CHEMICAL DIAGENESIS AND DOLOMITIZATION OF PALEOZOIC HIGH-Mg CALCITE CRINOIDS

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ABSTRACT: Geochemical analyses suggest that during early diagenesis, shortly after death and disarticulation of the organism, the stroma of crinoids is rapidly filled by cement. Skeletal port space is only preserved in specimens which were rapidly buried and sealed in either asphalt-impregnated or shale formations. Cement-filling of the stroma and subsequent alteration of the skeletal high-Mg calcite to diagenetic low-Mg calcite generally obliterates original microstructures and mineralogy. These changes are accompanied by redistribution of trace elements and stable isotopes, and lead to increases for $\delta^{13}C$, Mn and Fe by factors of 7 to 140. At the same time Mg, Sr, Na, $\delta^{18}O$ and in some instances $\delta^{13}C$ decrease by factors ranging from 26 to 1.5. No specific trends were detected for Al, Cu, Ni and Zn. Multiple and discontinuous chemical trends of the sample populations argue for the 'stepwise' alteration of originally biogenic high-Mg calcite.

Diagenetic microenvironments for the studied crinoids span the whole spectrum of water types as well as reaction processes/rates. Specimens from the Breathitt and Brush Creek most likely altered in the presence of meteoric water through diffusion-controlled reaction processes. On the other end of the spectrum are the specimens from the Burlington and Banff Formations which probably altered in diagenetic systems dominated by marine water with minor input of meteoric water via fluid-controlled reaction processes. Mixed-water and reaction process(es) account for the alteration of the crinoids from the Monte Cristo Formation of southern Nevada. Specimens from other units fall in between the fluid- to diffusion controlled to dominated reactions in the presence of marine to meteoric dominated to controlled waters.

Dolomitization of the diagenetically-stabilized web crinoids from the Irondequoit and Douro Formations probably proceeded in fluid-controlled systems in the presence of mixed water. The postulated K^{Sr}_D of about 0.02 is similar to the value based on high temperature experiments and thus supports the postulated diagenetic microenvironment. The $\Delta^{18}O$ value determined for the diagenetic low-Mg calcite-dolomite transformation is +2.5°/oo further supporting the postulated physicochemical parameters for dolomitizing fluid(s). Formation of ferroan dolomite depends on superjacent shale units and the redox condition of the dolomitizing fluid(s).

INTRODUCTION

Major advances have been made in delineating geochemical trends associated with the diagenetic transformation of both biogenic aragonite and low-Mg calcite (e.g. Land, 1967; Pingitore, 1976; Brand and Veizer, 1980; Buchardt and Weiner, 1981; Morse, 1983: Popp et al., 1986; Brand and Morrison, 1987; Brand, 1989a,b). The sum of these studies permits the selection and identification of pristine aragonite material as old as Carboniferous. However, to obtain pristine biogenic carbonates older than Carboniferous one is generally limited to low-Mg calcite shells of brachiopods. To supplement these data, major inroads have been made in characterizing the geochemistry and mineralogy of trilobites and consequently realizing their potential for identifying paleoenvironmental conditions (McAllister and Brand, 1989). Another group of biogenic carbonates, the

Table 1. Formation (*=this study), age, locality, lithology (L=limestone, S=shale, D=dolomite) and reference information for originally high-Mg calcite crinoids from North America.

Formation	Age	Locality	Lithology	Reference
CARBONIFEROUS				
Shawnee*	M. Virgillian	Kansas	S	von Bitter, 1972
Madera*	Missourian	New Mexico	L	Brand, 1989b
Kiewitz*	L. Missourian	Nebraska	S	Mudge & Yochelson, 1962
Brush Creek	E. Missourian	Pennsylvania	S	Norton, 1975; Brand & Morrison, 1987
Naco*	L. Desmoinesian	Arizona	S	Brew & Beus, 1976
Boggy*	M. Desmoinesian	Oklahoma	L	Blake et al., 1982; Brand, 1987a
Breathitt-Magoffin	E. Atokan	Kentucky	S	Dennis & Lawrence, 1979; Brand, 1987b
Breathitt-Kendrick	L. Morrowan	Kentucky	S	Jillson, 1919; Brand, 1987b
McCully*	L. Morrowan	Oklahoma	L	Sutherland & Henry, 1977
Bangor*	E. Chesterian	Tennessee	L	Smith, 1890
Monte Cristo*	Meramecian	Nevada	L	Langenheim & Webster, 1979
Lake Valley*	Osagean	New Mexico	L	Meyers, 1974
Banff*	L. Osagian	Alberta	L	Bamber et al., 1981
Edwardsville*	L. Osagean	Indiana	S	Lane, 1973
Burlington	M. Osagean	Missouri	L	Harris & Parker, 1964; Brand & Veizer, 1980
DEVONIAN				
Rundle*	L. Famennian	Alberta	L	Bamber et al., 1981
Hungry Hollow	Givetian	Ontario	LS	Popp, 1981; Popp et al., 1986
Speeds	Givetian	Indiana	L	Popp, 1981
Beechwood	Givetian	Indiana	L	Popp, 1981
Lingle	Givetian	Illinois	L	Popp, 1981
SILURIAN				
Douro	Ludlow-Pridoli	Arctic Canada	LD	Brand & Veizer, 1980, 1981
Irondequoit*	E. Wenlock	Ontario	LD	Milinkovitch & Brand, 1984

echinoderms, has received moderate attention in defining diagenetic processes (e.g. Richter, 1974; Towe and Hemleben, 1976; Heugebauer, 1978, 1979; Brand and Veizer, 1980; Blake et al., 1982). Despite these studies, less is known about the redistribution of trace elements and stable isotopes during the calcitization of crinoidal high-Mg calcite than of other biogenic carbonates (Brand and Veizer, 1980, 1981; Popp, 1981; Mackenzie et al., 1983).

The dolomitization process has been extensively discussed in the literature despite the fact that the actual mechanism still remains an enigma (e.g. Land, 1983; Dockal, 1988). Because limestone matrix, the precursor of mixed-water derived dolomite, is a melange of carbonate minerals, it would be better to characterize the dolomitization trend(s) using monomineralic carbonate grains (cf. Blake et al., 1982; Veizer and Demovic, 1974) such as crinoidal, stereom calcite (Blake et al., 1982; Budai

et al., 1987).

The first objective is to elucidate the microstructural, mineralogical, and geochemical changes that take place during the diagenetic alteration of originally high-Mg crinoidal calcite. During this procedure, we evaluate such aspects of the diagenetic process as possible as age dependence, lithological influence, environmental setting and water/rock ratio. The second objective is to delineate the morpho-chemical changes that take place during the subsequent dolomitization of diagenetically-stabilized crinoid calcite.

SAMPLE MATERIAL

Carboniferous, Devonian and Silurian crinoids were collected from a number of units in North America for this study and are supplemented by data of samples from other studies (Table 1). Included in the table is information on the general lithology of the host formation and at least one background reference for each unit.

Host rocks of the studied crinoids varied from wackestones to grainstones to shales. This variety allows for characterization of the possibly different diagenetic processes affecting originally high-Mg calcite crinoids and for determining whether these are controlled directly and/or indirectly by the composition of the host rock (e.g. Blake et al., 1982; Brand and Veizer, 1980; Neugebauer, 1979).

ANALYTICAL METHODS

Crinoids were separated manually from their enclosing rock matrix and then leached with 15% (v/v) HCl to remove any matrix and oxides remaining in skeletal crevices. After cleaning, a fragment of each sample was coated with gold-palladium in a sputter-coater. Fracture surfaces of fossil fragments were examined for skeletal microstructures using an ISI scanning electron

microscope.

