

# SULFATE REDUCTION RATES IN MICROBIAL MAT SEDIMENTS OF DIFFERING CHEMISTRIES: IMPLICATIONS FOR ORGANIC CARBON PRESERVATION IN SALINE LAKES\*

W. BERRY LYONS

*Hydrology/Hydrogeology Program, Mackay School of Mines, University of Nevada, Reno, Reno, Nevada 89557-0138  
(present address: Department of Geology, University of Alabama, Tuscaloosa, Alabama)*

MARK E. HINES

*Biogeochemical Systems Center, Institute for the Study of Earth, Oceans and Space, University of New Hampshire,  
Durham, New Hampshire 03824*

WILLIAM M. LAST

*Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2*

AND

ROBERT M. LENT

*Institute for the Study of Earth, Oceans and Space, University of New Hampshire, Durham, New Hampshire 03824  
(present address: United States Geological Survey, Water Resources Division, Blismark, North Dakota 58501)*

**ABSTRACT:** Kelts (1988) was the first to point out that the ionic composition of lacustrine waters could exert an important effect on the preservation of organic matter in the sediments of these systems. In lakes with high sedimentation rates, the sediments become devoid of molecular oxygen at or very near the sediment-water interface. The rates of anoxic (anaerobic) decomposition of organic matter vary with the amount and "type" of organic matter being buried as well as with the electron acceptor being reduced. The amount of energy produced per organic molecule being oxidized is more for microbial sulfate reduction than for methane production. Therefore, where sulfate is abundant, organic carbon should be more readily oxidized than where other anions such as  $\text{Cl}^-$  and  $\text{HCO}_3^-$  dominate the chemistry.

We have tested this hypothesis by determining *in-situ* sulfate reduction via radiolabel techniques in sediments from Freeflight Lake, a  $\text{Na}^+ \text{--} \text{Mg}^{2+} \text{--} \text{SO}_4^{2-}$  saline lake in southwestern Saskatchewan. These data are then compared to sulfate reduction rate measurements from other sedimentary environments. Of particular interest is our previous work on algal flat sediments from  $\text{Na}^+ \text{--} \text{Mg}^{2+} \text{--} \text{Cl}^-$  salt lakes and pans in Bonaire, N. A. The maximum sulfate reduction rate for the nearshore, algal flat sediments of Freeflight Lake was 400 nmol/ml/d. This is 2 to 2.5 times lower than rates from similar settings in Bonaire, even though the sulfate concentrations were 10–20 times higher at Freeflight Lake. In addition, the S:OC ratios of the Freeflight Lake sediments were extremely low, indicating the lack of sulfate reduction in these sediments. Although the total reduced sulfur concentration increased with depth at Freeflight Lake, an extremely high percentage of this total  $\text{S}^{2-}$  is in the form of acid-volatile sulfur. This would not have been predicted from the low sulfate reduction rates.

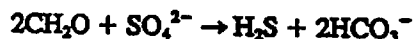
A number of important conclusions can be drawn from this work. They include the following: (1) sulfate reduction rates in salt lake sediments are not solely dependent on  $\text{SO}_4^{2-}$  concentrations nor on the ionic composition of the lake waters; (2) even though the organic carbon concentrations of these sediments are high, sulfate reduction is not rapid; and (3) the low sedimentation rate (0.03 cm/yr) may lead to the utilization of the most metabolizable of the carbon present in the oxic zone by aerobic bacteria, thereby slowing sulfate reduction rates.

## INTRODUCTION

The northern Great Plains of North America are characterized by flat to gently rolling topography and a cold semi-arid climate. This region contains an estimated  $3.5 \times 10^6$  salt lakes and saline wetlands. The composition of these waters varies dramatically, although  $\text{Na}^+ \text{--} \text{Mg}^{2+} \text{--} \text{SO}_4^{2-}$  waters dominate (Last, 1992). Because of the chemical diversity of the waters, these lakes can serve as important natural "beakers" in which to conduct various experiments. For example, Marino and others (1990) have utilized the sulfate-rich waters of northern Great Plains' lakes to establish what factors control nitrogen-fixation in cyanobacteria. These experiments were undertaken in these lakes solely because of their unique water compositions (Cole and others, 1986).

It has been argued that the ionic composition of the lacustrine waters should exert an important effect on the preservation of organic matter in these systems (Kelts, 1988). In lakes with high sedimentation and/or high primary production rates, depletion of molecular oxygen can occur at or above the sediment-water interface (Wetzel, 1975; Kelts, 1988). In aquatic systems, the rates of anoxic decomposition of organic matter vary with the amount and type of

organic matter being deposited and buried in the sediment (Bernier, 1978), as well as with the electron acceptor being reduced (Froelich and others, 1979). The amount of energy produced per organic molecule being oxidized is more for microbial sulfate reduction than for other anoxic biochemical pathways.



