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LA THÈSE A ÉTÉ
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GEOCHEMISTRY OF PALEOZOIC CORALS, CRINOIDS AND ASSOCIATED CARBONATE ROCKS FROM ARCTIC CANADA, IOWA AND MISSOURI

A Dissertation
Presented to
the School of Graduate Studies
University of Ottawa

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
in Geology

by
Uwe Brand
1979

Dr. J. Veizer Dissertation Supervisor

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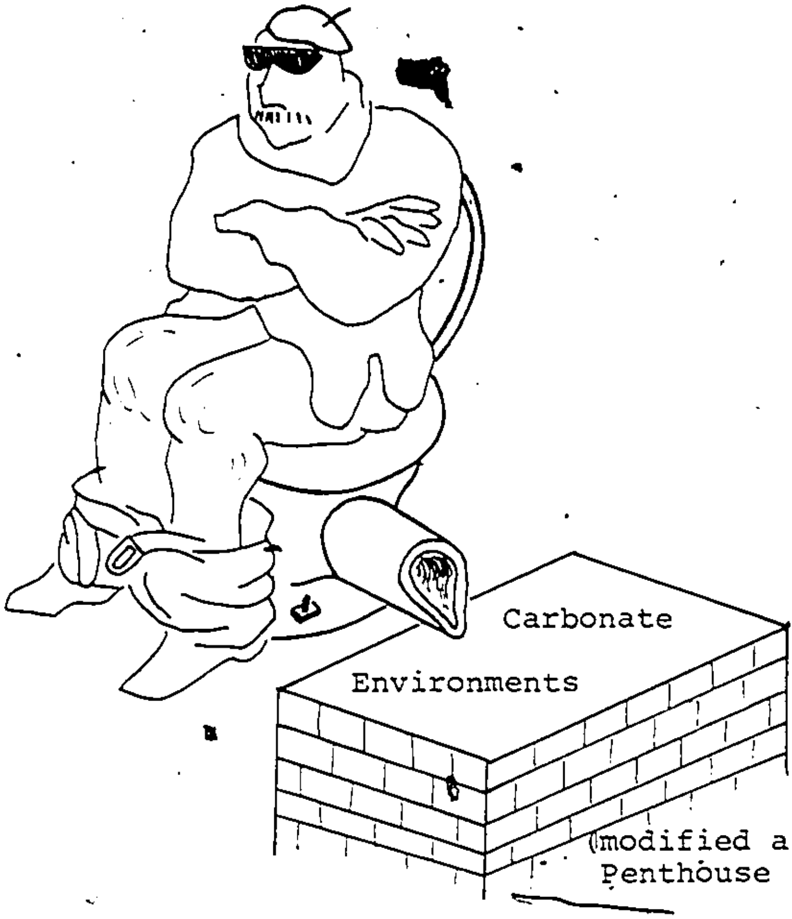

(modified after Penthouse '78)

IN DEALING WITH DIAGENETIC PROBLEMS, GEOLOGY BY ANALOGY MAY HAVE SERIOUS SHORTCOMINGS

R.K. MATTHEWS
1973

GENERAL ABSTRACT

Theoretical consideration of diagenetic stabilization by meteoric waters suggests that it leads to a decrease in $\delta^{18}O$, $\delta^{13}C$, Sr, Na and possibly Mg and increase in Mn and Fe in progressively altered carbonates.

The combination of elemental patterns and textural trends shows that the Burlington Limestone (Mississippian, Iowa and Missouri) was completely equilibrated with meteoric waters, while the Read Bay Formation (Silurian, Arctic Canada) was less affected.

As a consequence, in the Burlington Limestone the rock matrix (ie. biosparite), the enclosed crinoids (composed originally of high-magnesium calcite) and to some degree the rugose corals (composed originally of low-magnesium calcite) are chemically identical. The crinoid ossicles have an average Sr content of 160 ppm, rugose corals 180 ppm and the enclosing biosparite 120 ppm.

In contrast in the Read Bay Formation all the above mentioned internal components have specific chemistry, with 210 ppm Sr for the crinoids, 780 ppm for rugose corals and 360 ppm for their enclosing micritic matrix.

The rate at which a particular internal component approach the open system equilibrium is dictated by its respective mineralogical stability. The path of this equilibration for each fossil group can be traced across facies on Sr-Mn covariance diagrams.

Oxygen and carbon isotopic distributions in the separated fossil and matrix components of the Burlington Limestone and the Read Bay Formation can be reconciled with textural and trace element observations , only if it is accepted that the ^{18}O content of ancient oceans differred from that of the present day. Accepting these secular variations, the postulated $\delta^{18}O$ of Mississippian seawater was about 1 ‰ and of the Upper Silurian about 5 ‰ lighter than at present.

The estimated average diagenetic shift in $\delta^{18}O$ of the Burlington Limestone constituents is about −3 ‰ and for the Read Bay Formation constituents about −1‰ (PDB). Correcting for the magnitude of secular variation, the probable paleotemperature for the Mississippian sea of Iowa and Missouri was 31 ± 4°C and for the Upper Silurian sea of Arctic Canada 21 ± 2°C.

Calculations suggest that the Paleozoic rugose corals and crinoids were not enriched in ^{12}C and ^{16}O, rather they are in line with expected results for the studied brachiopods. The apparent "vital effect" of Recent scleractinian corals and crinoids may not be applicable to their Paleozoic [illegible]unterparts.

The $\delta^{13}C$ of the studied samples is bimodally distributed, with +0.5 ± 0.4 and +3.0 ± 0.7 ‰ as modes of the groups. The light-^{13}C group is characteristic of inorganically derived aragonite mud matrix and/or cement precipitated in equilibrium with ambient seawater. The heavy-^{13}C group is associated with samples from organic build-ups or from areas of high concentrations of skeletal debris. The cement of this group is organically derived high-Mg calcite and aragonite cement precipitated in carbon isotopic disequilibrium with ambient seawater.

Cementation of the Read Bay Formation sediments, which, in general, fall into the light-^{13}C group, proceeded in the submarine environment. On the other hand, most of the Burlington Limestone samples fall into the heavy-^{13}C group, and were initially cemented in the submarine environment, followed by subsequent cementation in the meteoric phreatic environment.

While the results show that the carbonate assemblage may act as a completely open diagenetic system (eg. Burlington Limestone), available data for the majority of studied sequences suggest that diagenetic equilibration ceases while some internal differences in chemical composition only are still preserved. This supports the concept of diagenetic stabilization in a partly closed reaction zone, which is not in equilibrium with the bulk aquifer water (eg. Read Bay Formation). If so, such chemical criteria could serve as a potential tool for evaluating the degree of diagenesis and for estimating the original composition of the different stabilized carbonate phases.

Also diagenetic dolomites from the Read Bay Formation were examined in this study. These late diagenetic dolostones form as a replacement of stabilized low-Mg calcite limestones with average Sr values of about 450 ppm. This replacement takes place in the "Dorag" fresh-seawater mixing zone.

This transformation is selective for the matrix (30 to 300 microns), while the allochems are usually replaced by larger crystals, but only after the original matrix has been dolomitized.

Any possible original isotopic or chemical differences within or between precursor limestones are eradicated during "Dorag" dolomitization, since this diagenetic transformation proceeds in a more or less open system with respect to the bulk aquifer (pore) water.

This precludes the use of trace elements and stable isotopes as facies, paleoenvironmental or paleoflow indicators for "Dorag" dolostones, while at the same time differentiating this group of dolostones from the "early diagenetic" varieties described by other authors.

GENERAL INTRODUCTION

The purpose of this study is to resolve geochemical gradients which may lead to a better understanding of diagenetic stabilization and "Dorag" dolomitization of carbonates, in other words, define the redistribution of trace elements and stable isotopes of different carbonate components and phases during limestone and dolostone diagenesis.

For this approach different fossil groups were selected to represent by analogy with their possible Recent counterparts, the different carbonate phases (eg. aragonite, high-Mg calcite and low-Mg calcite). Micrite represents the originally aragonite phase, while crinoids represent the originally high-Mg calcite phase and articulate brachiopods and possibly rugose corals represent the originally low-Mg calcite phase.

The fossil components and their enclosing matrix were collected from the Mississippian Burlington Limestone of Iowa and Missouri and the Silurian Read Bay Formation of Somerset and Cornwallis Islands, Arctic Canada.

The main objectives of the study are (1)to define elemental and isotopic behaviour in the course of increasing diagenetic equilibration of carbonate components with meteoric water. If successful, such criteria, combined with textural studies, may be utilized as diagenetic indicators, indicators of the original mineralogy of carbonate components and means to evaluate whether diagenetic stabilization of carbonate rocks is an equilibrium or disequilibrium process in relation to bulk aquifer (pore) water and (2) ascertain whether an increasing degree of dolomitization leads to the evolution of distinct redistribution patterns of trace, minor and major elements and stable isotopes in dolostones and if so, whether these changes are accompanied by textural evolution.

Secondary objectives of this study are (a) to evalute whether dolomitization proceeds via a dissolution - reprecipitation process either in equilibrium or disequilibrium with bulk aquifer (pore) water and (b) to determine whether diagenetic dolomite is formed by direct replacement of the original metastable $CaCO_3$ precursors or through an intermediate stable calcitic phase.

The dissertation is written in manuscript style to facilitate the publication of the results.

Chapter one deals with trace element diagenesis of the different carbonate components and phases. Chapter two is a follow-up of chapter one, in that it examines and attempts to reconcile the stable isotope results during carbonate diagenesis with those gleaned from trace elements. Chapter three is a combined elemental and isotopic study of "Dorag" dolomitization.

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CHAPTER I

TRACE-ELEMENT DIAGENESIS OF A MULTICOMPONENT PALEOZOIC CARBONATE SYSTEM

ABSTRACT

Theoretical consideration of diagenetic stabilization by meteoric waters suggests that it leads to a decrease in Sr, Na and possibly Mg and increase in Mn and Fe in progressively altered carbonates.

The combination of these elemental patterns and textural trends shows that the Burlington Limestone (Mississippian, Iowa and Missouri) was completely equilibrated with meteoric waters, while the Read Bay Formation (Silurian, Arctic Canada) was less affected.

As a consequence, in the Burlington Limestone the rock matrix (eg. biosparite), the enclosed crinoids (composed originally of metastable high-magnesium calcite) and to some degree the rugose corals (composed originally of stable low-magnesium calcite) are chemically identical. The crinoid ossicles have an average Sr content of 160 ppm, rugose corals 180 ppm and the enclosing biosparite 120 ppm.

In contrast in the Read Bay Formation all the above mentioned internal components have specific chemistry, with 210 ppm Sr for crinoids, 780 ppm for rugose corals and 360 ppm for their enclosing micritic matrix.

The rate at which a particular internal component approaches the open system equilibrium is dictated by its respective mineralogical stability. The path of this equilibration for each fossil group can be traced across facies on Sr-Mn covariance diagrams.

While the results show that the carbonate assemblage may act as a completely open diagenetic system (eg. Burlington

Limestone), available data for the majority of studied sequences suggest that diagenetic equilibration ceases while some internal differences in chemical composition are still preserved. This supports the concept of diagenetic stabilization in a partly closed reaction zone, which is not in equilibrium with the bulk aquifer water. If so, such criteria could serve as a potential tool for evaluating the degree of diagenesis and for estimating the original composition of the different stabilized carbonate phases.

RÉSUMÉ

Une considération théorique de la stabilisation diagénétique par les eaux atmosphériques semble indiquer que celle-ci mène à une réduction de la teneur en Sr, en Na et peut-être en Mg, et d'une augmentation de la teneur en Mn et en Fe dans les roches carbonées progressivement altérées.

La combinaison de ces modèles élémentaires et de ces tendances texturales indique que le calcaire de Burlington (Mississippien, Iowa et Missouri) était en équilibre complet avec les eaux atmosphériques tandis que la formation de Read Bay (Silurien, Canada arctique) était moins affecté.

Par conséquent, dans le calcaire du Burlington, la matrice (ex: biosparite), les Crinoïdes qui y sont contenus (composés primitivement de calcite métastable à haute teneur en magnésium), et, jusqu'à un certain point, les Tétracoralliaires (à l'origine, composés de calcite stable à faible teneur en magnésium) sont identiques au point de vue chimique. En moyenne, la teneur en Sr des ossicules des Crinoïdes est de 160 ppm; des Tétracoralliaires, de 180 ppm et de la matrice

(biosparite), de 120 ppm.

En contraste, dans la formation de Read Bay, les constituants internes ci-haut mentionnés ont une chimie caractéristique, avec une teneur en Sr de 210 ppm pour les Crinoïdes, de 780 ppm des Tétracoralliaires et de 360 ppm pour la matrice de micrite.

La vitesse à laquelle une constituant interne distinct s'approche de l'équilibre d'un système ouvert dépend de la stabilité minéralogique particulière du constituant. Le chemin suivi par chaque groupement fossile pour atteindre cet équilibre peut être tracé d'un faciès à un autre sur des diagrammes de covariance de Sr-Mn.

Quoique les résultats font voir que l'assemblage des roches carbonatées peut agir comme un système diagénétique complètement ouvert (ex: le calcaire de Burlington), les données disponibles pour la majorité des séquences étudiées semblent indiquer que l'équilibrage diagénétique cesse alors que certaines différences internes de composition chimique sont encore préservées. Ceci supporte le concepte de la stabilisation diagénétique dans une zone de réaction en partie fermée, qui n'est pas en équilibre avec la masse d'eau souterraine. S'il en est bien ainsi, de tels critères pourront éventuellement servir d'outil pour évaluer le degré de diagénèse et pour trouver la composition primitive des différentes phases stabilizées des roches carbonées.

ZUSAMMENFASSUNG

Die theoretische Betrachtung der diagenetischen Grundwasserstabilisierung deutet an, dass es zu einer Abnahme von Sr, Na und möglicherweise auch von Mg, und zu einer Zunahme

von Mn und Fe, in allmählich, mehr und mehr, veränderten Kalksteinen führt.

Die Kombination von diesen elementaren Mustern und den strukturellen Tendenzen zeigt, dass in den Gesteinen des Burlington Kalksteins (unteres Karbon, Iowa und Missouri) durch Umkristallisation ein geochemisches Gleichgewicht mit Grundwasser hergestellt wurde, während die Gesteine der Read Bay Formation (oberes Silur, kanadischen Arktis) weniger so beeintrachtigt wurden.

Das Ergebnis ist, dass die Gesteinsmatrix (z.B. der Biosparit), die eingeschlossenen Krinoiden (die ursprünglich aus halbstabilen Hoch-Mg Kalzit zusammengesetzt waren) und zum Teil die rugosen Korallen (die ursprunglich aus stabilen Tief-Mg Kalzit zusammengesetzt waren) des Burlington Kalksteins alle chemisch übereinstimmen. Die Krinoidenskelette haben einen Sr-Durchschnittsgehalt von 160 ppm, die rugosen Korallen haben 180 ppm, und der einschliessende Biosparit hat 120 ppm.

Im Gegensatz, zu den oben erwähnten, inneren Bestandteilen, haben dieselben in der Read Bay Formation eine arteigene Chemie, wie 210 ppm Sr in den Krinoiden, 780 ppm in den rugosen Korallen, und 360 ppm in der einschliessenden mikritischen Matrix.

Das Verhältnis, mit welcher jeder individueller innerer Bestandteil sich dem offenen Diagenesesystem nähert, wird von der mineralogischen Stabilität des betreffenden Bestandteils diktiert. Der Umwandlungsweg der verschiedenen Fossilgruppen kann durch Fazies, auf Sr-Mn Koveränderungsdiagrammen verfolgt werden.

Die Ergebnisse zeigen ausserdem, dass die Kalksteinzusammenfügung, sich wie ein vollständiges offenes Diagenesesystem (z.B. Burlington Kalkstein) verhalten kann, jedoch vorhandene Mehrheitswerte von studierten Karbonatschichten deuten an, dass die Diageneseumwandlung anhält, während noch einige innere Erhaltungsunterschiede in der chemischen Zusammensetzung erhalten sind.

Dies bestätigt die Auffassung, dass die diagenetische Stabilisierung in einer teilweise, geschlossenen Reaktionzone vor sich geht, welche zum Hauptteil nicht im Equilibrationszustand mit dem Grundwasser steht.

In diesem Fall können solche Normen als latente Instrumente benutzt werden, um den Diagenesegrad abzuschätzen, und um die ursprüngliche Beschaffenheit der verschiedenen, stabilisierten Karbonatphasen zu berechnen.

INTRODUCTION

Carbonate diagenesis has intrigued and puzzled geologists since Sorby in 1879 looked at carbonate rocks in thin sections. Up to the present diagenesis was usually defined as changes in the chemical distribution of elements, changes in the structure of individual carbonate particles and changes in texture of the accumulated sediment (Pettijohn, 1957, p. 365). These changes take place at or near earth-surface conditions and the transformation involves cementation, compaction and stabilization of the unconsolidated material to form indurated rock.

Previous studies of the above mentioned processes were usually confined to one or two major or trace elements, or isotopes, or were simply of a petrographic nature. In the last twenty years, these different approaches have been supplemented by Scanning Electron Microscope studies of different carbonate components.

Carbonate rock or sediment is a composite of various constituents, which differ structurally, texturally and chemically. In order to minimize the heterogeneity in observed diagenetic trends induced by the original components, the main constituents of the rocks were studied separately. These were the crinoids, brachiopods, rugose corals and their enclosing rock matrix and/or cement. This material came from the Pridolian (Upper Silurian) Read Bay Formation of Somerset and Cornwallis Islands and from the Osagian (Mississippian) Burlington Limestone of Iowa and Missouri (Uyeno, 1977; Harris & Parker, 1964).

The main objective of the present study is to define elemental behaviour in the course of increasing diagenetic equilibration of carbonate components with meteoric water. If successful, such criteria, combined with textural and isotope studies, may be utilized as (a) diagenetic indicators, (b) indicators of the original mineralogy of carbonate components, and (c) means to evaluate whether the diagenetic stabilization of carbonate rocks is an equilibrium or disequilibrium process in relation to bulk aquifer water.

REGIONAL GEOLOGY

Arctic Canada

The first systematic study of Arctic Geology was initiated in 1950 by Y.O. Fortier and R. Thorsteinsson of the Geological Survey of Canada. Thorsteinsson (1958) designated two type sections for the Read Bay Formation on the east coast of Cornwallis Island, one at Goodsir Creek for Members A and B, and one in an unnamed creek at Read Bay for Members C and D.

The Read Bay Formation of Somerset Island according to Gibling & Narbonne (1977, p. 1148) "... is composed of nodular and wavy-bedded, mottled and argillaceous limestones with rare oolitic and shelly calcarenites ...". Jones & Dixon (1977) gave a detailed account of the boundaries and stratigraphic descriptions of the formation on northern Somerset Island. The average thickness of the formation on Somerset Island is approximately 250 m (Jones, 1974; Jones & Dixon, 1977; Savelle, thesis, 1979). The Read Bay Formation of Somerset Island can be correlated with Member A of the Read Bay on Cornwallis Island (Gibling & Narbonne, 1977).

The material collected from the Read Bay Formation of Cornwallis Island came from Member C, which according to Thorsteinsson (1970, p.558-559) consists of 3775 feet (1151 m) of "... beds similar to Member A, but with biostromal and biohermal developments that are thicker and commonly dolomitized ...". Inclement weather in 1958 prevented Thorsteinsson from completing his work at Read Bay and a detailed account of Member C at its type section is still not completed. His graphic measurements indicated a thickness of about 4725 feet (1440 m) for Member C (Thorsteinsson, 1958).

