Short Communication

MINERALOGICAL AND BIOLOGICAL CONTROLS ON THE Fe/Ca AND Mn/Ca RATIOS OF LACUSTRINE CARBONATE ALLOCHEMS

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ABSTRACT

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The Fe/Ca and Mn/Ca ratios of lacustrine carbonate allochems are primarily controlled by the mineralogy of the carbonate polymorph. However, these ratios are subject to a significant degree of biological control among common biogenous carbonate forms of the same mineralogy. This suggests the trace-element ratios of the biogenous forms can serve as quantitative signals for estimating the primary mineralogy, original composition, and extent of diagenetic alteration of ancient lacustrine carbonates.

INTRODUCTION

Both the absolute and relative concentrations of certain trace elements (e.g., Sr, Mg, Fe, Mn) in diagenized carbonate sequences provide clues useful in paleoenvironmental reconstructions. This information also can serve as the quantitative basis for modeling the pathways and overall extent of diagenetic alteration (Pingetore, 1978; Brand and Veizer, 1980). provided that one can make an accurate estimate of the original trace-element composition of the carbonate deposits. This requirement poses little difficulty in most investigations of marine carbonate diagenesis; however, for reasons which are detailed below, it is far more difficult to satisfy in the case of freshwater carbonates.

We are interested in overcoming this problem by exploiting the biological fractionation capabilities of freshwater carbonate-secreting organisms. Biological fractionation refers to the ability of these organisms to regulate the amount of trace elements in their body fluids, and thus to exert some control over the trace-element composition of their shell material. This effect is of relatively minor significance in the marine realm, insofar as many marine organisms produce shells which have a trace-element composition nearly identical to that of inorganically precipitated carbonates (Brand and

Veizer, 1980). On the other hand, we have recently determined that the shell material of certain common taxonomic groups of freshwater organisms tends to have highly characteristic molar Sr/Ca and Mg/Ca ratios (Treese et al., 1981). In this short communication we report similar findings based on the analysis of Mn/Ca and Fe/Ca ratios of these same organisms. Collectively, these data suggest that trace-element ratios can be used to formulate better estimates of the original chemistry of ancient lacustrine carbonates and to gain insight into the processes involved in their diagenesis.

RESULTS AND DISCUSSION

The samples discussed here were collected from Littlefield Lake, a small (10.8 km^2) marl lake located in Isabella County in central Michigan, U.S.A. Murphy and Wilkinson (1980) have described the basin morphology, mechanisms of carbonate deposition, and facies distribution in Littlefield Lake, and we have monitored several chemical parameters of the lake water on a monthly basis for a period of 15 months. On the basis of these observations, Littlefield Lake is considered to be typical of hard-water marl lakes which occur extensively throughout the north-central U.S.A. (cf. Wetzel, 1960, 1975). A series of grab samples of lake sediment were sieved to obtain individual samples of the various carbonate allochems present. Calcite components include cyanophytic algal oncoids and encrustations on *Chara* as well as calcite sand and mud. The aragonite components include the three dominant gastropods *Amincola integra*, *Valvata tricarinota* and *Gyraulus deflectus*, and the dominant pelecypod *Sphaerium partumeium*. The concentrations of Ca, Fe, and Mn in these samples were determined by atomic absorption spectroscopy. Details concerning sample preparation and analytical procedures have been reported previously (Treese et al., 1981).

All of the samples collected during this study are Recent carbonates which formed in the lake under essentially the same environmental conditions. Consequently, we have assumed that differences in the composition of the different genetic groups of carbonates examined here must be due primarily to differences in mineralogy and/or biological fractionation rather than variations in the temperature and/or water chemistry of Littlefield Lake. This assumption probably is not strictly true since, for example, different taxa may achieve optimum growth rates at slightly different temperatures. However, the results of controlled laboratory studies (cf. Buchardt and Fritz, 1978) suggest that such bio-specific responses have a negligible effect on the partition coefficient, at least over the temperature range typical of lakes.

