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Jellyfish Lake, Palau: Regeneration of C, N, Si, and P in anoxic marine lake sediments

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Abstract

Sediment cores from Jellyfish Lake were processed under an inert atmosphere and the pore waters extracted and analyzed for the following parameters: pH, titration alkalinity (TA), Cl^-, H_4SiO_4, $PO_4{}^{3-}$, $NH_4{}^+$, Ca^{2+}, Mg^{2+}, $SO_4{}^{2-}$, and H_2S. Additionally, in one set of pore-water samples (core 10), the $\delta^{13}C$ of the ΣCO_2 was also determined. The TA, H_4SiO_4, $PO_4{}^{3-}$, $NH_4{}^+$, and H_2S increased with depth in the pore waters above anoxic bottom-water values. H_2S values increased to 3.8 μM. In one case, both H_4SiO_4 and $PO_4{}^{3-}$ concentrations increased to a maximum value and then decreased with depth, suggesting removal into solid phases. The H_4SiO_4 concentrations are equal to or greater than pore-water values observed in sediments underlying upwelling areas. $PO_4{}^{3-}$ concentrations are, in general, lower than pore-water values from terrigenous nearshore areas but higher than nearshore carbonate pore-water values from Florida Bay or Bermuda. The Ca^{2+}, Cl^-, and $Mg^{2+}:Cl^-$ ratios show slight decreases in the top 15–20 cm, suggesting that authigenic carbonate may be forming. This suggestion is supported by the fact that the pore waters are saturated with respect to $CaCO_3$ due to the very high TAs. The $\delta^{13}C$ measurements of the pore-water ΣCO_2 are from a shorter core. These measurements reach their most negative concentration at 72 cm and then become slightly heavier. This change is accompanied by a decrease in TA, suggesting the onset of methanogenesis at this location in this core.

The study of the formation of authigenic minerals in modern marine anoxic environments provides important insights into understanding the ancient sedimentary rock record. The formation and preservation of phosphate minerals, calcium carbonate, and biogenic silica are greatly dependent on the diagenesis of organic matter after sediment burial (Berner 1974).

In its bottom waters, Jellyfish Lake has dissolved sulfide concentrations among the highest reported for any marine system (Burnett et al. unpubl.). Therefore, the biogenic debris reaching the sediment–water interface has been exposed to anoxic conditions prior to burial. The chemical diagenesis of organic matter in the lake sediments could be somewhat analogous to marine sediments in the geologic past, such as during the Cretaceous period, when widespread anoxia occurred (Arthur and Jenkyns 1981).

One of the initial motivations for our study of Jellyfish Lake was to assess the possibility that stratified marine lakes on uplifted carbonate platforms may be analogs for the environment in which the numerous insular phosphate deposits scattered throughout the tropical Pacific Ocean formed. The conventional wisdom regarding the

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Table 1. Analytical techniques for pore-water samples.

Titration alkalinity	Titration	±0.1 meq liter^{-1}	Strickland and Parsons 1972
Phosphate	Colorimetric	±2%	Strickland and Parsons 1972
Silicate	Colorimetric	±7%	Strickland and Parsons 1972
Ammonium	Colorimetric	±2%	Orem 1982
Fluoride	Specific ion electrode	±2%	Froelich et al. 1983
ΣH_2S	Specific ion electrode	±5%	—
Sulfate	Indirect titration	±1%	Howarth 1978
Choride	Mohr titration	±2%	—
Calcium	Flame AAS with Cs and LA for matrix modification	±2%	—
Magnesium	Flame AAS with Cs and La for matrix modification	1%	—
pH	Electrode	±0.1 pH units	—

origin of these deposits states that insular phosphates are a result of interactions of solutions leached from avian guano with the underlying carbonate bedrock. Although guano-derived phosphate deposits clearly do form, as shown by studies of modern deposits off Peru and on some equatorial Pacific islands (Gulbrandsen 1975; Piper et al. 1990), we suspect, for reasons given below, that some deposits may be marine or specifically marine-like in origin.

Jellyfish Lake was selected for this study because it is located near known insular deposits and because of what was learned about its unusual chemistry during an earlier study (Hamner et al. 1982). Phosphate deposits of various sizes are found throughout the southern Palau islands. Phosphate was mined on Angaur and Peleliu until about 1950 (U.S. Army 1956). Eil Malk, the island where Jellyfish Lake is, contains ~15 small scattered phosphate deposits totaling 500,000 t. An old sketch map originally prepared by the South Seas Development Company (U.S. Army 1956) shows that these small deposits are mostly circular to oval and are found in depressions in the carbonate terrane. Their size, shape, and locations make them look very much as if they could be remnants of former marine lakes. We decided, therefore, to investigate this possibility by studying early diagenesis via pore-water analysis of sediments from a modern lake.

Here we present pore-water concentrations of various inorganic constituents from a series of gravity- and diver-operated cores from the central portion of the lake. These data allow us to determine the effect of anoxic diagenesis on the fate of organically derived materials in the sediments. This paper is one in a series describing the geochemistry of Jellyfish Lake. The others include the organic geochemistry of the sediments (Orem et al. 1991), the sulfur geochemistry of the sediments (Bates et al. 1993), and the nutrient and trace metal geochemistry of the water column (Landing et al. 1991).

Study area, materials, and methods

The location and general character of Jellyfish Lake and the coring methodology are presented elsewhere (Burnett et al. unpubl.; Orem et al. 1991).

Sediment samples were extruded, sectioned, and placed into precleaned polyethylene centrifuge tubes with tight-fitting caps. The nylon and plastic centrifuge tubes and utensils had previously been cleaned in 10% vol/vol HCl and washed copiously with distilled deionized water. The sediment samples were centrifuged at approximately in situ temperatures. The centrifuged pore water was passed through 0.4-μm Nuclepore filters held in Millipore polycarbonate filter holders. All procedures except the centrifugation were conducted in a glove bag under an inert atmosphere (He) to minimize any oxidation of reduced species (Loder et al. 1978; Lyons et al. 1979).

