

## Sr/Ca and Mg/Ca ratios in polygenetic carbonate allochems from a Michigan marl lake

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**Abstract**—Rapid accumulation of  $\text{CaCO}_3$  is occurring in Littlefield Lake, a marl lake located in central Michigan. The sediment, which is 95%  $\text{CaCO}_3$ , primarily consists of eight different genetic groups of carbonate allochems. These include calcite muds, sands, algal oncoids and *Chara* encrustations, as well as the dominant aragonitic gastropods *Valvata tricarinata*, *Gyraulus deflectus* and *Ammicola integra*, and the dominant aragonitic pelecypod *Sphaerium partumeium*. Samples of each of these groups were analyzed for Ca, Sr and Mg. Molar Mg/Ca ratios are primarily controlled by allochem mineralogy, with calcitic forms having Mg/Ca ratios 5–10 times larger than aragonitic (shelled) forms. The Sr/Ca ratios are primarily controlled by biochemical fractionation, and are significantly lower than Sr/Ca ratios of inorganically precipitated aragonite from other settings. Partition coefficients were determined for both Sr and Mg for each carbonate allochem group and, based on comparisons with results reported by other workers, the partition coefficients determined here are generally considered 'typical' or representative values for biogeneous freshwater carbonates. An analysis of variance of the data indicates that most genera and species of carbonate-secreting organisms in marl lakes have highly characteristic Sr/Ca and Mg/Ca ratios. These ratios can potentially serve as geochemical tracers in future investigations of lacustrine carbonate diagenesis. Both Sr and Mg are influenced by grain size and/or surface area, probably due to the presence of these elements in non-lattice-held (exchangeable) positions.

### INTRODUCTION

MARL LAKES are hardwater lakes that precipitate calcium carbonate. They occur extensively throughout temperate regions of the world and, within the continental U.S., are found in many of the northern and midwestern states, particularly Indiana, Michigan, Minnesota, and New York. Marl lake sediments are typically 90–95% carbonate, primarily precipitated through biochemical processes, although inorganic precipitation has been reported for some systems (TERLECKY, 1974). The important biogenous components in marl lakes include cyanophytic oncoids, encrustations on *Chara* (a submergent macrophyte common in most marl lakes) and shell material from gastropods and pelecypods (cf. MÜLLER, 1968; ODUM, 1957).

Carbonate sediments in marl lakes are the modern analogs to many freshwater limestone deposits in the stratigraphic record and, as such, are potentially significant in investigations aimed at reconstructing paleoenvironmental conditions. A critical aspect of this type of investigation is that the authors must either: (1) assume or demonstrate that the carbonate material has retained its original composition; or, alternatively (2) ascertain the degree of compositional

change due to diagenesis. Inasmuch as the first approach above can be considered a 'no diagenesis' case, the second approach represents the more general situation. Thus the subject of freshwater carbonate diagenesis has received increased attention in recent years (cf. MÜLLER *et al.*, 1972; STOFFERS and HECKY, 1978; MÜLLER and WAGNER, 1978). The fact remains, however, that there have been few comprehensive analyses of modern marl lake carbonates (cf. BRUNSKILL, 1968; TERLECKY, 1969, 1974). In contrast, investigations of modern marine carbonates have provided a much broader data base for use in diagenetic interpretations. A particularly fruitful approach in this regard has involved the examination of elemental partitioning patterns. For example, based on a knowledge of the composition of modern marine carbonates, investigations have shown that variations in the amounts of Sr and Mg (and other elements) present in calcite and aragonite lattices can serve as key indicators of different depositional environments and/or the extent of subsequent diagenetic alteration (cf. CURTIS and KRINSLEY, 1965; DODD, 1965; SCHROEDER, 1969; WALLS *et al.*, 1977). A more detailed knowledge of elemental partitioning patterns in modern freshwater carbonates presumably would make such an approach equally viable for this type of deposit.