A total of 281 samples was analyzed. Approximately 0.5 g of each sample was digested in 18 mL of 5% (v/v) HCl for 5 h; this method limits leaching of elements from the non-carbonate portion still adhering to the samples (Brand and Veizer, 1980). All samples were analyzed for Ca, Mg, Sr, Mn, Na, Al, Fe, Ba, Zn, Cu, Ni and Pb on a Varian 1475 atomic absorption spectrophotometer. Average accuracy compared with recommended values for N.B.S. (633, 634, 636) standard rocks, and average precision based on duplicate analyses were better than 5 relative percent for Ca, Mg, Sr, and Mn, 10% for Na, Fe, and Cu, and 15% for Al, Ba, Zn, Ni and Pb. Average precision of the insoluble residue (I.R.), determined by thermo-gravimetry, was better than 5 relative percent. All discussion in the text is based on elemental concentrations recalculated on a 100% carbonate (insoluble residue-free) basis. Additional material was procured from the studies of Brand and Veizer (1980, 1981), Milinkovitch and Brand (1984). Brand (1987a,b), Brand and Morrison (1987), Popp (1981) and Popp et al. (1986) for a total trace-element data base of 368 samples.

Ninety-one samples were also analyzed for carbon and oxygen isotopes on a V.G. Micromass 602D mass spectrometer. These samples were selected after evaluation of trace element data. Approximately 10 mg of powder of each sample was reacted with 100% phosphoric acid at 50°C for 1/2h. The isotopic ratios are expressed in the conventional (δ) notation relative to PDB in°/oo. The ^{17}O correction of Craig (1957) was applied to the data. Average accuracy and precision of data (duplicate analyses) as compared to recommended values for N.B.5. 20 (Solenhofen Limestone) standard rock (cf. Craig, 1957) were:δ^{18}O (0.18,0.11) andδ^{13}C (0.12, 0.15)°/oo, respectively. Further data were obtained from the studies listed above (Table 1) for a total base of 153 stable isotope values.

Tables of geochemical data (Appendix) are available for a nominal charge from the Depository of Unpublished Data, CISTI National Research Council of Canada, Ottawa, Ontario Canada K1A 0S2.

HIGH-Mg CALCITE DIAGENESIS

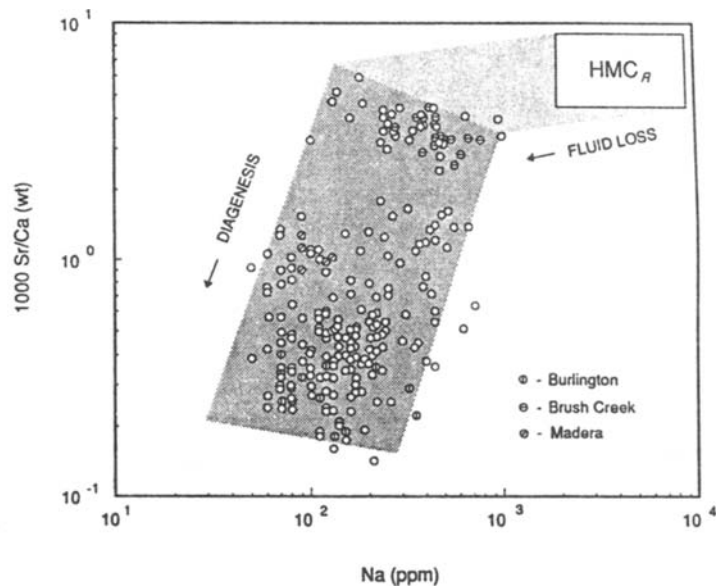### Trace Elements

Evaluation of Lower Paleozoic crinoids from

Figure 1.-- *Strontium/calcium and sodium diagenetic trends of originally high-Mg calcite crinoids (Table 1). The high-Mg calcite field (HMCR) defines the ranges of Sr and Na contents observed in Recent echinoderms (Morrison and Brand, 1986). The 'fluid loss' area and trend represent loss of body fluids and organics from the stroma during early diagenesis. The selected crinoid populations represent material with relatively high (Brush Creek), intermediate (Madera) and low (Burlington) trace element contents. Shaded area encompasses about 98% of the studied material.*

North America shows considerable variation in trace element content with post-depositional alteration. The Sr and Na contents of originally high-Mg calcite decrease in a sequential but discontinuous diagenetic alteration pattern (Figure 1; Plummer and Mackenzie, 1974). Specimens from a particular locality/unit do not span the whole diagenetic range, instead they cluster in sequentially distinct areas (e.g. Burlington, Madera and Brush Creek). This distinct elemental distribution is also noted in crinoids from the other formations. Also note the apparent significant drop in the Na content observed between modern crinoids and the least-altered material from the Brush Creek and Kiewitz.

Modern echinoderms contain large quantities of Na in skeletal calcite, body fluids and fluid inclusions. It is postulated that the large discrepancy in Na between modern and least-altered ancient echinodermal material is related to loss of body fluids during the early stages of death and disarticulation of the organism(s). This loss of body fluids accounts for
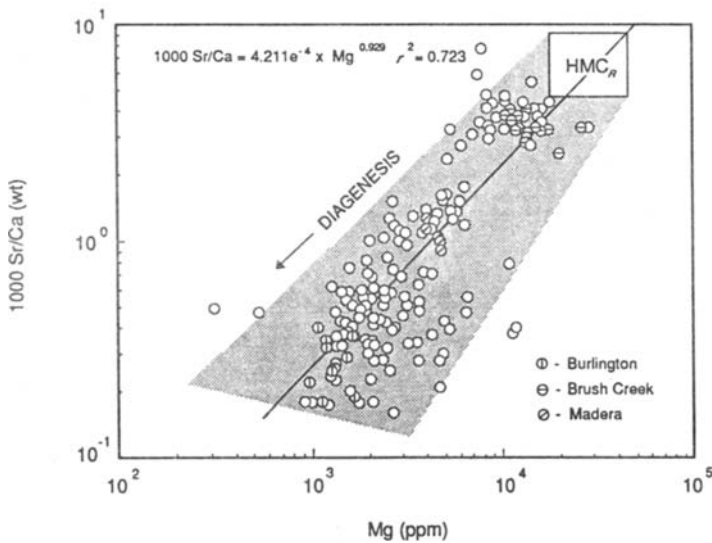
Figure 2.--Redistribution of Sr/Ca and Mg during the diagenetic alteration of originally high-Mg calcite crinoids. The correlation equation defines the functional relationship between the changes in Sr and Mg contents of crinoids with progressive alteration relative to elemental contents encountered in unaltered modern counterparts; the significance of the relationship is explained by the coefficient of determination (r^2). Explanations for other fields and symbols as in Fig. 1.

a reduction of Na by factors of about 5 and 9 in crinoidal calcite for the least-altered Kiewitz and Brush Creek specimens, respectively (Figure 1). But at the same time, Sr contents do not change with this loss of body fluids. It is believed that the consequent change in Na with the concomitant lowering of both Mg and Sr contents is related to changes in mineralogical and chemical integrity during skeletal carbonate diagenesis (Figures 1, 2). The distinct chemical 'character' of individual populations is maintained with alteration for the three test units and for all the others.

Segregation of data into limestone and shale units presents a clear separation of Mn and Fe contents for all the crinoids (Figure 3). Similar observations have been made by other authors on this apparent redox dependence displayed by the data (e.g. Veizer, 1977: Morrison et al., 1985; Brand, 1981, 1987a, 1989a). Samples from limestones show decreases in Sr, Na and Mg contents with increases of both Mn and Fe with increasing 'stepwise' alteration (Figures 3,4). The trend for crinoid material from shales is more complex; some populations show a decrease of both Mn and Fe with progressive altera-
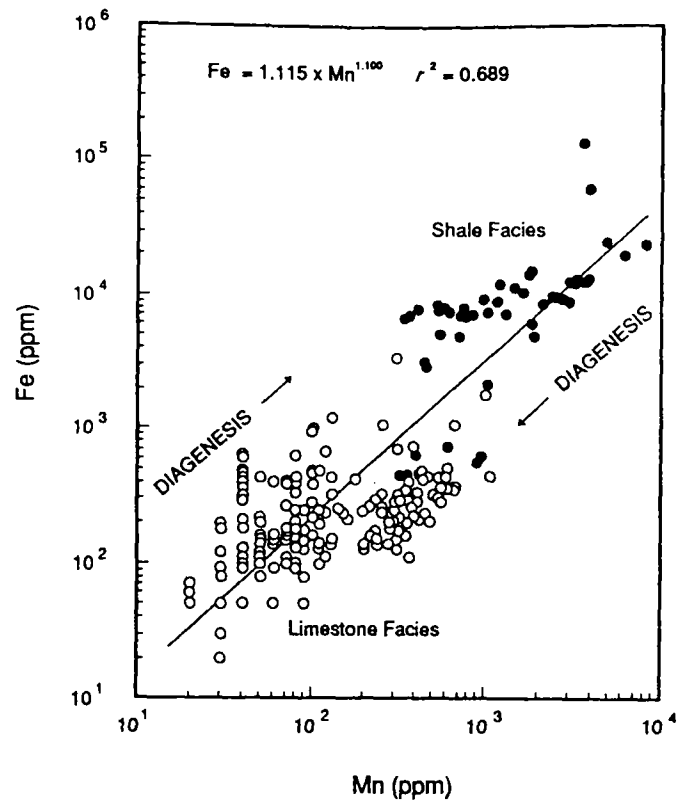