In the summer of 1977 the author measured the thickness of Member C at Read Bay as 1310 m. This compares closely to graphic and bed-by-bed measurments (1290 m and 1272 m, respectively) obtained by J.J. Packard (1978, pers. comm.).

Arctic samples came from the Read Bay Formation at Garnier Bay, Fury Beach, Creswell Bay and Cape Garry of Somerset Island and from Member C of the Read Bay Formation at Goodsir Creek, Depot Point Lake, Read Bay and Cape Rescue on the east coast of Cornwallis Island (Fig. I-1). For detailed lithologic and stratigraphic descriptions of these localities see Jones (1974), Jones & Dixon (1977), Mayr (1978) and Gibling & Narbonne (1977) and Appendix I.

Iowa and Missouri

The Burlington Limestone from which the remainder of the samples were collected was named by James Hall (1857) to replace the term "Encrinital Group of Burlington" of Owen (1852). The type section of the Burlington Limestone is in Crapo Park, Burlington, Iowa (Owen, 1852). There the formation forms a northeast-facing escarpment overlooking the Mississippi River.

According to Spreng (1961, p. 149) the formation generally has a "... coarse grained, crinoidal, light-colored, stylolitic character ...". Harris & Parker (1964) studied the formation in detail in Iowa and subdivided it into the Dolbee Creek, Haight Creek and Cedar Fork Creek Members. These subdivisions

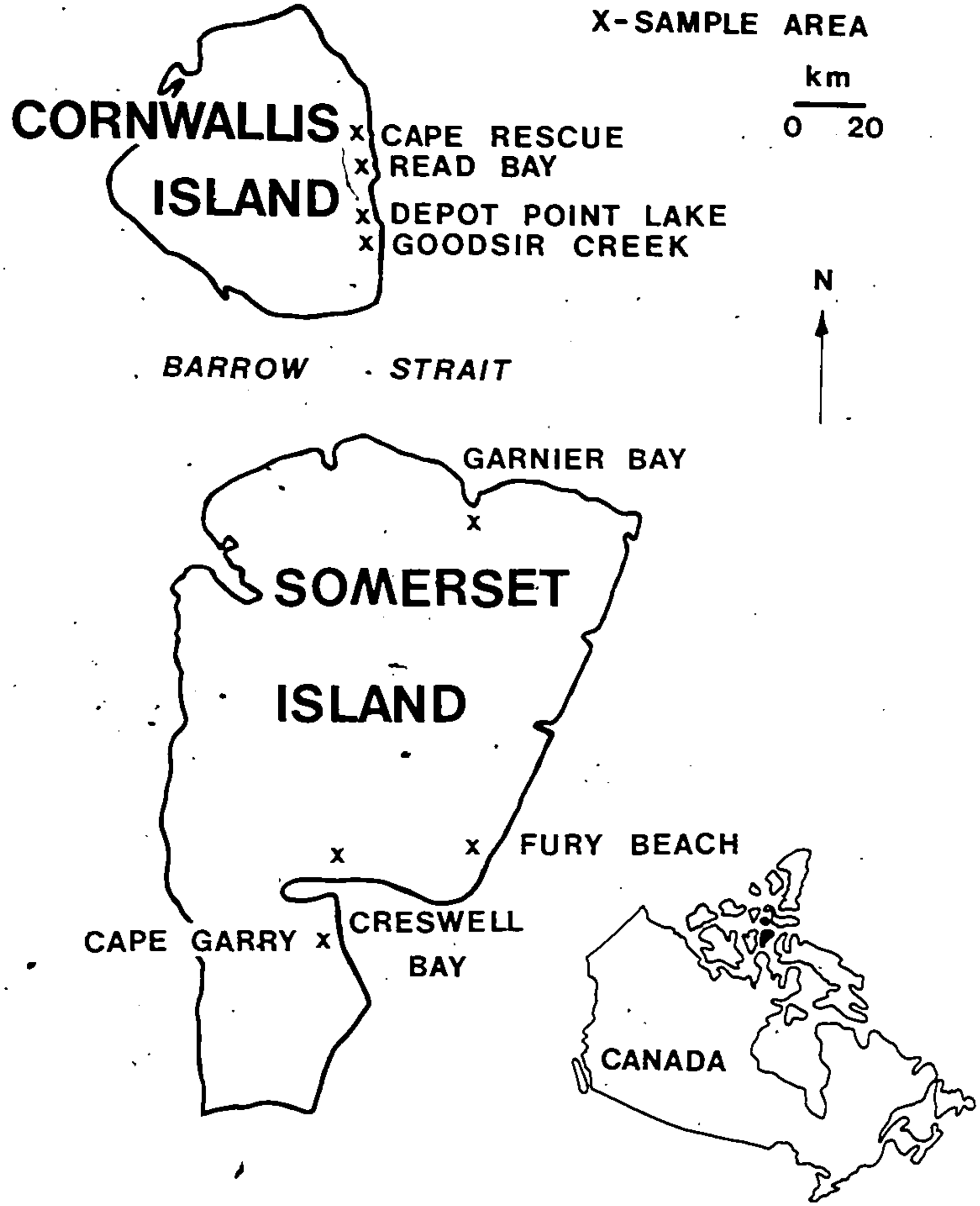


Fig. I-1. Geographic setting and locations of sections in the Read Bay Formation on Cornwallis and Somerset Islands, Arctic Canada.

could be followed into the subsurface of northwestern Iowa and into adjacent counties in northeastern Missouri.

However, in other parts of Missouri these subdivisions cannot be recognized. For example, in southwestern Missouri, the Burlington Limestone is difficult to distinguish lithologically from the overlying Keokuk Formation. Thus some authors such as Thompson & Fellows (1969) combine the two formations into one unit. However, they can be distinguished by means of their distinct crinoid faunas (S. Fagerlin, 1978, pers. comm.). In northeastern Missouri, the Burlington Limestone is divided into Lower and Upper Members on the basis of its crinoid fauna (Moore, 1928).

Samples from the Burlington Limestone were collected in the Burlington and Mediapolis areas of Iowa, and the Columbia and Springfield areas of Missouri (Fig. I-2). For detailed locality and faunal descriptions see Moore (1928), Thompson & Fellows (1969) and Harris & Parker (1964) and Appendix I.

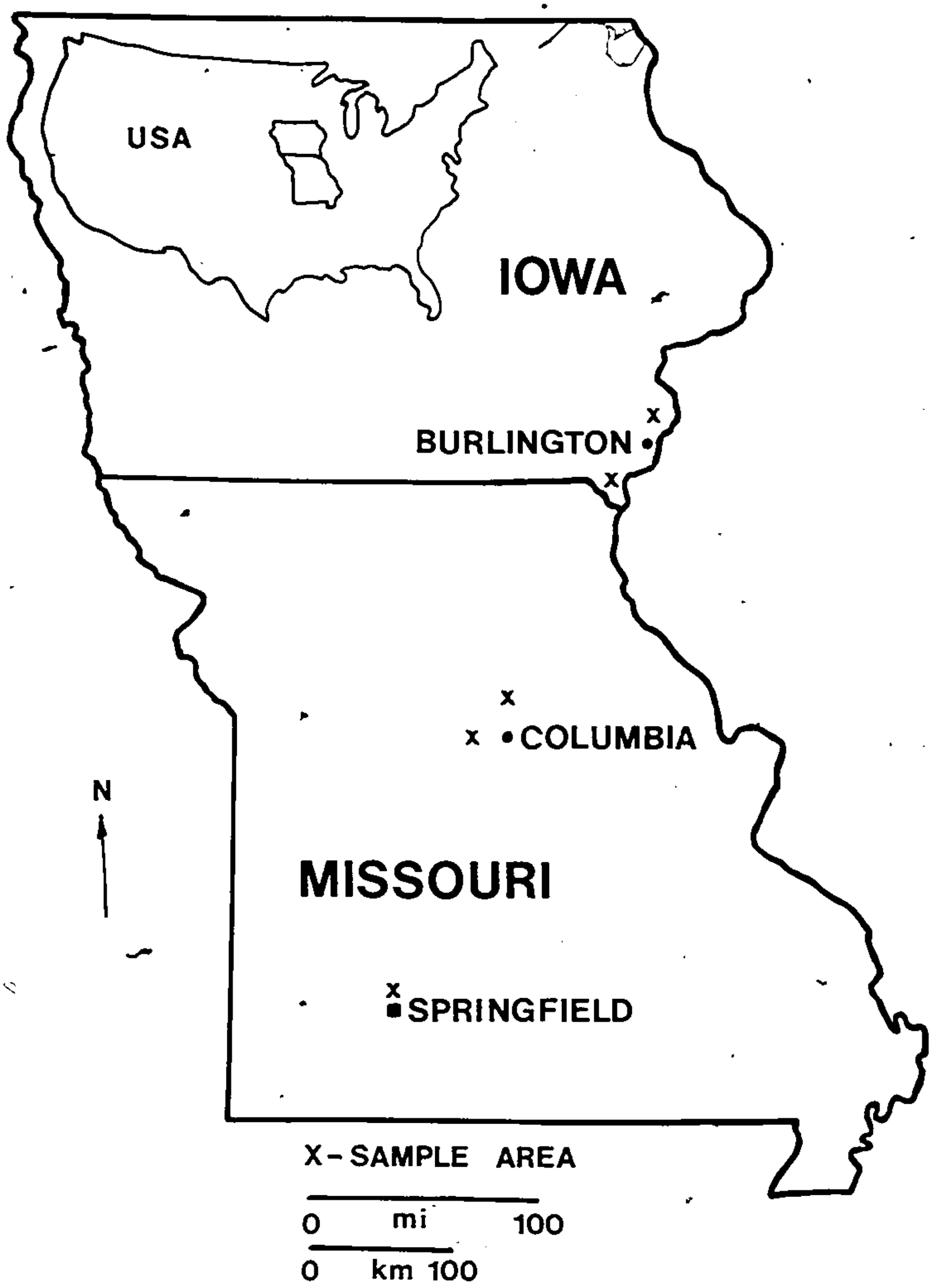


Fig. I-2. Geographic setting and locations of studied sample areas of the Burlington Limestone in Iowa and Missouri.

PETROGRAPHY

Read Bay Formation

The Read Bay Formation of Somerset Island consists of micrite and biomicrite with brachiopods and crinoids being the most abundant allochems (Table I-1). The samples from Member C of the Read Bay Formation of Cornwallis Island are lithologically more complex. Variations from micrite to microspar, biomicrite to biosparite (neomorphic spar) and various degrees of dolomitization are all represented (Table I-1 and Appendix II). Extensive bioherm and reef developments are commonly dolomitized. The most abundant allochems of the bioherms and biostromes are brachiopods, crinoids, corals and gastropods.

In general the Read Bay Formation of Cornwallis and Somerset Islands according to Mayr (1978, p. 21) "... consists of light to medium brown-grey lime mudstone with interbeds of skeletal or lump grainstone and light to medium brown limestone interbedded with light grey-brown dolomite ...".

The rugose corals used (Mucophyllum and similar forms with massive theca; W.G. Parkins, 1979 pers. comm.) are well preserved, even with fine trabecular structures recognizable in some thin sections. Their systematics and paleoecology are currently being studied by W.G. Parkins at the University of Ottawa. Silicification of the corals is not extensive and usually restricted to their rootlets and/or a thin layer just beneath their thecal walls.

FORMATION Location	biomicrite	biosparite	dolo. biomicrite	dolo. biosparite	brachiopods	bryozoans	corals	crinoids	gastropods	pelecypods	pellets	trilobites	syntaxial overgr.	equant	2-generations	diss.-ppt	neomorphism	dolomitization	-incipient	-fossil	-matrix	silicification	-fossil	stylolites
READ BAY FM.																								
Somerset Is.																								
Garnier Bay	x				x	x	x	x	x			x	x	x		x	x		x		x		x	
Fury Beach	x				x	x	x	x	x			x	x	x		x	x		x		x		x	
Creswell Bay	x				x		x	x						x										x
Cape Garry	x				x		x	x						x										x
Cornwallis Is.																								
Cape Rescue			x	x	x	x	x	x	x			x	x	x					x	x	x		x	x
Read Bay			x		x	x	x	x	x	x		x		x		x	x		x		x		x	x
Depot Pt Lake	x				x	x	x	x				x	x	x		x	x		x		x		x	x
Goodsir Creek			x	x	x	x	x	x			x	x	x	x		x	x		x	x	x		x	x
BURLINGTON LST.																								
Iowa																								
Burlington		x			x	x		x					x	x	x	x			x				x	x
Mediapolis		x		x	x			x				x	x	x		x			x		x		x	x
Missouri																								
Columbia		x			x	x		x				x	x	x	x	x	x?		x				x	x
Springfield		x			x		x	x					x			x			x					x

Table I-1. Summary of micro- and macroscopic petrographic observations of the studied samples. For a more detailed account of each locality see Appendix II. (Note x = present)

The crinoids sampled included Carpocrinus arcticus (Frest & Strimple, 1977) and a new unidentified crinoid. Preservation overall is good, with dolomite replacement most extensive in the samples from Cape Rescue. This is discussed more fully in chapter III.

Burlington Limestone

The Burlington Limestone of Iowa and Missouri is mainly bioclastic limestone composed of crinoidal stem and plate fragments (Table I-1). It ranges from calcarenite to calcirudite (crinoidal biosparrudite) (Harris & Parker, 1964). The formation contains chert nodules which constitute up to 5 percent of the formation. However, these were not sampled for the present study.

Brachiopods in the Burlington Limestone are usually well preserved and exhibit the distinctive single or two layered shell structure (cf. Bathurst, 1971). The brachiopods used in this study belong to the genus Dictyoclostus.

The crinoids collected from the Burlington Limestone belong to the genus Platycrinites. The ones from Iowa are extensively silicified (up to 30 percent), while the crinoid ossicles from Missouri are less silicified.

The rugose corals used are the genera Triplophyllites and Amplexus. Their overall poor preservation and fragmented nature made more precise identification impossible. The specimens from Iowa are extensively replaced by chalcedony (up to 50 percent); the samples from Missouri are considerably less silicified.

ORIGINAL COMPONENT MINERALOGY

Crinoids

All authors agree that on the basis of mineralogical and fine structural observations both Recent and fossil crinoids secreted a high-Mg calcite (= HMC, 8-16 mole % $MgCO_3$) endoskeleton (Table I-2). Therefore the crinoids were selected to serve as the standard for the HMC phase.

Brachiopods

All authors, except one, agree that on the basis of mineralogical and fine structural observations both Recent and fossil articulate brachiopods were, as already stated by Chave (1954, p.279) "...composed of calcite containing less than 4 per cent magnesium carbonate..." (Table I-2). Therefore, brachiopods were selected as the low-Mg calcite (=LMC) standard.

Rugose Corals

There is no general agreement as to the original mineralogy of the rugose corals (Table I-2). This was seen as an opportunity to utilize chemical techniques and textural studies simultaneously to test whether they could shed some light on the original mineralogy of this particular component. The reader is referred to Sandberg (1975) for a concise and encompassing synopsis of the structures and mineralogy of the rugose corals.

Micrite

About half of the fossil components for this study were collected from the limestones of the Read Bay Formation, which for the most part are mottled micrites and biomicrites. These samples are mostly a uni-component assemblage, with

Table I-2. Summary of the original mineralogy of the different fossil groups (Note C* = calcite with unspecified Mg content).

	AUTHORS	A	HMC	LMC	C*
CRINOIDS	Chave,1954		x		
	Lowenstam,1963		x		
	Weber,1969		x		
	Bathurst,1971		x		
	Richter,1972		x		
	McQueen et al.,1974		x		
	Milliman,1974		x		
	Neugebauer,1978		x		
BRACHIOPODS	Chave,1954			x	
	Lowenstam,1961			x	
	Williams,1968			x	
	Bathurst,1971			x	
	Veizer,1971			x	
	Richter,1972			x	
	Sandberg,1975			x	
	Jaanusson,1966	x			
RUGOSE CORALS	Sorauf,1971	x(?)	x(?)		
	Oekentorp,1972	x			
	Fenninger & Flajs,1974	x			
	Flügel,1975;1976	x			
	Richter,1972		x		
	Sorauf,1977		x		
	Richter & Füchtbauer, 1978		x		
	Lowenstam,1963			x	
	Veizer,1978			x(?)	
	Stehli,1956				x
	Lowenstam,1961				x
	Kato,1963				x
	Bathurst,1971				x(?)
	Sandberg,1975				x
	Zorn,1977				x

(Note ? uncertainty of author as to mineralogy).

only minor amounts of other mineralogical components. In analogy with their Holocene counterparts these micritic limestones are believed to be diagenetically stabilized aragonitic muds (Veizer et al., 1978), since most shallow water muds and cements (eg. Read Bay Formation) are aragonite (Milliman & Müller, 1978). Therefore, the micritic bulk rock, excluding the extracted fossil allochems is believed and used here to represent an original aragonitic (= A) mineralogical phase.

ANALYTICAL TECHNIQUES

The crinoid ossicles, the coral coralla and the brachiopod valves, were manually separated from their enclosing rocks. The extracted fossils were treated with 15 % ($^v/v$) HCl to remove their outermost layer. This was done to minimize possible contamination of the irregular outer layers of the fossils by their enclosing rock.

A total of three hundred and seventeen fossil and rock samples were treated with 40 ml of 3 % (8 % $^v/v$) HCl for 5½ hours. Leaching experiments showed that the insoluble residue (I.R.) stabilized after about 4-7 hours for limestones and after about 5-8 hours for dolostones. After this time the I.R. was extensively leached. Furthermore, to keep Na contamination to a minimum gloves were worn during all preparatory stages.

Strontium, manganese, sodium, iron, aluminium, magnesium and calcium were determined on a Varian-Techtron 6R Atomic Absorption Spectrophotometer. Sr and Al were analysed in an acetylene-nitrous oxide flame, while Mn, Na, Fe, Mg, and Ca were determined in an air-acetylene flame.

Ca was added only to Na calibration solutions (Veizer _et al_., 1977); $Sr(NO_3)_2$ was added to Mg sample, calibration and standard rock solutions (Abbey _et_ _al_., 1974); KCl was added to Al sample, calibration and standard rock solutions (Kretz, 1970); $LaCl_3 \cdot 6H_2O$ was added to Ca sample, calibration and standard rock solutions (Abbey _et_ _al_., 1974); KCl (2000 ppm K) was added to Sr sample, calibration and standard rock solutions.

Average accuracy and reproducibility, as compared with recommended values for N.B.S. (1b, 88a, 1014); Z.G.I. (TB, KH) and U.S.G.S. (G-2, BCR-1) standard rocks (Flanagan, 1973; Abbey, 1975) were as follows: Sr (8.3, 2.1), Mn (8.1, 2.2), Na (11.0, 6.2), Fe (8.4, 2.2), Al (5.4, 9.3), Mg (8.5, 2.5) and Ca (6.3, 1.6) relative percent, respectively.

Insoluble residue was determined gravimetrically by ashing the filter paper at 900°C for 2 hours. Average reproducibility was 5.0 relative percent.

The chemical data is presented in Appendix III.