Titration alkalinity (TA), reactive phosphate, reactive silicate, ammonium, fluoride, and dissolved sulfide (ΣH_2S) were analyzed in the laboratory at the Micronesian Mariculture Demonstration Center (MMDC) in Koror, Palau, within 36 h of collection. Sulfate and chloride were analyzed later in Palau, while calcium and magnesium were determined on acidified samples upon return to the U.S. Analytical procedures and their estimated precision as percent relative standard deviation are shown in Table 1. We used the PC-WATEQ2 computer program (Ball et al. 1987) to calculate mineral saturation indices.

Samples for stable isotope and concentration analyses of ΣCO_2 were stored in rubber-capped, completely full, 14-ml glass bottles in which 200 μl of saturated mercuric chloride had been evaporated to dryness before sample addition. For the isotopic analyses, 1–2-ml samples of accurately known weight were transferred to a stripping line by a double-needle technique that obviated the need to open bottles to atmosphere. The CO_2 was extracted by stripping with He after addition of 100% phosphoric acid. The gas was purified with two traps containing dry ice-acetone and a final trap containing melting ethanol. Gas yields were measured by electronic manometer calibrated with pure dry $CaCO_3$ and solutions of $NaHCO_3$ of known strength. Blank values were negligibly small. The accuracy and precision of the ΣCO_2 analysis was shown to be better than ±1% RSD by replicate analysis of coastal seawater run repeatedly as a line monitor and duplicate analysis of some samples. Isotopic analysis was done on a modified MS 12 mass spectrometer at the Research School of Earth Science, Australian National University. Calibration was performed with RSES in-house standards that

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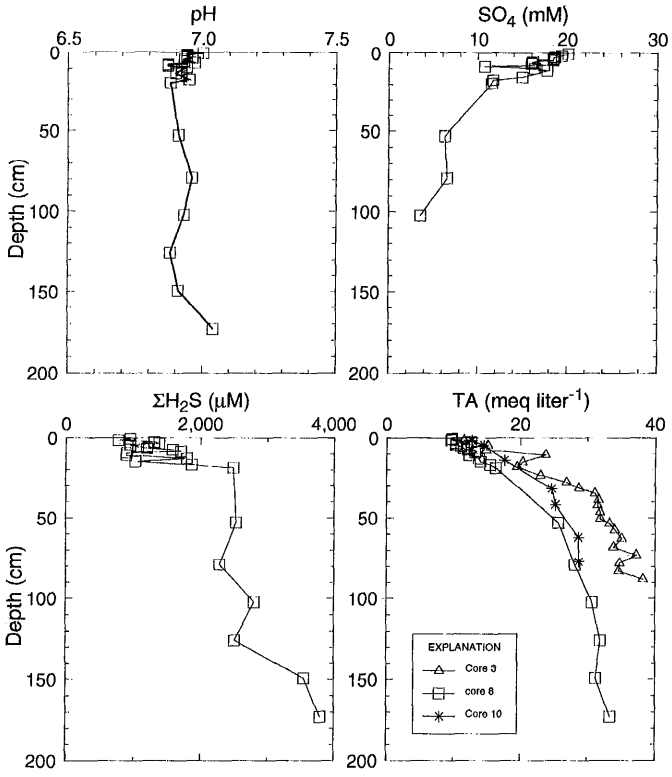

Fig. 1. Pore-water pH, SO_4^{2-}, ΣH_2S (core 8), and titration alkalinity (TA) vs. depth in cores 3, 8, and 10.

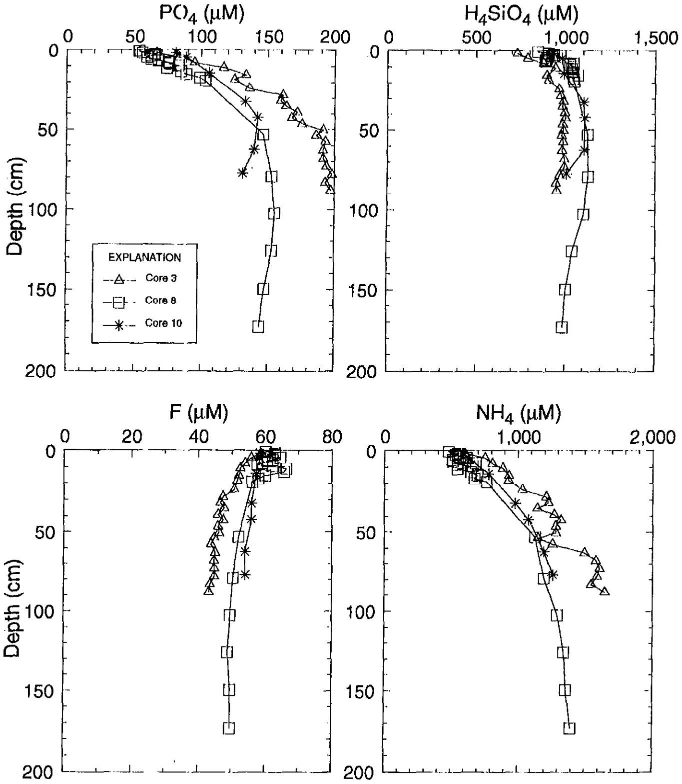

Fig. 2. As Fig. 1, but of pore-water phosphate, silicate, ammonium, and fluoride.

were themselves calibrated with respect to international standards. The precision of the isotopic analysis of pore water was ≤0.10‰. Replicate analysis of six samples of coastal seawater analyzed as run monitors during the analysis gave $\delta^{13}C$ values of +0.63±0.06‰.