Therefore, where the sulfate ion is abundant, organic carbon should be more readily oxidized and, hence, not preserved in the sediments where other anions such as  $\text{Cl}^-$  and  $\text{HCO}_3^- + \text{CO}_3^{2-}$  dominate the solution chemistry (Kelts, 1988). This hypothesis is of great consequence in understanding why organic matter is preserved in some lacustrine environments and not in others.

## IMPORTANCE OF LAKE STUDIES TO PETROLEUM GEOLOGY

From the perspective of petroleum geology, one of the major tasks challenging earth scientists is to gain a more complete understanding of the mechanisms and conditions which promote the production and preservation of organic matter in lacustrine (and marine) environments. As detailed in Kelts (1988), in order to better understand the source rock potential of ancient lake sediments, details of the car-

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bon cycle in modern "end-member" lakes must be studied. In particular, data on organic matter production, sedimentation, and preservation in saline lakes are sparse (Warren, 1986). The effects of changes in circulation, climate, and salinity on organic matter production/sedimentation are almost totally unquantified. Similarly, the bottom water conditions that offer the best potential for significant preservation are only known qualitatively for a very limited range of depositional settings.

Much has been written on the relationship between closed basin lake sedimentation and petroleum production and preservation (Kirkland and Evans, 1981; Warren, 1986; Kelts, 1988). Probably the best studied ancient deposit is the Eocene Green River Formation of the western United States (Eugster and Hardie, 1975; Desborough, 1978; Tissot and others, 1978; Surdam and Stanley, 1979; Johnson, 1981; Boyer, 1982; Smoot, 1983; Sullivan, 1985). There is considerable debate and disagreement over the exact nature of the depositional setting of the oil shale member, but it has been concluded that it represents either a playa lake complex or a chemically stratified lake setting, or both. Although Sullivan (1985) has suggested that it is unlikely that one modern lake can serve as an analog for ancient Lake Gosiute, Freeflight Lake has components of both these two settings. Therefore, the behavior of carbon within the Freeflight Lake system should provide some analogies with ancient saline systems that have developed petroleum potential.

In addition, Freeflight Lake is a true "end-member" lake in that it is an alkaline lake whose major anion is sulfate, not  $\text{HCO}_3^- + \text{CO}_3^{2-}$ . Prevailing theories hold that large amounts of organic matter necessary to generate oil cannot be preserved in environments that are sulfate-rich (Kelts, 1988). In such environments sulfate-reducing bacteria can rapidly oxidize organic matter to  $\text{H}_2\text{S}$  and  $\text{HCO}_3^-$ , leading to the authigenic production of  $\text{CaCO}_3$  with light  $\delta^{13}\text{C}$  values. This process has been observed in marine marginal, hypersaline lakes such as Solar Lake in the Sinai (Aharon and others, 1977; Lyons and others, 1984a). Therefore an important question is, can organic matter survive early diagenesis in sulfate-rich lake systems? Freeflight Lake provides an excellent opportunity to test this hypothesis.

We have tested the hypothesis relating sulfate concentration to organic matter preservation by relating water anionic composition to organic carbon preservation. This is determined via *in-situ* sulfate reduction by radiolabel techniques on sediments from Freeflight Lake, a  $\text{Na}^+\text{-Mg}^{2+}\text{-SO}_4^{2-}$  saline lake in southwestern Saskatchewan. These data are then compared to sulfate reduction rate measurements from other hypersaline sedimentary environments, where  $\text{SO}_4^{2-}$  is present but are not the major anionic species. Results have shown that in these environments sulfate reduction rates can be very rapid (Jorgensen and Cohen, 1977; Lyons and others, 1984a, b).

#### FREEFLIGHT LAKE

Freeflight Lake is located about 350-km east of Regina, Saskatchewan in western Canada (Fig. 1). The lake occupies a narrow closed basin that was created by glacial meltwater runoff ~15 ka BP. It has a mean depth of approxi-

mately 20 m and a maximum depth of 25 m, which is unusually deep compared to other prairie lakes. The lake has a thin layer (~6 m) of relatively dilute brine (110‰ TDS), overlying a much more saline (180‰) water column (Last and Slezak, 1987). The upper dilute layer undergoes seasonal variation in salinity due to runoff and evaporation, but the upper and lower brines never mix. Both water masses are dominated by  $\text{Na}^+$  and  $\text{SO}_4^{2-}$ . However, the monimolimnion has a higher proportion of  $\text{HCO}_3^-$  relative to the surface waters (Table 1).