For data reduction and compilation, the SPSS package, version 6 (Nie *et al.*, 1975) was utilized. Factor analyses were done using the PA 2 procedure with Varimax rotation. Analyses were performed on a IBM 360 computer.

All discussion in the text is based on concentrations recalculated on the total carbonate (insoluble residue-free) basis.

THEORETICAL CONCEPTS

The post-depositional stabilization of an original metastable carbonate assemblage is achieved through complimentary textural, mineralogical and chemical changes. The chemical behaviour of a simplified carbonate system is treated in detail by Garrels & Christ (1965), and the overall reaction can be written as:

$$CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca(HCO_3)_2 \qquad (I-1)$$

The process as represented by equation (I-1) is a wet dissolution - reprecipitation reaction (Bathurst,1971,p.239).Trace elements such as Sr^{2+}, Mn^{2+}, Mg^{2+}, Fe^{2+}, Pb^{2+}, Zn^{2+} and Na^+ will substitute, to varying degrees, for Ca^{2+} in the $CaCO_3$ lattice. This substitution can be in the following forms: 1) diadochic, 2) interstitial, 3) adsorption for unsatisfied charges and 4) filling of unoccupied lattice positions in lattice defects of the structure.

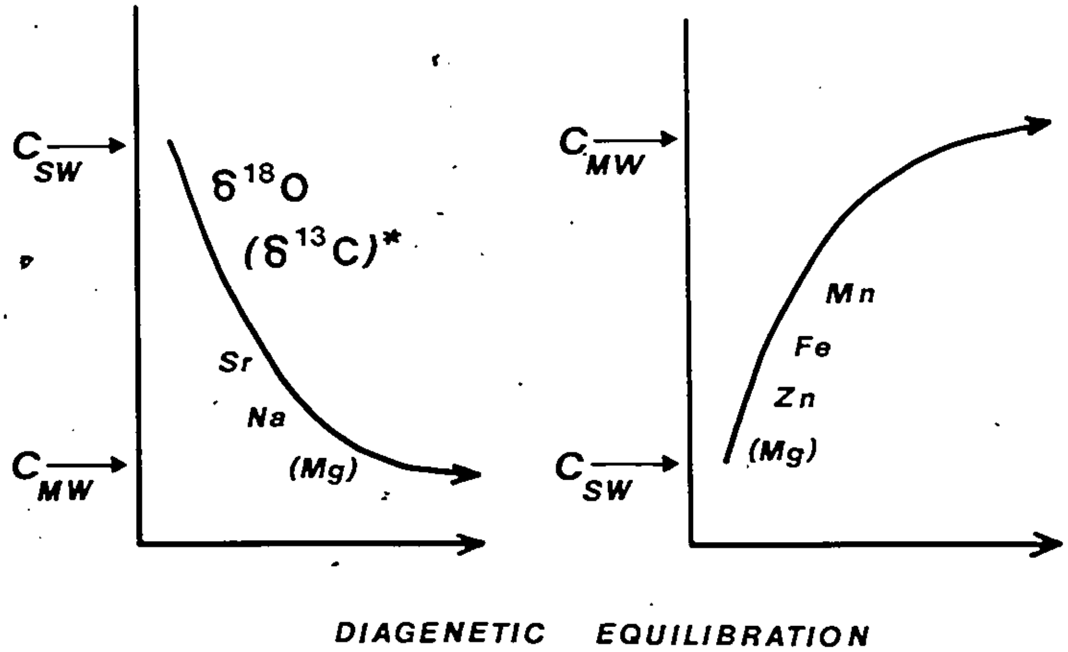
The original carbonate phase, precipitated in inorganic or biogenic equilibrium with seawater will incorporate its trace elements and stable isotopes in equilibrium with the ambient seawater. This phase, upon exposure to meteoric water, will dissolve partially or fully, exchange and mix its trace elements and stable isotopes with those in the interstitial water, and reprecipitate as diagenetic low-Mg calcite (dLMC). The dLMC will have trace element and isotopic composition, which is shifted in the direction of equilibrium with the interstitial meteoric water. Since such water, in general, contains less Sr, Na and Mg (and lighter $\delta^{18}O$, $\delta^{13}C$) and more Mn, Fe and Zn (cf. Turekian, 1972, Table 6-3), the above process should lead to a lowering of Sr and Na and an increase in Mn, Fe and Zn in dLMC (Fig. I-3). It can lead to either depletion or enrichment of Mg depending on whether the original phase was either HMC or LMC and A. The rate at which the composition of the dLMC approaches equilibrium with meteoric water depends on the water/rock ratio involved. The higher this ratio (due to increasing openness of the diagenetic system and/or increasing number of dissolution - reprecipitation events) the closer the equilibrium with meteoric water will be.

The above reasoning applies to the transformation of the original metastable carbonate components and matrix into dLMC. The concomitant occlusion of pore space in the matrix is achieved by compaction and cementation. If the latter proceeds in the marine environment, the precipitated cement will be subject to a sequence of events similar to that affecting the matrix and components during subsequent meteoric stabilization. In contrast, cement precipitated in the meteoric environment is LMC in equilibrium with ambient meteoric water. Therefore, depending on the proportion of either cement, the sample would be further from or closer to equilibrium with meteoric water.

Furthermore, for fully or partly open diagenetic systems (the point to be argued later in the text), single or multiple solution - precipitation events will lead, in general, to a decrease of concentrations for the elements with $K_{\text{calcite-water}}$

Fig. I-3. Elemental and isotopic changes during diagenetic stabilization of $CaCO_3$ with meteoric water. C_{SW} = calcium carbonate in equilibrium with seawater; C_{MW} = calcium carbonate (dLMC) in equilibrium with meteoric water. The isotopic compositions of C_{SW} and C_{MW} are from Gross (1964), Keith & Weber (1964), Choquette (1968), Degens & Epstein (1964), Murata et al. (1969), Veizer & Fritz (1976) and Hudson (1977). The following are ranges for partition coefficients at earth surface conditions for calcite: $K^c_{Sr} = 0.055$ to 0.27 (Holland et al.,1964; Holland,1966; Kinsman,1969; Katz et al.,1972; Ichikuni,1973); $K^c_{Na} = 2.0 \cdot 10^{-5}$ to $3.0 \; 10^{-5}$ (Möller et al., 1976; White,1978); $K^c_{Mg} = 0.02$ to 0.06 (Winland,1969; Benson & Matthews,1971; Alexandersson,1972; Richter & Füchtbauer,1978); $K^c_{Fe} = 1$ to 20 (Veizer,1974; Richter & Füchtbauer,1978); $K^c_{Zn} = 5.2$ to 5.5 (Crocket & Winchester,1966; Dardenne,1967); $K^c_{Mn} = 5.4$ to 1700 (Bodine et al.,1965; Crocket & Winchester, 1966; Michard,1968; Ichikuni,1973). The large ranges for some of the partition coefficients are possibly due to the different nature of the experiments (ie. direct precipitation from solution; dissolution-precipitation; etc.; for further discussion and details the reader is referred to the authors).

The following are the fractionation factors for $^{18}O/^{16}O$, $\alpha_c \frac{R_c}{R_w} = 1.0286$ (O'Neil & Epstein,1966) and for $^{13}C/^{12}C$, $\alpha_c \frac{R_c}{R_{HCO_3}} = 1.00185$ (Emrich et al.,1970). The increase and/or decrease of (Mg) depends on the original carbonate phase (A, HMC, LMC). The decrease of $(\delta^{13}C)^*$ is discussed in chapter two.


C SW
C MW
δ18O
(δ13C)*
Sr
Na
(Mg)
C MW
C SW
Mn
Fe
Zn
(Mg)
DIAGENETIC EQUILIBRATION

< 1 (Sr, Na, Mg) and to an increase for those with $K > 1$ (Mn, Fe, Zn) (cf. Fig. I-3). The greater the deviation of a particular partition coefficient from unity the stronger the depletion or enrichment for a given degree of diagenetic equilibration.

The partition coefficient is defined at low activities by the following equation:

$$K = \frac{(m_t \;/\; m_c)_s}{(m_t \;/\; m_c)_l} \qquad \text{(I-2)}$$

In equation (I-2), t stands for the trace (minor) element, c is the carrier (major) element, s is the solid phase, l is the liquid (solution), m is the moles of the trace and carrier elements and K is the partition coefficient (McIntire, 1963). This partition coefficient defines inorganically precipitated carbonates (A, HMC, LMC and Dolomite). Usually this relationship also applies to biologically precipitated carbonates. However, when $K^{\text{c-biol.}}_{\text{element}} \neq K^{\text{c-inorg.}}_{\text{element}}$ this is referred to as biological fractionation (ie. vital effect), and the controls of this fractionation process are as yet not fully understood (Lowenstam, 1961; Milliman, 1974). For more details and a comprehensive discussion of partition theory see McIntire (1963).

The thermodynamic stability of a particular carbonate phase in seawater and meteoric water will, to some degree, control the rate at which the above discussed equilibration will take place. HMC, A and LMC are stable in the original depositional marine environment (Kitano & Hood, 1962; Winland, 1969; Möller & Kubanek, 1976; LMC is stable because seawater is supersaturated with respect to calcite). In the diagenetic meteoric environment HMC and A are metastable, while LMC is the stable phase (Jansen & Kitano, 1963; Friedman, 1964; Taft & Harbaugh, 1964; Land, 1967; Schroeder, 1969; 1972; 1973). The two metastable phases (HMC and A) will undergo rapid alteration to a more stable phase in meteoric water, while LMC should resist alteration in this diagenetic environment. The latter should retain its original chemical imprint, while the former will this characteristic with stabilization.

Finally, solid - state diffusion could affect the chemical make-up of the carbonate phase. However, diffusion has been found to be slow, so that it only plays minor part in elemental equilibration and redistribution (Urey et al., 1957; Anderson, 1969; Billings & Ragland, 1968; Bathurst, 1971, p.464).

In summary, increasing diagenetic alteration (equilibration with meteoric water) should lead to an enrichment of Mn and Fe and depletion of Sr, Na and possibly Mg in the final product (dLMC). It should be noted, that this diagenetic equilibration is achieved by a combination of factors. As a consequence of different compositions of sea and meteoric water and variable partition coefficients as well as water/rock ~~ratios~~, the progression in dissolution - reprecipitation events should lead to a more pronounced displacement in chemical composition as well as to greater textural maturity. Thus a textural alteration trend (eg. micrite - microspar - pseudospar) should be accompanied by Sr, Na and possibly Mg depletion and Mn and

Fe enrichment. This covariance is solely a result of post-depositional phenomena. In contrast, a biomicrite - biosparite sequence may conform with the above predicted chemical trends not only due to metastable precursor to dLMC transformation, but also because the original porosity of the latter was higher and thus it contains a higher proportion of meteoric cement in a given sample volume. Most natural situations involve a combination of the above factors. However, as a generalization, the high porosity facies are probably characterized by more meteoric cement as well as greater equilibration of the matrix (due to higher water/rock ratio of the stabilizing meteoric system).

The above described approach has been previously utilized by Veizer (1974) and Veizer & Fritz (1976) in their study of belemnites and by Pingitore (1976; 1978) evaluating the diagenetic history of scleractinian corals and the reader is referred to these papers for further details.

EVALUATION OF RESULTS

General considerations

Following the discussion in the previous section, Sr, Na and possibly Mg should decrease, while Fe and Mn should increase with increasing diagenetic equilibration. Factor analysis of the data shows that three factors account for all variations in the measured variables (Table I-3). Factor 1, which controls most of the variance for I.R., Al and Fe, represents leaching of the two elements during acid digestion of the samples from the I.R. (cf. chapter two for additional discussion of Fe distribution). The second most important factor is dolomitization with an inverse relationship between Mg and Ca. This will be discussed further in chapter three. Factor 3 depicts the changes with diagenetic equilibration. As was predicted from theory, an excellent negative correlation exists between Mn and Sr and to some degree with Mg. Since Sr-Mn (Fig. I-4) gives the best resolution for the diagenetic trend, this covariance will be utilized in the subsequent discussion.

The above chemical trend is accompanied by an increase in textural maturity (from micrite in Field 2 to micrite, microspar and minor pseudospar in Field 3), and by an increase in the amount of cement (Fig. I-4). The trend of the dolomite field (3a) will be discussed in chapter three.

The biosparite samples of the Burlington Limestone also conform to the predicted textural - chemical covariance pattern. Field 4 represents crinoids and associated biosparite, while

	Factor 1	Factor 2	Factor 3
log I.R.	0.63213	-0.06898	0.10141
log Mn	0.17713	-0.22754	-0.95470
log Sr	0.27129	-0.27737	0.57112
log Fe	0.80661	0.28347	-0.10275
log Al	0.91194	0.23865	0.13602
log Na	0.23138	0.20617	-0.08390
log Mg	0.31302	0.80008	0.37986
log Ca	-0.05703	-0.71196	0.09544

Factor	Pct. of Var.	Diagnosis
1	51.4	laboratory leaching*
2	28.1	dolomitization
3	20.5	diagenetic equilibration

Table I-3. Factor analysis (Varimax rotated factor matrix) of all the studied samples (N = 317). (Note * additional interpretation in chapter II).

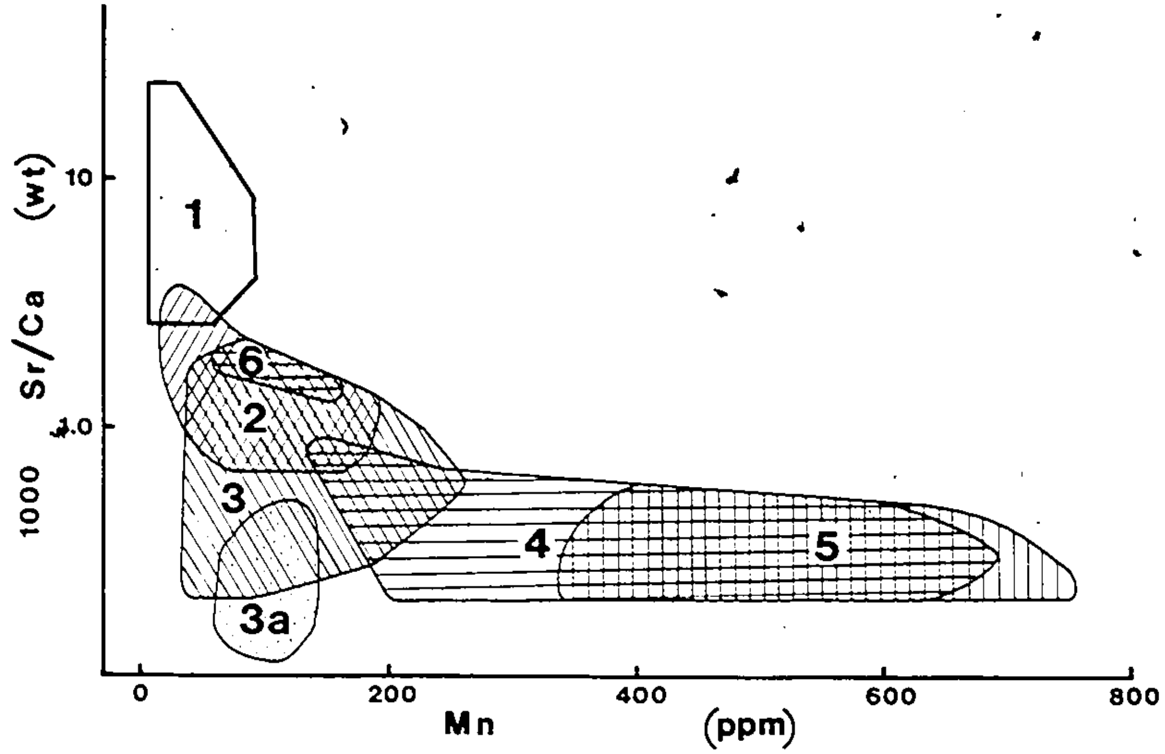


Fig. I-4. General trend for the samples from the different regional localities. Field 1 represents the theoretical possible ranges for A, HMC and LMC in inorganic and organic equilibrium with present day seawater (Chave, 1954; Lowenstam, 1961; Bathurst, 1971 and Milliman, 1974). Field 2 represents samples from the Read Bay Formation of Somerset Island. Field 3 represents the Read Bay Formation samples from Cornwallis Island; field 3a represents dolomitic Read Bay Formation samples from Cape Rescue, Cornwallis Island. Field 4 and 6 represent samples from the Burlington Limestone of Missouri. Field 5 represents Burlington Limestone samples from Iowa.

Field 6 represents LMC-fossils from the Burlington Limestone of Missouri. The biosparite of Field 4 shows a marine stage of cementation (1st-generation non-ferroan calcite) followed by a non-marine one (2nd-generation ferroan calcite I and II) (Richter & Füchtbauer, 1978) (Table I-1 and Appendix II). In Field 5 a similar sequence is observed, except that the non-marine cement is more pronounced and also silicification is extensive (Table I-1). Therefore, the biomicrite (fields 2-3) to biosparite (fields 4-5) chemical trend is a consequence of increasing proportions of meteoric cement as well as of the greater equilibration of the associated matrix and allochems with meteoric water.

In order to discount variations in this chemical trend due to pooling of data for various mineralogical phases, the results will be discussed separately for each mineralogy.

High-Mg calcite

Factor analysis of the presumed original HMC-crinoids depicts a two stage diagenetic trend (factors 1 and 3) (Table I-4). Factor 1, though can be divided into two parts, where the Ca and I.R. variation can be related to silicification (evident in the crinoids from Iowa), while Mn and Na and, possibly Mg, variation relates to diagenetic equilibration of the Burlington crinoids. Laboratory leaching of Al and Fe from aluminosilicates (I.R.) is represented by factor 2 (see chapter two for additional discussion). The two diagenetic factors, 1 and 3, are evident on the Sr-Mn graph for HMC (Fig. I-5).

	Factor 1	Factor 2	Factor 3
log I.R.	0.45495	0.67591	-0.09477
log Mn	0.72525	0.24365	-0.30013
log Sr	-0.00285	0.08781	0.46143
log Fe	-0.08642	0.72470	-0.04338
log Al	-0.05807	0.82579	0.01290
log Na	0.23682	0.09227	-0.44958
log Mg	-0.95275	0.22561	-0.15989
log Ca	0.47170	-0.29726	0.69720

Factor	Pct. of Var.	Diagnosis
1	42.2	diagenetic equilibration I and silicification
2	40.2	laboratory leaching*
3	17.7	diagenetic equilibration II

Table I-4. Factor analysis (Varimax rotated factor matrix) of HMC - crinoids (N = 118).

(Note * additional interpretation in chapter II).