Figure 3.--Chemical variation of the Fe and Mn contents of altered crinoidal specimens. This trend is only partly explained by leaching from insoluble residue and/or oxide coatings (Table 2). Instead, diagenetic trends are superimposed on primary environmental and lithological differences (cf. Brand, 1989a). Explanations for statistics as in Fig. 2.

tion, whereas others show only slight increases to none in Mn and Fe contents (Figure 4). Some of this dichotomy may be related to leaching of these two elements from oxide coatings that were not removed during the cleaning stage (cf. Brand, 1989b).

Microstructures

Microstructures are useful indicators of the degree of diagenetic alteration in biogenic carbonate grains (cf. Blake et al., 1982: Brand and Morrison, 1987; Brand, 1989 a,b). Skeletons of modern echinoderms consist of the calcitic stereom and the stroma filled by organic tissue and body fluids. These skeletal structures are preserved in some of the crinoids from the Brush Creek (Figure 5, plate A: Brand and Morrison, 1987). But, this open meshwork is not preserved in specimens from the Kiewitz (Figure 5, plate B), although they have geochemical signatures similar to those from the Brush Creek. In

Table 2. Varimax rotated factor matrix (Nie et al., 1975) of diagenetically altered Carboniferous and Silurian crinoids (N=153). Interpretations are based on geochemical trends derived from theoretical considerations and applied data (e.g., Brand and Veizer, 1980; Pingitore, 1976, 1982).

	Factor 1	Factor 2	Factor 3	Communality
log I.R.	-0.11466	0.49718	0.46786	0.47923
log Ca	-0.44203	-0.37912	-0.15549	0.36029
log Mg	0.93011	0.10555	-0.-3826	0.87771
log Sr	0.90344	0.19453	-0.13949	0.87350
log Mn	0.02781	0.98212	0.13898	0.98464
log Na	0.61883	0.11339	0.07997	0.40221
log Al	0.25156	0.52951	0.55335	0.64986
log Fe	0.38197	0.80463	0.09704	0.80275
log Zn	-0.04622	0.09299	0.69745	0.49723
log Cu	0.23550	0.12733	0.26422	0.14148
log Ni	0.20424	-0.05569	0.13150	0.06211

Factor	Eigenvalue	Pct. of Var.	Interpretation
1	3.61999	59.0	*Diagenetic Alteration*
2	1.85170	30.2	*Depositional Environment & Leaching*
3	0.65932	10.8	*Laboratory Leaching*

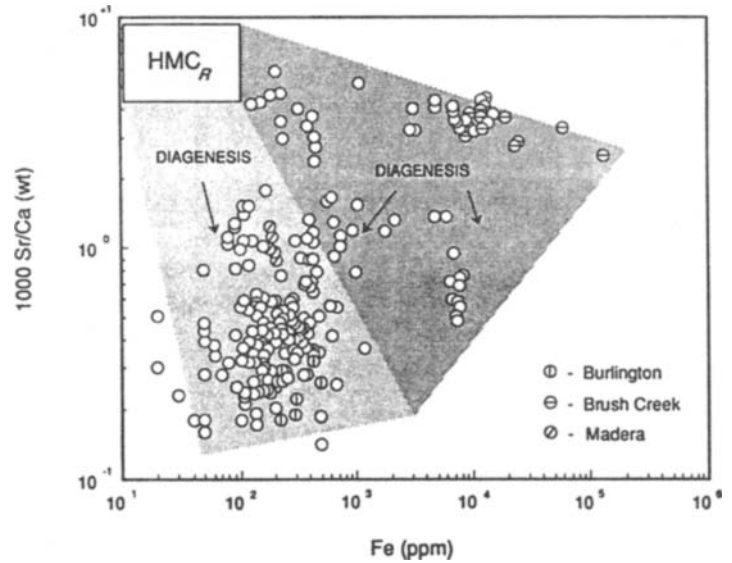Note: covariant parameters are italicized or underlined (> 0.4500).

Figure 4.--Chemical variation of the Sr and Fe contents with progressive diagenetic alteration with consideration for environmental/lithological influences. The specimens in the lightly shaded area are from limestones, whereas the other fields represents specimens from shales. Explanations of field and symbols as in Fig.1.

another unit, the Magoffin marine horizon of the Breathitt Formation which contains an aragonite mollusc fauna, the crinoid skeletons are filled and replaced by diagenetic low-Mg calcite (Figure 5, plate C). No significant difference in appearance is noted between specimens from the Kiewitz, Magoffin and Madera Formations (Figure 5, plates B-D). In contrast, there are definite differences in mean Mg, Sr and Na contents between specimens from the Kiewitz-Magoffin (16030-13850 ppm, 1400-1320 ppm; 850-340 ppm, respectively) and Madera (4470 ppm, 380 ppm; 100 ppm; Appendix). Microstructural features in these specimens are sharp and well defined, whereas in more extensively altered (Mg, 4280 ppm: Sr, 130 ppm: Na, 180 ppm) specimens from the Rundle of Alberta, some rounding of the calcite surfaces is visible in SEM (Figure 5, plates E,F). This rounding is probably related to dissolution of the diagenetic calcite in a later, more corrosive diagenetic environment. Thus, microstructures of crinoids are useful in characterizing least-altered and most-altered specimens, but are of only limited value for the mass of specimens in the broad geochemical range related to intermediate stages of post-depositional alteration.

Stable Isotopes

The stable isotope values of the crinoids fall into two distinct fields (Figure 6). Furthermore,

samples closest to the original field display two divergent trends. Those in trend one generally maintain their $\delta^{13}C$ values, but their $\delta^{18}O$ values show a steady enrichment in ^{17}O with progressive stepwise alteration. Most of the samples in this group are Carboniferous in age. The Burlington Limestone crinoids, based on trace element contents, include some of the most altered specimens, but their stable isotope values stipulate a possible marine origin for the diagenetic fluid(s). In contrast, the specimens from the Madera Formation, which are less altered based on trace elements, have isotope values postulated to be derived during post depositional alteration in the presence of mixed marine-meteoric water. On the other hand, the specimens from the Brush Creek (Pennsylvania) and Breathitt (Kentucky) most likely altered in the presence of meteoric waters (cf. Brand and Morrison, 1987; Brand, 1987b).