Few data exist on elemental partitioning patterns in

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freshwater carbonates. ODUM (1957) has reported mean Sr/Ca ratios for general groups of biogenous carbonates (calcite encrustations on algae, aragonite gastropods and pelecypods) for "freshwaters of humid climates" and has shown that these values are considerably lower than the corresponding ratios for biogenous marine carbonates. The most comprehensive set of Sr/Ca measurements (and some Mg/Ca data) for freshwater carbonates to date were obtained in an analysis of various carbonate allochems from Lake Constance in Western Europe by MÜLLER (1968). However, as MÜLLER (1968, 1978) has pointed out, these data probably do not reflect 'normal' freshwater environments because of exceptionally high Sr/Ca ratios in carbonate skeletal material due to anomalously high Sr concentrations in Lake Constance waters. MÜLLER (1968) also suggested that certain Sr/Ca ratios are characteristic of certain taxonomic groups, although he did not attempt to verify this by statistical analysis.

The specific objectives of this study are: (i) to determine values for Sr/Ca and Mg/Ca ratios in freshwater carbonate allochems from a 'typical' marl lake, and (ii) to determine if either or both of these ratios can serve as a distinguishing characteristic for each of the specific types of carbonates allochems which commonly form marl sediments.

## METHODS

Littlefield Lake, a typical marl lake located in Isabella County in central Michigan, was chosen as the study area for this investigation (Fig.1). The lake is 2.5 km long and 0.5 km wide. A wide marl bench surrounds the entire shoreline, and three well-developed lakemounds have built to the lake surface (MURPHY and WILKINSON, 1980).

Biogenous forms of calcium carbonate were isolated from Littlefield Lake sediments by carefully sieving a series of grab samples collected from the marl bench platform along the south shore of the lake. The following biogenous forms were identified: calcite algal oncoids (19 samples); calcite *Chara* encrustations (20 samples); the three aragonitic gastropods *Amnicola integra* (14 samples), *Valvata tricarinata* (8 samples) and (*Gyraulus deflectus* (11 samples); and the aragonitic pelecypod *Sphaerium partumeium* (4 samples). In addition, 20 samples of calcite mud and 20 samples of calcite sand were selected for analysis.

Each sample was dried for 10 hr at 110°C and ground to less than 2  $\mu$ m. All samples of shell material were sonically cleaned before grinding in order to remove any inclusive non-molluscan carbonate and residual organic material. Aliquots of each sample were then dissolved in 1 M acetic acid. This acid digestion procedure dissolves carbonates and associated metals while leaving clay lattices and other minerals intact (SATYABRATA *et al.*, 1957). The digestion solutions were agitated for 8 hr to insure complete carbonate dissolution, filtered through 0.45  $\mu$ m filters, and analyzed by atomic absorption spectroscopy (AAS) for Sr, Mg and Ca. The concentrations for these same elements were determined by AAS on 30 samples of Littlefield Lake water collected between April and November of 1979.