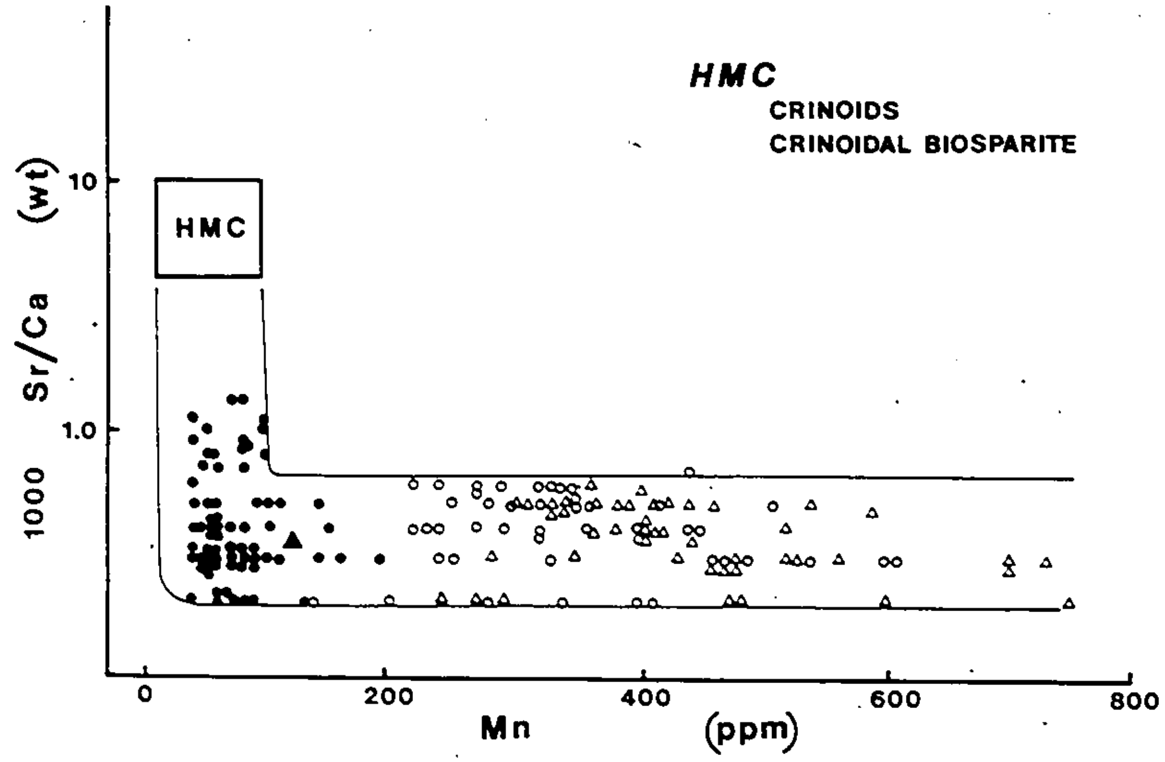


Fig. I-5. HMC alteration with diagenetic stabilization by meteoric water. The HMC field defines the theoretical possible range of this phase in inorganic and organic equilibrium with present day seawater (Chave, 1954; Bathurst, 1971; Milliman, 1974). The ● denotes the crinoid samples from the Read Bay Formation of Somerset and Cornwallis Islands. The ○ represents the crinoids from Iowa and Missouri, while △ represents their enclosing crinoidal biosparite (Burlington Limestone). The ▲ is an average value of a crinoidal biosparite from the Mesozoic of Czechoslovakia (Veizer & Demovič, 1974). Population I (≲ 210 ppm Mn) is represented by the material from the Read Bay Formation and from the Mesozoic of Czechoslovakia, while Population II (≳ 210 ppm Mn) is defined by the material from the Burlington Limestone.

On the left side of the diagram (≲ 210 ppm Mn) representing the Read Bay Formation samples, the Sr depletion is five times faster than the Mn enrichment (factor 3, Table I-4). This is accompanied by Mg depletion (factor 1), which perhaps is related to the increasing "purification" of dLMC of microdolomite inclusions (cf. Lohmann & Meyers, 1977, for further discussion). Population two (≳ 210 ppm Mn; Burlington Limestone samples) shows only small Sr depletion with increasing Mn content (factor 3, Table I-4) (Fig. I-5). Both populations also display increasing silicification (I.R. in factor 1) with increasing Mn content. The relatively stable Sr content of dLMC suggests that the measured concentrations are close to its equilibrium value with the interstitial meteoric water, while Mn (being controlled by Eh) could have been variable, and mostly associated with precipitated meteoric syntaxial cement (Table I-1, Appendix II).

The crinoidal biosparites (this study and Veizer & Demovič, 1974) follow a pattern similar to that for the crinoids, even though these are multi-component and multi-phase bulk samples. This substantiates the assertion of Lohmann & Meyers (1977) that the crinoidal syntaxial cement (1st-generation only, Table I-1 and Appendix II) most likely was originally HMC.

Aragonite

Factor analysis of the presumed original A-micrite samples shows that laboratory leaching is the dominant controlling factor of trace element variations, particularly those of Al and Fe (Table I-5) (see chapter two for further discussion).

	Factor 1	Factor 2	Factor 3
log I.R.	0.93359	-0.20271	0.14690
log Mn	-0.01477	0.05124	-0.41447
log Sr	0.47455	-0.60146	0.31866
log Fe	0.84654	0.19429	-0.15442
log Al	0.87848	-0.05564	0.15633
log Na	0.42800	0.64622	0.40915
log Mg	-0.05644	0.92032	-0.05366
log Ca	0.01539	-0.91076	0.13440

Factor	Pct. of Var.	Diagnosis
1	50.6	laboratory leaching*
2	42.2	dolomitization
3	7.2	diagenetic equilibration

Table I-5. Factor analysis (Varimax rotated factor matrix) of A - micrite (N = 96).

(Note * additional interpretation in chapter II).

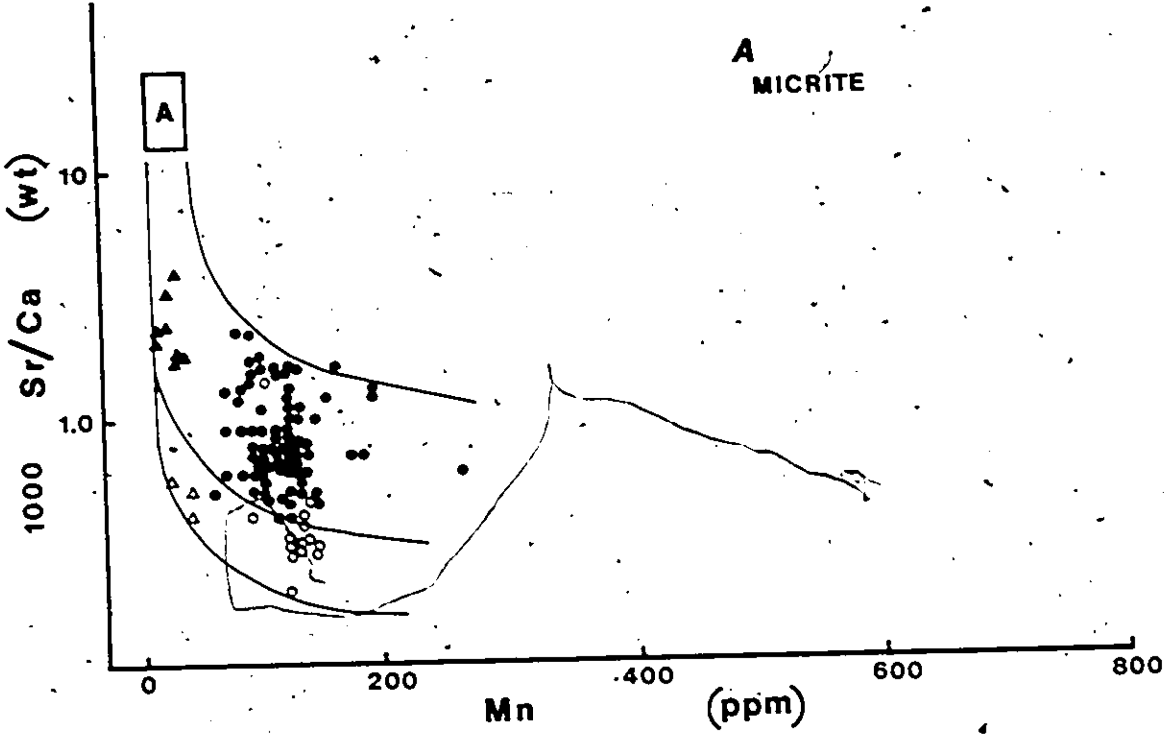


Fig. I-6. Equilibration trend of A - micrite with meteoric water. The A field outlines the theoretical possible range of inorganic aragonite in equilibrium with present day seawater (Kinsman, 1969; Bathurst, 1971; Milliman, 1974). The ● and ○ represent micrite and dolomitic samples from the Read Bay Formation of Somerset and Cornwallis Islands; they contain ≲ 30,000 ppm Mg and > 30,000 ppm Mg, respectively. The ▲ and △ represent average concentrations of similar facies from the Mesozoic of the Carpathians (Czechoslovakia) (Veizer & Demovič, 1974). All the studied A - micrite samples fall into Population I (≲ 210 ppm Mn).

Dolomitization, factor 2, causes an increase in Mg and Na and a simultaneous decrease in Ca and Sr (see chapter three for further discussion). Factor 3 is diagenetic equilibration leading to repartition of Sr, Na and Mn.

Dolomitization and diagenetic equilibration account for the rapid loss of Sr (~1-2 orders of magnitude; Fig. I-6) and Na as well as the slight increase in Mn (factors 2 and 3, Table I-5). This trend is similar to that for population one (≳ 210 ppm Mn; Fig. I-5). Unfortunately, the majority of the material is micrite-microspar with minor amounts of pseudospar and sparite. Further research is needed to investigate the complete transition of micrite to pseudospar.

Low-Mg calcite

LMC fossils should behave differently from the two previous phases since LMC is stable both in the marine (due to supersaturation; Garrels & Christ, 1965, p. 375; Krauskopf, 1967, chapter three; Bathurst, 1971, chapter six) and the diagenetic meteoric environments (cf. the section, "Theoretical Concepts").

Factor analysis of the presumed LMC phases shows that diagenetic equilibration (inverse relationship between Sr and Mn and to some degree Mg) is the dominant factor (Table I-6). Laboratory leaching of Al and Fe from the I.R. and biological fractionation account for the remainder of the total chemical variation (factors 2 and 3, respectively).

The rugose coral data fall close to the predicted theoretical LMC field and with increasing diagenetic equilibration

	Factor 1	Factor 2	Factor 3
log I.R.	0.19502	0.92112	0.02931
log Mn	-0.98645	0.14906	0.03826
log Sr	0.96076	-0.06305	0.16065
log Fe	-0.36937	0.75090	-0.09816
log Al	0.01284	0.86960	-0.04927
log Na	0.03941	0.00897	0.93259
log Mg	0.66734	0.25214	-0.51585
log Ca	0.39412	0.32615	-0.24540

Factor	Pct. of Var.	Diagnosis
1	43.4	diagenetic equilibration
2	38.6	laboratory leaching*
3	18.0	biological fractionation

Table I-6. Factor analysis (Varimax rotated factor matrix) of LMC - fossils (brachiopods and rugose corals). (Note * additional interpretation in chapter II). (N = 40)

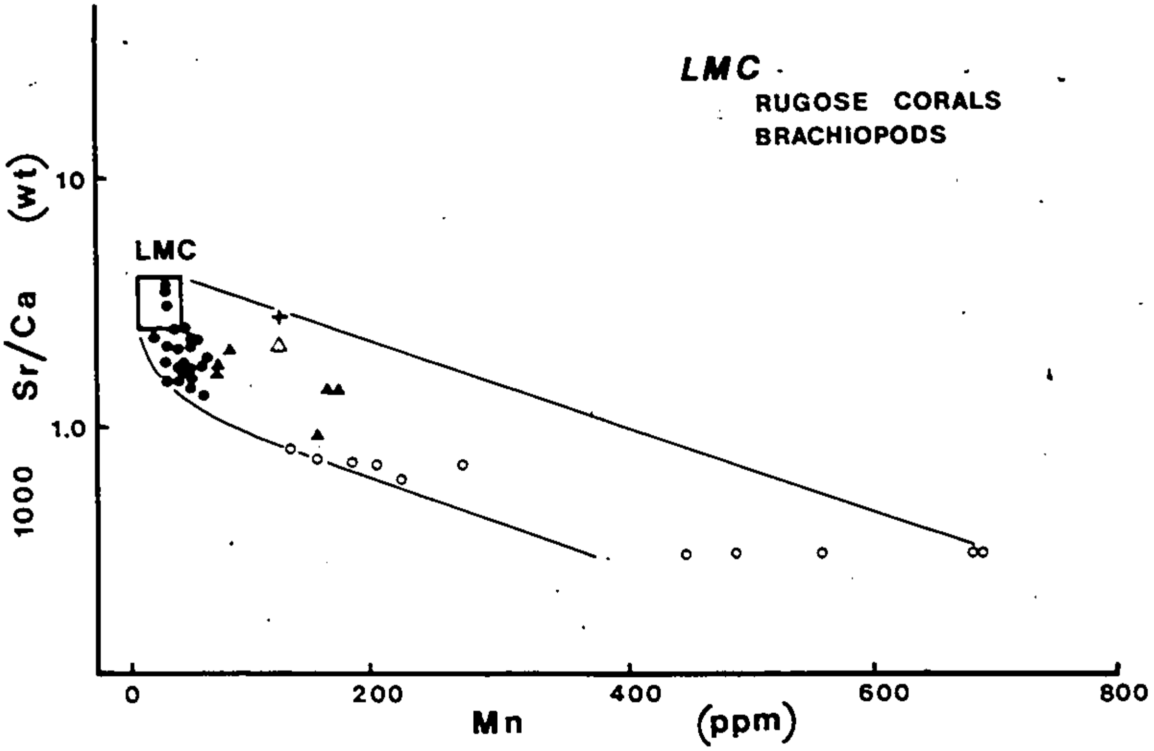


Fig. I-7. Diagenetic equilibration of LMC-fossil groups with meteoric water. The LMC field delineates the theoretical possible range of LMC in inorganic (?) and organic equilibrium with present day seawater (Lowenstam, 1961, 1963; Bathurst, 1971; Milliman, 1974). The ● and ○ represent rugose corals from Arctic Canada and Iowa and Missouri, respectively. The ▲ represents brachiopods from the Burlington Limestone (Iowa and Missouri). The △ and + represent average values for Paleozoic brachiopods and Mesozoic belemnites, respectively (Veizer, 1971, 1974).

follow mostly the trend of the brachiopods and belemnites (Fig. I-7).

In the Read Bay Formation, the rugosans and HMC crinoids are closely spatially associated and enclosed in the same micritic matrix. Therefore, during diagenetic stabilization both groups were subjected to similar hydrologic conditions, yet their trace element diagenetic trends diverge (Figs. I-5 and I-7). This discrepancy combined with the above-noted conformity of the rugosan, brachiopod and belemnite trends, suggests that the herein studied Paleozoic rugose corals secreted a corallum that was originally LMC instead of either A or HMC. However additional data are required to confirm the validity of this assertion for the whole group of Rugosa.

Overall, LMC is a "stable" phase in diagenetic meteoric water, yet it, too, will eventually reequilibrate to some degree. Although the bulk of the samples fall close to the original LMC field, a few show extreme alteration. These samples are from the Burlington Limestone and their extreme alteration can perhaps be explained by their extreme silicification. An additional possibility is that not all interseptal spar cement was removed during the laboratory preparation of the samples.

LMC - Biological fractionation

Despite the relative stability of LMC, both groups (rugose corals and brachiopods) lose some of their Mg and Na during diagenetic stabilization, as exemplified by the weak negative correlation of Mg and Na with Mn (Fig. I-8). Extrapolation of these trends to the "least altered" values

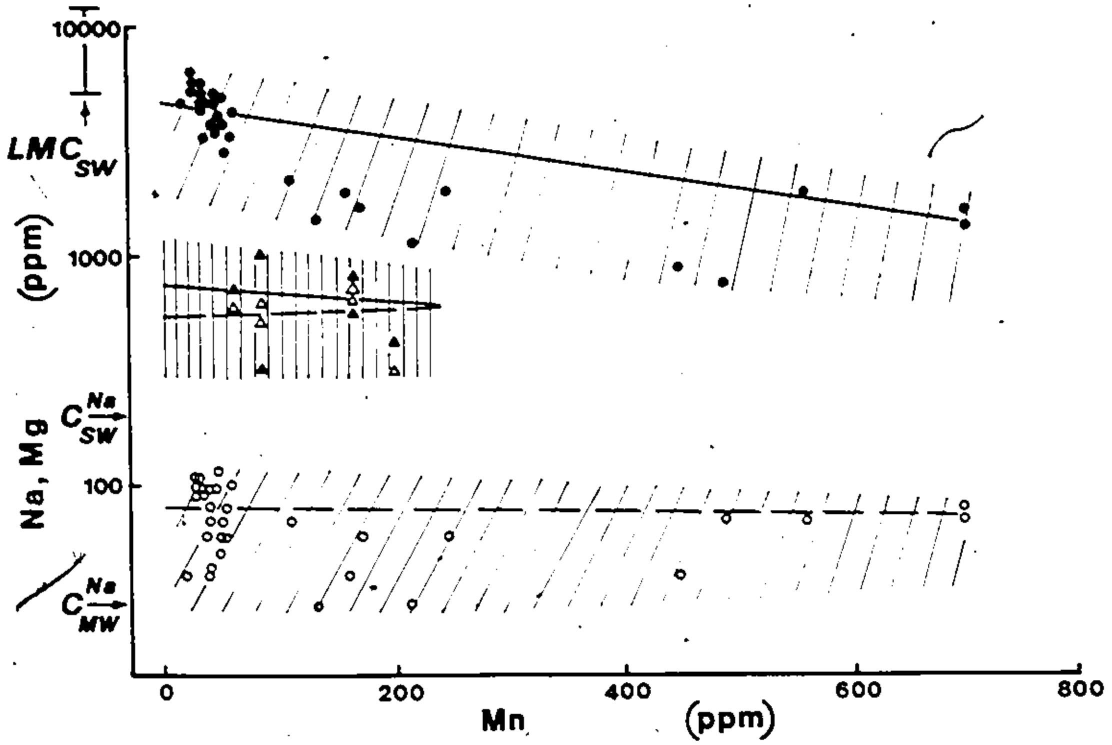


Fig. I-8. Sodium and magnesium biological fractionation in corals and brachiopods. C^{Na}_{SW} - Na concentration for calcite in inorganic equilibrium with present day seawater; C^{Na}_{MW} - Na concentration for calcite in inorganic equilibrium with average meteoric water (White, 1978; Turekian, 1972, Table 6-3). LMC_{SW} - delineates the Mg range (2 to 4 mol % $MgCO_3$) for LMC in inorganic equilibrium with present day seawater (Chave, 1954). The ● and ○ represent Mg and Na values of the rugose corals, respectively. The ▲ and △ represent Mg and Na values of the brachiopods, respectively. The solid lines represent the Mg linear regression trends of the rugose corals and brachiopods, while the dashed lines represent the Na linear regression trends of the rugosans and brachiopods.

for both rugose corals and brachiopods, suggests that diagenetic equilibration with meteoric water depleted their Mg and Na content by a factor of less than 2.

As predicted by factor analysis, Mg and Na are subject to biological fractionation (factor 3, Table I-6). The rugose corals incorporated Mg into their corallum in apparent equilibrium with their ambient seawater (upper field, Fig. I-8). However, the rugose corals appear to have discriminated against Na, which is in contrast to their temperature and salinity tolerance (Milliman, 1974, p. 88). This Na discrimination in the Paleozoic rugose corals could be a mechanism or driving force for the precipitation of LMC. The loss of the complexing power of Na for CO_3^{2-} would allow the LMC precipitation to proceed (Garrels & Christ, 1965, p. 107; Garrels et al., 1961). The Na content of the rugosan coralla is approximately ($\sim$80 ppm) half of that expected for calcite in equilibrium with present day seawater ($\sim$200 ppm) (lower field, Fig. I-8).

