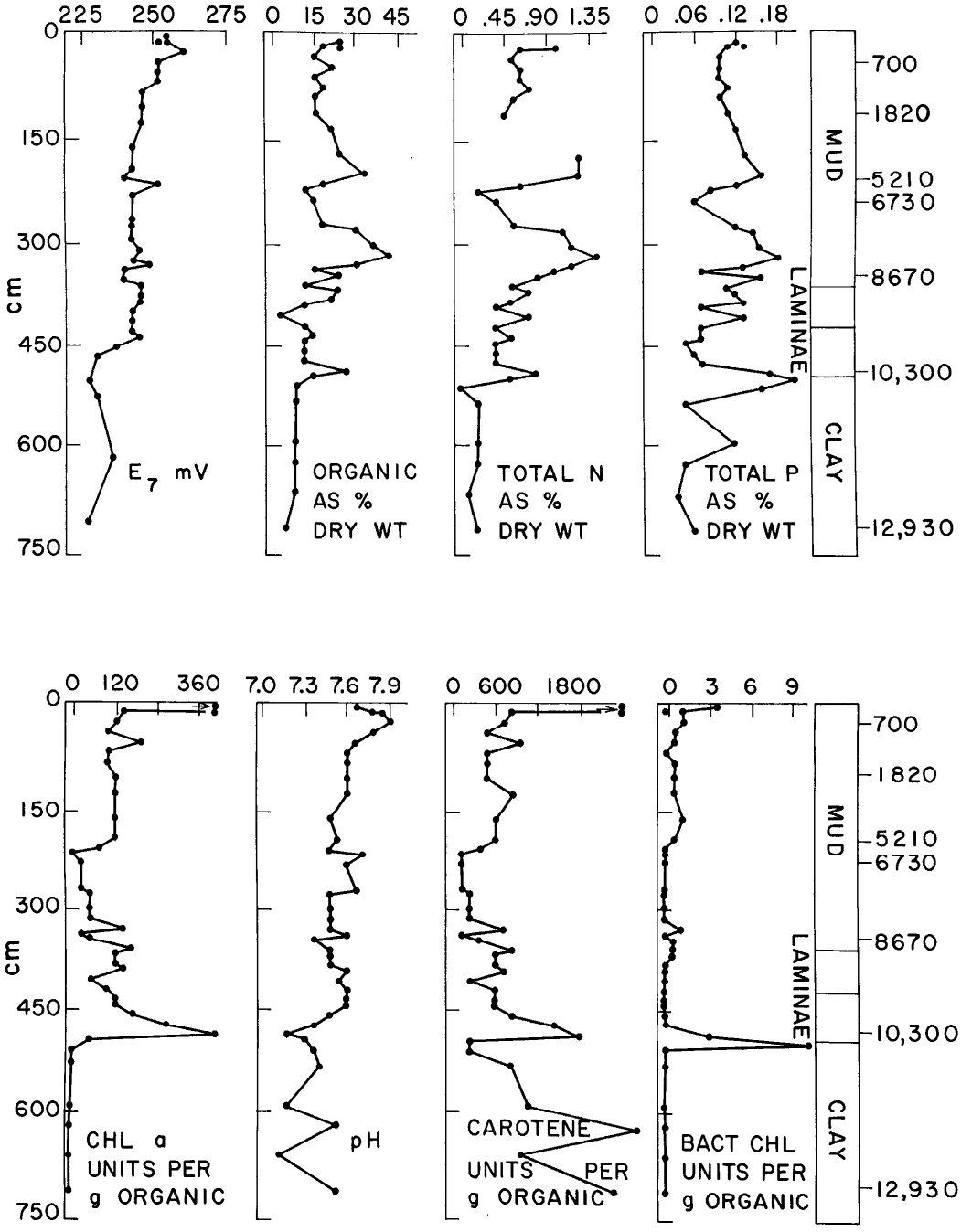


Fig. 9. Profiles of Eh, organic matter, total nitrogen and phosphorus, pH, and sedimentary pigments in 7.5-m core.

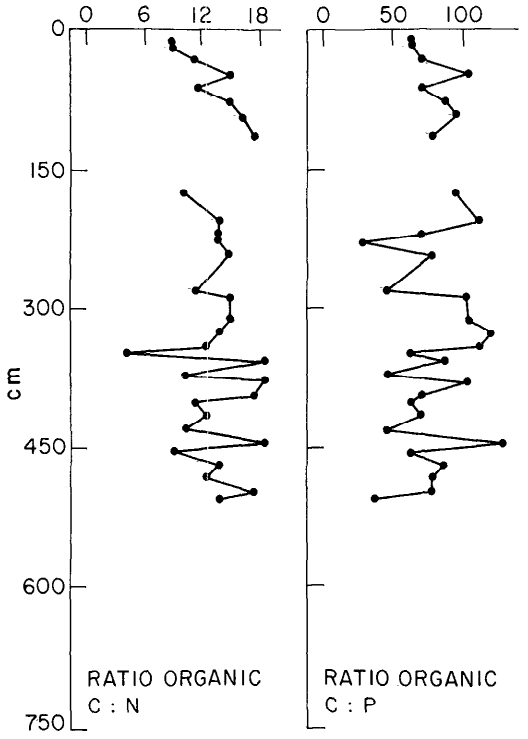


Fig. 10. Ratios of organic C to total N and organic C to total P on a weight basis in 7.5-m core.

most part between 8 and 18 and thus overlap the range in living phytoplankton (Parsons et al. 1977), which is now and probably always has been the major source of sedimenting organic matter in Lake Valencia.