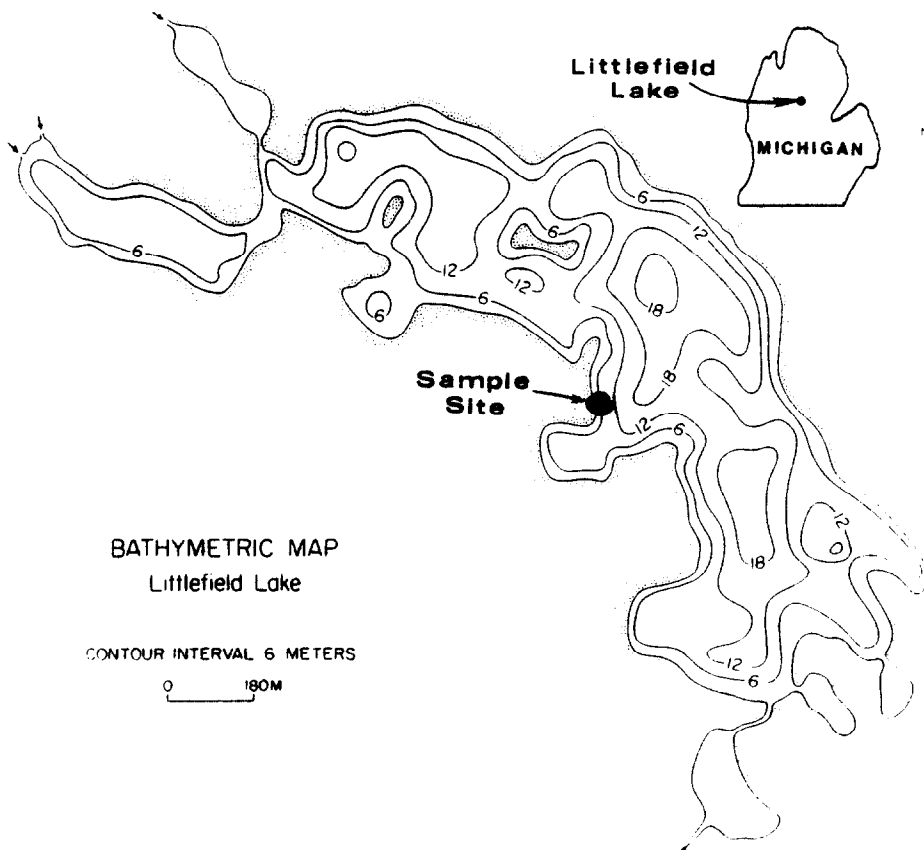


Fig. 1. Bathymetric map of Littlefield Lake, Isabella County, Michigan.

Finally, the mineralogy of the various carbonate groups was determined by X-ray diffraction analysis. Statistical analysis of the geochemical data was accomplished using MIDAS, a package of multivariant statistical programs available at The University of Michigan.

## RESULTS AND DISCUSSION

The behaviors of trace elements of double positive charge which substitute for calcium in calcium carbonate lattices are described by partition theory (cf. PINGATORE, 1978). The partition coefficient for a particular trace element,  $K_{TE}$ , is defined by the relationship (cf. MACINTYRE, 1963)

$$K_{TE} = \frac{(M_{TE}/M_{Ca})_s}{(M_{TE}/M_{Ca})_l}$$

where  $M_{TE}$  = moles of trace element,  $M_{Ca}$  = moles of calcium, and s and l = subscripts denoting the solid and liquid phases, respectively.

Partition coefficients of sedimentary carbonates are primarily controlled by four factors (AMIEL *et al.*, 1973): (a) temperature of formation; (b) water chemistry (i.e. concentration of trace elements and calcium in the precipitating solution); (c) the mineralogy of the precipitate, and (d) biochemical fractionation (physiology of the organism). The Sr/Ca and Mg/Ca molar ratios determined in this study and, consequently, the calculated values for  $K_{Sr}$  and  $K_{Mg}$ , show considerable variation between the different genetic groups (Table 1). Inasmuch as the different groups of carbonate from Littlefield Lake have formed under essentially the same environmental conditions of temperature and water chemistry, observed differences between groups can be attributed to their mineralogy and/or to biochemical fractionation. It is probably true that the different taxonomic groups have not formed under exactly the same environmental conditions because they may grow at slightly different rates according to the specific biological response to temperature, sunlight, etc. (S. V. SMITH, personal communication). Subtle variations due to these factors cannot be detected when analyzing field samples.

BUCHARDT and FRITZ (1978) have recently investigated Sr uptake in the freshwater gastropod *Limnaea stagnalis* in carefully controlled laboratory tank experiments. They concluded that water chemistry (which was measured in the present study) had an important influence on Sr uptake, while neither variations in temperature (between 13 and 28°C) nor growth rate had any measurable influence on Sr partitioning in shell aragonite.

The effect of mineralogy on the distribution of trace elements in carbonates is well documented (cf. MACINTYRE, 1963; FYFE and BISCHOFF, 1965). The calcite lattice tends to accept ions of a smaller radius than Ca, such as Mg, Fe and Mn, while excluding larger ions. The aragonite lattice, on the other hand, will tend to accept ions of larger radius; such as Sr, Ba and Pb; and may even be stabilized by such substitutions (FYFE and BISCHOFF, 1965). This mineralogical effect is evident in our data, particularly with respect to Mg (Table 1). The Mg/Ca molar ratios and  $K_{Mg}$  values of calcite groups are 5–10 times higher than the corresponding values for the aragonite groups. In contrast, our Sr data do not reveal a sharp distinction between the various groups on the basis of mineralogy.