The samples in the other group, with increasingly lighter $\delta^{13}C$ and ^{18}O values, are the Silurian (Brand and Veizer, 1981) and Devonian crinoids (Popp, 1981). The Silurian specimens are postulated to have altered in the presence of meteoric-dominated diagenetic waters.
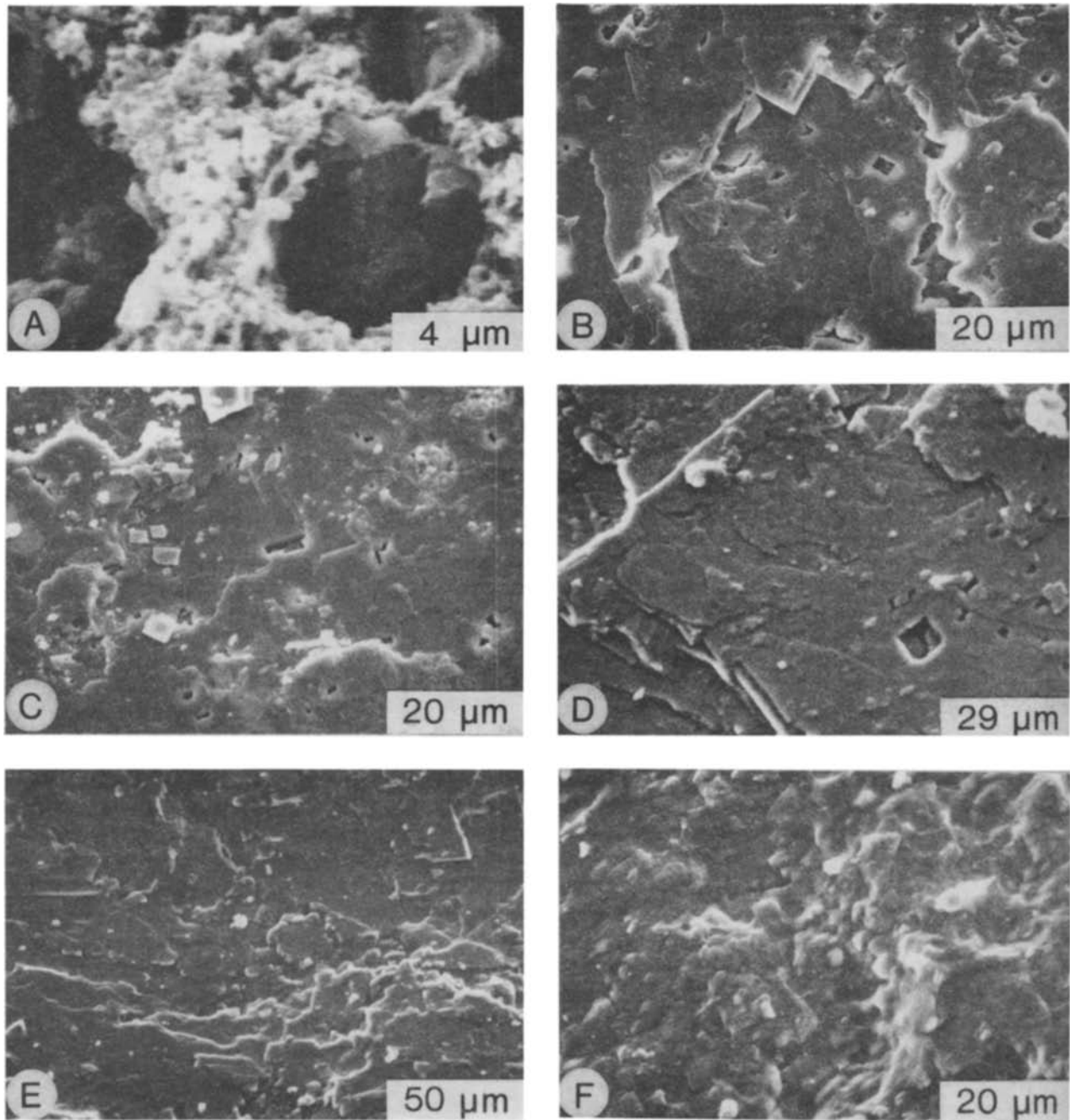
Figure 5.--Scanning electron photomicrographs of some originally high–Mg calcite crinoids. Plate A is a specimen from the Brush Creek Member at Sewickley, Pennsylvania (Brand and Morrison, 1987). Plate B is a crinoid from the Kiewitz Shale at Ash Grove, Nebraska. Plate C is a specimen from the Magoffin Member of the Breathitt Formation at locality 4 of Dennis and Lawrence (1979; Brand, 1987b). Plate D represents a crinoid from the Madera Formation at Sierra Lucero, New Mexico. Plates E and F are examples of microstructures in specimens from the Rundle Group near Moose Mountain, Alberta.
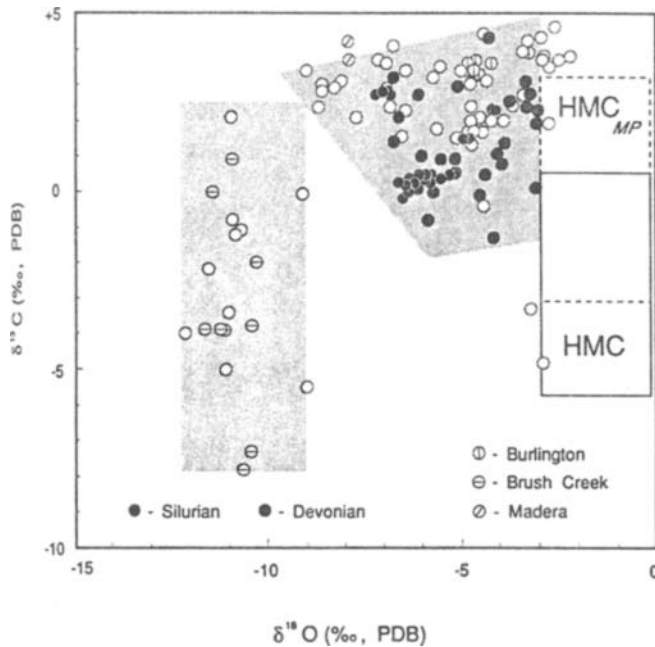
Figure 6.--Stable isotope compositions of Carboniferous (open symbols), Devonian and Silurian crinoids. The HMCR and HMCMP fields represent the isotopic ranges measured and postulated for echinodermal calcite precipitated in modern and mid Paleozoic seawater, respectively (Brand, 1989b). The lightly shaded field represents specimens which altered in the presence of meteoric water, whereas those in the other field probably were subjected to alteration by fluid(s) of marine/meteoric derivation. Symbols as Fig. 1.

Factor Analysis

Varimax-rotated factor analysis of the Silurian and Carboniferous crinoids shows that three factors account for all the resolvable geochemical variation observed in these samples (Table 2). Factor 1, which accounts for 59.0% of the variation is interpreted to represent the diagenetic alteration of the originally high-Mg calcite skeleton of crinoids. This factor shows about equal loading for Mg and Sr (cf. Figure 2) and slightly lower loading on Na (cf. Figure 1). The lower loading for Na reflects the postulated early-diagenetic loss of body and inclusion fluids from the stereom and stroma. The trends for the other two diagenetic tracers is highly significant with good communality (Table 2).

Factor 2, which represents about 30% of the total geochemical variation, is loaded by I.R., Al, Mn and Fe. Based on similarities of loadings and geo-

chemical comparison of data, the I.R. and Al are paired and interpreted to represent laboratory leaching, whereas Mn and Fe are paired and represent a strong control of depositional conditions (Veizer, 1977; Brand, 1987 a,b). Comparative evaluation of Fe contents and I.R. shows no significant correlation between these two variables. Instead, the redox sensitivity of Fe and Mn generally subdues other trends such as diagenetic trends as well as some minor leaching from matrix and coatings not removed during the cleaning process. Factor 3, with its similar loadings on I.R., Al and Zn, represents leaching of these elements from the noncarbonate fraction of the sample(s) during weak-acid digestion in the laboratory.

HIGH-Mg CALCITE DIAGENESIS MODEL

Diagenetic trends

Considering the chemistry of depositional and diagenetic fluids, physicochemical parameters of the diagenetic microenvironment, partition coefficients and other thermodynamic properties of high-Mg calcite allows for the postulation of first-order trends for elemental and isotopic redistribution with progressive and stepwise alteration of these biogenic carbonates (cf. Veizer, 1983b; Brand, 1989a,b). In his 1983b paper, Veizer presented hypothetical trends for both aragonite and high-Mg calcite diagenesis. For the calcitization of high-Mg calcite, he listed in decreasing order Fe, Cu, Co, Mn, Ba and Zn as being enriched in the diagenetic product. Concomitantly, Na, Mg, U, ^{13}C, Sr and ^{18}O decrease in magnitude during the alteration process (Veizer, 1983b, Figure 14). However, he based these trends on theoretical information of least- and most-altered biogenic carbonates, while considering all the kinetic and thermodynamic properties of the minerals, waters and diagenetic systems.