The C:P ratios of the sediments are considerably higher than would be expected even in P-starved phytoplankton and are certainly higher than in particles of the deep water in present-day Lake Valencia (Table 1), indicating much more extensive loss of P than of N from the sediments.

The pigment profiles may be informative because of their potential relation to standing crop and even production (e.g. Wetzel 1970; Sanger and Gorham 1972). The uppermost samples are extremely rich in pigments, which could result either from incomplete pigment degradation or from recent accelerated eutrophication. Below the first 10 cm, the Chl *a* profile is essentially uniform over the upper 2 m except for a marked peak at 55 cm (1200 B.P.). This peak corresponds to a silicon and diatom frustule peak at the same level (Fig. 6).

Between 210 and 270 cm, coincident with the high allogenic mineral plateau, the relative amounts of chlorophyll are very low. The salinity, although higher than in the periods just preceding or following, would not, at this time, have approached the earlier high salinity conditions (10,500–9200 B.P.), as the indicators of highest salinity (aragonite, *Cyclotella*) are absent over the plateau. The drastic decrease in all pigments relative to organic matter could be explained by an influx of refractory organic matter from the watershed, as might occur with the more drastic seasonal changes in water and material fluxes typical of a drier watershed. Alternatively, production may have been suppressed by turbidity deriving from the high clastic input.

From the clay layer up to 270 cm there is a decrease in chlorophyll corresponding to the proposed decrease in salinity and increase in lake level. The high pigment levels just above the clay layer seem to be associated with high salinities ($>10$ g·liter$^{-1}$), rapid nutrient recycling, and high blue-green algal production and standing stock like those found by Iltis (1974) and Melack and Kilham (1974) in shallow, saline lakes in Africa.

The profile of carotenoid pigments is similar to the profile of Chl *a* except in the clay layer, which is essentially devoid of chlorophyll but rich in carotenoids, indicating the strong nonlacustrine influence on these sediments. Above the clay layer, the ratio of chlorophylls to carotenoids is very high, indicating strong autochthonous control of carbon flow (Sanger and Gorham 1972).

The amounts of bacteriochlorophyll are extremely small over most of the range but show a sharp peak just at the clay interface (475 cm). The algal chlorophyll maximum is actually one sample above this (488 cm). The sequence indicates dominance of photosynthetic bacteria under the most extreme salinity conditions.

*Conclusion*

Our interpretation of the chemical data is summarized in Fig. 11. The chronology of the 7.5-m core begins with a dry or seasonal lakebed accumulating fine clastic materials low in organic matter and essentially devoid of aquatic microfossils. The associated pollen indicates dry conditions in the watershed (Salgado-Labouriau 1978). After 12,500 B.P., the climate became wetter, resulting in formation of a saline and extremely eutrophic lake about 10,500 B.P. This lake became deep rather quickly, as indicated by the presence of sediments in the 10,000 B.P. age range near the present shoreline. The lake remained quite saline, however, until about 9200 B.P., as indicated by intense aragonite deposition. The lake during this period would have been sensitive to slight moisture change because of its lack of outlet, which has magnified the variation in chemical and mineral indicators within this zone. Salinity was sufficient to cause Ca depletion but not advanced brine evolution and would thus seem to have fluctuated in a range somewhat above today's salinities (e.g. 2–10 $g \cdot liter^{-1}$ solids). The diatom data (Bradbury in press) are consistent with this view.

The trend toward freshness and high lake level appears to have peaked about 8000 B.P., at which time the lake must have discharged water. Pollen from this period indicates the presence of moist forest in the watershed (B. Leyden pers. comm.), and the diatoms are a low salinity assemblage. Aragonite deposition stopped well before this. Calcite deposition occurred, and the Ca:Mg ratio of the carbonates indicates salinities well below present ones, as does the presence of *Melosira granulata.*

The moisture peak around 8000 B.P. was brief. Chemical indicators show an abrupt return to more saline conditions about 7400 B.P., accompanied by high Mg:Ca ratios in the precipitating carbonates, the disappearance of *Melosira,* and pollen indicators associated with disturbed vegetation. Two peculiarities are typical of this return to drier conditions.