Partition coefficients for Sr are highly dependent upon whether precipitation occurs via an inorganic or organic mechanism (BATHURST, 1976). For example, at a constant temperature of 25°C, HOLLAND *et al.* (1964) have reported  $K_{Sr}$  values of  $0.14 \pm 0.02$  and  $1.0 \pm 0.1$  for inorganically precipitated calcite and aragonite, respectively. However,  $K_{Sr}$  values for biogenically precipitated carbonates from both marine and freshwater environments are significantly lower than the corresponding values for inorganically precipitated forms (MÜLLER, 1968). This difference has been attributed to biochemical fractionation (MÜLLER, 1968; MILLIMAN, 1974); i.e. the ability of some organisms to regulate the amount of certain trace elements in their body fluids, such that their shell material is derived from a solution of different composition than the environment in which they live.

Table 1. Generic carbonates in Littlefield Lake

Carbonate Form*	PM**	Mg/Ca <sup>†</sup> ( $\times 10^2$ )	Sr/Ca <sup>†</sup> ( $\times 10^4$ )	$K_{Mg}$ <sup>‡</sup> ( $\times 10^2$ )	$K_{Sr}$ <sup>‡</sup>
Calcareous mud (20)	C	3.38±.28	7.52±.50	6.50	3.79
Calcareous sand (20)	C	3.04±.09	7.74±.41	5.80	3.89
Oncooids (19)	C	2.36±.03	4.75±.27	4.50	2.42
<i>Chara</i> encrust. (20)	C	2.55±.13	7.36±.26	5.00	3.74
<i>Ammicola</i> i. (14)	A	0.31±.12	8.45±.37	0.59	4.29
<i>Valvata</i> t. (8)	A	0.55±.15	7.21±.18	1.06	3.64
<i>Gyalulus</i> d. (11)	A	0.60±.12	5.86±.21	1.15	2.98
<i>Sphaerium</i> p. (4)	A	0.24±.05	8.81±1.3	0.47	4.44

\* Number of samples shown in ( )

\*\* PM=Primary Mineralogy; C=Calcite; A=Aragonite

† Mean value of molar ratio ± standard deviation

‡ For Littlefield Lake water: Mg/Ca=0.52±.03; Sr/Ca=0.0020±0.0002

Table 2. Comparison of molar Sr/Ca and  $K_{Sr}$  values

Carbonate Form	Lake Constance			Littlefield Lake			FWHR	
	No.*	Sr/Ca ( $\times 10^4$ )	$K_{Sr}$	No.	Sr/Ca ( $\times 10^4$ )	$K_{Sr}$	No.	Sr/Ca ( $\times 10^4$ )
CALCITE ALGAE								
Oncoids	21	10.6	.18	19	4.75	.24	-	-
Other forms	-	-	-	20	7.36	.37	-	-
Average	21	10.6	.18	39	5.90	.31	3	5.8
CALCITE SAND	4	13.0	.22	20	7.74	.39	-	-
GASTROPODS								
<u>Valvata</u>	2	14.0	.23	8	7.21	.36	-	-
<u>Gyroulus</u>	1	14.9	.25	11	5.86	.29	-	-
Other forms	14	15.3	.26	14	8.45	.43	-	-
Average	17	15.2	.25	33	7.30	.37	33	7.5
PELECYPODS								
Sphaerium	3	21.6	.36	4	8.81	.44	-	-
Other forms	12	22.0	.37	-	-	-	-	-
Average	15	21.9	.37	4	8.81	.44	-	-

Lake Constance (Müller, 1968); Littlefield Lake (this study);  
FWHR=Fresh Waters of Humid Regions (Odum, 1957)

\* No.=Number of samples

This biochemical effect, rather than mineralogy, appears to be the major factor controlling the Sr/Ca ratios and  $K_{Sr}$  values of the various generic groups of carbonates from Littlefield Lake.

ODUM (1957) and MÜLLER (1968) have reported average values for the Sr/Ca ratio in calcite algal encrustations, calcite sands (Müller, only), gastropods and pelecypods for "freshwaters of humid climates" and Lake Constance, respectively. Müller's data are presented in sufficient detail to allow a comparison between his data and ours on the genus level for some organisms. These comparisons are summarized in Table 2.