MINERALOGY AND NON-STOICHIOMETRIC EFFECTS

The stoichiometric substitution of various trace elements for Ca in carbonate polymorphs is related to the geometry of the lattice structure and the size difference between the substituted ion and Ca^{2+}. Ions larger than Ca^{2+}

(e.g., Sr^{2+}, Ba^{2+}, $U(VI)$) are most readily accepted in the orthorhombic structure of aragonite, while smaller ions such as Fe(II) and Mn(II) are preferentially incorporated into the rhombohedial structure of calcite (McIntyre, 1963; Fyfe and Bischoff, 1965; Milliman, 1974). Furthermore, since the size difference in ionic radius between Mn(II) and Ca^{2+} is 14.3% vs. a 21.7% difference between Fe(II) and Ca^{2+}, Mn(II) substitutes more extensively for Ca^{2+} in calcite than does Fe(II) (Berry and Mason, 1959).

These expected mineralogical trends are generally evident in our data (Table I). The Mn/Ca ratios of calcite components are 3.1—11.1 times greater than those of the aragonite components and, except for *S. partumeium*, the Fe/Ca ratio of the calcite components are 1.4—4.6 times greater than those of the aragonite components. Also, within calcite groups, the Mn/Ca ratio is consistently higher than the Fe/Ca ratio as would be anticipated from differences in their ionic size. The reason for the relatively high Fe/Ca ratio of the aragonite shell of *S. partumeium* is not readily apparent.

TABLE I

Molar Fe/Ca and Mn/Ca values for Littlefield Lake

Carbonate form	N[1]	Fe/Ca[2] ($\times 10^4$)	Mn/Ca[2] ($\times 10^4$)
CALCITE FORMS:			
Pisoliths	19	5.28 ± 0.55	16.8 ± 4.5
Chara	20	6.56 ± 0.69	15.3 ± 1.0
Sands	20	15.9 ± 1.3	18.4 ± 1.0
Muds	15	6.61 ± 0.96	20.0 ± 1.4
ARAGONITE FORMS:			
Valvata tricarinota	8	3.43 ± 0.57	3.70 ± 0.62
Gyraulus deflectus	11	3.57 ± 0.49	4.94 ± 0.79
Amnicola integra	14	3.72 ± 0.58	2.56 ± 0.64
Sphaerium partumeium	4	6.16 ± 1.5	1.79 ± 0.36

[1] N = number of samples.
[2] Value determined ± one standard deviation.

It could be a biological fractionation effect (see following discussion); however, since we were able to isolate only four individuals of this species from our samples, it may simply result from the relatively high error associated with determining a mean value based on so few specimens.

Trace elements which occupy non-stoichiometric positions relative to Ca in carbonates may be: (1) associated with organic matter, (2) present as anomalous mineral inclusions, and/or (3) present in exchangeable (adsorbed) positions (Amiel et al., 1973). The pre-analysis treatment of the samples was designed to minimize the effect of the first of these factors and all sample groups except calcite sand and mud were sonically treated to remove non-

carbonate mineral grains. No attempt was made to remove trace elements adsorbed on the samples because the leaching techniques commonly used for this purpose do not provide a quantitative removal (Walls et al., 1977). Based on these considerations, and noting that the calcite sand and mud in Littlefield Lake are primarily derived from the disintegration of *Chara* encrustations (Treese et al., 1981), it is possible to estimate the influence of the latter two non-stoichiometric effects by comparing the trace-element ratios determined for these three sample group. For example, Fe/Ca ratios determined for *Chara* encrustations and calcite mud are nearly identical, while the relatively high value for calcite sand suggests the presence of non-carbonate, Fe-bearing mineral grains in sand samples. A similar argument can be made for the presence of non-carbonate-bearing minerals in both the sand and the mud. Finally, if we assume that the difference in the Mn/Ca ratio between sand and mud is due entirely to a difference in grain size, i.e. greater adsorption of because of increased surface area with smaller size, then as much as 8—9% of the Mn could be present in adsorbed positions in the mud. This difference is actually quite small considering that surface area may increase by a factor of at least 10^5 between these two size fractions (Filipek and Owen, 1979), several orders of magnitude larger than the observed increase in Mn concentration.