Unfortunately, the hydrology of Freeflight Lake is still largely unknown. The area receives about 28 cm of precipitation per year, but up to 4–5 times this amount can be lost through evaporation. The lake also receives water from diffuse runoff and small ephemeral streams. The largest components of the hydrologic budget appear to be groundwater input and loss by evaporation (Slezak, 1989). There are numerous subaerial springs and areas of diffuse groundwater discharge located within the basin. It is also likely that subaqueous spring discharge occurs. The basin is topographically closed. During the ice-free season, the lake shows an unusual temperature profile with a temperature minimum of 1 to 2°C occurring at the chemocline. This is likely due to the influx of cold, but relatively fresh water into the lake from marginal and subaqueous springs. Another explanation may be a temperature decrease caused by mirabilite dissolution, a strongly endothermic reaction (Last, 1993a).

Several major sedimentary environments exist in the Freeflight Basin (Last, 1993a). The samples discussed in this paper were obtained in the "algal mat-carbonate platform" facies. The sediments of this facies range from well laminated carbonate and quartz sands to organic-rich carbonate mud. Much of the lake bottom near the shore is dominated by microbial mats and stratiform stromatolites. Further offshore, at the break in slope, this carbonate bank grades into a debris slope and fan facies. The sediment here consists of poorly sorted and commonly organic-rich sand and gravel. Finally, in water depths greater than about 8 m, the bottom sediments consist of coarsely crystalline soluble salts (mainly mirabilite, epsomite, and bloedite) mixed with fine grained organics, pyrite, and clays.

The algal flat facies, together with the slope and debris apron facies, is spatially the least extensive of the six sedimentary facies in the basin. The algal flats extend basinward from approximately the low water level to water depths of about 2.5 to 3 m. The sediments of the algal flats are mainly biolaminated clays and silty to sandy clays. The sediments have a high organic matter content (20–70 percent) and normally a high moisture content (greater than 75 percent). The sediment is composed of subequal proportions of organic matter, fine grained siliciclastics, and endogenic/authigenic carbonate minerals.

The surface of the algal flat facies is mostly covered with a thin leathery mat. Although the precise species composition of this mat has not yet been determined, it is assumed that cyanobacteria are the dominant organisms responsible for its generation and development. Even though the algal flat facies is everywhere within the reach of wind-driven waves, the mat is very tough and resistant to water turbu-