The average Sr/Ca ratios determined for the biogenous forms in all three studies display the same trend: i.e. pelecypods > gastropods > calcite algae. Very good agreement exists between ODUM's (1957) values and the values reported for Littlefield Lake, whereas the Lake Constance values are significantly higher. This difference is undoubtedly due to the exceptionally high Sr/Ca ratio in Lake Constance waters ( $6.0 \times 10^{-3}$ ) as compared to average freshwaters ( $2.4 \times 10^{-3}$ ) of the world (BOWEN, 1966). MÜLLER (1968) deliberately elected to examine carbonates from freshwaters containing high Sr concentrations in order to demonstrate that the Sr/Ca ratios of the carbonates are not indicators of salinity but of the Sr/Ca ratio of the depositional environment. However, despite the high Sr content of Lake Constance waters, one might expect the  $K_{Sr}$  values reported by MÜLLER (1968) to be representative of freshwaters provided a linear relationship exists between the Sr/Ca ratio of the carbonates and that of the lake waters over the range of Sr/Ca ratios between typical freshwaters and Lake Constance. An examination of the  $K_{Sr}$  values reported in Table 2 indicates that this is not the case. The average Sr/Ca ratio ( $6.0 \times 10^{-3}$ ) in Lake Constance is three times the

average ratio in Littlefield Lake ( $2.0 \times 10^{-3}$ ), but the Sr/Ca ratios for the various carbonates in Lake Constance are only about 1.7–2.5 times the corresponding values in Littlefield Lake. Consequently, the  $K_{Sr}$  values reported by MÜLLER (1968) are 15–45% lower than the  $K_{Sr}$  values determined in this study. Based on the agreement between the Sr/Ca ratios of the carbonates determined in this study and that of ODUM (1957), and the fact that the Sr/Ca ratio of Littlefield Lake waters ( $2.0 \times 10^{-3}$ ) is close to the world average ( $2.4 \times 10^{-3}$ ) for freshwaters (BOWEN, 1966), we consider the  $K_{Sr}$  values reported here to be representative values for 'normal' freshwater carbonates.

MÜLLER's (1968) study also reported Mg concentrations in the various carbonate allochems and waters of Lake Constance. These data were used to calculate Mg/Ca ratios and  $K_{Mg}$  values for Lake Constance carbonates for comparison with our data (Table 3). The average Mg/Ca ratios determined in each study display the same trend: i.e. calcite sand > calcite algae > gastropods > pelecypods.

The world average Mg/Ca ratio for freshwater is about 0.45 (BOWEN, 1966). Littlefield Lake waters are fairly close to this value (0.52), while the average for Lake Constance (0.26) is half the Littlefield Lake value. However, this difference in water chemistry apparently has little effect on Mg partitioning within the calcite forms, as evidenced by the agreement that exists between the  $K_{Mg}$  values calculated for oncoids, calcite algae and carbonate sands. These values are considered representative for 'normal' freshwater carbonates.

In contrast to the calcite forms, the  $K_{Mg}$  values calculated for the aragonite forms in Lake Constance are 4–7 times higher than the corresponding values for Littlefield Lake. The reason(s) for this difference are not apparent from the available data. We do not note that the  $K_{Mg}$  values calculated for Littlefield Lake dis-

Table 3. Comparison of molar Mg/Ca  $K_{mg}$  values

Carbonate Form	Lake Constance			Littlefield Lake		
	No.*	Mg/Ca ( $\times 10^2$ )	$K_{mg}$	No.	Mg/Ca ( $\times 10^2$ )	$K_{mg}$
CALCITE ALGAE						
Oncoids	21	1.28	.05	19	2.36	.04
Other forms	-	-	-	20	2.55	.05
Average	21	1.28	.05	39	2.46	.05
CALCITE SANDS	4	1.92	.07	20	3.04	.06
GASTROPODS						
Valvata	2	1.63	.06	8	.55	.01
Cyraulus	1	1.84	.07	11	.60	.01
Other forms	14	.95	.04	14	.31	.006
Average	17	1.07	.04	33	.46	.01
PELECYPODS						
Sphaerium	3	.53	.02	4	.24	.005
Other forms	12	.84	.03	-	-	-
Average	15	.78	.03	4	.24	.005

Lake Constance (Muller, 1968); Littlefield Lake (this study)

\* No.=Number of samples

play the sharp difference expected on the basis of mineralogy, whereas this is generally not true for the  $K_{Mg}$  values calculated for Lake Constance carbonates, particularly the gastropods. This could result from the presence of some contaminant, e.g. calcite sand particles in some of the Lake Constance gastropod and pelecypod samples. WALLS *et al.* (1977) have analyzed various marine calcite and aragonite mollusk shells, and their data suggest that the  $K_{Mg}$  values of the calcite forms are about 5–15 times larger than the aragonite forms. If this same relationship is true for freshwater mollusks, then only a small amount of calcite contamination would result in anomalously high  $K_{Mg}$  values for the aragonite forms.