BIOLOGICAL FRACTIONATION: IMPLICATIONS CONCERNING LACUSTRINE CARBONATE DIAGENESIS

We have calculated an analysis of variance of our data to determine the extent that Fe/Ca and Mn/Ca ratios are characteristic for the various taxonomic groups obtained from Littlefield Lake. The results of this analysis, in matrix form in Table II, indicate the level of statistical significance at which each generic group can be distinguished from all other groups on the basis of

TABLE II

Analysis of variance matrix of Fe/Ca ratios (above diagonal) and Mn/Ca ratios (below diagonal)

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

*1 *1* = pisoliths; *2* = *Chara*; *3* = *Gyraulus deflectus*; *4* = *Valvata tricarinota*; *5* = *Amnicola integra*; *6* = *Sphaerium partumeium*.
*2 Letters indicate degree of statistical significance between Fe/Ca and Mn/Ca ratios for each comparison. A = $p < 0.01$; B = $p < 0.1$; C = $p > 0.1$; X = diagonal.

these geochemical ratios. For Mn/Ca ratios, the analysis of variance indicates that all of the pairings are significantly different ($p < 0.1$) and that these differences are highly significant ($p < 0.01$) in all but one case. Four of the 15 pairings show no significant difference ($p > 0.1$) in Fe/Ca ratios. However, three of the four cases involve pairings between the three gastropod species: *A. integra*, *V. tricarinota* and *G. deflectus*. Apparently each of the gastropods examined here incorporates Fe to the same extent, although Fe/Ca ratios do serve to differentiate gastropods from the other biogenous forms. The remaining instance where no significant difference in trace-element signatures exists is the pairing between *Chara* encrustations and *S. partumeium*. These two groups may also incorporate Fe to the same extent, but this interpretation is considered tenuous because the analysis of only four samples of *S. partumeium* may have precluded detection of a small but significant difference in Fe/Ca ratios of these two groups.

Trace-element ratios are useful for studying carbonate diagenesis only if fairly narrow limits can be established for the composition of each trace element in the original carbonate, so that compositional changes which occurred during diagenesis can be quantified by composition to a fixed reference point. Investigations of marine carbonate diagenesis have satisfied this condition by examining either carbonates which originally were formed via inorganic precipitation or biogenous carbonate form which incorporate trace elements to the same extent as the inorganic forms. The incorporation of trace elements into the solid phase during carbonate precipitation is described by the relationship (McIntyre, 1963)

$$K_T = \frac{(M_T/M_{Ca})_s}{(M_T/M_{Ca})_l}$$

where K_T = the partition coefficient for trace element T; M_T and M_{Ca} = moles of trace element and Ca^{2+}, respectively; and the subscripts s and l denote the solid and liquid phases, respectively. Experimentally determined inorganic partition coefficient values for several elements are reported in the literature [e.g., see Brand and Veizer (1980) and references therein]. Hence, given the constancy of composition of marine waters for elements such as Ca, Mg and Sr, and a knowledge of the appropriate K_T values, it is possible to make reasonably accurate estimates of the original composition of these elements in inorganic (and some biogenous) forms of marine carbonates.

Estimates of the original Fe and Mn concentrations of diagenized marine carbonates are less accurate because the concentrations of these elements in marine waters are more variable. Despite this greater uncertainty, these elements are still useful for monitoring diagenetic transformations because their concentrations in meteoric waters (a common liquid phase in carbonate diagenesis) are significantly greater than in seawater (Turekian, 1972). Because of this concentration difference, elements with $K_T > 1.0$ (Fe and Mn) are preferentially incorporated into solids during diagenesis, while elements with

$K_T < 1.0$ (Sr and Mg) are preferentially left in the liquid phase (Pingetore, 1978; Brand and Veizer, 1980). Consequently, even though the initial Fe and Mn content of a original marine carbonate is not precisely known, there occurs a trend of increasing Fe and Mn concentrations in the solid phase with increasing degree of alteration and re-equilibration. Finally, since Sr and Mg will display an opposite trend during meteoric diagenesis, it should be possible to extrapolate back from these diverging elemental trends and define an approximate concentration "window" for the original concentration of the diagenized carbonate sequence.

Inorganic lacustrine carbonates present a more complex situation because, compared to marine waters, the concentrations of Sr, Mg, Fe and Mn in lake waters are highly variable (Müller et al., 1972; Wetzel, 1975, p. 254). Even if the trace-element partition coefficients for inorganic lacustrine carbonates were known, it would be difficult to estimate the original trace-element signature of a diagenetically altered carbonate owing to the uncertainty of the chemistry of the lake waters from which it was derived. Furthermore, an increasing degree of diagenetic alteration would probably not lead to pronounced enrichment or depletion of these elements because their concentrations in meteoric waters may be quite similar to that of the lake waters in which they formed.