Results and discussion

From our unpublished radiochemical work on the sediment cores (Burnett pers. comm.), it seems that there may have been a loss of up to 13 cm from the tops of all the gravity cores taken. (Although a number of cores were obtained, only three were processed for pore water.) This core-top loss is because the surficial sediment in Jellyfish Lake is extremely porous, with in situ bulk densities of ~0.07 g cm^{-3}. Therefore, a fluff layer of some depths (perhaps 13 cm) acts as a transition from the water column to the more dense and compacted sediments at depth. A similar fluff layer has been described in Lake Superior (McKee et al. 1989) and in Mangrove Lake, Bermuda (Orem et al. 1986). We are confident that the diver-obtained core (core 8) represents a complete sediment column sample. Some mixing of the surficial part of this core took place during transport back to the laboratory at Koror. The pore-water data from gravity cores 3 and 10 will be used where necessary, however, because useful information regarding chemical diagenesis of these sediments is still available. If we compare the pore-water nutrient data from core 3 to data from core 8, it seems that as little as 1–2 cm (for H_4SiO_4) or as much as ~7–8 cm (for PO_4^{3-} and TA) of core 3 may have been lost during sampling. In core 10, the comparison of the TA pore-water to bottom-water data indicates very little of the surficial sediment was lost.

Pore-water concentrations vs. depth for pH, sulfate, sulfide, TA, ammonium, phosphate, silicate, and fluoride are shown in Figs. 1 and 2. The pH at the sediment–water interface is 7.0, decreases to 6.9 at 20 cm, and remains relatively constant to 150 cm (Fig. 1). The pH below 170 cm is 7.05. In core 8, the SO_4^{2-} concentrations decrease from between 19 and 20 µM at the sediment–water interface to 0 at 126 cm; the most rapid decrease takes place from 0 to 50 cm (Fig. 1). This sulfate loss corresponds to the decrease in sedimentary organic carbon at the same depths (Orem et al. 1991). This decrease indicates that sulfate reduction continues in the surficial sediment of the lake, which can also be demonstrated with the ΣH_2S data, where dissolved sulfide increases from values of 1.0–1.4 µM in the surface sediments to values of 3.8 µM at ~175 cm (Fig. 1). Lack of any substantial source of iron in the system helps account for these high ΣH_2S values (Landing et al. 1991). Sulfur isotopic measurement of the sediments also indicates that sulfate reduction has occurred (Bates et al. 1993).

Interestingly, the surficial pore waters have lower ΣH_2S concentrations than do the bottom waters (~2.5 vs. 1–1.5 µM). This decrease of ΣH_2S across the sediment–water interface is curious and may be related to the abovemen-

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tioned core loss. Similar decreases have been observed in other marine-influenced anoxic basins. For example, in the Pettaquamscutt River estuary, Rhode Island, Henrichs and Farrington (1987) observed a similar decrease of ΣH_2S across the sediment–water interface. It is possible that the ΣH_2S reacts with sedimentary organic matter and produces the very high organic sulfur values found in these sediments (Orem et al. 1991). The removal of ΣH_2S by reaction with organic matter such as humic acid is well documented (Nissenbaum and Kaplan 1972; Francois 1987). The data suggest high in situ rates of sulfate reduction within the anoxic water column or the fluff zone of Jellyfish Lake. It is highly possible that the fluff zone may be an important focus for sulfate reduction in this system.

TA in the bottom water increases from between 8.4 and 9.2 meq liter^{-1} to 33.48 meq liter^{-1} at 173 cm (Fig. 1). Again, the most rapid increase occurs between the sediment–water interface and ~50 cm, suggesting that this is the region of extensive sulfate reduction. Core 3 had TA values as high as 34 meq liter^{-1} at much shallower depths (Fig. 1). Whether this difference is due to the difference in coring technique (i.e. surface sediment loss plus more compaction with the gravity-coring unit) or real spatial variation cannot be documented at present. TA values in core 10 slowly increase below 60-cm depth.

Ammonium concentrations increase across the sediment–water interface from fluff layer values of ~390 μM to ~500 μM (core 2). The concentration of NH_4^+ increases with depth to values as high as ~1.65 μM in core 3 and 1.4 μM in core 8 (Fig. 2). Reactive phosphate concentrations also increase from 47 μM in the fluff layer to 53 μM at 0.5 cm in core 8. In cores 8 and 10, the PO_4^{3-} concentrations proceed through a maximum value of 140–155 μM at ~100 and ~40 cm, respectively, and then decrease. In core 3, maximum values of ~200 μM are reached at ~70 cm and are then maintained (Fig. 2).

H_4SiO_4 concentrations increase from ~570 μM in the bottom water to ~650 μM in the fluff layer to 845 μM at 0.5-cm depth in the pore waters of core 8 (Fig. 2). Our values are similar to those reported by Hamner et al. (1982) for Jellyfish Lake bottom water. There seems to be very rapid recycling of H_4SiO_4 in anoxic waters and surficial pore waters of the lake. The concentrations are an order of magnitude higher than concentrations observed in the anoxic bottom waters of the Cariaco Trench (Fanning and Pilson 1972) and ~5 times higher than those found in Saanich Inlet bottom waters (Nissenbaum et al. 1972; Murray et al. 1978). In all three pore-water cores, the concentration of H_4SiO_4 proceeds through a maximum at ~20–80 cm and then decreases (Fig. 2). Maximum values are ~1.1 μM in cores 8 and 10. These values are extremely high and are similar to concentrations observed in oceanic pore waters, where biological productivity is great and the delivery of biogenic silica to the ocean floor is extremely high (Schink et al. 1974; Jahnke et al. 1983).