MÜLLER's (1968) contention that certain genera and species of freshwater carbonate secreting organisms have characteristic Sr/Ca ratios has important implications as far as understanding freshwater carbonate deposition. Investigations of modern marine biogenous carbonates do show consistent differences in strontium content between various genera (LIVINGSTON and THOMPSON, 1971; WEBER, 1973; SMITH *et al.*, 1979). Studies such as these typically have included samples from various geographic areas. Consequently, there has been much debate about the significance of the chemical differences because of uncertainty concerning the extent to which skeletal chemistry is determined by environmental versus genetically controlled factors (cf. discussions by WEBER, 1973; SMITH *et al.*, 1979). Because of this problem SMITH *et al.* (1979) went to considerable lengths to control the relevant environmental variables in their study and thus support the conclusion that the Sr content of their samples (Pacific corals) does indeed show a significant genetic dependence. In a similar vein, we consider the freshwater samples collected in this study to represent the maximum amount of experimental control over environmental factors that can be achieved

outside the laboratory. All samples are modern lacustrine carbonates from the same lake, and all have presumably been subject to the same environmental influences. Thus any similarities or differences in skeletal chemistry should be primarily due to genetic factors.

A knowledge of the similarities and differences in skeletal chemistry is also important to understanding the behavior of Sr and Mg during diagenesis. Obviously, the efficacy of using Sr/Ca or Mg/Ca ratios as paleoenvironmental indicators depends upon the extent they are preserved during diagenesis or, more realistically, upon an accurate assessment of how much they have been altered during diagenesis. Unfortunately, formulating such an assessment is not a straightforward process. The behavior of trace elements in carbonates during diagenesis is affected by a variety of factors, including the primary mineralogy, the temperature and chemistry of the diagenetic solution, the openness of the system to water flow, and non-carbonate mineral reactions (PINGATORE, 1978). Because of the variance introduced by these factors, multivariate statistical analyses (e.g. factor analysis) of large data sets often provide the best means of gaining insight into trace element behavior during diagenesis.

We have calculated and analysis of variance of our data to determine the extent that Sr/Ca and Mg/Ca ratios are characteristic indicators for various taxonomic groups, carbonate sands, and carbonate muds from Littlefield Lake. The results of this analysis are summarized in matrix form in Table 4, which reports the level of statistical significance at which each generic group can be distinguished from all other groups on the basis of these geochemical ratios. With this information in hand, subsequent investigations can be directed at interpreting the geological significance of variations in trace elements ratios for each

Table 4. Analysis of variance matrix of Sr/Ca ratios (below diagonal and Mg/Ca ratios (above diagonal) in Littlefield Lake

	1*	2	3	4	5	6	7	8
1	X**	A	A	A	A	A	A	A
2	A	X	A	A	A	A	A	A
3	A	B	X	A	A	A	A	A
4	A	A	C	X	A	A	A	A
5	A	A	A	A	X	A	A	C
6	A	A	B	C	A	X	C	A
7	A	A	A	A	A	A	X	A
8	A	A	A	A	C	A	A	X

\* 1=Oncoids; 2=Cal. Sands; 3= Cal. Muds; 4=Chara; 5=Amnicola i.; 6=Valvata t.; 7=Gyraulus d.; 8=Sphaerium p.

\*\* Letters indicate degree of statistical significance of the difference between Sr/Ca and Mg/Ca ratios for a given comparison. A= $p < 0.01$ ; B= $p < 0.1$ ; C= $p > 0.1$ ; X=diagonal

generic carbonate group within a lacustrine sedimentary sequence.

For the Sr/Ca ratio, the analysis of variance indicates that all but two of the individual pairings are significantly different ( $p < 0.1$ ). Moreover, the observed differences are highly significant ( $p < 0.01$ ) in the majority of cases. The pairings of *Chara* incrustations vs calcareous mud and *Sphaerium p.* vs *Amnicola i.* are not significantly different ( $p > 0.1$ ). The *Chara* vs carbonate mud pairing is probably indistinct because of a common source effect; i.e. the calcareous muds are primarily derived from the breakdown of *Chara* fragments, and thus the two groups have essentially the same Sr/Ca ratio. The similarity between the Sr/Ca ratios of *Sphaerium p.* and *Amnicola i.* suggests that these groups incorporate Sr to the same extent. However, since only four samples of *Sphaerium p.* are included in this study, the analysis of this limited number of samples may have precluded detection of a small but significant difference in the Sr/Ca ratio of these two groups.