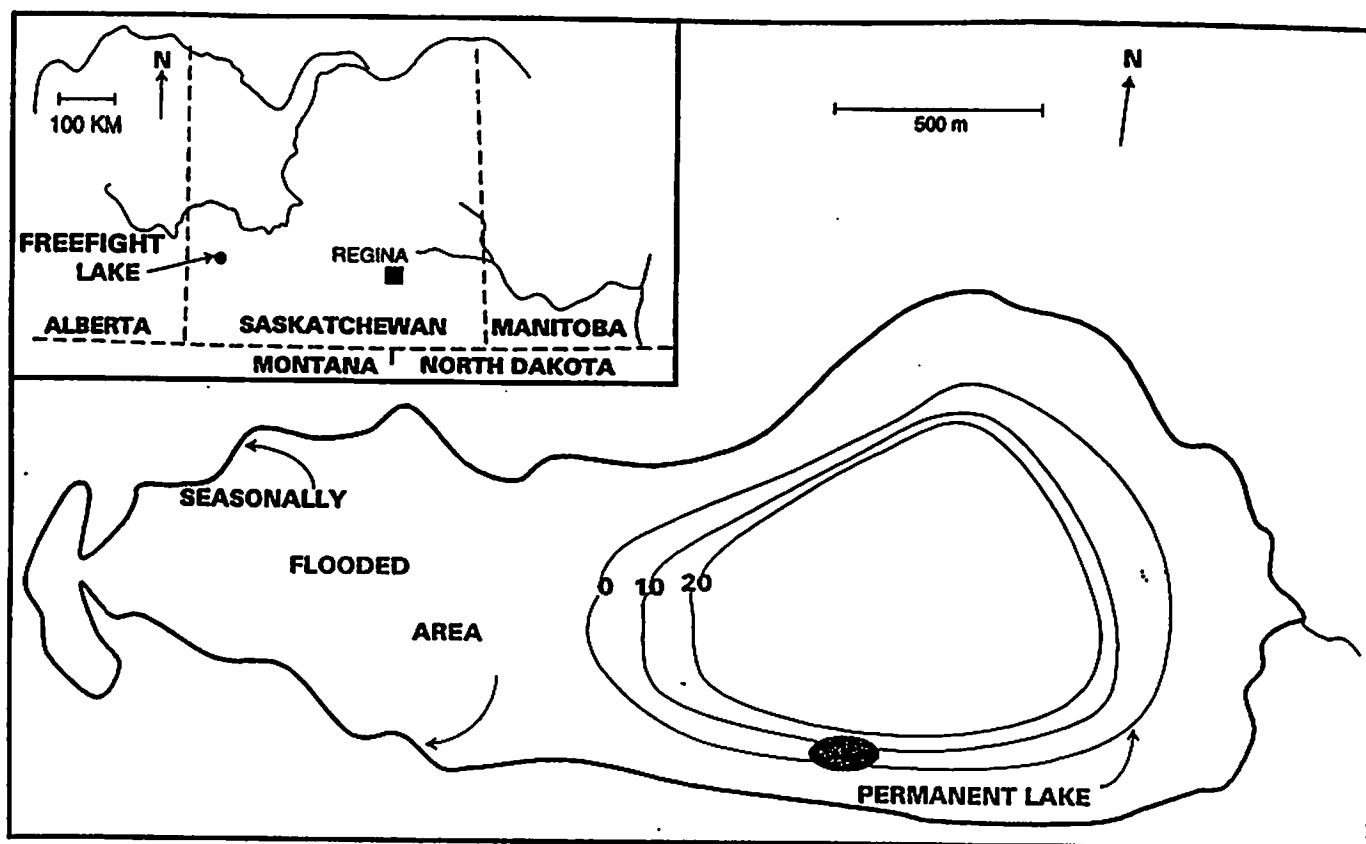


FIG. 1.—Generalized bathymetric map of Freefight Lake. Shaded area indicates the location of the reduction rate studies. Inset map shows the location of Freefight Lake in the northern Great Plains of western Canada.

TABLE 1.—MORPHOLOGICAL AND CHEMICAL DATA FOR FREEFIGHT LAKE (FROM LAST, 1993a).

Surface Area:		
at mean water level		1.02 km <sup>2</sup>
at seasonally flooded level		2.94 km <sup>2</sup>
Depth:		
Mean	19.52 m	
Maximum	24.96 m	
Average Brine Chemistry (mol/l):		
	Micromol/l	Millimol/l
Ca <sup>2+</sup>	0.004	0.011
Mg <sup>2+</sup>	0.444	0.498
Na <sup>+</sup>	0.709	1.31
K <sup>+</sup>	0.059	0.065
Cl <sup>-</sup>	0.194	0.199
HCO <sub>3</sub> <sup>-</sup>	0.051	0.265
SO <sub>4</sub> <sup>2-</sup>	0.666	0.957
TDS (ppt)	111.7	179.1
pH	9.2–8.0	7.4

lence and wave erosion. Only where gas vacuoles have created an undulose surface morphology is the surface mat locally broken and interrupted. The algal mat is also characterized by abundant rooted vegetation throughout. These macrophytes develop a mucilaginous sheath during their growth which further acts to trap and bind fine grained clastic particles.

Measurements were made at four locations in the algal mat-carbonate platform facies (Fig. 1). Sites A, B and C

represent a series of samples running perpendicular to the lake margin with site C at 3-m offshore, site B at 1.5-m offshore and site A at ~0.1-m offshore. Site X was also 1.5-m offshore but ~40-m east of site B. All samples were taken in water depths of less than 1 meter. Radiocarbon based sedimentation rates have been determined from cores from the area of the lake where our short cores and pore water samples were taken. The long term sedimentation rate in the algal mat-carbonate platform facies, based on these <sup>14</sup>C dates, is 0.3 mm yr<sup>-1</sup> (Last, 1993a). This relatively low sedimentation rate contrasts sharply with much higher sedimentation rates (up to ~20 mm yr<sup>-1</sup>) in the deep basin area of the lake (Last, 1993b).

#### METHODS

Sediment cores were obtained by hand using polycarbonate core tubes similar to the techniques described in Lyons and others (1984a). The cores were immediately sealed and returned to our laboratory facilities (approximately one hour's drive from the lake). The cores were extruded into an N<sub>2</sub>-filled glove bag and sectioned for sulfate reduction measurements. The rates were determined radiometrically using <sup>35</sup>SO<sub>4</sub><sup>2-</sup> by injecting the label into sediment-filled syringes and incubating the syringes in the dark, as outlined by Hines and others (1989, 1992). The reaction was stopped by freezing. Both acid volatile and chromium reducible sulfide

were determined (Hines and others, 1989). Pore water samples were obtained using *in-situ* "sipper" samples (Hines and others, 1989, 1992). Sippers are lysimeters Teflon with a porous Teflon collar that allows movement of water from the sediment into the sipper, upon the application of a vacuum. Sipper samples were obtained within 10 cm of the cores used for sulfate reduction measurements. Only a small portion of the pore water data is presented here; the full data set is given on a detailed manuscript describing mineral equilibrium modeling of the pore water data in preparation. Titration alkalinity ( $A_T$ ) was measured immediately after pore water collection using a titration technique with a Gran plot.  $Ca^{2+}$  was determined on acidified samples using flame atomic absorption after dilution with a matrix modifier (Spader and Lyons, 1985).  $Cl^-$  and  $SO_4^{2-}$  were measured after dilution with distilled-deionized water by ion chromatography.  $\Sigma H_2S$  was determined colorimetrically using the methylene blue method (Hines and others, 1989).