Sediment analyses indicate that the Jellyfish Lake sediments contain abundant diatom frustules as well as extremely high opaline silica concentrations (Burnett et al. unpubl.). Net primary production is very high in the surface waters. It is estimated to be 0.52–3.1 g C m^{-2} d^{-1} by Hamner et al. (1982) and must provide a continual high flux of biogenic silica into the bottom waters. Hamner et al. (1982) have shown that the major phytoplankton species include the chain-forming centric diatoms, such as *Chaetoceros* sp. The source of the H_4SiO_4 in the anoxic water column, as well as the high concentrations observed in the pore waters, must be due to the dissolution of this biogenically produced silica.

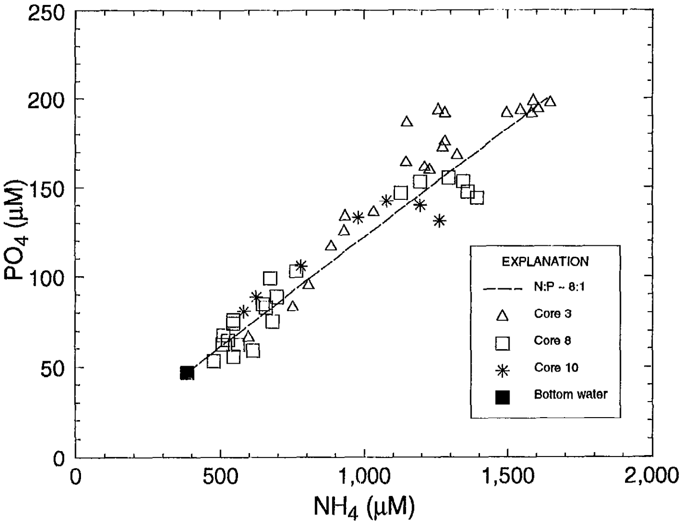

Fig. 3. Dissolved phosphate vs. ammonium in pore waters from cores 3, 8, and 10. The dashed line is drawn with a N:P atomic ratio of 8:1.

The fluoride concentrations generally decrease from bottom-water values of 65 μM across the sediment–water interface to 58–60 μM in the fluff layer to 49–50 μM below 125-cm depth (Fig. 2).

Nutrient regeneration processes—The C:N ratio of the organic matter being buried in Jellyfish Lake ranges from 28 to 16 (Orem et al. 1991). In core 8, the surface values are as high as 28, and the deeper values are ~21. The pore-water $NH_4^+ : PO_4^{3-}$ ratio for cores 3, 8, and 10 is 8:1 (Fig. 3). N:P pore-water ratios from nearshore carbonate sediments yield much lighter N:P ratios (Hines and Lyons 1982), probably indicating the more rapid adsorption of PO_4^{3-} onto carbonate grains (Berner 1974). After the pore-water N:P ratio is corrected for the effects of differential diffusion and adsorption (Martens et al. 1978; Krom and Berner 1980, 1981; Froelich et al. 1988), the N:P ratio of the organic matter is 20:1, yielding a C:N:P of 106:3.8:0.2. If we assume that the C:N:P ratio of the phytoplankton in the lake is similar to that of ocean phytoplankton (106:16:1), the surficial organic matter in core 8 is greatly depleted in both N and P relative to C. Krom and Berner (1981) have found the C:N:P ratio of organic matter in nearshore clastic sediments to be 106:11:0.3. Gulf of Trieste organic matter has been found to have a mean C:N:P ratio of 106:8:0.2 (Faganeli et al. 1988). The Jellyfish Lake organic mat-

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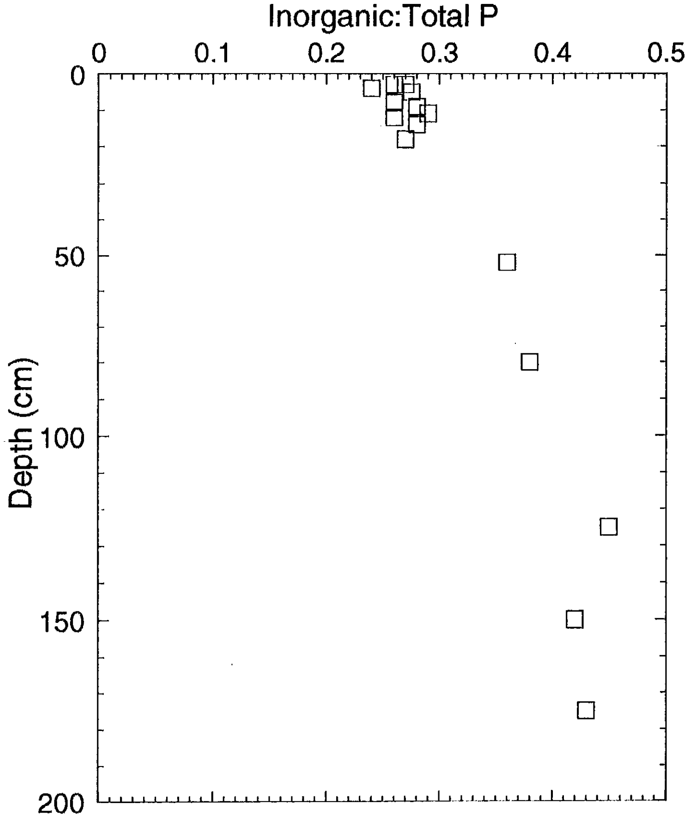

Fig. 4. Ratio of inorganic to total P for core 8 vs. depth. Inorganic P was determined by standard molybdate blue spectrophotometry after leaching the dried and powdered sediment with 1 N HCl. Total P was determined after ashing the sediment at 550°C.

ter is similar in P but greatly depleted in N compared to these values. This depletion could be due to the more rapid regeneration of N and P at the oxic–anoxic interface or in the anoxic bottom waters or to a significant percentage (~50%) of the organic matter that is deposited on the lake floor being derived from a more carbon-enriched, terrestrial source. The P depletion could also be due to removal via carbonate mineral reaction (*see below*).