There is general agreement between the postulated diagenetic redistribution trends and directions (Veizer, 1983b, Figure 14) and measured ones based on a large number of crinoids from many different depositional and diagenetic settings (Figure 7). The Mn and Fe contents increase, and at the same time, ^{18}O, Na, Sr and Mg decrease with "step-wise" diagenetic alteration of originally high-Mg calcite. The Mn contents increase faster at lesser degrees of alteration and eventually level off, whereas Fe tends to increase with increasing alteration (Figure 7). At the other end of the spectrum, the ^{18}O and Na
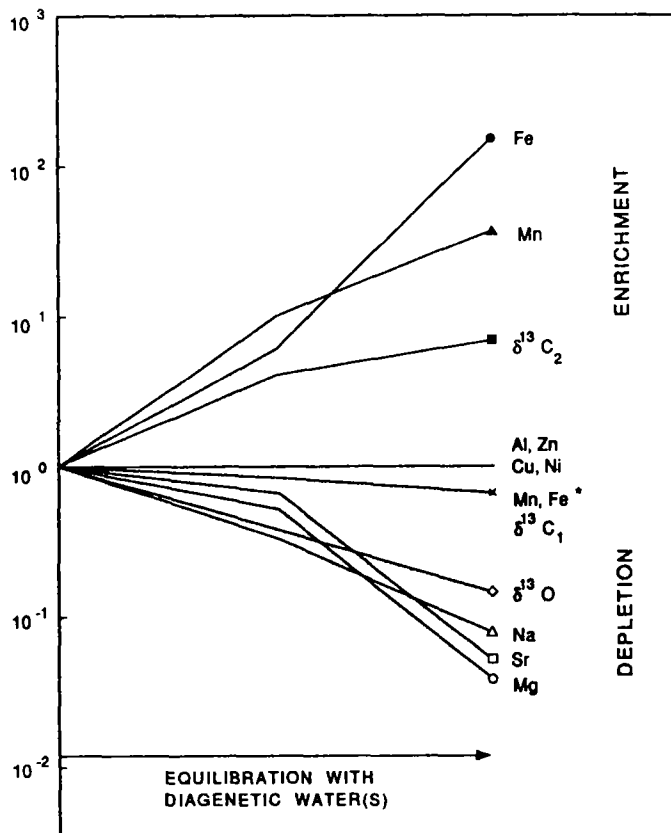
Figure 7.--Summary diagram of changes in trace element contents and stable isotope compositions during the diagenetic alteration of originally high-Mg calcite. The increase/decrease for the $\delta^{13}C$ compositions depends on the type of diagenetic water involved in the alteration process. The trends for the re-distribution of Fe and Mn contents depends on the chemical parameters (redox) of the diagenetic and/or depositional fluids. Fe and Mn, with an asterisks, define diagenetic trends of specimens from shales, whereas those without symbols represent trends for specimens from limestones.

contents consistently decrease with increasing degrees of diagenetic alteration, whereas the tempo increases for both Sr and Mg (Figure 7). No significant changes in elemental contents with post-depositional alteration of originally high-Mg calcite were recorded for Al, Zn, Cu and Ni. This lack of trends for these elements may be related to low instrument sensitivity, insufficient knowledge about partitioning coefficients, water chemistries of both epeiric seas and diagenetic waters and/or some yet undefined factor(s) (cf. Brand, 1989a).

A few exceptions were noted in the elemental and isotopic redistribution trends. Mn and Fe con-

Table 3. Equations defining the elemental and isotopic diagenetic trends for the high-Mg calcite-calcite transformation process and the magnitudes of the diagenetic alteration.

Element	Enrichment-depletion equation	r^2	Magnitude (xA/xUn)	Veizer (1983b)
Mg	$\Delta Mg = 3.3e^{+4} - 327.1$ D.A.	0.997	-26	-18
Sr	$\Delta Sr = 2131.7 - 19.7$ D.A.	0.989	-20	-5
Na	$\Delta Na = 1764.7 - 16.2$ D.A.	0.988	-13	-70
$\delta^{18}O$	$\Delta^{18}O = -0.8 - 9.9e^{-2}$ D.A.	0.940	-7	-2
$\delta^{13}C_1$	$\Delta^{13}C_1 = -2.7 - 7.71e^{-3}$ D.A.	0.998	-1.5	-9
$\delta^{13}C_2$	$\Delta^{13}C_2 = -2.6 + 5.9e^{-2}$ D.A.	0.996	+7	
Mn	$\Delta Mn = 17.2^* 10(1.6e-2$ D.A.)	0.973	+37 (-2)	+100
Fe	$\Delta Fe = 37.4^* 10(2.3e-2$ D.A.)	0.974	+150 (-2)	+7000
Cu			0	+700
Zn			0	+9
Ni			0	N.D.
Al			0	N.D.
Co			N.D.	+200
Ba			N.D.	+20
U			N.D.	-18

Note: -,+ denote decrease and increase of respective element/isotope during high-Mg calcite diagenesis; N for elements is 368, and for isotopes it is 153. D.A. - the degree of diagenetic alteration; r^2 - coefficient of determination; xA, xUn - chemical means of altered and unaltered sample populations, respectively; N.D. - not determined. Magnitudes of Veizer (1983b, p. 285) were taken from his Figure 14. $\delta^{13}C_1$ and $_2$ trends are alteration by pre-dominantly meteoric and mixed waters, respectively. Enrichment trend for Mn and Fe applies to most sample populations, whereas the depletion trends are for some material from shales (Fig. 7).

tents decrease with increasing diagenetic alteration in some of the specimens from the Brush Creek and Breathitt Formations (Figure 4). Also, the ^{13}C content either increases ($\delta^{13}C_3$) or decreases ($\delta^{13}C_1$) depending on the fluid involved in the process during diagenetic alteration. It is postulated that mixed and meteoric waters were involved in these diagenetic alterations, respectively.

Magnitudes of diagenetic trends

Elemental and isotopic contents vary significantly betweendepositional high-Mg calcite and diagenetic calcite (Table 3). The hypothetical enrichment/depletion factors range from +7000 for Fe to -2 for $\delta^{18}O$, with intermediate values for the other elements/isotopes for alteration in fluid-controlled diagenetic systems (Veizer, 1983a, b). It is difficult to envisage diagenetic environments with suitable physicochemical conditions required by these large enrichment/depletion factors. Problems between hypothesized and measured magnitudes of alteration trends for carbonate grains may be related variation in the modes of reprecipitation and openness of the diagenetic microenvironment (cf. Pingitore et al., 1989; Brand, 1989a).

Trends and especially magnitudes are significantly different for the sample populations of this study (Figure 7, Table 3) compared to those postulated by Veizer (1983b) for high-Mg calcite altered in open (fluid-controlled) systems. Enrichment/depletion magnitudes are higher by factors of about 1.5 to 4 for Mg, Sr and $\delta^{18}O$, whereas they are lower by factors of about 3 to 50 for Mn, Na, $\delta^{13}C$ and Fe (Table 3). The difference in the Na magnitudes between the two studies probably relates to the high sodium content of body fluids and fluid inclusions of originally high-Mg calcite (cf. Figure 1). This influence of fluids was not included in the computations for the diagenetic enrichment-depletion equation of Na (Table 3). The other differences in magnitudes between hypothesized and measured magnitudes may be related to uncertainties in the physicochemical conditions of the diagenetic waters and/or in the partition/fractionation coefficients (Brand and Veizer, 1980). This argument most likely applies to the re-distribution of Sr, Mn and Fe in carbonate grains. Greater uncertainty is noted for the magnitudes of Cu and Zn with enrichments postulated by Veizer (1983b), whereas no significant changes in their magnitudes were observed in the studied material.