#### RESULTS AND DISCUSSION

Sulfate reduction rates (SRR) are plotted versus depth in Figure 2 while the acid volatile sulfide (AVS) and chromium reducible sulfide (CRS) are reported in Table 2.  $Ca^{2+}:Cl^-$ ,  $A_T:Cl^-$  ratios and  $\Sigma H_2S$  pore water concentrations are shown in Table 3.

#### Sulfate Reduction Rates

The sulfate reduction rates in the algal mat-carbonate platform facies of Freeflight Lake are very low (Fig. 2), especially considering that the organic matter concentrations in these sediments range from 20–70 percent. It is well established that organic matter is the limiting factor to

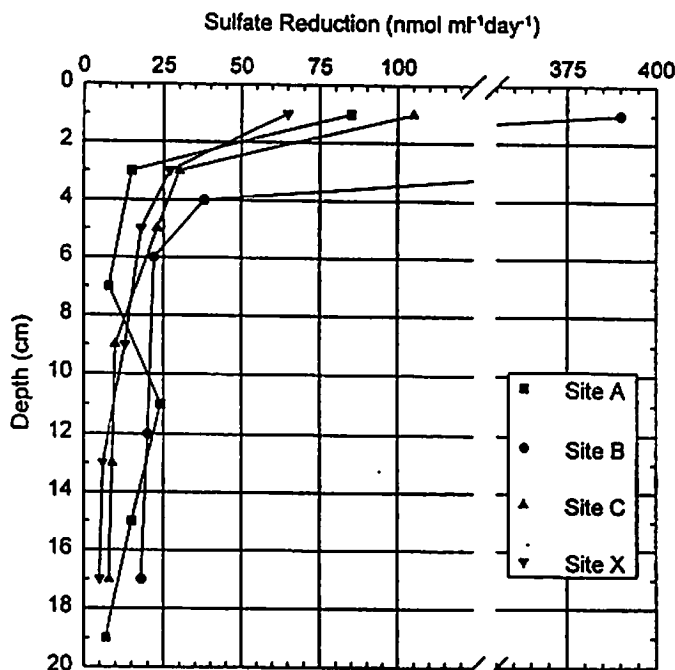


FIG. 2.—Sulfate reduction rates (SRR) for the four Freeflight Lake sites.

TABLE 2.—ACID VOLATILE SULFIDE (AVS) AND CHROMIUM REDUCIBLE SULFIDE (CRS) IN FREEFLIGHT LAKE SEDIMENTS

Sample	Depth cm	AVS $\mu\text{mol ml}^{-1}$	CRS $\mu\text{mol ml}^{-1}$
C	0–2	11 $\pm$ 2	0.1 $\pm$ 0.1
	2–4	21 $\pm$ 10	0.3 $\pm$ 0.1
	4–6	59 $\pm$ 1	3 $\pm$ 3
	8–10	18 $\pm$ 5	3 $\pm$ 3
	12–14	23 $\pm$ 2	2 $\pm$ 2
	16–18	25 $\pm$ 2	2 $\pm$ 2
B	0–2	10 $\pm$ 0	1.8 $\pm$ 0.3
	2–4	13 $\pm$ 0	2 $\pm$ 1
	4–6	19 $\pm$ 6	0.9 $\pm$ 0.1
	8–10	34 $\pm$ 18	4*
	12–14	28 $\pm$ 2	4*
	16–18	17 $\pm$ 3	3*
A	0–2	48 $\pm$ 34	2.1 $\pm$ 0.5
	2–4	24 $\pm$ 12	3.2 $\pm$ 0.3
	6–8	29 $\pm$ 6	3.1 $\pm$ 0.8
	10–12	40 $\pm$ 10	ND
	14–16	18 $\pm$ 2	ND
	18–20	18*	ND
X	0–2	77 $\pm$ 17	4 $\pm$ 1
	2–4	131 $\pm$ 9	6 $\pm$ 0
	4–6	99 $\pm$ 74	6 $\pm$ 1
	8–10	241*	ND
	12–14	183*	ND
	16–18	207*	ND

(Mean of two measurements except where noted.)