The analysis of variance on the basis of the Mg/Ca ratio shows highly significant differences ( $p < 0.01$ ) for all but two pairwise comparisons. *Sphaerium p.* and *Amnicola i.* again are indistinguishable, probably for the same reason(s) discussed above for the Sr/Ca ratio. *Gyraulus d.* and *Valvata t.* also cannot be distinguished; both are gastropods with mixed calcite-aragonite mineralogy and both apparently incorporate Mg to the same extent.

In addition to their presence in calcite and aragonite lattices, both Sr and Mg may occupy non-stoichiometric positions relative to Ca in carbonate skeletal material. They may be (1) associated with organic compounds, (2) present as mineral inclusions, and/or (3) present in exchange (adsorbed) positions (SCHROEDER, 1969; AMIEL *et al.*, 1973; WALLS *et al.*, 1977). The pre-analysis treatment of our samples was

designed to minimize the effects of the first two factors listed above. However, no attempt was made to remove any Sr and Mg that were adsorbed on the samples, because the leaching techniques used for this purpose probably do not provide a quantitative removal (WALLS *et al.*, 1977). Thus, one parameter which could affect our data is the size (surface area) of the carbonates.

A comparison of the trace element ratios determined for calcareous sands and muds, both of which are primarily derived from *Chara*, should reveal any influence due to size/surface area. If there were no significant size/surface area effect influencing our data, we would expect the trace element ratios of the sands and muds to be essentially the same. On the other hand, if Sr and Mg occupy exchange positions in the samples, significant differences should exist between the sands and muds. The analysis of variance indicates that size/surface area does influence our data. The mean Sr/Ca ratios of the sands and muds are different at the 0.1 significance level but not the 0.01 level, while the mean Mg/Ca ratios are different at the 0.01 level. These differences are consistent with experimental data. Dissolution experiments and measurements of the exchange capacity of sedimentary carbonates indicate that as much as 9–12% of the Mg, but only about 1% of the Sr, are present in adsorbed positions (AMIEL *et al.*, 1973; WALLS *et al.*, 1977).

## SUMMARY AND CONCLUSIONS

1. The primary factor controlling the Mg/Ca ratio of sedimentary carbonates in Littlefield Lake is mineralogy. The Mg/Ca ratios and  $K_{Mg}$  values of calcite forms are 5–10 times larger than corresponding values for aragonite forms. The primary factor controlling the Sr/Ca ratios and  $K_{Sr}$  values is biochemical fractionation.

2. A comparison of geochemical data pertaining to sedimentary carbonates from Littlefield Lake (this study), Lake Constance (MÜLLER, 1968) and "freshwaters of humid climates" (ODUM, 1957) indicates that the Sr/Ca ratio follows the trend: pelecypods > gastropods > calcite algae. The Mg/Ca ratio displays an opposite trend: calcite sand > calcite algae > gastropods > pelecypods.

3. The  $K_{Mg}$  values determined for the calcite carbonates from Littlefield Lake and the  $K_{Sr}$  values determined for both the calcite and aragonite forms are considered representative values for typical marl lakes. However, the  $K_{Mg}$  values of the aragonite forms in Littlefield are significantly different from those calculated for Lake Constance. Further studies are needed to determine which of these sets of partition coefficients should be considered representative for typical marl lakes.

4. Most of the genera and species of carbonate secreting organisms in marl lakes have highly characteristic Sr/Ca and Mg/Ca ratios. Thus, it should be possible

ible to use these ratios as indicators in future studies aimed at understanding the mobility of Sr and Mg during the diagenetic alteration of lacustrine carbonates.

5. Statistically significant compositional differences exist between calcareous sands and muds, both of which are primarily derived from *Chara*. Thus the data are influenced by a grain-size or surface area effect which is probably due to the presence of Sr and Mg in non-lattice-held (exchangeable) positions.

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