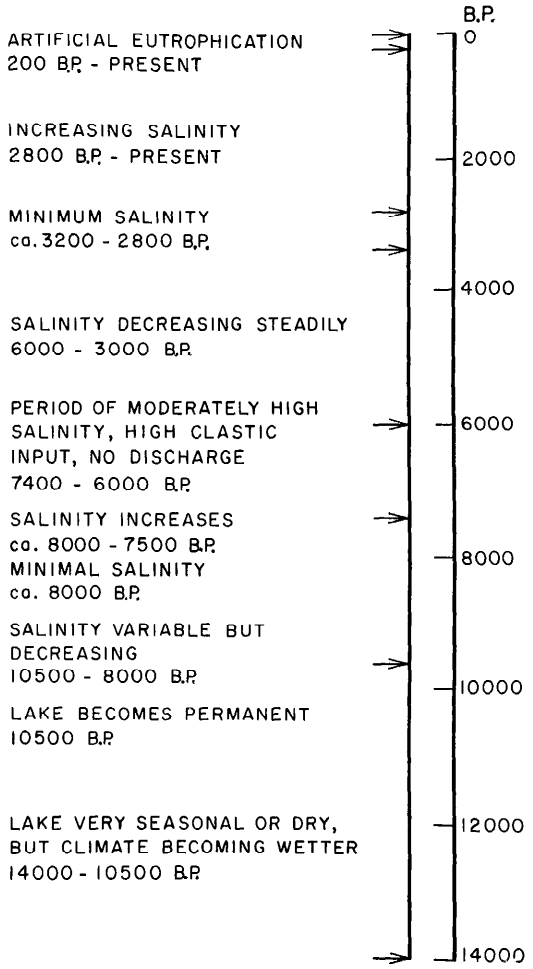


Fig. 11. Summary of chronology as reconstructed from chemical data.

First, there was a great increase in clastic loading of the lake, leading to clastic domination of the sediment mineralogy and chemistry. This increased role of allogenic minerals in a drying episode is repeated in the most recent sediments, which serve as a confirmation of the likelihood of high clastic loading under moderately dry conditions and lowered lake levels (*see* Sly 1976). The second peculiarity is very low chlorophyll content of the sediment for the dry period of 7400–6000 B.P., in contrast to the more recent drying, which has produced very high chlorophyll concentrations. The lake is now subject to major artificial eutrophi-

cation (Lewis and Weibezahn 1976), but this may not be sufficient to account for the contrast. The allogenic component is so pronounced in the earlier drying episode that production in the lake may have been suppressed by high inorganic turbidity. The possibility of human alteration of the watershed should not be dismissed, although archaeological information suggests that this is too early for major agricultural impact (Cruxent and Rouse 1958).

The dry episode began to ameliorate about 6000 B.P., as indicated by reduced clastic input (presumably due to increased vegetation cover and greater water depth in midlake), by increase in the Ca:Mg ratio of carbonates, and by change in diatom species composition. A peak of moisture was apparently reached about 3000 B.P. Chemical indicators and the return of *Melosira* suggest salinities $<500$ mg·liter$^{-1}$ for as long as several hundred years. The lake must have discharged water at this time.

About 2800 B.P., a slow drying episode began which has continued to the present day, as uniformly indicated by chemical and biological data. About 1200 B.P. a unique event occurred, possibly through anthropogenic influence, involving intense production and high diatom populations.

A growing body of evidence from the tropics indicates the existence of dry conditions at the end of the Pleistocene and generally increased wetness within the last 12,000 years (van der Hammen 1974; van Zinderen Bakker 1972; Tricart 1974; Livingstone 1975; Colinvaux and Schofield 1976). The universality of this trend is uncertain, but the Lake Valencia data reinforce the impression of low rainfall within the tropics at the end of the Pleistocene. Evidence for subsequent marked increase in rainfall is equally impressive, but on a given continent the details of variation within the Holocene may differ considerably between regions (Livingstone 1975).

It has been shown for the Columbian and Venezuelan Andes that the last Andean glaciation was essentially synchronous with north temperate glaciation (van der Hammen 1974; Salgado-Labouriau and Schubert 1976; Salgado-Labouriau et al. 1977). The Andean glacial retreat is dated at 12,000–13,000 B.P. and would thus exactly coincide with the conversion of the Valencia basin from a dry or seasonally wet area to a permanent lake. Increased moisture is thus associated with local deglaciation. Both the Andean work and the Valencia work reported here indicate significant changes in humidity within the Holocene as well, but details are too shadowy to allow geographic generalization.

Our study and the apparent convergence of data on major moisture changes in the lowland tropics since the late Pleistocene reinforce a major point brought out by Livingstone's (1975) review of climatic change in Africa. We can expect to find that lakes of the lowland tropics have shown radical changes in chemistry, nutrient budgets, and water levels over the relatively recent past.

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*Submitted: 12 December 1979*
*Accepted: 12 February 1981*