\* Only one measurement

ND = no data

TABLE 3.—PORE WATER DATA FROM FREEFLIGHT LAKE SEDIMENTS

Sample	Depth cm	$Ca:Cl$ mM	$A_T:Cl$ meqM	$\Sigma H_2S$ mM
C	1–3	0.012	0.35	0
	3–8	0.011	0.30	0
	8–13	0.016	0.36	0.34
	13–18	0.014	0.42	1.88
	18–23	0.015	0.50	3.44
B	1–6	0.015	0.35	0.86
	6–11	ND	ND	0
	11–16	0.018	0.49	2.96
	16–21	ND	ND	2.83
A	1–6	0.006	0.31	0.58
	6–11	0.016	0.36	1.37
	11–16	0.016	0.36	1.46
	16–21	0.014	0.31	3.14
X	1–6	0.014	0.31	2.58
	6–11	0.014	0.37	2.62
	11–16	0.017	ND	2.68
	16–21	0.016	0.41	3.08
	21–26	0.009	0.39	4.07
Overlying Water		0.21	0.26	0

sulfate reduction where sulfate is present (Westrich and Berner, 1984). High sulfate concentrations are present in all our samples (Table 3). Our measured rates are much lower than those observed in similar geologic settings dominated by seawater compositions where  $Cl^- \rightarrow SO_4^{2-}$ , i.e., Bonaire, N.A. and Solar Lake, Sinai (Table 4). For example, in the Bonaire algal mats, the mean sulfate reduction rate is ten times greater while  $SO_4^{2-}$  concentration is 10 to 20 times less (Table 4). In fact, although the SRRs

TABLE 4.—COMPARISON OF THREE SALT LAKE ALGAL MAT SEDIMENTS

Site	SO <sub>4</sub> <sup>2-</sup> Reduction (mmol ml <sup>-1</sup> d <sup>-1</sup> )	TDS (ppm)	SO <sub>4</sub> <sup>2-</sup> (mmol)	Organic Matter (mg ml <sup>-1</sup> )	Reduced S (μmol ml <sup>-1</sup> )
Freeflight	100 (500)	125	700	140	27
Solar Lake	4000 (6700)	180	130	70	22
Bonaire	1000 (6400)	40	30	ND	ND

in Freeflight Lake are higher than those found in continental shelf sediments (Hines and others, 1991), they are lower than those observed in shallow water marine and estuarine sediments where the organic matter concentrations are an order of magnitude lower (Hines and Jones, 1985; Lyons and others, 1984a).

Although the SRRs are low at Freeflight Lake, sulfate reduction does have a geochemical impact on these sediments. Authigenic sulfide minerals are forming (Table 2) from dissolved sulfide produced through sulfate reduction (Table 3). We have measured dissolved Fe<sup>2+</sup> in the pore waters of these sediments and the values are all below 5 μM suggesting that the build up of high concentrations of ΣH<sub>2</sub>S in these pore waters even at low SRRs is due to lack of iron in the system.

The decrease with depth of the SRR in the Freeflight Lake sediments, similar to those observed in nearshore marine environments, is due to the bacterial utilization of the most metabolizable organic carbon (Berner, 1980). Therefore, the fastest rates are closest to the sediment-water interface where the organic matter is being introduced into the sediments. Unlike observations both at Bonaire (Lyons and others, 1984a) and Solar Lake (Jørgensen and Cohen, 1977), however, the organic matter concentrations in the sediments at Freeflight Lake do not decrease as sulfate reduction proceeds. Last (1990) and Slezak (1989) have shown that in the algal mat—carbonate platform area, very near to our coring sites, the organic matter concentration fluctuates slightly but does not decrease with depth. In two cores from this region, the surface organic matter values range from 24–30 percent, but values between 90- and 100-cm depth are essentially the same (i.e., 24–30 percent). Therefore, although sulfate reduction is occurring in these sediments, large amounts of organic carbon are being preserved. This is because sulfate reduction rates are too low to convert organic carbon effectively into inorganic carbon. This is in contrast to both Bonaire and Solar Lake. In Solar Lake, the carbon fixed by the algal mat community as organic matter is almost totally converted to inorganic carbon by the depth of 70 cm (Jørgensen and Cohen, 1977; Aharon and others, 1977; Lyons and others, 1984b). At Bonaire, this conversion happens in the uppermost centimeters. Our work has indicated that 83 percent of the photosynthetic carbon that is fixed in the mat is decomposed via sulfate reduction in the top 2.5 cm of the sediment.

#### Sedimentary Sulfur

In all cases observed (Table 2), the AVSs (monosulfides) are much greater than the CRS (pyrite) concentrations in these sediments. This is not what is observed in nearshore

marine sediments where pyrite becomes the dominant form of sedimentary sulfide close to the sediment-water interface (Berner, 1970; Sweeney and Kaplan, 1973). Although more recent work suggests a higher percentage of AVS to total reduced S in anoxic marine sediments (Morse and Cornwell, 1987), nowhere has such a high percentage of AVS been observed in marine systems. This is particularly true at the lower sedimentation rates observed at Freeflight Lake (Goldhaber and Kaplan, 1975). In salt marshes, on the other hand, the distribution of the reduced sulfur pool can vary annually with depth and season (Hines and others, 1989). High AVS:CRS ratios were observed in a number of these samples especially in the summer when SRRs were highest. Yet even when compared to salt marsh sediments, the Freeflight Lake sediments show much higher percentages of AVS to total S than many salt marsh sediments. For example, Lord and Church (1983) report this ratio to be ~50 percent whereas at Freeflight Lake the ratios at locations C and B at 18 cm are 92 and 85 percent, respectively. At present we cannot explain why these systems seem similar.