On the other hand, the brachiopods appear to have discriminated against Mg (middle field, Fig. I-8). Similar observations ($MgCO_3$ as low as 0.21 mol %) have also been noted for Recent and fossil brachiopods by Lowenstam (1961) and Jope (1965). Both authors suggest that the incorporation of Mg is temperature dependent. However, their advocated Mg-temperature relationships are of opposing signs. In any case, the exclusion of Mg from cell fluids in the brachiopods would cause the precipitation of $CaCO_3$, due to the loss of the complexing power of Mg (Garrels & Christ, 1965, p. 107).

In contrast to the corals, the brachiopods, which in general, are intolerant of low and high salinities (Rudwick, 1965, p. H211) have Na concentrations about 3 times higher than that expected for calcite in equilibrium with the present day seawater (middle field, Fig. I-8).

Summary of trends

The previously discussed trends for particular components are summarized in Fig. I-9. From this figure it is evident that progressive equilibration with meteoric water will lead to an assemblage where all internal components are in chemical equilibrium. However, a review of published data as well as the present results suggest that most of the stabilized carbonates do not exceed the range of Mn values (and thus the degree of open system diagenetic alteration) defined by $\bar{x} \pm s$ (Fig. I-9). Within this range the original Sr gradients of mineralogical phases are still to some degree preserved, although the absolute concentrations are lowered. This preservation of chemical gradients imposes constraints on the diagenetic system involved in mineralogical stabilization and at the same time promises to provide a tool for evaluation of the original mineralogy of a given component as well as the degree of its diagenetic alteration.

Consequences and diagenetic model

The studied fossils (mineralogical components) were separated from the same enclosing host rock, commonly in immediate proximity. The dispersed fossils were, therefore,

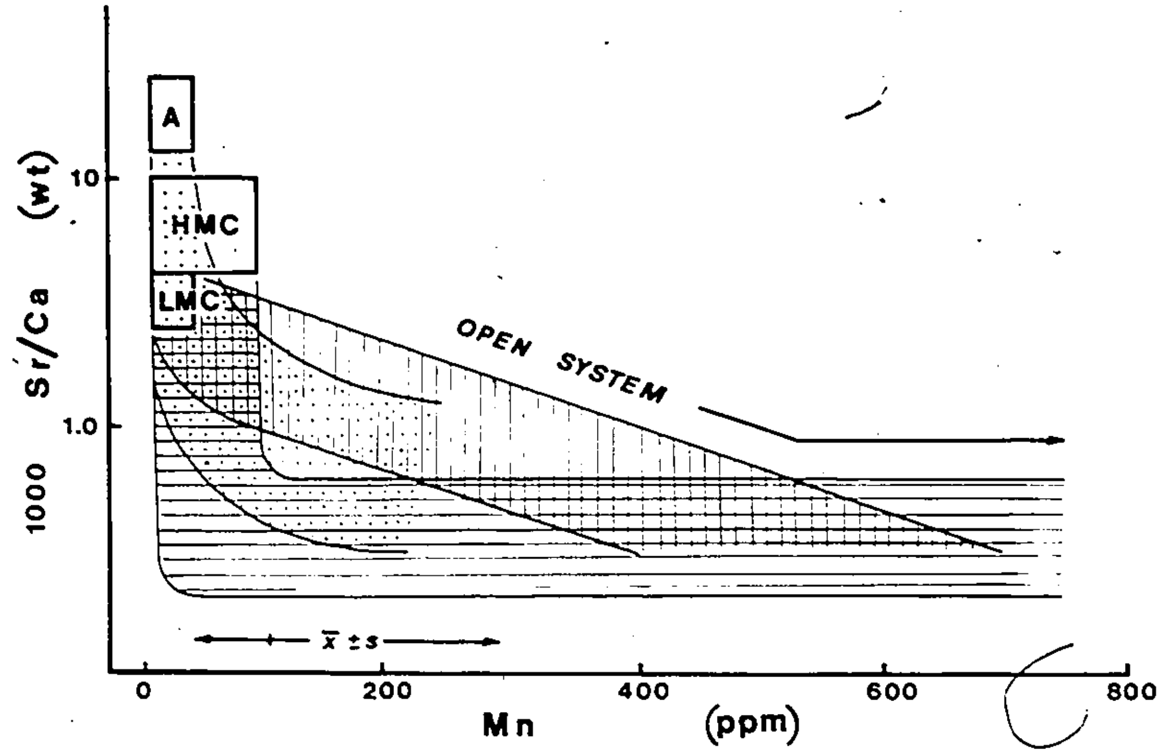


Fig. I-9. Summary of diagenetic trends for A, HMC and LMC with stabilization by meteoric water (Figs. I-5 to I-7). The x̄ ± s (geometric mean and standard deviation) represents literature review of app. 2100 samples from various carbonate facies, localities and ages (Wangersky & Joensuu, 1964; Dittmar & Vogel, 1968; Friedman, 1969; Honjo & Tabuchi, 1970; Veizer & Demovič, 1974 [unpublished Mn results for samples included in this study] ; Veizer & Wendt, 1976; Veizer, 1977; Pingitore, 1976, 1978; Veizer <u>et</u> <u>al</u>., 1978; this study). "Open system" designates the field where no chemical differences between fossil and matrix/cement are evident.

subjected to comparable external conditions (eg. permeability, porosity, mineralogy and chemistry of the host rock as well as to a similar volume and chemistry of the interstitial diagenetic water). Yet for the typical Mn range ($\bar{x} \pm s$) they show clear chemical differences, with LMC components consistently enriched while the HMC components are depleted in Sr with respect to their enclosing rock matrix (Fig. I-10). It is evident in this figure that these gradients diminish as the openness of the diagenetic system (water/rock ratio) increases. However, in the presently studied crinoidal biosparite, represented by the right side of Fig. I-10, the absence of chemical gradients may be due to the possibility that the crinoid ossicles and some of the syntaxial cement were of similar HMC mineralogy (see Theoretical Concepts for discussion). Since the external conditions were comparable for all components, the preserved chemical gradients of the sampled dLMC representatives suggest that the components themselves controlled the chemical composition of the final phase. Thus the original chemical compositions of different carbonate phases and their thermodynamic stability are reflected in their stabilized counterparts. With increasingly open diagenetic conditions the role of the original phase diminishes.

It is generally believed that diagenetic stabilization of carbonate sequences proceeds after exposure of the metastable assemblage to meteoric water (Bathurst, 1971, chapter 8). Dissolution of the metastable phases supersaturates the aquifer water with respect to calcite and induces the precipitation of

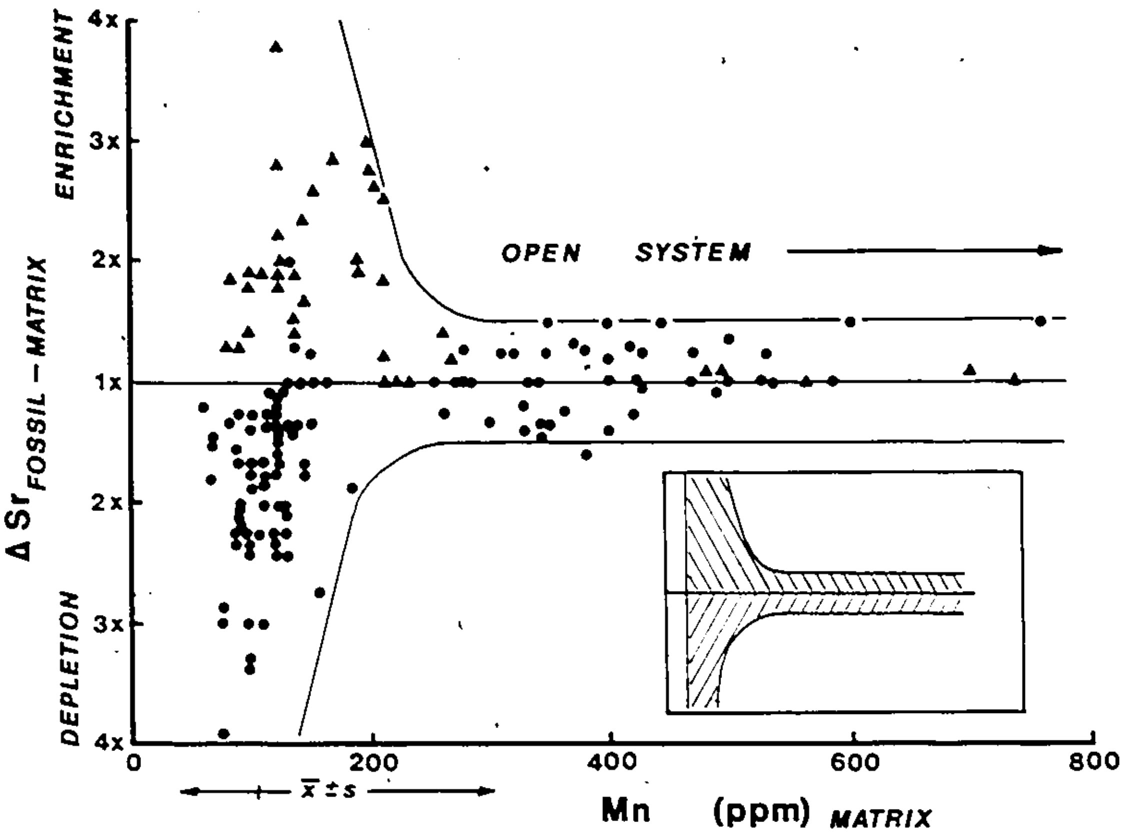


Fig. I-10. Enrichment - depletion graph (fossil-matrix). The ▲ represents the LMC-fossils (rugose corals and brachiopods) from the Read Bay Formation and the Burlington Limestone. The ● represents crinoids from the Canadian Arctic and from Iowa and Missouri. The material from the Read Bay Formation (Canadian Arctic) falls into Population I, while the material from the Burlington Limestone falls into Population II (= open system). The x̄ ± s and "open system" as in Fig. I-9. Populations I and II as in Figs. I-5 to I-7. Upper field of inset represents area of fossil-matrix enrichment, whereas the lower field designates the area of fossil-matrix depletion, all with respect to the matrix.

dLMC. Furthermore, this dLMC is believed to precipitate in equilibrium with the bulk aquifer (pore) water. Consequently, the composition of the stabilized limestone is controlled to a large extent by the interstitial meteoric water. Such a model is applicable to the "open system" part of Figs. I-9 and I-10 (cf. Pingitore, 1976, 1978 for further discussion). However, this system appears to be the exception rather than the rule as shown by the Mn values usually encountered in ancient carbonate facies.

It is evident that the components on the left side of Figs. I-9 and I-10 could not have been in equilibrium with the same bulk aquifer water. Furthermore, their close proximity in the same matrix precludes the existence of separate hydrologic systems for the corals, brachiopods, crinoids and their matrix. This leads to the conclusion that diagenetic mineralogical stabilization proceeds in discrete self-contained "reaction zones" established on solid-liquid interfaces (Fig. I-11). These reaction zones perhaps similar to those postulated by Katz and Matthews (1977), Pingitore (1976) and Veizer (1977, 1978), are termed here "Partly Closed Reaction Zones" (Fig. I-12). Such reaction zones derive their dissolved ions from both the dissolving metastable phase and the surrounding bulk aquifer (pore) water. The proportion of ions from each source in the reaction zone water film (= Messenger Film) will depend on the rate of dissolution - reprecipitation [A, HMC, (LMC) → dLMC] versus the rate of diffusion and flow transport between the water in the

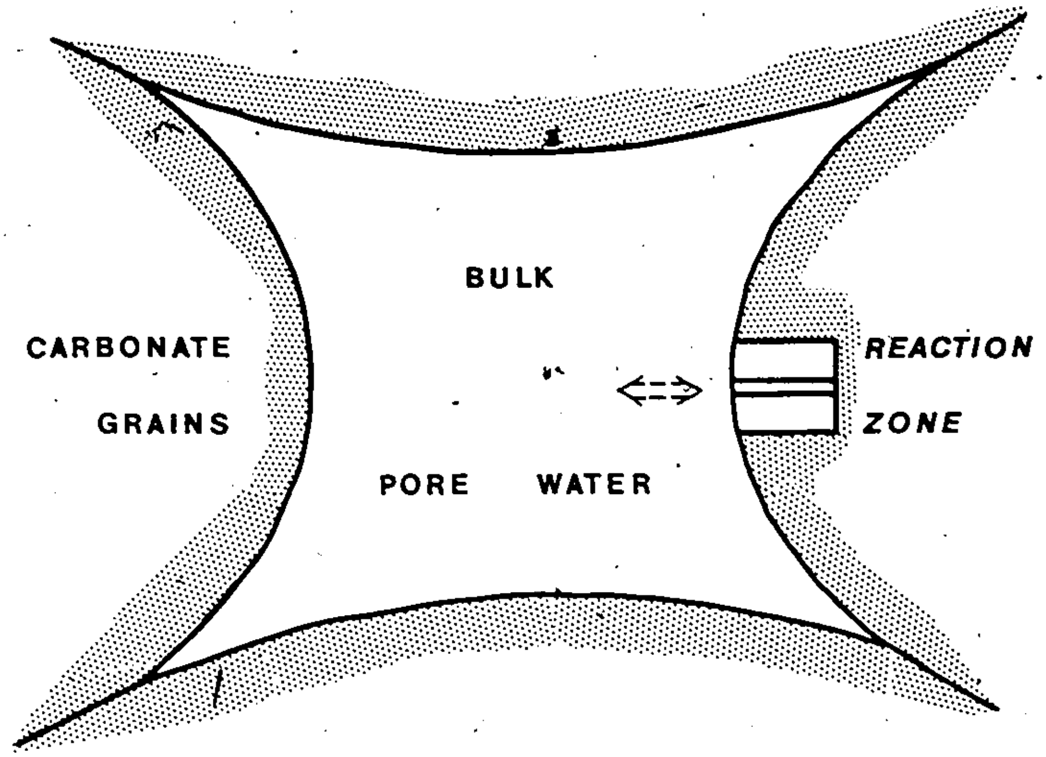


Fig. I-11. Functional and spatial relationship between the reaction zone, carbonate grains and bulk pore water. The carbonate grains could be a multitude of phases (ie. A, HMC and LMC). The bulk aquifer system (pore water) comprises the meteoric vadose and phreatic zones.

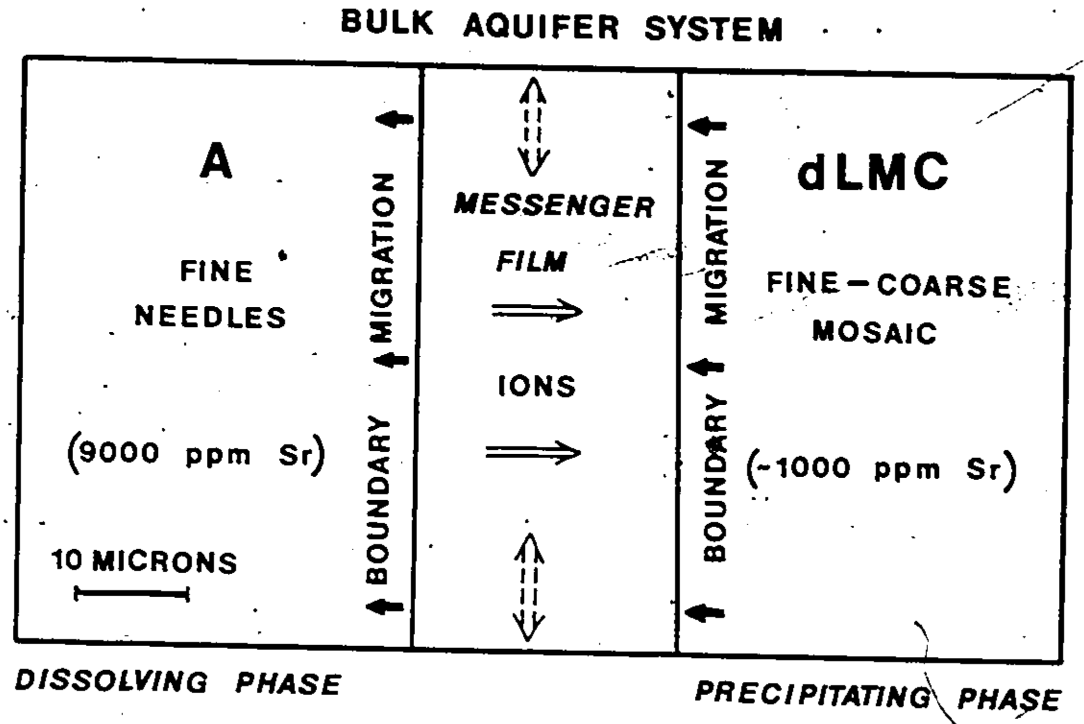


Fig. I-12. Partly Closed Reaction Zone (modified from Pingitore, 1976). Transfer of chemical and textural information takes place via the "Messenger Film". The Messenger Film (reaction zone) water is in disequilibrium with that of the bulk aquifer (pore water). Substituting HMC (or LMC (?)) for A would alter the chemical information of the donor (dissolving) and receptor (precipitating) phase accordingly. The stabilization process through boundary migration will proceed until all of the original metastable phase is transformed into dLMC.

reaction zone and the surrounding pore water. Since the rate limiting step of the dissolution - reprecipitation process is the precipitation of dLMC (Bathurst, 1971, p. 451), the chemistry of the reaction zone water will be "buffered" by the dissolving metastable phase. If diffusion and flow transport is relatively slow, a concentration gradient (spike) may persist in the vicinity of the dissolving phase. On the other hand with fast transport these gradients will dissipate into the pore water and an open system is approached. This could explain the consistent elemental gradients observed in the present study as well as the fact that the diagenetic redistribution of trace elements appears to have been controlled by the chemical composition and stability of the original mineralogical phases.

A similar mineralogical control was advocated already by Veizer & Demovič (1974) and Veizer (1977) from their studies of the Mesozoic and Paleozoic carbonates of Czechoslovakia and Australia, respectively. They recognized a bimodal distribution, with low- and high-Sr groups (lower portion of Fig. I-13). They concluded that the low-Sr group contained mostly originally HMC samples as well as rocks which underwent multistage solution-precipitation alteration (= open system in the present study). The high-Sr group, they classified as composed of originally A and LMC facies. This bimodal model can be expanded to a trimodal one, with distinct populations for the HMC, A and LMC phases (top in Fig. I-13).