Post et al. (1985) have demonstrated that tropical wet forest organic matter has C:N value of ~30. This ratio is very similar to the value of 28 observed by Orem et al. (1991) in the surficial sediments of core 8. Marine algae has a value of ~7, and marine sedimentary organic matter has a value of ~10 (Krom and Berner 1981). If we assume a simple two end-member system of terrestrial rain-forest organic matter with a C:N value of 30 and an allochthonous lake end-member with a C:N value of 10, and a composite Jellyfish Lake C:N value of 28, then, of the total organic matter present, only 10% is from the lake and 90% is from the surrounding rain forest. The 90% value seems to be very similar to that obtained by organic geochemical means (Orem et al. 1991) and suggests that high ratios of C:N are probably due to rapid regeneration of lake organic matter above the chemocline and selective burial of the vascular plant material from the forest.

Orem et al. (1991) have demonstrated that 20–50% of the labile carbohydrate of the particulate organic C of the lake is lost prior to sedimentation, and only 5–9% is lost from the sediment–water interface to the 100-cm depth in core 8. This indicates rapid C, N, and P regeneration and return to the waters of the lake. The C:N:P ratio of the anoxic bottom water is 106:6:0.5. The comparison between this water column ratio and that of the pore waters indicates that much of the N and P is regenerated from organic matter at the sediment–water interface and (or) in the fluff layer. The 18:1 C:N ratio suggests that the organic matter falling through the water column has N preferentially regenerated from it or that the organic matter is about a 50:50 mix of vascular plant remains and lake algal debris. Based on the organic geochemical results, however, this apparently is not the case, because the lake sediments are dominated by organic matter from vascular plant remains (Orem et al. 1991).

Phosphate diagenesis—The pore-water profiles for phosphate (Fig. 2) show concentrations at the core top significantly higher than bottom water (~ 30 μM liter^{-1}) increasing steadily to values of ~150 μM liter^{-1} in cores 8 and 10 and to nearly 200 μM liter^{-1} in core 3. Two of the three cores (8 and 10) have a phosphate maximum at depth and a significant and apparently linear decrease at deeper levels.

We also determined pore-water fluoride in an attempt to use its distribution as a tracer of authigenic phosphorite precipitation, as was demonstrated for phosphate mineralization in Peru shelf sediments (Froelich et al. 1983, 1988). Fluoride is an essential element of carbonate fluorapatite (CFA), the principal phosphatic mineral phase of marine phosphorites. Although other phosphatic minerals are known to occur on oceanic islands, CFA is one of the chief mineral phases found (Altschuler 1973).

The fluoride profiles (Fig. 2) are characterized by concave-downward trends, starting at approximately bottom-water concentrations (65 μM liter^{-1}) and leveling off at around 44 μM liter^{-1} in the deeper parts of these cores. These profiles thus suggest F^- uptake, which can be modeled as first-order removal (Froelich et al. 1983). We used this approach and calculated that F^- is removed at a rate between 0.2 (core 8) and 0.3 (core 3) μM F cm^{-2} yr^{-1}. If we assume this occurs solely by precipitation of CFA with a P:F mode ratio of ~2.5, the equivalent phosphate removal is ~0.5–0.9 μM P cm^{-2} yr^{-1} in these sediments. If this estimate is divided by the net sediment mass accumulation rate (0.67 g cm^{-2} yr^{-1}, Burnett pers. comm.), an "expected" authigenic concentration of inorganic phosphorus is ~0.2–0.04 wt%. In fact, the actual inorganic P concentration in core 8 ranges from 0.03 to 0.05%, with the lowest values near the sediment surface and a systematic increase downcore; this can best be seen in a plot of the ratio of inorganic to total phosphorus down core (Fig. 4). Thus, the F^- flux model reasonably explains almost all the inorganic P observed in these sediments. We have been unable to verify the presence of CFA within

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the sediment (a virtually impossible task at these low concentrations). We recognize the possibility that F uptake may not be linked to CFA precipitation, but may instead be controlled by adsorption onto one of the sediment constituents. Ruttenberg (unpubl.) has shown, for example, that F^- can adsorb onto ferric oxyhydroxide surfaces in oxic marine sediments. Because of the anoxic nature of the Jellyfish Lake sediments, surfaces of this type probably are not present. It is possible that F^- has adsorbed onto some other phase, such as organic matter or silica. However, the F^- uptake model is clearly consistent with the amount of inorganic phosphate observed in these sediments. Additionally, the increase of inorganic phosphate downcore argues in favor of authigenic precipitation.

If the F^- uptake is controlled by CFA precipitation, mineralization occurs mainly in the upper parts of the sediment column. The pore-water phosphate profiles (Fig. 2) do not show any inflection within this interval, probably because the regenerative input from organic matter dominates the phosphate distribution in the upper sediment layers. The source of the dissolved PO_4 in these pore waters is clearly organic matter, as shown by a plot of dissolved $PO_4{}^{3-}$ vs. $SO_4{}^{2-}$ (Fig. 5). Most of the points fall along a trend with a $\Delta PO_4/\Delta SO_4$ slope of ~1 : 150, the stoichiometric relationship expected for the regenerative release of phosphate from Jellyfish Lake organic matter during sulfate reduction.