#### C:S Ratios

The C:S ratios in sediments and sedimentary rocks have been utilized with great success to determine the environment of deposition (Berner and Raiswell, 1983, 1984). The basic premise behind this usage is that sediments containing high C:S are derived from freshwater (i.e., low sulfate concentrations), while sediments deposited in "euxinic" conditions (i.e., highly anoxic bottom waters) have very low C:S ratios. Little data are available from hypersaline sedimentary environments.

Sedimentary C:S ratios can be calculated from our data knowing the porosity of the sediments and assuming that ~40 percent of the organic matter present is organic carbon (Aller and Yingst, 1980). Using data from all locations at 18 cm, the C:S ratios (by mass) range from 16 to 120. Using standard interpretations of their C:S ratios, these sediments would be classified as freshwater lacustrine (Berner and Raiswell, 1983; Berner, 1985), even though high concentrations of dissolved sulfate are present in the environment.

The C:S ratios at Freeflight Lake resemble those observed recently for organic-rich Cretaceous sediments in the Negev region of southern Israel (Minster and others, 1992). These Negev sediments contain oil shales. The high ΣH<sub>2</sub>S pore water concentrations (Table 3), the low dissolved Fe<sup>2+</sup> concentrations in the pore waters (<5 μM) and the lack of pyrite or CRS indicate that the mat environment at Freeflight Lake is extremely iron deficient. The lack of Fe<sup>2+</sup> prevents of pyritization in anoxic sediments (Calvert and Karlin, 1991; Minster and others, 1992). This also appears to be the case in the Freeflight Lake sediments as the other possible explanation, that is, sulfate limitation (Bein and others, 1990), is certainly not the case (Table 3).

#### Pore Water Data

The pore water data set from the algal mat sediments is shown in Table 3 and the SO<sub>4</sub><sup>2-</sup>:Cl ratios are plotted vs. depth in Figure 3. Three general statements can be made

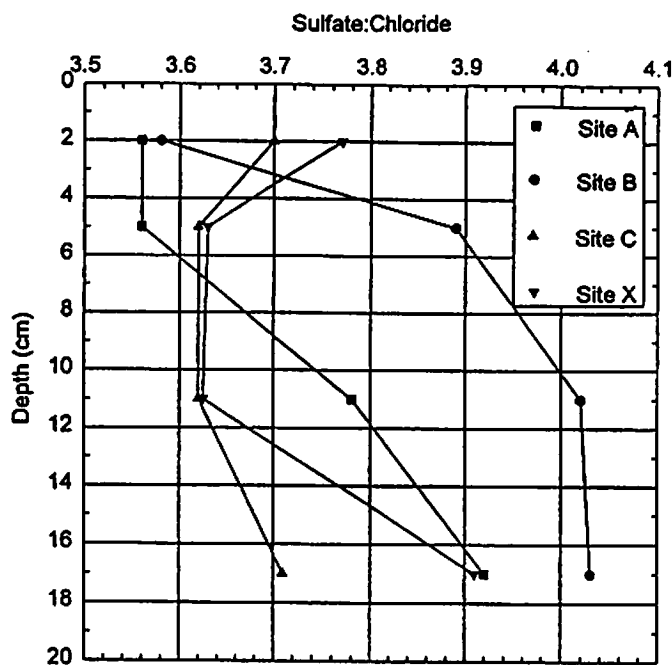


FIG. 3.—Sulfate:chloride porewater ratios for the four Freeflight Lake sites.

regarding these data: (i) sulfate:chloride ratios are greater than the overlying water value, (ii)  $A_T:Cl$  are greater than the overlying water value, and (iii) the  $Ca:Cl$  ratios are less than the overlying water value (Table 3).