Diagenetic Models

The studied sample populations, based on all diagenetic indicators (mineralogy, microstructures, trace elements and stable isotopes), reflect fluid and diffusion-controlled reaction systems and water regimes of marine, meteoric and mixed origins. Specimens from the Burlington Limestone of Iowa and Missouri probably were cemented and altered in fluid-controlled and slightly reducing marine water-dominated diagenetic microenvironments (Figure 8). This assertion deviates from the results of Brand and Veizer (1980) and Kauffman et al. (1988) who postulated a meteoric water source for the crinoids/cements and cements, respectively. It is highly possible that the alteration of the metastable crinoid mineralogy preceded the general cementation and lithification of the Burlington sediments. This may well account for the lithification of the crinoids in a marine water-dominated (minor mixing of meteoric water) diagenetic system, and with continual uplift of the sediments into the terrestrial environment, alteration and cementation processes were controlled by meteoric water.
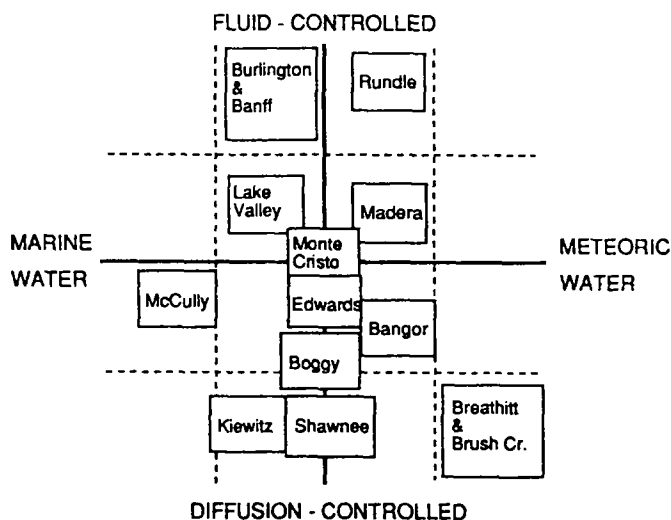
Crinoids from the Madera Formation of cen-

Figure 8.--Model of diagenetic system for the diagenetic alteration of biogenic high-Mg calcites. Fluids of the Model are from left to right; marine water-controlled, marine water-dominated (minor meteoric component), meteoric water-dominated (minor marine component), and meteoric water-controlled. Diagenetic processes of the Model are from top to bottom; fluid-controlled, fluid-dominated (minor diffusion reaction), diffusion-dominated (minor fluid reaction), and diffusion-controlled reactions. Placement of individual sample populations is based on both trace element contents and isotopic values.

tral New Mexico are postulated to have altered in a meteoric water-dominated and fluid-controlled system (Figure 8). At the other of the spectrum are the crinoids from both the Breathitt and Brush Creek which altered in systems controlled by meteoric waters and diffusion reactions (Figure 8; cf. Brand, 1987b: Brand and Morrison, 1987). Meyers and Lohmann (1985) postulated that Lake Valley crinoids altered in the presence of meteoric waters in a relatively open system. This is partly confirmed by the crinoid data of this study. It is postulated here that the studied crinoids from the Lake Valley altered in a fluid-dominated system wetted by marine water-dominated (with minor meteoric water) fluids (Figure 8). Another unusual occurrence are the crinoids from the Kiewitz Shale of Nebraska. Their high elemental and ^{18}O contents but relatively light $\delta^{13}C$ values (+1.2 to -0.4°/oo) suggest alteration in a diffusion-controlled and marine water-dominated system with the input of isotopically-light CO_2 from decomposing organic matter.

Blake et al. (1982) and Brand (1989a) postulated that the echinoderms and molluscs from asph-
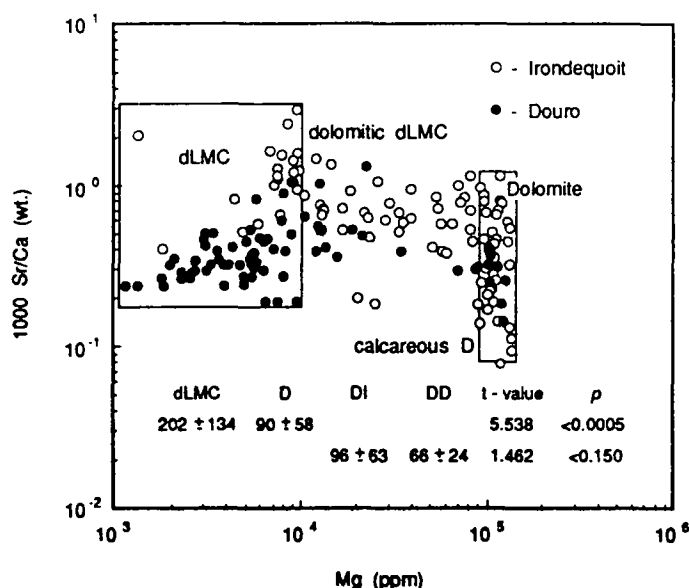
Figure 9.--Dolomitization trends of Silurian crinoids from the Irondequoit Limestone, southern Ontario, and the Douro Formation, Arctic Canada (Table 1). The dLMC fields are from data of this study and Brand and Veizer (1980). The dolomite fields represent stoichiometric dolomite compositions. Statistical data are for Sr contents of diagenetic low-Mg calcite (dLMC) and dolomites (D) from both the Irondequoit (DI) and Douro (DD) Formations.

altic-rich units of the Boggy Formation in the Buckhorn quarry altered in a closed or nearly-closed (diffusion-controlled to dominated) system mediated by small volumes of meteoric water. The Boggy crinoids of this study came from the creek locality (Squires, 1973) which is southwest of the quarry; asphalt is only a minor component at this site. Therefore, aragonitic fossils are rare and echinoderms are more altered than those from the quarry. Thus, the diagenetic regime which affected the crinoids of this study differs from those hypothesized by Blake et al. (1982) and Brand (1989a) for the quarry sediments. It is postulated to have been a microenvironment controlled by mostly diffusion-dominated reactions with mixed water (Figure 8). This reflects the slightly different trace element and stable isotope chemistries of the crinoids compared to those of the biogenic carbonates from the quarry. Therefore, the diagenetic history of the lower Boggy sediments involved mixed water, progressing into meteoric water regimes for the later sediments of the quarry (Blake et al., 1982; Brand, 1989a), and possibly a third phase of alteration/cementation involving CO_2-charged formation waters (Sadd, 1986) during injection of the oil into the upper sediments

of the formation.

The crinoids from the other units such as Banff, Rundle, Monte Cristo, Edwardsville, Bangor, Shawnee, and McCully fall into different diagenetic regimes based on their microstructure, trace element and stable isotope data (Figure 8). The multitude of diagenetic regimes postulated for the alteration of the different sample populations supports the concept of "stepwise" alteration for high-Mg calcite crinoids (e.g. Plummer and Mackenzie, 1974). This reiterates the observation that biogenic carbonates have to be evaluated on an individual basis (cf. Brand, 1989a,b).

DOLOMITIZATION

Trace elements

Trace element content has been used to differentiate between the various types of dolomite (e.g. Land, 1980). However, the mixture of depositional mineralogies for carbonates complicates the establishment of reliable diagnostic criteria. The mineralogical uncertainty is removed in this study by using crinoid material from the Irondequoit of southern Ontario and from the Douro of Cornwallis Island (Table 1, Brand and Veiwer, 1980; Brand and Milinkovitch, 1984). In some localities the crinoids and matrix have been extensively dolomitized by obviously 'secondary' processes. Trace chemistries of the diagenetically altered material from both localities are slightly different, probably reflecting physicochemical differences in the diagenetic microenvironments (Figure 9). Based on all geochemical data, it is postulated that the crinoids of the Irondequoit Formation altered in a system controlled by meteoric water via diffusion-dominated reactions. In contrast, the crinoids of the Douro Formation probably altered in meteoric- and fluid-dominated diagenetic systems.

The Sr chemistry is significantly different between the crinoids of the dLMC and D populations ($p \leq 0.0005$). This is not an artifact of Sr differences between the two populations, because the slight difference in chemistry of the dLMC-crinoids is homogenized by the subsequent dolomitization process ($p \leq 150$, Figure 9).