In addition to phosphate precipitation, which may accompany CFA formation in the uptake (shallow) portion of the F profile, there also seems to be phosphate removal deeper in these sediments. This removal is clearly shown by the series of data points that plot below the line that describes the pore-water N : P ratio of 8 : 1 (Fig. 3). The approximate removal flux (J_p) of phosphate in these portions of the profiles was estimated from

$$J_p = -\phi_z D_s (\mathrm{dP}/\mathrm{d}z)_z.$$

ϕ_z is the average porosity over the interval z, D_s the whole sediment diffusion coefficient for PO_4 (estimated as 3.6×10^{-6} cm^2 s^{-1}; Krom and Berner 1980), and $(\mathrm{dP}/\mathrm{d}z)_z$ the linear portion of the phosphate gradient below a maximum over depth range z. Although we did not directly measure porosities, we were able to make reasonable estimates based on measured water contents (88–93%) and assumed grain densities of the major sediment components ($CaCO_3$, opaline silica, and organic matter). Our estimates for porosity (0.93–0.95 ml cm^{-3}), together with the measured linear $PO_4{}^{3-}$ gradients and a reasonable value for the diffusion coefficient, resulted in estimated authigenic phosphate production rates of 0.02 (core 8)–0.03 (core 10) μM P cm^{-2} yr^{-1} for these deeper sediment layers. These rates are about an order of magnitude lower than those estimated for the phosphate mineralization associated with fluoride uptake in the upper sediment layers. The vast majority of the inorganic phosphate contained in Jellyfish Lake sediments, therefore, does not seem to be associated with the removal that occurs in the deeper, extremely anoxic part of the sediment column. The linear trend of this portion of the pore-water $PO_4{}^{3-}$ vs. depth profile (Fig. 2) suggests that the removal occurs at a deeper level than our cores penetrated. One possibility is that this removal takes place at the contact of these sediments with the underlying carbonate bedrock.

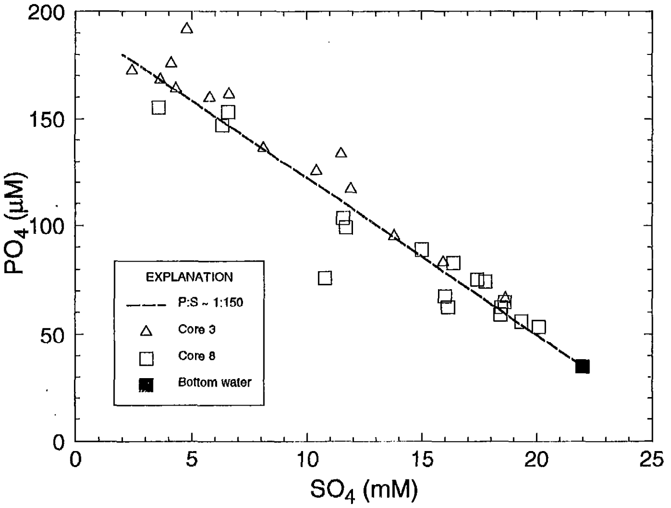

Fig. 5. Dissolved phosphate vs. sulfate in pore waters from cores 3 and 8.

These calculations show that the authigenic removal *fluxes* of phosphate into Jellyfish Lake sediments are fairly high (at least in the upper sediment column), comparable to removal fluxes measured for Peru shelf sediments (Froelich et al. 1988). The extremely high bulk sediment accumulation (~0.7 cm yr^{-1}), however, dilutes the authigenic phosphate to such an extent that authigenic phosphate *concentrations* are very low. Clearly, no phosphate deposit will form under these conditions.

Sulfate reduction model—Given the pore-water $SO_4{}^{2-}$ data and the sedimentation rate (W), the first-order rate constant for microbial sulfate reduction (k_s) can be determined (Berner 1974; Murray et al. 1978). The sedimentation rate for the deepest portion of the lake was determined via ^{210}Pb to be 0.7 cm yr^{-1} (Burnett unpubl. data). The resulting k_s, depending on the $SO_4{}^{2-}$ profile used, is $4\text{–}26 \times 10^{-10}$ s^{-1}.

Murray et al. (1978) determined k_s for the Saanich Inlet anoxic basin sediments to be $43\text{–}61 \times 10^{-10}$ s^{-1}, yet the organic C (OC) concentration of surface sediments in Saanich Inlet is only 3.8%. Interestingly, the Jellyfish Lake surficial sediments are 26.5% OC on a total bulk sedimentary basis (Bates et al. 1993), yet their k_s is 2.5–10 times lower than those of Saanich Inlet. This further supports the notion proposed by Orem et al. (1991) that most organic matter reaching the floor of Jellyfish Lake is refractory in nature or already highly degraded. This slower rate is due to the rapid degradation of organic matter in the water column as well as the high percentage of vascular plant debris entering the lake. Hamilton and Hedges (1988) have shown that the rate of decomposition of nitrogen-containing organic matter and carbohydrates is about twice that of lignin material in anoxic basin sedi-

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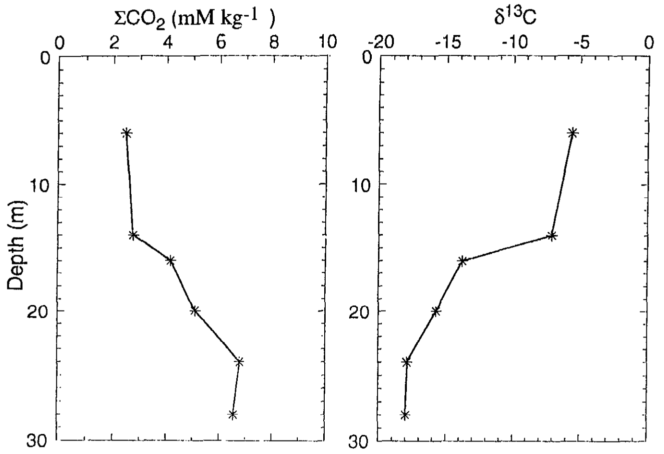

Fig. 6. Water-column ΣCO_2 and $\delta^{13}C$ (‰) of ΣCO_2 concentrations.