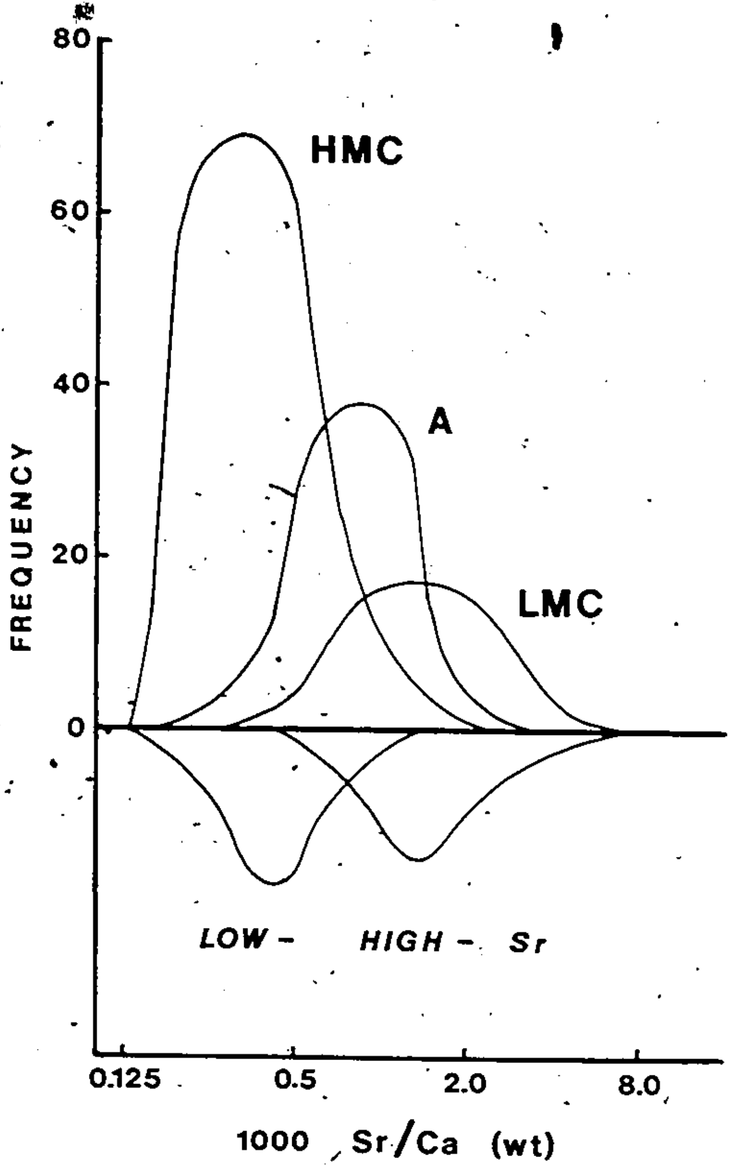


Fig. I-13. Strontium distribution in the studied components. For detailed facies analyses of the "low-Sr" and "high-Sr" groups see Veizer & Demovič (1974, p. 104). The modes of the carbonate phases of the present study are: HMC (0.4 Sr/Ca), A (0.9 Sr/Ca) and LMC (1.8 Sr/Ca).

CONCLUSIONS

Petrographic and elemental studies of different fossil groups and host rocks and comparison with published data lead to the following conclusions:

(1) Increasing diagenetic equilibration in meteoric water (due to textural alteration, precipitation of interparticle cement, and their combination) is reflected by concomitant changes in trace element composition, particularly Sr and Mn;

(2) Although diagenetic equilibration leads to a decrease in Sr content, the original different chemical gradients of A and HMC are partly preserved. LMC because of its stability in meteoric water, retains Sr concentrations which are only slightly altered;

(3) The above trace element relationship can be utilized to identify the original mineralogy of the dLMC phases. Such criteria suggest that the herein studied Paleozoic rugose corals secreted originally a LMC corallum;

(4) Since all internal components in the Burlington Limestone have identical chemistry it is suggested that its diagenetic stabilization proceeded in an open diagenetic system controlled by the chemistry of the bulk aquifer water;

(5) In contrast, stabilization of most carbonate systems appears to proceed in discrete reaction zones on solid-liquid interfaces. The chemistry of a reaction zone is controlled by the dissolving phases and by disequilibrium exchange with the surrounding bulk aquifer water. Thus all internal components

can retain measureable chemical differences, which mark the gradients. This stabilizing process is applicable to the Read Bay Formation.

CHAPTER II

STABLE ISOTOPE DIAGENESIS OF A MULTICOMPONENT PALEOZOIC CARBONATE SYSTEM

ABSTRACT

The present study deals with oxygen and carbon isotopic distributions in the separated fossil and matrix components of the Mississippian Burlington Limestone (Iowa and Missouri) and the Upper Silurian Read Bay Formation (Arctic Canada). The results can be reconciled with textural and trace element observations only if it is accepted that the ^{18}O content of ancient oceans differred from that of the present day. Accepting these secular variations, the postulated δ^{18}O of Mississippian seawater was about 1 ‰ and of the Upper Silurian about 5 ‰ lighter than at present.

The estimated average diagenetic shift in δ^{18}O of the Read Bay Formation constituents (stabilized in a partly closed diagenetic system) is about -1 ‰ and for the Burlington Limestone constituents (stabilized in an open diagentic system) is about -3 ‰ (PDB). Correcting for the magnitude of secular variation, the probable paleotemperature for the Mississippian sea of Iowa and Missouri was $31 \pm 4^{\circ}$C and for the Upper Silurian sea of Arctic Canada $21 \pm 2^{\circ}$C.

Calculations suggest that the Paleozoic rugose corals and crinoids were not enriched in ^{12}C and ^{16}O, rather they are in line with expected results for the studied brachio[illegible]ds. The apparent "vital effect" of Recent corals and crinoids may not be applicable to their Paleozoic counterparts.

The δ^{13}C of the studied samples is bimodally distributed, with $+0.5 \pm 0.4$ and $+3.1 \pm 0.7$ ‰ as the modes of the groups. The

light-^{13}C group is characteristic of inorganically derived aragonite mud matrix and/or cement precipitated in equilibrium with ambient seawater. The heavy-^{13}C group is associated with samples from organic build-ups or from areas of high concentrations of skeletal debris. The cement of this group is organically derived high-Mg calcite and aragonite precipitated in carbon isotopic disequilibrium with ambient seawater.

Cementation of the Read Bay Formation sediments, which, in general, fall into the light-^{13}C group, proceeded in the submarine environment. On the other hand, most of the Burlington Limestone samples fall into the heavy-^{13}C group, and were initially cemented in the submarine environment, followed by subsequent cementation in the meteoric phreatic environment.

RÉSUMÉ

Ces recherches traitent de la distribution des isotopes d'oxygène et de carbone dans la matrice et les fossiles séparés, constitutifs du calcaire de Burlington (Mississipien, Iowa et Missouri) et de la formation de Read Bay d'âge Silurien supérieur (Canada arctique).. Les résultats peuvent se concilié avec les données obtenues sur la texture et les oligo-éléments seulement si l'on admet que la teneur des océans anciens en ^{18}O était différente de celle des océans actuels. Si l'on accepte ces variations séculaires, le δ^{18}O postulé pour l'eau de mer du Mississippien aurait été environ 1 ‰ et pour l'eau de mer du Silurien supérieur environ 5‰ moins que le δ^{18}O des océans actuels.

La modification diagénétique moyenne en $\delta^{18}O$ calculée pour les éléments constitutifs de la formation de Read Bay (en équilibre dans un systeme diagénétique partiellement isolé) est d'environ 1 ‰ et pour les éléments constitutifs du calcaire de Burlington, d'environ 3 ‰ (PDB). La paléotempérature probable calculée pour la mer d'âge Mississippien en Iowa et au Missouri était de 31 ± 4°C et pour la mer dans le Canada arctique, d'âge Silurien supérieur, de 21 ± 2°C, compte tenu des corrections apportées pour l'ampleur des variations séculaires.

D'apres les calculs la teneur des Tetracoralliaires et des Crinoïdes Paléozoiques en ^{12}C et en ^{16}O n'était pas élevée, mais etait plutot conforme aux résultats prévus pour les Brachiopodes examinés. Le "vital effect" apparent des Coraux et des Crinoïdes Récents pourrait donc ne pas être applicable aux Coraux et aux Crinoïdes Paléozoiques.

Le $\delta^{13}C$ des échantillons examinés a une distribution bimodale, dont +0.5 ± 0.4 et +3.1 ± 0.7 ‰ sont les modes des groupes. Le groupe du ^{13}C-léger est caractéristique d'une matrice de boue aragonite d'origine inorganique et/ou d'un ciment précipité en équilibre avec l'eau de mer ambrante.

Le groupe du ^{13}C-pesant est associé aux échantillons venant d'accumulations organiques ou de régions où il y a en concentration élevée de debris squelettiques. Ce groupe a un ciment d'aragonite et de calcite de haute teneur en Mg, de nature organique et qui a été précipité dans un milieu dans lequel les isotopes de carbone étaient en diséquilibre avec l'eau de mer ambrante.

La cimentation des sédiments de la formation Read Bay qui font partie generalement du groupe ^{13}C-leger c'est passé dans un milieu sous-marine. Par contre la plupart des échantillons de calcaire Burlington font partie du groupe ^{13}C-pesant; leur cimentation a été d'abord dans un milieu sous-marine, et ensuite par une cimentation dans un milieu météorique phréatique.

ZUSAMMENFASSUNG

Die vorliegende Mitteilung befasst sich mit der Sauerstoff- und der Kohlenstoffisotopenverteilung in den getrennten Fossilien und den Matrixbestandteilen des Burlington Kalksteins des unteren Karbons (Iowa und Missouri), und der Read Bay Formation des oberen Silurs (kanadischen Arktis).

Die Isotopenergebnisse, können mit den Struktur- und den Spurenelementbeobachtungen in Einklang gebracht werden, aber nur dann, wenn man akzeptiert, dass der ^{18}O Inhalt der vormaligen Ozeane anders als der der heutigen war. Nimmt man diese Säkularveränderungen an, dann war der vorausgesetzte δ^{18}O Wert für das Meerwasser des unteren Karbons, ungefähr 1 ‰, und der δ^{18}O Wert für das Meerwasser des oberen Silurs, ungefahr 5 ‰ niedriger, als der für heutige Ozeane.

Die geschätzte, durchschnittliche Diageneseverschiebung der δ^{18}O Werte, für die Bestandteile der Read Bay Formation (die in einem zum Teil geschlossenen Diagenesesystem stabilisierten) ist ungefähr -1 ‰, und der, für die Bestandteile des Burlington Kalkstein (die in einem offenen Diagenesesystem stabilisierten) ist ungefähr -3 ‰ (PDB).

Wenn das Säkularveränderungsausmass richtig gestellt ist, dann war die Paläomeertemperatur des unteren Karbons von Iowa und Missouri, 31 ± 4 °C, und die Paläomeertemperatur des oberen Silurs der kanadischen Arktis, 21 ± 2 °C.

Berechnungen deuten an, dass die paläozoischen rugosen Korallen und Krinoiden nicht mit ^{12}C und ^{16}O angereichert waren, vielmehr stimmen deren Ergebnisse mit denen von den Brachiopoden überein. Der sogenannte "vital effekt" der rezenten Korallen und Krinoiden, ist wahrscheinlich für deren paläozoischen Gegenstücke nicht angängig.

Der $\delta^{13}C$ Wert der studierten Gesteinsproben ist bimodal verteilt, mit Gruppenmodalitäten von $+0{,}5 \pm 0{,}4$ und $+3{,}1 \pm 0{,}7$ ‰. Die leichte-^{13}C Gruppe ist charakteristisch für anorganisch herleitbare Aragonitschlammmatrix, und/oder Aragonitzement, welche im Equilibrium mit dem umgebenden Meerwasser ausfielen.

Die schwere-^{13}C Gruppe ist mit Gesteinsproben von organischen "Aufbauten", oder mit Gesteinsproben von Gegenden mit hoher Skeletttrümmerkonzentration verbunden. Der Zement dieser Gruppe ist organisch herleitbarer Hoch-Mg Kalzit und Aragonit, der in Kohlenstoffisotope Nichtequilibrium mit dem umgebenden Meerwasser ausfiel.

Die Zementierung der Sedimente der Read Bay Formation, die meistens in die leichte-^{13}C Gruppe gehören, nahm in der unterseeischen Umgebung statt. Statt dessen, die meisten

Gesteinsproben des Burlington Kalksteins, deren Werte in die schwere-^{13}C Gruppe fallen, wurden zuerst in der unterseeischen Umgebung zementiert, und später, anschliessend in der phreatischen Grundwasserumgebung zementiert.

INTRODUCTION

Changes in the isotopic ratios of diagenetically stabilized limestones indicate that most of their alteration, involving mineralogical transformation of the original marine metastable assemblage into stable low-Mg calcite (dLMC), occurred in the phreatic fresh water zone (Gross, 1964; Land, 1970; Allan & Matthews, 1977; Hudson, 1977). In addition, the presence of secondary calcite in the pores of the rock causes a similar shift in the isotopic composition of the rock, because the $^{18}O/^{16}O$ and $^{13}C/^{12}C$ ratios of secondary calcites are markedly different from those of the constituent grains (Gross, 1964).

In the previous chapter it was shown that the above diagenetic stabilization process is reflected by the degree of textural preservation as well as the trace element composition of the carbonate components. This is particular evident from Sr versus Mn scatter diagrams, with Sr decreasing and Mn increasing in the process of equilibration with meteoric water. Furthermore, it was documented that the rate of this wquilibration was controlled by the stability of the original mineralogical phases.

The preservation of primary textures in the rugose corals (eg. trabecular structure) and brachiopods (eg. two layer shell structure) from the Burlington Limestone and Read Bay Formation suggest that diagenetic stabilization (transformation of HMC, A and possibly LMC into dLMC) took place probably at rather shallow depths under near earth surface conditions (ie. pressure and temperature). This assertion is also substantiated by the compaction experiment of Shinn et al. (1977), which showed that neither great depths nor large volumes of water are required to compact and cement carbonate sediments. This applies in particular to the biomicrites of the Read Bay Formation which show few signs of extensive compaction, even though depth of burial has been calculated in excess of 3 km (Kerr, 1977). However, the biosparites of the Burlington Limestone were never buried to great depth (Harris & Parker, 1964).

The above points are important in evaluating the diagenetic redistribution of ^{18}O in carbonates, since the fractionation (thus ^{18}O content) of oxygen isotopes is temperature dependent (O'Neil & Epstein, 1966). Therefore the temperature factor for oxygen fractionation during carbonate diagenesis will be only of second order importance. Thus changes in $\delta^{18}O$ will be of a "primary" nature, which will be discussed later on in this paper.

Since mineralogical stabilization is a dissolution-reprecipitation process (Bathurst, 1971, chapter 8) each solution-precipitation step involves equilibration with meteoric water not only of the trace elements but also of oxygen and carbon isotopes. The degree of stabilization of each sample with meteoric water has been determined by consideration of its textural features and trace element composition.

The aim of this chapter is to evaluate the behaviour of carbon and oxygen isotopes during diagenetic equilibration of each mineralogical component and phase under shallow earth surface conditions.

THEORETICAL CONCEPTS

The original isotopic composition of marine $CaCO_3$ depends on a) the isotopic content of ambient seawater, b) the vital effect of biogenic carbonates and c) the temperature and salinity of the seawater. All of these are discussed in detail by Faure (1977) and Hudson (1977).

The diagenetic isotope exchange between an original marine carbonate phase and dissolved HCO_3^- of meteoric waters can be represented simply as:

$$^{13}C^{18}O_3^{2-} + H_2{}^{16}O + {}^{12}CO_2 \rightleftharpoons {}^{12}C^{16}O_3^{2-} + H_2{}^{18}O + {}^{13}CO_2 \quad \text{(II-1)}$$

The depletion in ^{18}O and ^{13}C (Fig. I-3, chapter one) is due to the fact that meteoric water is enriched in ^{16}O (Gross, 1964; Faure, 1977) and the dissolved CO_2, if soil-derived, is enriched in ^{12}C (Craig, 1953; Vogel, 1959; Gross, 1964). The degree of this isotopic exchange will depend in general on the proportions of the isotopes in the stabilized phase derived from the carbonate precursor and the interstitial meteoric water. The higher the influence of the latter is – the more open the diagenetic system will be, and the closer to equilibrium with such water the precipitated dLMC will be.

The temperature dependence of oxygen and carbon can be represented by equation II-2 (from Faure, 1977, p. 352 and 384):

$$1000 \ln \alpha_c = A\, 10^6\, T^2 + B \quad \text{(II-2)}$$

In this equation A and B are experimental constants, T is the absolute temperature and α is the isotope fractionation factor. The oxygen and carbon isotope fractionation factors are given in Fig. I-3 (chapter one). However, to calculate paleotemperatures of carbonates the equation of Epstein et al. (1953) is generally used, which was modified by Craig (1965) and Shackleton & Kennett (1975). The modified equation can be represented by:

$$T^{o}C = 16.5 - 4.3\ (\delta_c - \delta_w) - 0.14\ (\delta_c - \delta_w)^2 \quad \text{(II-3)}$$

in which δ_c is the measured $\delta^{18}O$ of the carbonate, δ_w is the measured or assumed $\delta^{18}O$ of the water and T is the temperature in degree Celsius. If the $\delta^{18}O$ of seawater is constant relative to present day ocean water, then δ_w would be zero, whereas if this is not the case then δ_w will be some value other than zero. For additional discussion of isotope fractionation see Faure (1977, chapters 18, 19 and 20).

The composition of surface meteoric water is temperature dependent which varies with latitude, altitude, season, etc. (Dansgaard, 1964) with $\delta^{18}O$ ranging from about −2 at the equator to about −30 ‰ (SMOW) at the poles. However, since most of the stabilization occurs relatively rapidly after deposition of the carbonate sequence, these latitudinal variations are probably of small significance. The Silurian Read Bay Formation of Somerset and Cornwallis Islands was deposited at approximately 20 ± 5°N latitude (Irving, 1973, fig. 1). The Mississippian Burlington Limestone was deposited at approximately 10 ± 5°S latitude (Keppie, 1977, fig. 3).

The Quaternary glaciation is believed to have caused about 1.5 ‰ fluctuation in $\delta^{18}O$ of seawater and thus its derived meteoric water (Shackleton, 1968; Emiliani & Shackleton, 1974). At this stage it is not possible to estimate the influence of such a factor for the Paleozoic hydrosphere, but any such influences will probably be of second order importance only.

REGIONAL GEOLOGY - PETROGRAPHY - ORIGINAL COMPONENT MINERALOGY :

The detailed discussion of regional geology, location of samples, petrography and mineralogy of carbonate components has been presented in chapter one (this thesis) and in Appendices I and II.

ANALYTICAL TECHNIQUES

The initial preparation of samples (separation and powdering) was described in chapter one of this thesis.

Approximately 10 mg of 156 samples were reacted with 100 % phosphoric acid (McCrea, 1950). P_2O_5 was added to the acid to ensure absence of free water.

Oxygen and carbon were measured on a V. G. Micromass 602 D Twin mass spectrometer. Their isotopic ratios are expressed in the usual notation (δ) and given relative to PDB :

$$\delta^{18}O\ (‰) = \left[\frac{(O^{18} / O^{16})_S - (O^{18} / O^{16})_{St}}{(O^{18} / O^{16})_{St}} \right] \times 1000$$

$$\delta^{13}C\ (‰) = \left[\frac{(C^{13}/C^{12})_S - (C^{13}/C^{12})_{St}}{(C^{13}/C^{12})_{St}} \right] \times 1000$$

Furthermore, the ^{17}O correction of Craig (1957) was employed.

Average accuracy and reproducibility, as compared to recommended values for N. B. S. (20, Solnhofen Limestone) standard rock (cf. Craig, 1957; Hoefs, 1973), were as follows: $\delta\ ^{18}O$ (0.12, 0.05) and $\delta\ ^{13}C$ (0.05, 0.05) permille, respectively.