Partition coefficients for K^{Sr}_D range from 0.07 to 0.02 with arguments presented for the validity of both end members (see Land, 1980). Using a K^{Sr}_D of 0.05 for the high-Mg calcite to calcite transformation
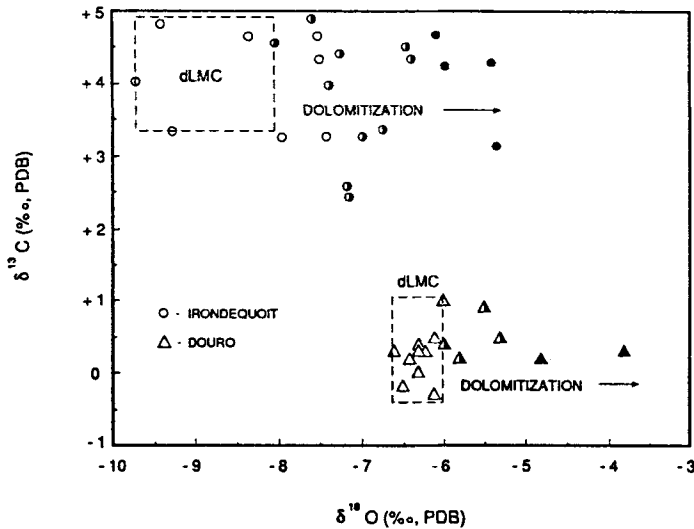
Figure 10.--Geochemical characterization of the different dolomite varieties from the Irondequoit and Douro Formations. The divisions and concentration limits for the ferroan dolomite and ankerite fields are based on data from Goldsmith et al. (1962) and from Beran and Zeman (1977), respectively. Statistical trends include dLMC data of each population.

and chemistries of the postulated waters, the observed Sr levels in the studied material are similar to the calculated ones. However, in subsequent calculations for the dolomitization process, a K^{Sr}_D of 0.07 and water mixtures ranging from 10-50% seawater give results (>200 ppm Sr) which are inconsistent with the observed data (Figure 9). However, with a K^{Sr}_D of about 0.02 and mixed water chemistry, the calculated Sr concentration (90 ppm) is identical to the mean of all the dolomitized crinoid data (Figure 9). This simple calculation supports the assertion of Katz and Matthews (1977) for a low $(K^{Sr}_D \sim 0.025)$ partition coefficient for the dolomitization of diagenetically stabilized high-Mg calcite in a fluid-controlled system (Land and Epstein, 1970; Fritz and Smith, 1970).

Although the dolomitized crinoids from the Irondequoit and Douro have similar Sr and Mg chemistries, their Fe and Mn contents differ significantly. Two divergent trends are evident for the material from the two formations (Figure 10). This divergence in Fe content is also demonstrated by Mn (not shown) and staining of thin sections (Brand and Veiwer, 1980; Brand and Milinkovitch, 1984). Statistical tests discount laboratory leaching of matrix and/ or oxides as causes for these trends. Instead, it is
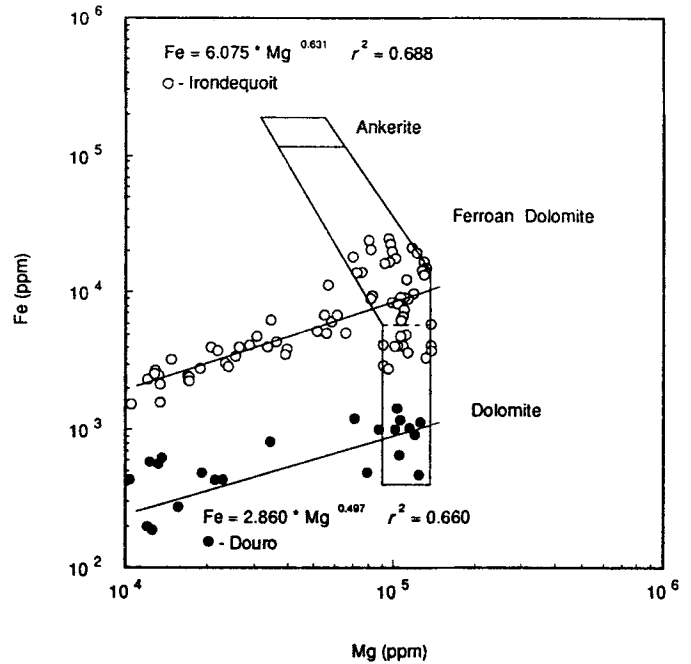

Figure 11.--Stable isotope re-distribution of the diagenetically stabilized crinoids from the Irondequoit and Douro Formations and their subsequent transformation into dolomite. The trend towards heavier $\delta^{18}O$ values is in agreement with dolomitization by mixed waters (e.g. Land, 1980,1983; Budai et al. 1987).

postulated that the dolomitizing fluids of the Douro were oxic and shales, which may be a source for Fe and Mn, are not closely associated with the Douro. In contrast, the Irondequoit is overlain by the Rochester shale and it is postulated to be the source for these two elements in the dolomitizing fluids migrating over and through the sediment column of southern Ontario at that time.

Stable Isotopes

The diagenetically and dolomitized crinoids from the Irondequoit and Douro fall into isotopically two distinct fields. The $\delta^{13}C$ values of the Irondequoit crinoids are heavier by about 4°/oo compared to those from the Douro (Figure 11). This difference in $\Delta^{13}C$ does not diminish with progressive dolomitization of the specimens from both localities. It is postulated that this difference is a reflection of fluctuations in salinity, oxidation/fermentation of organic matter in the depositional and/or diagenetic environments. Secular variation of the oceanic bicarbonate reservoir is discounted because of the similar age for the two units. Also, latitude is not a viable explanation, because both units were within

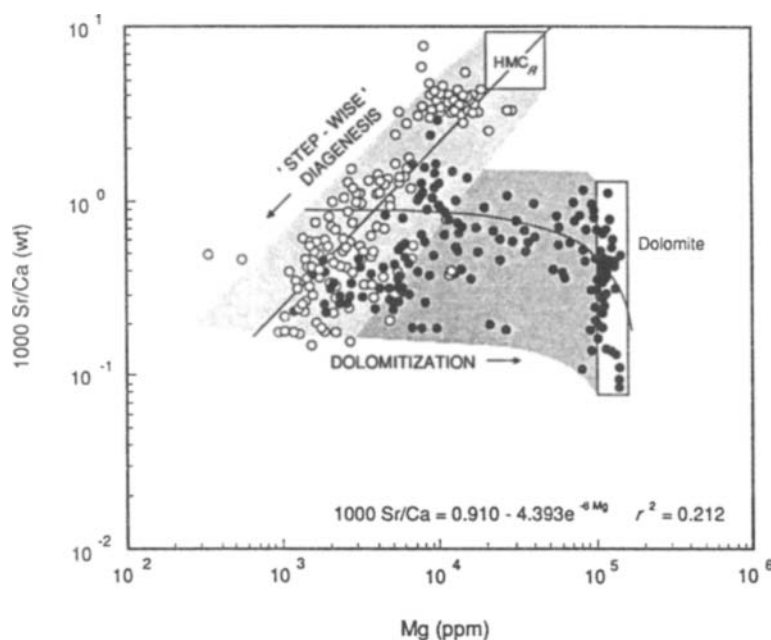$$1000 \, Sr/Ca = 0.910 - 4.393e^{-4\,Mg} \qquad r^2 = 0.212$$

Figure 12.--Summary trends for the diagenetic alteration and subsequent dolomitization of originally high-Mg calcite. The correlation equation represents the dolomitization trend of crinoidal Sr/Ca and Mg. The equation for the diagenetic trend as in Fig. 1. Heavily stippled area represents dolomitic and calcareous dolomite specimens. Fields as explained in Figs. 1 and 9.

the paleotropics and subject to meteoric waters with isotopic compositions of about $-2^{\circ}/oo$ relative to contemporaneous seawater (Anderson and Arthur, 1983). Using $\delta^{13}C$ values of Silurian brachiopods from the Ludlowville Formation, it was postulated that a habitat influenced by differential input of light carbon from the oxidation of terrestrial/marine organic matter is the most plausible explanation for the differential $\delta^{13}C$ values of the two crinoid populations (Brand, 1989b).