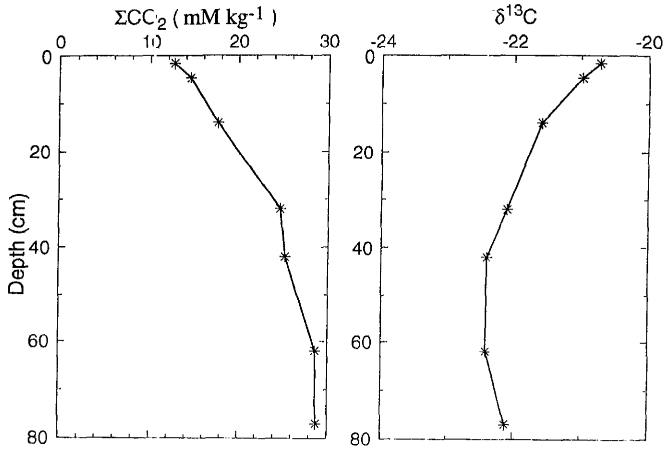

Fig. 7. Pore-water ΣCO_2 and $\delta^{13}C$ (‰) of ΣCO_2 concentrations from core 10.

ments. Therefore, much of the organic matter produced in the oxic portion of the lake is rapidly degraded before burial. Much of this degradation may occur at the oxic–anoxic boundary of the lake, where there is a 1–2-m-thick bacterial plate, and particulate OC concentrations reach a maximum and then decrease rapidly with depth (Hammer et al. (1982).

The amount of OC reaching the sediment surface can be calculated by means of modification of the equation of McNichol et al. (1988):

$$C_b = w[\mathrm{OC}]_d\rho.$$

C_b is the amount of OC buried in the sediments, ρ the density of solids (=0.07 g cm^{-3}), $[\mathrm{OC}]_d$ the surficial sediment OC concentration (= 265 mg C g^{-1}) (from Bates et al. 1993), and w the sedimentation rate (=0.7 cm yr^{-1}).

This calculation yields a value of 130 g C m^{-2} yr^{-1} for the amount of OC buried in the deepest portion of the lake. This value is 68% of the total C fixed (190 g C m^{-2} yr^{-1}) in the euphotic zone of the lake (Hammer et al. 1982). This value, coupled with the observation (Bates et al. 1993) that there is little loss (~3.5% on a total sedimentary basis) of OC from the surface to a depth of 151 cm, suggests again that most organic matter that reaches the sediment–water interface of the lake is refractory. This conclusion also supports the data of Orem et al. 1991).

Reimers and Suess (1983) have shown that 35–85% of the total OC flux in marine systems is utilized at or near the sediment–water interface. Martens and Klump (1984) found that ~24% of the C sedimented at Cape Lookout Bight is rapidly recycled back into the water column. Klump et al. (1989) have shown that 15–40% of the C deposited in the eastern basins of Lake Superior is recycled into the water column. Although this does not seem to be the case in Jellyfish Lake, the rapid decrease of particulate organic matter at the chemocline (Hammer et al. 1982) suggests that this interface plays a predominant role in carbon cycling in this environment. In fact, Venkateswaran et al. (1993) indicate very high levels of total bacterial biomass at the chemocline of the lake. They found that the total numbers of cells is comparable to eutrophic coastal waters. All this information combined suggests rapid and efficient turnover of the most labile C compounds at the chemocline and not at the sediment–water interface.

Carbon isotopes in Jellyfish Lake waters—$\delta^{13}C$ of the ΣCO_2 was measured in both water column and pore-water samples. These data are shown in Figs. 6 and 7. The oxic surface waters are the heaviest of all the waters in the lake, yet even they are much lighter than ocean waters. The $\delta^{13}C$ values in South Pacific surface waters range between +1‰ (Kroopnick 1985) and +2.2‰ (Craig 1970), yet the oxic waters of the lake at 6 m are ~−5‰. This isotopic value indicates that much of the ΣCO_2 in the surface waters of the lake has been derived from the degradation of organic matter in the water column. This value is much lower than oceanic bottom water of ~+0.5‰, suggesting that indeed a high percentage of the ΣCO_2 in the lake is respiration derived (~30%). This low value is even more impressive when one considers the high productivity in the lake itself, which should enrich the lake ΣCO_2 in ^{13}C as phytosynthesis occurs.

There is a rapid decrease in $\delta^{13}C$ values across the chemocline (Fig. 6). This decrease supports the premise that the bacterial plate at the redox boundary serves an important role in organic matter degradation and nutrient recycling in the lake and as a diffusive barrier to upward movement of CO_2 from respiration. The $\delta^{13}C$ values decrease to values approaching −18‰ at depth in the anoxic waters and then remain relatively constant.

There is another rapid decrease in the $\delta^{13}C$ value across the sediment–water interface, from values ~−18‰ to values approaching −21‰. (This large change suggests a portion of the top of the core may have been lost during sampling.) The $\delta^{13}C$ value decreases again to −22.4‰ at 40 cm, remains constant, and then actually increases below 60 cm (Fig. 7). Although SO_4^{2-} does not go to zero in this core, this increase in $\delta^{13}C$ is at a depth similar to

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that at which SO_4^{2-} reached zero in core 3. It is possible that methane is produced at depths below 60 cm (Nissenbaum et al. 1972; Martens and Berner 1977). Bubbles were observed in many of the cores, and it is highly probable that methane production is a major process in the lake sediments below the sulfate reduction zone. The $\delta^{13}C$ values of the ΣCO_2 of the pore waters are extremely negative and similar to those reported in the literature in sediments dominated by microbial sulfate reduction as the major biogeochemical pathway for oxidation of organic matter (Presley and Kaplan 1968; Nissenbaum et al. 1972; Goldhaber 1974).