BIOLOGICAL FRACTIONATION

Brachiopods

Recent articulate brachiopods have been shown not to display any "vital effect". Lowenstam (1961, p. 243), from extensive studies of this phylum in various physical environments, concluded "...that brachiopods lay down shell carbonate in isotopic equilibrium with the surrounding waters...". Thus this group should be well suited to serve as the low-Mg calcite (LMC) standard.

Rugose corals

Recent aragonitic scleractinian corals display a vital effect (Lowenstam & Epstein, 1957; Keith & Weber, 1964; Weber & Raup, 1966; Weber & Woodhead, 1969, 1970, 1972a). Weber & Woodhead (1970) suggested that the $\delta^{18}O$ of reef-building corals will be temperature and metabolic process dependent, which explains the apparent isotopic disequilibrium or vital effect between skeletal carbonate and ambient seawater. They proposed these criteria to explain the variability of $\delta^{18}O$ in their sampled corals from Heron Island, Australia.

In addition, Weber & Woodhead (1972b) showed that some coelenterates of the class Hydrozoa (skeletal carbonate is A; Milliman, 1974, table 26, p. 92-93) and Octocorallia (skeletal carbonate is A and HMC; Milliman, 1974, table 26, p. 92-93) secrete $CaCO_3$ in oxygen isotopic equilibrium with ambient seawater. They (Weber & Woodhead, 1972b, p. 296) suggested that "...with faster excretion of CO_2 to seawater, little or no metabolic carbon dioxide is incorporated in the skeleton." This proposed process is, at present, speculation, which deserves more research to delineate the non-vital effect in these corals.

At this stage it is not known if the Paleozoic rugose corals analogous to the Recent hydrocorals and octacorals, precipitated their skeletons in isotopic equilibrium with ambient seawater. Also, possibly due to the different presumed LMC mineralogy (p. 40, chapter one) of the rugose corals the apparent vital effect for Recent scleractinian corals may not be applicable to Paleozoic rugosans. Later in the text the brachiopod and coral samples will be compared to test whether any isotopic vital effect can be detected.

Crinoids

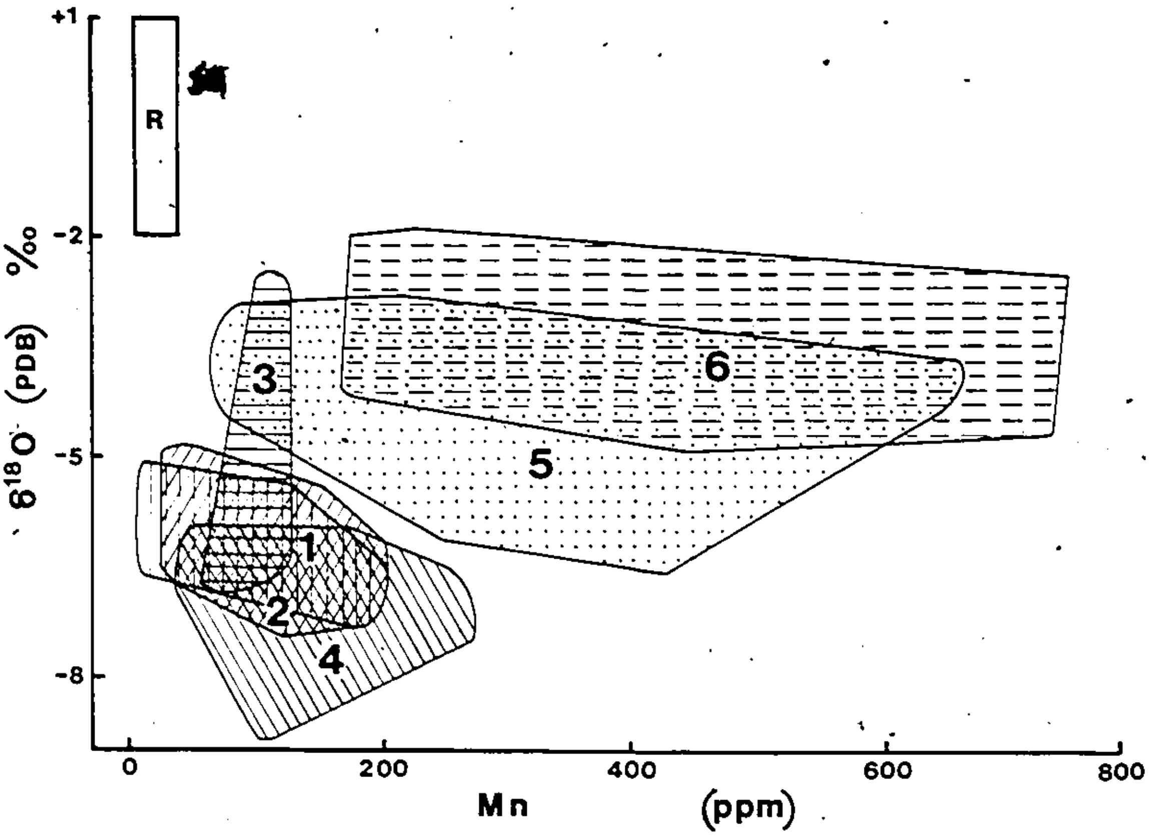
Recent crinoids display a vital effect and are as a group enriched in ^{12}C and ^{16}O (Lowenstam & Epstein, 1957; Weber & Raup, 1966; Weber, 1968). The same inconsistencies as already noted for the corals (eg. discrepancies in the procedures for temperature calculations, such as not mentioning the water correction; comparison of Recent representatives with Paleozoic ones) apply also to the crinoids. Consequently, more definitive studies are required to confirm the vital effect in the Recent (and by analogy in the Paleozoic crinoids).

EVALUATION OF RESULTS

The role of secular variations

Previous extensive studies of the $\delta^{18}O$ of sedimentary carbonates, cherts and phosphates show ^{18}O depletion with increasing geologic age (Degens & Epstein, 1964; Keith & Weber, 1964; Perry, 1967; Fritz, 1971; Perry & Tan, 1972; Veizer & Hoefs, 1976). This trend is believed to be either (a) secondary, caused by continuous post-depositional equilibration of the carbonate sediment with percolating meteoric water, or (b) primary. In the latter case, it is ascribed either (1) to higher temperatures of the ancient oceans (Knauth & Epstein, 1976), or (2) to the depleted ^{18}O nature of ancient seawater (Perry, 1967; Fritz, 1971; Perry & Tan, 1972; Veizer, 1977).

As shown in the previous chapter, the manganese concentration of a carbonate component will increase with increasing equilibration with meteoric water. The plot of all $\delta^{18}O$ data vs. Mn content (Fig. II-1) shows that, regardless of whether it is in the same or more "equilibrated" Mn range, the Mississippian Burlington Limestone contains heavier $\delta^{18}O$ than the Upper Silurian Read Bay Formation. Thus the equally or more altered (on the basis of textures and trace element data) Mississippian corals, crinoids and brachiopods contain heavier (less"altered") oxygen isotopes than their Silurian counterparts (cf. also Veizer, 1977, p. 572-573). If this $\Delta^{18}O$ is not primarily a post-depositional feature, then the Δ can be linked to a higher Silurian ocean temperature.



~~Fig. II-1. Scatter~~ diagram of $\delta^{18}O$ vs. Mn for all studied samples. The R-Recent field defines the observed range of organic and inorganic carbonate in equilibrium with present day seawater (Gross, 1964; Keith & Weber, 1964, Milliman, 1974). Field 1 represents micrites and associated fossils from the Read Bay Formation of Somerset Island. Field 2 represents micrites-microspar and fossils from the Read Bay Formation at Read Bay and Depot Point Lake. Field 3 represents dolomitic micrites and fossils from the Read Bay Formation at Cape Rescue. Field 4 represents dolomitic micrites, minor sparites and fossils from the Read Bay Formation at Goodsir Creek. Field 5 represents biosparites and fossils from the Burlington Limestone of Missouri. Field 6 represents biosparites and partly siliceous fossils from the Burlington Limestone of Iowa.

However, this would demand ~ 25°C higher temperature (~ 21 vs. 46°C) for the Silurian habitats. Such a difference and temperature variation does not appear to be realistic. Therefore, the alternative least contradictory to the present data is related to an increase of ^{18}O content of the oceans with decreasing geologic age (b-2). Extrapolation of the $\delta^{18}O$ - Mn trends (Fig. II-1) into the range of the "least altered" Mn values suggests that on average, the Mississippian skeletal components are ~ 1 ‰ and the Silurian ones ~ 5 ‰ lighter than their Holocene counterparts. Since the variations in the degree of diagenetic equilibration were corrected for by this extrapolation, the maximal diagenetic component in the least altered specimens is $\lesssim$ 1 ‰ and the $\Delta^{18}O$ Mississippian-Silurian is therefore real.

Based on the above discussion it can be concluded that the oceans became progressively enriched in ^{18}O during geologic history and, therefore, each respective carbonate component age group must be considered separately.

Phanerozoic carbonate rocks (cf. Veizer & Hoefs, 1976, for summary) have $^{13}C/^{12}C$ ratios mostly within the range 0 ± 2 ‰ PDB. Recently, Veizer <u>et al</u>. (in prep.) advocated that within this overall scatter, there may exist real secular variations of $^{13}C/^{12}C$ of seawater bicarbonate. However the mean $\delta^{13}C_{carbonate}$ of the Silurian, Carboniferous and Quaternary are all about 0 ‰ PDB. Thus possible secular variations in $\delta^{13}C$ will be only of secondary importance.

Oxygen isotopes

In this chapter only those factors will be discussed which have a direct bearing on the isotope variables. For discussion of the other factors the reader is referred to chapter one.

High-Mg calcite

The variation in oxygen isotopic composition of the HMC components of the Burlington Limestone can be explained almost entirely by factor 2 (Table II-1). This factor, identified as diagenetic equilibration with meteoric water, causes the loss of Sr and Mg and simultaneous enrichment in ^{18}O, this enrichment cannot be explained at this time.

In contrast, the oxygen isotopic composition of the HMC components in the Read Bay Formation is controlled primarily by the frequently observed dolomitization (factor 1, Table II-2), which causes ^{18}O enrichment. This process will be discussed in detail in chapter three.

No systematic trend in δ^{18}O is apparent for the pooled Burlington Limestone and Read Bay Formation populations if one accepts that the ^{18}O composition of ocean water has remained constant during geologic history (Fig. II-1). However, in the previous section it was concluded that average ocean water was depleted by about 1‰ and 5‰ for the Mississippian and Silurian, respectively. Accepting this secular variation, the agreement between conclusions based on textural and trace element data (chapter one) and oxygen isotope distribution patterns becomes

	Factor 1	Factor 2	Factor 3	Factor 4
log I.R.	0.76034	0.55073	0.17943	-0.21773
log Mn	0.85666	0.13770	0.20905	0.44570
log Sr	-0.16233	-0.74623	0.13753	0.11200
log Fe	0.85831	-0.08148	0.01370	-0.23044
log Al	0.83389	0.32218	-0.28327	0.04034
log Na	0.05271	-0.02330	0.08777	-0.62178
log Mg	0.08467	-0.65491	0.66101	-0.09021
log Ca	-0.17670	0.09531	-0.72564	0.30448
$\delta^{18}O$	0.13574	0.93173	0.01573	0.23781
$\delta^{13}C$	-0.51818	0.05639	0.74947	0.32828

Factor	Pct. of Var.	Diagnosis
1	46.4	laboratory leaching and silicification
2	26.1	diagenetic equilibration
3	17.2	dolomitization
4	10.3	?

Table II-1. Factor analysis (Varimax rotated factor matrix) of the HMC - phases of the Burlington Limestone samples (N = 16 crinoids; 31 crinoidal biosparite).

	Factor 1	Factor 2	Factor 3
log I.R.	-0.03231	0.57700	0.28676
log Mn	0.10052	-0.01552	0.31868
log Sr	-0.26843	0.94851	-0.15407
log Fe	0.48413	0.45200	0.50759
log Al	0.28125	0.46335	0.64433
log Na	0.55068	-0.40458	-0.16553
log Mg	0.94264	-0.02500	0.10213
log Ca	-0.87553	0.27314	-0.21569
$\delta^{18}O$	0.77945	0.11121	0.38899
$\delta^{13}C$	0.01804	-0.08982	-0.80463

Factor	Pct. of Var.	Diagnosis
1	52.8	dolomitization
2	35.9	diagenetic equilibration and laboratory leaching
3	11.3	silicification (?)

Table II-2. Factor analysis (Varimax rotated factor matrix) of the HMC - phase of the Read Bay Formation samples (N = 35).

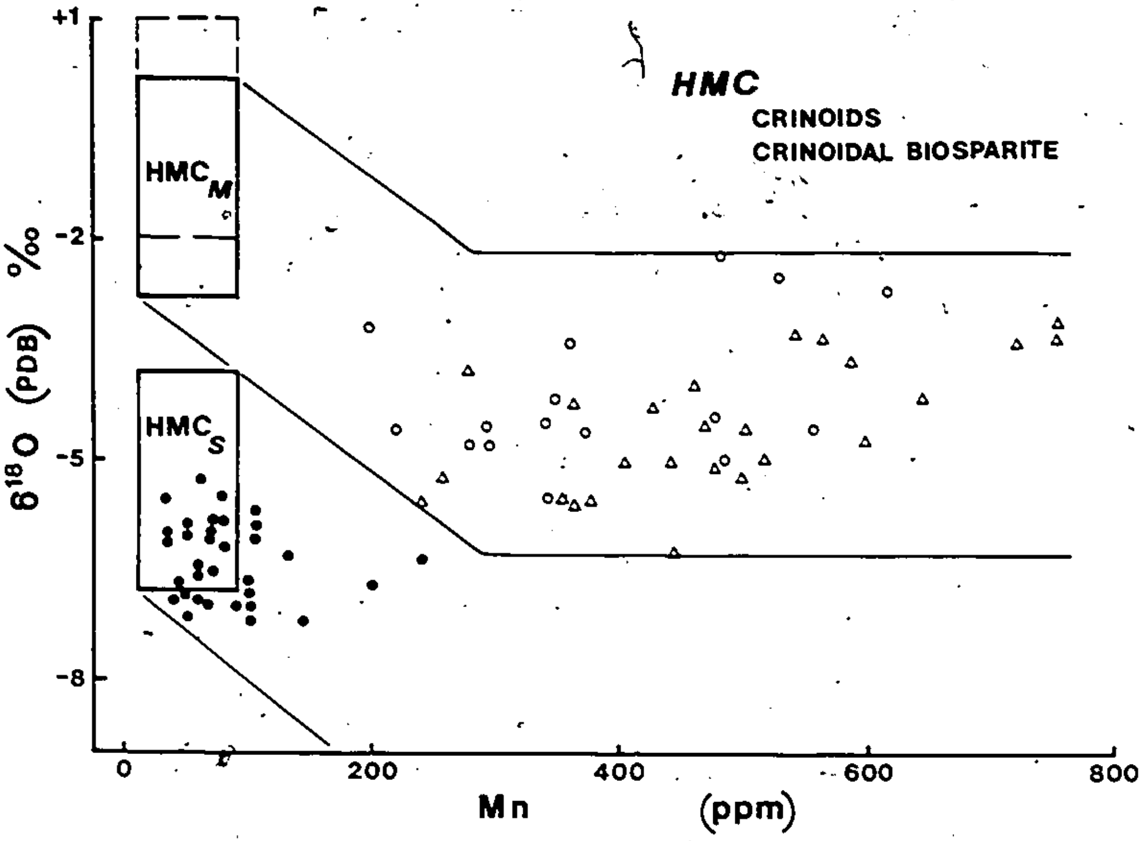


Fig. II-2. Scatter diagram of $\delta^{18}O$ vs. Mn for the presumed originally HMC carbonate components. The dashed HMC field defines the observed range of Recent HMC in organic and inorganic equilibrium with seawater (Gross, 1964; Keith & Weber, 1964; Milliman, 1974). The solid fields are the postulated ranges for the equivalent HMC components of the Mississippian (HMC$_M$) and the Upper Silurian (HMC$_S$) (Perry, 1967; Fritz, 1971; Milliman, 1974; Veizer & Hoefs, 1976). The ● represents crinoids from the Read Bay Formation. The ○ and △ represent crinoids and biosparites, respectively from the Burlington Limestone.

satisfactory.

The less altered (equilibrated) Read Bay Formation HMC components fall into or close to the postulated Silurian compositional field; with average depletion in ^{18}O of about 1 ‰ (Fig. II-2). In contrast, the more altered Burlington Limestone HMC components show an average depletion of about 3 ‰ (Fig. II-2).

Aragonite

The total variation of trace elements and isotopes in the micrite to dolomite variation in rock type of the Read Bay Formation is controlled by three factors (Table II-3). Factor 1, diagnosed as laboratory leaching and salinity, can be separated into I.R. and Fe and Al for the former diagnosis and Na and $\delta^{18}O$ and $\delta^{13}C$ for the latter one, where an increase in Na is accompanied by an increase in ^{18}O but decrease in ^{13}C. Factor 2, diagnosed as dolomitization and controlling most of the $\delta^{18}O$ variation, will be discussed in chapter three. Factor 3, which accounts for 12.7 % of the total elemental and isotopic variation, is diagnosed as representing diagenetic equilibration with meteoric water; Mn and ^{13}C are loaded positively and ^{18}O negatively on this factor.

The scatter diagram $\delta^{18}O$ vs Mn shows that the results for the Read Bay Formation cluster close to the postulated field for A in equilibrium with Silurian seawater (Fig. II-3). The few samples that are enriched in ^{18}O are dolomitized

	Factor 1	Factor 2	Factor 3
log I.R.	0.91516	-0.17976	-0.18084
log Mn	0.03304	0.04525	0.55667
log Sr	0.40221	-0.71276	-0.08493
log Fe	0.86715	0.17113	0.38751
log Al	0.93155	0.04871	-0.17695
log Na	0.43210	0.65642	-0.07374
log Mg	-0.01458	0.93793	0.22752
log Ca	-0.00131	-0.95996	0.05040
$\delta^{18}O$	0.51494	0.64940	-0.41905
$\delta^{13}C$	-0.53250	-0.03355	0.59670

Factor	Pct. of Var.	Diagnosis
1	48.6	laboratory leaching and salinity
2	38.7	dolomitization
3	12.7	diagenetic equilibration (?)

Table II-3. Factor analysis (Varimax rotated factor matrix) of the A (aragonite) -phase of the Read Bay Formation samples (N = 47).