Experimental work suggests that secondary dolomite should be enriched relative to coeval calcite in ^{18}O by about $4-7^{\circ}/oo$ (e.g. O'Neil and Epstein, 1966; Friedman and O'Neil, 1977; Land, 1983). The dolomitized crinoids of this study are enriched in ^{18}O relative to their non-dolomitized counterparts (Figure 11). The $\Delta^{18}O$ for the dLMC-dolomite of the two populations is consistent with about $+2.5^{\circ}/oo$, and fits the postulated range of $+1$ to $+7^{\circ}/oo$ based on experimental and applied data (Land, 1983, p. 92). The difference in $\delta^{18}O$ between the two populations is ascribed to secular variation of seawater-^{18}O content and/or habitat (e.g. Brand, 1989b). However, the relative similarity in paleolatitude setting (trop-

ics) for the two localities decreases the importance of this factor. If it is secular variation this would demand a shift of about $2^{\circ}/oo$ between Wenlockian and Pridolian epeiric seawater (Figure 11). More data of preserved Silurian biogenic carbonates are required to test this hypothesis.

The trace element and stable isotopes chemistries of the Irondequoit and Douro crinoids support the assertion that dolomitization of these two units took place in a fluid-controlled (open) system (Land and Epstein, 1970; Fritz and Smith, 1970; Land, 1983), dominated or control led by meteoric water with admixtures of marine water.

SUMMARY

This work demonstrates that biogenic carbonates from different units have to be evaluated individually for their diagenetic regime (Figure 8), and the material studied from the Boggy and Burlington Formation require separate evaluations even for the different horizons/cement stages.

Despite all these differences in water types and reactions involved in the diagenesis of originally high-Mg calcite crinoids, alteration of the stereom and cementation of the stroma leads to progressively lower Sr and Mg contents (Figure 12). However, we must distinguish between progressive alteration (e.g. Pingitore, 1978; Brand and Veizer, 1980) where the degree of alteration within a particular unit was control led by sediment size and type, water type and water/rock ratio of the diagenetic microenvironment, and 'Stepwise' alteration (Plummer and Mackenzie, 1974) where variations in both water type(s) and reaction(s) are involved in the post-depositional alteration of carbonate grain(s) (Figure 12).

Dolomitization of precursor dLMC derived from originally high-Mg calcite supports the postulated re-partitioning trends and magnitudes of elements determined by experiment (Figure 12). In addition, chemical and isotopic values support the assertion that dolomitization of precursor dLMC is a fluid-controlled reaction dominated by meteoric water with variable admixtures of marine waters (Ward and Halley, 1985).

CONCLUSIONS

Microstructural, geochemical and statistical analyses of crinoids in conjunction with published

results suggest the following conclusions regarding the diagenetic alteration and dolomitization of biogenic high-Mg calcite.

1. During early alteration the stroma of crinoids was rapidly filled by cement, while the specimen(s) still resided in the marine environment or shallow sediment column. Skeletal pore space is only preserved in specimens effectively shielded from diagenetic fluids by either asphalt and/or shale formations in conjunction with rapid burial. Cementation and alteration of skeletal high-Mg calcite generally obliterates primary microstructures and mineralogy.

2. These morphological/mineralogical alterations are accompanied by concomitant trace-element and stable isotope changes. Alteration of high-Mg calcite to diagenetic low-Mg calcite generally leads to an increase in Fe and Mn contents for most crinoids, although a few specimens from shales showed decreases in their Fe and Mn contents with alteration. Conversely, it leads to a decrease in Na, Sr and Mg, and to lighter $\delta^{18}O$ values. The direction for $\delta^{13}C$ appears to be strongly controlled by the CO_2 composition of the diagenetic water(s). Other elements, such as Al, Cu, Ni and Zn show no significant trends.

3. The redistribution of tracers leads to increases between depositional and diagenetic phases by factors of 7 to 150 for $\delta^{13}C_2$, Mn, and Fe, respectively. In contrast, for Mg, Sr, Na, $\delta^{18}O$ and $\delta^{13}C_1$, compositions decrease by factors ranging from 26 to 1.5. These trends and the multimethod approach can be used to determine the degree of alteration for biogenic high-Mg calcite skeletal material.

4. Alteration of the crinoids was dominated by marine- and meteoric-water systems with minor inputs from the other water type. Reaction processes vary from fluid- to diffusion-controlled. For example, the Burlington and Banff crinoids most likely altered in a diagenetic system dominated by marine waters proceeding via fluid-controlled reactions. In contrast, the specimens from the Breathitt and Brush Creek altered in the presence of meteoric waters through diffusion-controlled reaction processes. A more complex scenario, is depicted by the mollusc, brachiopod and crinoid material from the Boggy Formation, where early alteration of the crinoids (from DB I-Ill) proceeded in mixed waters followed by meteoric alteration of the aragonitic molluscs in the Buckhorn asphalt quarry, with a possible later

cementation event. This multitude of diagenetic settings suggests that alteration of high-Mg calcite is a 'stepwise' diagenetic process controlled by water types and amounts.

5. Based on geochemical data, dolomitization of the diagenetically stabilized crinoids proceeded in a fluid-controlled system in the presence of mixed waters. The postulated K^{Sr}_D of about 0.02 is similar to the experimentally determined value. The $\Delta^{18}O$ value for the diagenetic low-Mg calcite-dolomite is about +2.5°/oo which lends further support to the postulated physicochemical parameters of the dolomitizing microenvironment. Formation of ferroan dolomite depends source and the redox condition of the dolomitizing fluid.

ACKNOWLEDGEMENTS

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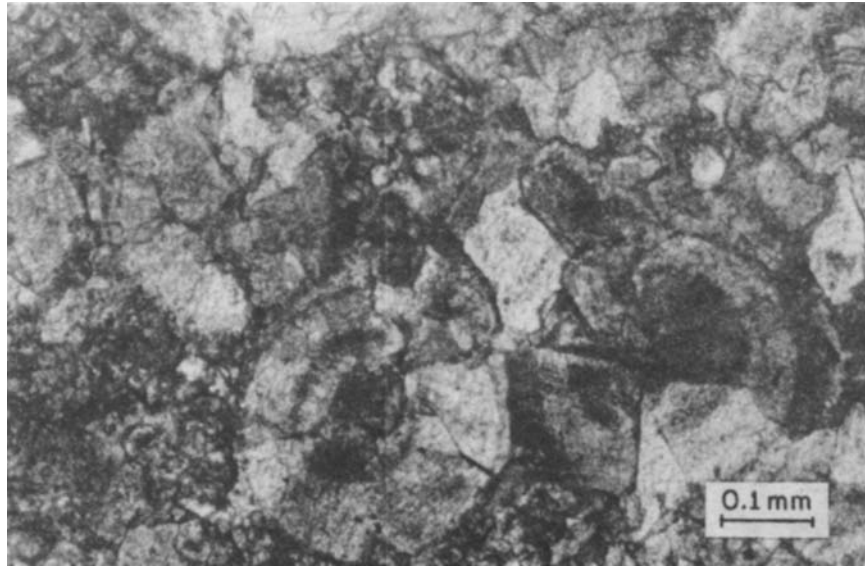
Photomicrograph of dolomitized ooid grainstone. Note that despite pervasive dolomitization, ooid nuclei and concentric laminae are visible. Tribes Hill Formation, Lower Ordovician, Mohawk Valley, New York (Figure 10 on page 231 in Curl, M.W., Zagorski, T.W. and Friedman, G.M., 1984, Depositional environments and diagenesis of subsurface Tribes Hill Formation (Lower Ordovician), Mohawk Valley, New York: The Compass of Sigma Gamma Epsilon, v. 61, p. 216-243).

Photomicrograph of skeletal grainstone. Fossil fragments have created shelter porosity. Euhedral dolomite crystals surround allochems. Tribes Hill Formation, Lower Ordovician, Mohawk Valley, New York (Figure 15 on page 236 in Curl, M.W., Zagorski, T.W., and Friedman, G.M., 1984, Depositional environments and diagenesis of subsurface Tribes Hill Formation (Lower Ordovician), Mohawk Valley, New York: The Compass of Sigma Gamma Epsilon, v. 61, p. 216-243).