Biogenic silica diagenesis—The apparent kinetic constant (k_{Si}) for biogenic silica dissolution can be calculated by techniques similar to those outlined by Vanderborght et al. (1977). For core 8, a value of 3.5×10^{-8} s^{-1} is obtained. This value is an order of magnitude lower than what has been calculated for nearshore clastic sediments (Vanderborght et al. 1977). This k_{Si} is misleading because the H_4SiO_4 concentrations at 0.5 cm in the pore water are already extremely high (845 μM). Berner (1974) concluded that in sediments containing appreciable biogenic silica, sediment pore waters should attain saturation values with respect to silica at very shallow depths. This situation is certainly the case in Jellyfish Lake (Fig. 2). In core 8, the pore waters are in equilibrium with amorphorous silica at the sediment–water interface and become supersaturated below a few centimeters depth (Fig. 8). In core 3, the pore waters are slightly undersaturated in the top 2 cm, in equilibrium at 3 cm, and supersaturated below this depth.

Therefore, the low k_{Si} is probably related to the saturation state of the pore waters as outlined by Berner (1974). The high concentrations of H_4SiO_4 in the fluff layer, at the sediment–water interface, and in the top 0.5 cm of the pore waters suggest that the rate of biogenic silica dissolution is most rapid at the sediment–water interface and(or) in the water column and not in the sediment column. The pore waters in both cores are undersaturated with less soluble forms of SiO_2, but due to the dearth of clastic silicate minerals in these sediments, this is of little consequence.

Calcium carbonate diagenesis—In both cores 3 and 8, the pore waters are at equilibrium with respect to calcite and slightly supersaturated with respect to aragonite at the sediment–water interface and are supersaturated with respect to both mineral phases at depth.

The high total carbonate concentrations (~30% $CaCO_3$) in the sediments (Orem et al. 1991) are partly due to the input of detrital carbonate from the surrounding limestone terrane. However, the production of TA via sulfate reduction (Fig. 1) increases the total carbonate concentrations in the pore waters, leading to log saturation indices >0. Similar situations have been observed in other anoxic sediments (Presley and Kaplan 1968) as well as in anoxic waters (Anderson et al. 1987). Whether authigenic carbonate minerals are actually forming in the sediments of Jellyfish Lake is unknown.

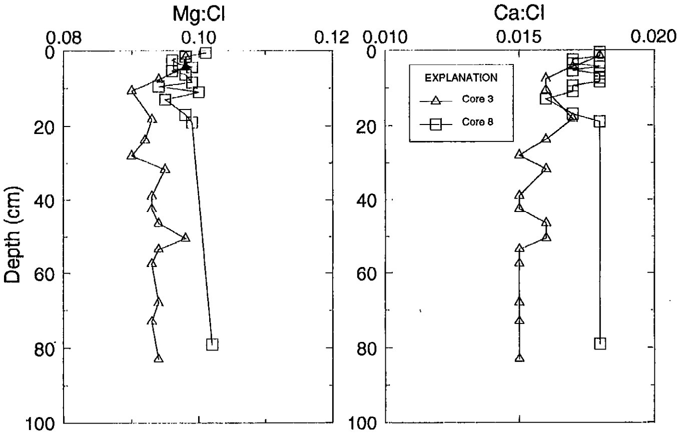

Fig. 8. Pore-water Mg : Cl and Ca : Cl molar ratios vs. depth in Jellyfish Lake sediments in cores 3 and 8.

The Ca : Cl ratios in the pore waters do decrease with depth, suggesting in situ carbonate mineral precipitation (Fig. 8). This is especially true in core 3. The value at the sediment–water interface is slightly lower than the oceanic value of 0.019, indicating that authigenic $CaCO_3$ may also be forming in the highly anoxic bottom waters—similar to what has been observed in Framvaren, Norway (Anderson et al. 1987). In core 3, the Mg : Cl ratios also decrease with depth (Fig. 8). In this low SO_4^{2-} environment where sulfate reduction is rapid, the possibility exists for dolomite or protodolomite formation (Baker and Kastner 1981); however, we have not examined the sediments extensively enough to document its occurrence.

Conclusions

The extremely high productivity in Jellyfish Lake and the close proximity of the lake to tropical rain-forest vegetation provide high fluxes of organic matter through the anoxic hypolimnion of the lake into the sediments. Although much of this organic matter is apparently degraded at the midwater redox boundary and in the highly anoxic bottom waters, high concentrations of OC are found in the sediments of the lake. The diagenesis of this buried organic debris leads to very high TA, ammonium, phosphate, silicate, and ΣH_2S in the pore waters of the sediments. The initial rapid regeneration of C, N, P, and Si in the surficial sediments apparently leads to PO_4^{3-}, SiO_2, and $CaCO_3$ removal at depth.

Our calculations show that there are fairly high removal fluxes of phosphate into the sediments, yet because of the high sedimentation rate, this authigenic phosphate material is diluted out. This conclusion does not necessarily rule out the marine lake model of insular phosphate formation. It is possible, for example, that the phosphate mineralization process is accelerated when a lake reaches a more mature stage in its evolution. Spooky Lake, another lake on Eil Malk that we did not have the opportunity to investigate, has many of the same characteristics as Jellyfish Lake but is shallower and contains much higher levels of dissolved PO_4^{3-} (W. Hamner pers. comm.).

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Another possibility is that subsequent subaerial weathering of exposed marine lake sediments could result in a phosphatic soil or perhaps an insular phosphate deposit after the more soluble and more easily oxidized components have been removed. A final possibility is that the acidic, organic, and phosphate-rich pore solutions of these sediments interact with the underlying carbonate to produce phosphorite by a replacement process. This type of phosphorite is well known on phosphate islands. This possibility could be evaluated at a later date by recovery of a sediment core that extends to the underlying limestone.

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