The increase in the  $SO_4:Cl$  ratio in the pore waters is undoubtedly due to the dissolution of authigenic and endogenic  $SO_4^{2-}$  minerals that have been deposited within the mat. These minerals include mainly gypsum, bloedite, epsomite, and mirabilite (Last, 1993a). We have observed a similar phenomenon in evaporitic-mat sediments in Bonaire (Spader and Lyons, 1985) where gypsum dissolution dominates  $SO_4^{2-}$  input to the pore fluids. Similar observations have been made in Solar Lake. By observing the pore water profile alone, one would conclude sulfate reduction is not occurring because in many cases  $SO_4^{2-}$  increases with depth. On the other hand, the increase in  $A_T$  indicates that sulfate reduction is occurring because  $HCO_3^-$  is a major product of sulfate reduction (Berner, 1980). In addition, the decrease in  $Ca^{2+}$  relative to  $Cl^-$  suggests that authigenic  $CaCO_3$  is precipitating in the mat. This is similar to that documented in both Solar Lake (Aharon and others, 1977; Lyons and others, 1984b) and Bonaire (Spader and Lyons, 1985) mat sediments. Analyses of the Freeflight Lake sediments indicate that the following carbonate minerals are present: aragonite, magnesian calcite, normal (low-Mg) calcite, stoichiometric and well-ordered dolomite, Ca-rich "protodolomite" (poorly ordered, nonstoichiometric dolomite), magnesite, hydromagnesite, and huntite (Last, 1993a). Stable carbon isotopic measurements of the aragonite in the upper meter of sediment in the algal flat area indicate a gradual decrease (i.e., increase in  $\delta^{13}C$ ) from +3.2‰ to -0.7‰ with depth in the core (Last, 1990). These data support the notion that *in-situ* precipitation of  $CaCO_3$  is oc-

curing in this environment. The increase in  $CaCO_3$  enriched in  $^{13}C$  with depth suggests that this  $CO_2$  is derived from the decomposition of organic matter ( $\delta^{13}C = -18.6$  to  $-26.3$ ‰) within the sediment.

#### Organic Carbon Preservation

The most surprising observation of this study is the relatively low SRR seen at Freeflight Lake. Although the dissolved sulfate concentrations are high and the sedimentation rate is low, a large amount of organic carbon is buried rather than oxidized by sulfate reduction or any other microbial pathway. Compared to other hypersaline algal mat environments like Solar Lake and Bonaire (Table 4) this is an unusual finding. In these latter two settings, organic matter is rapidly converted to inorganic carbon via sulfate reduction.

Of course, the obvious question is why Freeflight Lake's organic matter is preserved even while concentrations of high dissolved sulfate exists? There is no doubt that in coastal marine environments, sulfate reduction is the major process in organic matter mineralization (Jørgensen, 1982). This prompted the notion that sulfate-rich waters are not conducive to organic matter preservation in lacustrine sediments (Kelts, 1988). It is obvious from our work, that the preservation of organic matter in lacustrine environments is controlled, in part, by factors other than the anionic composition of water and pore water. Recent work on the origin of marine, organic-rich rocks has suggested that high primary production rather than anoxia is the most important control on the preservation of organic matter (Pederson and Calvert, 1990). Using our integrated SRR data and assuming that for every mole of sulfate reduced, two moles of organic carbon are consumed, we have calculated the rate of OC consumption via SR at our four sites at Freeflight Lake (Table 5). The organic carbon burial rate at Freeflight Lake is  $\sim 500 \text{ nmol cm}^{-2} \text{ d}^{-1}$ . Therefore, the gross OC primary production rate in the algal mat in this location at Freeflight Lake varies from  $\sim 3000 \text{ nmol cm}^{-2} \text{ d}^{-1}$  to  $1160 \text{ nmol cm}^{-2} \text{ d}^{-1}$ . These should be considered minima as loss by other modes of decomposition have not been accounted for. The photosynthetic rate at Solar Lake (assuming a 12 hour period of light and the hourly rates of Cohen and others, 1977) is  $50 \mu\text{mol cm}^{-2} \text{ d}^{-1}$ . Therefore, the photosynthetic rate at Solar Lake is about sixteen times greater than at Freeflight Lake. This value must be considered a minimum. These calculations suggest that rates of primary production are not the only factors controlling preservation of organic carbon in Freeflight and Solar Lakes. The rate of primary production in Solar Lake is 16 times greater than in Freeflight Lake but far more organic matter is preserved in Freeflight Lake sediments.

TABLE 5.—ESTIMATED ORGANIC CARBON CONSUMPTION RATE AT FREEFLIGHT LAKE

Site	Rate ( $\text{nmol cm}^{-2} \text{ d}^{-1}$ )
A	960
B	2514
C	1070
X	660

Degens and Paluska (1979) suggested that organic matter is preserved and petroleum formed in hypersaline environments due to a "pickling" effect. Although they offer no detailed information on how this should occur, it is an intriguing notion. Obviously it does not occur everywhere as organic matter is rapidly decomposed in some hypersaline, anoxic settings such as Solar Lake. Perhaps higher pH in the mixolimnion of the Freeflight Lake waters aids in organic matter preservation. However, the mystery of why organic matter accumulates here and not in similar marine hypersaline settings remains. There is no doubt that these high accumulations of organic matter at Freeflight Lake could make it a potential oil-shale environment.

## CONCLUSIONS

Our work indicates that sulfate reduction rates in salt lakes are not directly related to the anionic composition of the lake water. As in marine sediments, the rate of decomposition and, hence preservation, of organic matter in salt lake sediments is related to the quality and quantity of the organic matter being buried as well as the sedimentation rate.

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