Based on these considerations, the trace-element compositions of inorganic lacustrine carbonates, unlike their marine counterparts, are likely to be too variable to be useful in detecting small but significant changes resulting from chemical diagenesis. The strong control of trace-element ratios by biological fractionation, on the other hand, suggests that lacustrine biogenous forms are well-suited for the purpose of estimating original allochem compositions in diagenetic studies. In fact, given the highly characteristic ratios determined for different taxa thus far, the number of independent geochemical signals which could theoretically be used to monitor diagenetic processes should approach the product of the number of trace elements and different taxonomic forms which are examined.

SUMMARY AND CONCLUSIONS

Molar Fe/Ca and Mn/Ca ratios were determined for various carbonate allochems collected from a typical temperate-region marl lake. The primary factor which controls these ratios is allochem mineralogy (calcite or aragonite). Both Fe/Ca and Mn/Ca ratios are larger in calcites than in aragonites and, within calcites, Mn/Ca is consistently higher than Fe/Ca. These differences are consistent with the known ability of different $CaCO_3$ polymorphs to accomodate ions of different size which substitute stoichiometrically for Ca. Among biogenous allochems of the same mineralogy, biological fractionation controls the trace-element ratios to the extent that various taxa have highly characteristic compositions. Inorganic lacustrine carbonates, unlike their marine analogs, probably are too variable in composition to be use-

ful in diagenesis studies. However, the influence of biological control on trace-element ratios suggests that biogenous forms can serve as quantitative geochemical signals for estimating the primary mineralogy, original composition, and extent of diagenetic alteration of ancient lacustrine carbonates.

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REFERENCES

Amiel, A., Friedman, G.M. and Miller, D.S., 1973. Distribution and nature of incorporation of trace elements in modern aragonitic corals. Sedimentology, 20: 47—64.

Berry, L.G. and Mason, B., 1959. Mineralogy. W.H. Freeman, San Francisco, Calif., 612 pp.

Brand, U. and Veizer, J., 1980. Chemical diagenesis of a multicomponent carbonate system, 1. Trace elements. J. Sediment. Petrol., 50: 1219—1236.

Buchardt, B. and Fritz, P., 1978. Strontium uptake in shell aragonite from the freshwater gastropod. *Limnaea stagnalis.* Science, 199: 291—292.

Filipek, L.H. and Owen, R.M., 1979. Geochemical associations and grain-size partitioning of heavy metals in lacustrine sediments. Chem. Geol., 26: 105—117.

Fyfe, N.S. and Bischoff, J.L., 1965. The calcite aragonite problem. In: L.C. Pray and R.C. Murray (Editors), Dolomitization and Limestone Diagenesis: A Symposium. Soc. Econ. Paleontol. Mineral., Spec. Publ., 13: 3—13.

McIntyre, W.L., 1963. Trace element partition coefficients, a review of theory and applications to geology. Geochim. Cosmochim. Acta, 27: 1209—1264.

Milliman, J.D., 1974. Marine Carbonates — Recent Sedimentary Carbonates, I. Springer, New York, N.Y., 1st ed.

Müller, G., Irion, G. and Förstner, U., 1972. Formation and diagenesis of inorganic Ca—Mg carbonates in the lacustrine environment. Naturwissenschaften, 59: 158—164.

Murphy, D.A. and Wilkinson, B.H., 1980. Carbonate deposition and facies distribution in a central Michigan marl lake. Sedimentology, 27: 123—135.

Pingetore, Jr., N.E., 1978. The behavior of Zn^{2+} and Mn^{2+} during carbonate diagenesis: theory and applications. J. Sediment. Petrol., 48: 799—814.

Treese, T.N., Owen, R.M. and Wilkinson, B.H., 1981. Sr/Ca and Mg/Ca ratios in polygenetic carbonate allochems from a Michigan marl lake. Geochim. Cosmochim. Acta, 45: 439—445.

Turekian, K.K., 1972. Chemistry of the Earth. Holt, Reinhart and Winston, New York, N.Y., 131 pp.

Walls, R.A., Ragland, P.C. and Crisp, E.L., 1977. Experimental and natural study of diagenetic mobility of Sr and Mg in biogenic carbonates. Geochim. Cosmochim. Acta, 41: 1731—1777.

Wetzel, R.G., 1960. Marl encrustations on hydrophytes in several Michigan Lakes. Oikos, 11: 223—236.

Wetzel, R.G., 1975. Limnology. W.B. Saunders, Philadelphia, Pa., 743 pp.

Wineland, H.D., 1969. Stability of calcium carbonate polymorphs in warm, shallow seawater. J. Sediment. Petrol., 39: 1579—1587.