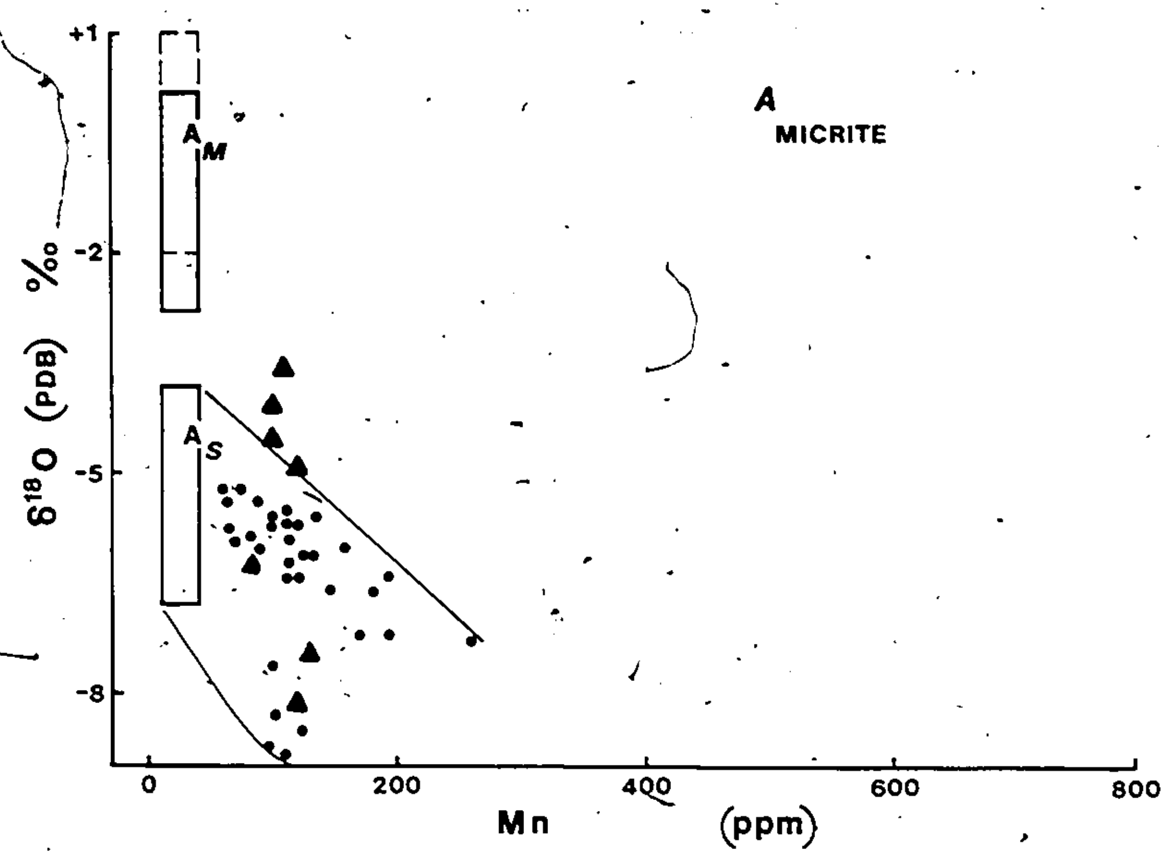


Fig. II-3. Scatter diagram of $\delta^{18}O$ vs. Mn for presumed originally aragonite (A) carbonate components. The dashed A field defines the observed range of Recent A in organic and inorganic equilibrium with seawater (cf. Fig. II-1). The solid fields are the postulated ranges for the equivalent A carbonate components of the Mississippian (A_M) and Upper Silurian (A_S) (cf. Fig. II-2). The ● represent micrites ($\lesssim$ 30,000 ppm Mg) and ▲ represents dolomitic micrites (> 30,000 ppm Mg) from the Read Bay Formation.

(samples from Cape Rescue, Fig. I-1, chapter one), in accordance with the conclusions based on factor analyses.

The trend of increasing diagenetic equilibration with meteoric water (approximated by the increase in Mn) is accompanied by depletion in ^{18}O. The more altered samples are those from Cornwallis Island. This is in general agreement with conclusions based on trace element and textural observations (Fig. I-3). If the average $\delta^{18}O$ composition of A in equilibrium with Silurian seawater is about -5 ‰ (PDB), the observed average isotopic alteration for A is then about 1.5 ‰.

Low[illegible]g calcite

Factor analysis of the presumed original LMC Burlington Limestone samples shows that oxygen isotopic composition varies antithetically with Ca (Factor 3, Table II-4), but the meaning of this factor is not clear. Perhaps dilution of $CaCO_3$ by combined weight of other components in the rock (eg. Mg, Si,...) leads to a depletion of ^{18}O. In the LMC samples of the Read Bay Formation, $\delta^{18}O$, together with Na is positively loaded on factor 4 (Table II-5), which again is not clearly understood. Perhaps salinity, during either deposition or early diagenesis, could influence Na and ^{18}O distribution (cf. Craig & Gordon, 1965; White, 1978). More work is required for qualification of this relationship.

The data from the Burlington Limestone occupy most of the horizontal part of the diagenetic pathway as defined by

	Factor 1	Factor 2	Factor 3
log I.R.	0.94484	0.15950	0.11387
log Mn	0.80038	-0.57792	-0.04558
log Sr	-0.57799	0.75223	0.25387
log Fe	0.84011	-0.20993	0.00052
log Al	0.84446	0.18685	-0.18979
log Na	0.04867	0.87711	0.37510
log Mg	-0.06809	-0.56172	0.24660
log Ca	0.26648	0.15925	-0.76132
$\delta^{18}O$	0.16368	0.24831	0.63375
$\delta^{13}C$	-0.74836	0.11006	0.57934

Factor	Pct. of Var.	Diagnosis
1	57.4	laboratory leaching and silicification
2	25.9	diagenetic equilibration
3	16.6	total calcite (?)

Table II-4. Factor analysis (Varimax rotated factor matrix) of the LMC - phases of the Burlington Limestone samples (N = 13).

	Factor 1	Factor 2	Factor 3	Factor 4
log I.R.	0.89130	0.07315	-0.07922	0.23633
log Mn	0.21517	-0.59216	-0.03171	-0.04126
log Sr	0.20894	0.75063	0.14035	0.05678
log Fe	0.81385	-0.05151	0.47355	0.01297
log Al	0.93241	-0.00010	0.18531	0.03832
log Na	0.59888	-0.24100	0.05038	0.70568
log Mg	0.33483	0.19002	0.86066	0.01577
log Ca	0.13782	0.69192	-0.68559	-0.09812
$\delta^{18}O$	0.03693	0.22702	0.02243	0.68628
$\delta^{13}C$	-0.01981	0.80703	-0.06802	0.11577

Factor	Pct. of Var.	Diagnosis
1	44.7	laboratory leaching
2	29.8	diagenetic equilibration
3	15.1	dolomitization
4	10.4	salinity (?)

Table II-5. Factor analysis (varimax rotated factor matrix) of the LMC - phase of the Read Bay Formation samples (N = 14).

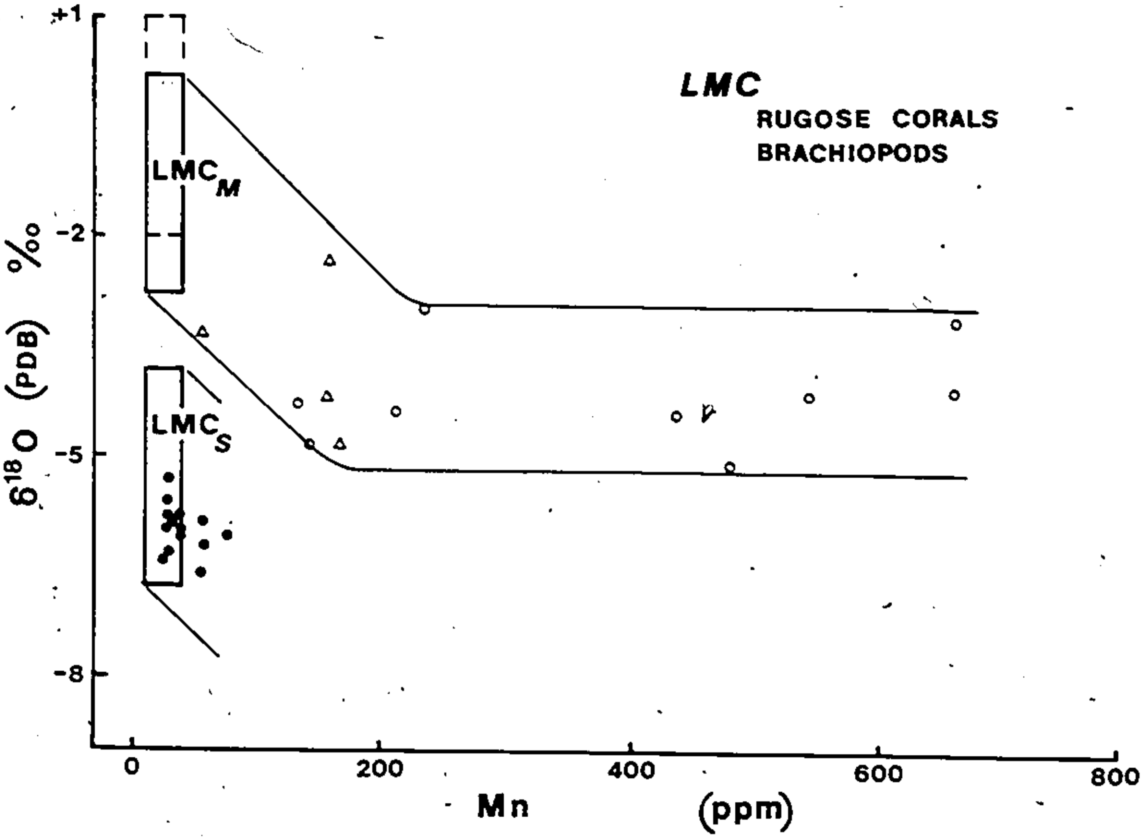


Fig. II-4. Scatter diagram of $\delta^{18}O$ vs. Mn for presumed originally LMC carbonate components. The dashed field defines the observed range of Recent LMC in organic and inorganic (?) equilibrium with seawater (Lowenstam, 1961; Gross, 1964; Milliman, 1974). The solid fields are the postulated ranges for equivalent LMC carbonate components of the Mississippian (LMC_M) and Upper Silurian (LMC_S) (cf. Fig. II-2). The ● represents rugose corals from the Read Bay Formation. The ○ and △ represent rugose corals and brachiopods, respectively from the Burlington Limestone.

the δ^{18}O vs Mn covariance diagram (Fig. II-4). All the Burlington Limestone LMC δ^{18}O values fall below and well beyond the realm of the postulated original LMC field in equilibrium with Mississippian seawater. The average δ^{18}O depletion appears to be about 3 ‰ (PDB).

The Read Bay Formation results for the presumed LMC components are almost exclusively clustered within or near the postulated original LMC field in equilibrium with Silurian seawater (Fig. II-4). Even though most of the samples fall within the postulated original field, they are depleted in ^{18}O, on average, by about 1 ‰. This depletion is about a third of that for the Burlington samples.

Summary

The Burlington Limestone is, on average, depleted in ^{18}O by about 3.0 with respect to $CaCO_3$ precipitated in equilibrium with the postulated Mississippian seawater (Fig. II-5). The presumed HMC and LMC components are limited mostly to the horizontal part of the diagenetic pathway. The higher scatter of the HMC measurements could be related to their stronger diagenetic alteration due to lower stability of HMC as well as to the higher original porosity of the crinoid ossicles vs. the LMC coral skeletons and brachiopod shells.

On the other hand, all the Read Bay Formation results fall within or near the $CaCO_3$ field in equilibrium with the postulated Silurian seawater (Fig. II-5). The samples appear to be, on average, depleted by about 1 ‰ in δ^{18}O. The data

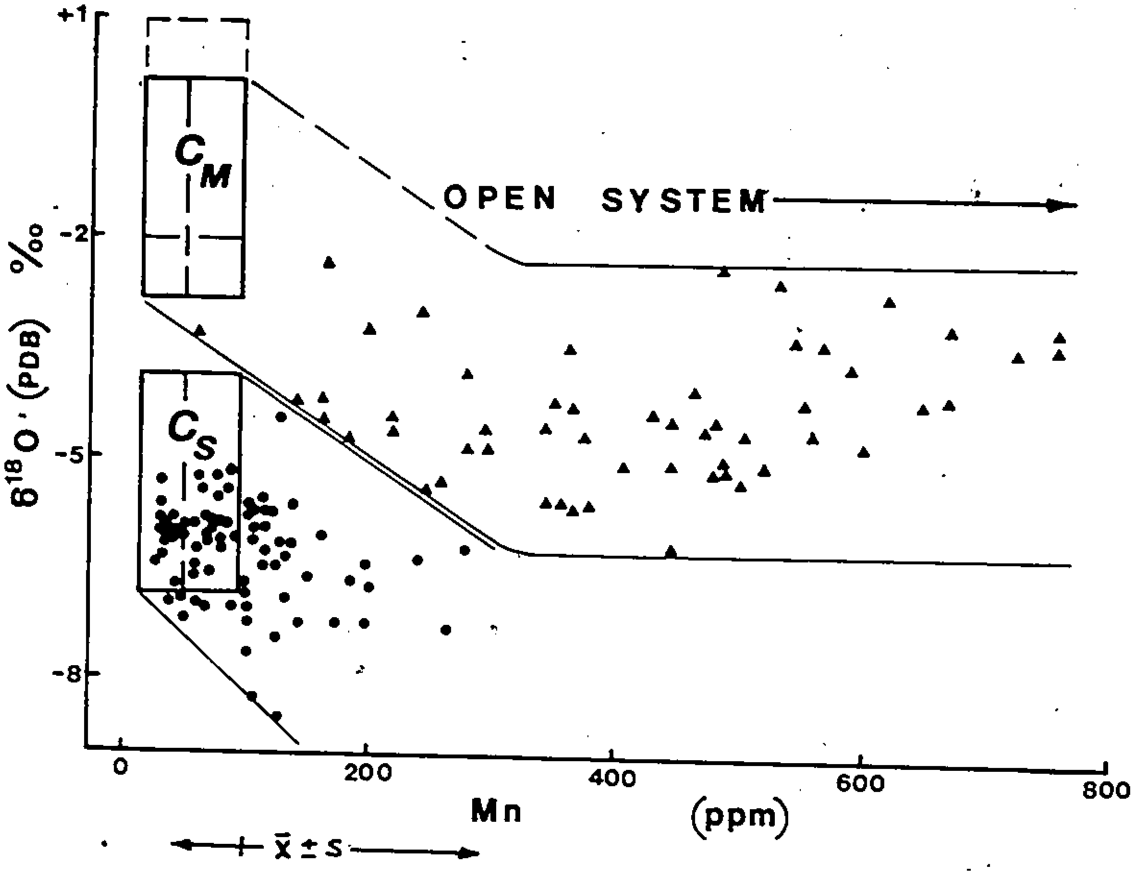


Fig. II-5. Summary of $\delta^{18}O$ diagenetic stabilization trends for HMC, LMC and A. The Recent (dashed field), Mississippian (C_M) and Upper Silurian (C_S) fields are the postulated ranges for carbonates (HMC, A, LMC) in equilibrium with contemporaneous seawater (cf. Figs. II-2, 3, 4). The $\bar{x} \pm s$ distribution and "open system" as in fig. I-9 (chapter one). The ● represents all the samples from the Read Bay Formation. The ▲ represents all the samples from the Burlington Limestone.

are all restricted to the declining part of the diagenetic pathway.

These results show that the Mississippian Burlington Limestone components show stronger ^{18}O depletion (by a factor of $\sim$3) than the Silurian Read Bay Formation equivalents. In other words, the former were subjected to stronger diagenetic equilibration with meteoric water. This is in accord with conclusions based on trace element data that the Mississippian assemblage was mineralogically stabilized in an open meteoric diagenetic system, whereas the Silurian one was stabilized in a partly closed "reaction zone" system. The absence of clear relative mineralogical (LMC, HMC, A) gradients in $\delta^{18}O$ at similar alteration levels (Mn concentrations) is due to the fact, that, contrary to their Sr content, the original mineralogical phases were not typified by large $\delta^{18}O$ differences.

If the secular variations of seawater ^{18}O with geologic age are correct, then the extension of the oxygen paleothermometer beyond the Mississippian depends not only on elimination of altered samples (in the way discussed by Veizer & Fritz, 1976; and in chapter one), but also on the knowledge of the correction factors for secular variations in the isotopic composition of seawater.

If the Mississippian seawater was about 1‰ and the Silurian seawater was about 5‰ lighter than present day seawater, the average calculated Temperature would be about

31 ± 4°C for the Mississippian brachiopods and corals ($\delta^{18}O$, $\bar{x} = -3.0$, SD = 0.8 ‰) and about 21 ± 2°C for the Upper Silurian corals ($\delta^{18}O$, $\bar{x} = -1.0$, SD = 0.35 ‰).

Similar temperature values are obtained for the Upper Silurian using the Read Bay Formation crinoids (22 ± 5°C) instead of the corals. This kind of similarity can also be shown for the Mississippian using the different components of the Burlington Limestone such as brachiopods (29.5 ± 5.5°C), rugose corals (32 ± 3° C) and crinoids (31 ± 6°C).

These results suggest that biological fractionation did not play a major part in the ^{18}O incorporation into the skeletons of the Paleozoic rugose corals, possibly due in part to their different original mineralogy (LMC, chapter one) or the Paleozoic crinoids. More research is needed to clarify the "vital effect" of Recent scleractinian aragonitic corals and crinoids and Paleozoic rugose corals and crinoids.

Carbon isotopes

A considerable portion of the observed variation in carbon isotopic composition of the HMC components can be explained by factors, which suggest depletion of ^{13}C with increasing Fe (Factor 1, Table II-1 - Burlington Limestone; Factor 3, Table II-2 -.Read Bay Formation). This may suggest that the increasing proportion of phreatic, ^{13}C depleted, ferroan calcite cement is the cause of this relationship (cf. Richter & Füchtbauer, 1978). Replacement of (or filling of pores in) the original skeletal HMC by dLMC (by ferroan calcite) may account for simultaneous Mg and ^{13}C depletion and Ca enrichment in the Burlington Limestone components (Factor 3, Table II-1). Therefore, the variation of Fe in the studied limestone samples is not only controlled by laboratory leaching from aluminosilicates in the I.R. (Tables I-4,5 and 6, chapter one), but also by pore filling and replacement ferroan calcite.

Factor analysis of the A component with respect to ^{13}C has already been discussed under oxygen isotopes.

The total isotopic variation of ^{13}C of the LMC components of the Burlington Limestone is explained by factors 1 and 3 (Table II-4). Factor 1 is analysed as laboratory leaching and silicification, with the latter component of this factor controlling the variation of Mn, Sr and $\delta^{13}C$. Factor 3, diagnosed as total calcite, is not well understood at this time. Factor 2 (Table II-5) of the LMC components of the Read Bay Formation is diagnosed as diagenetic equilibration and has been extensively discussed in chapter one and in the oxygen isotope section (this chapter).

Consideration of $\delta^{13}C$ shows that the samples fall into two ^{13}C groups (Fig. II-6). This bimodal distribution is independent of age (both Silurian and Mississippian samples contribute to each group) and of the degree of alteration as approximated partly by $\delta^{18}O$ values. Furthermore, this distribution is independent of the diagenetic system (both partly closed and open system stabilized samples contribute to each group, chapter one). The two $\delta^{13}C$ groups show a slight decrease in ^{13}C with diagenetic equilibration (app. 1 ‰). However, any secular variation of ^{13}C is not taken into consideration in deriving the value (Fig. II-6). This decrease is probably a result of partial diagenetic equilibration with isotopically light meteoric water. The trends do not converge and this suggests that we are dealing with two different fundamental processes controlling the $\delta^{13}C$ of the different components.

Since diagenetic processes and secular variations in ^{13}C are only of secondary importance; the other possibility is that this bimodal distribution is of a "primary" nature. The following are possible factors involved in this primary control: (1) the textural nature of the limestone matrix, (2) the role of decomposing organic matter in the environment of $CaCO_3$ precipitation, (3) the type and source of cement (eg. methane derived; marine; meteoric; or a combination of these), (4) the

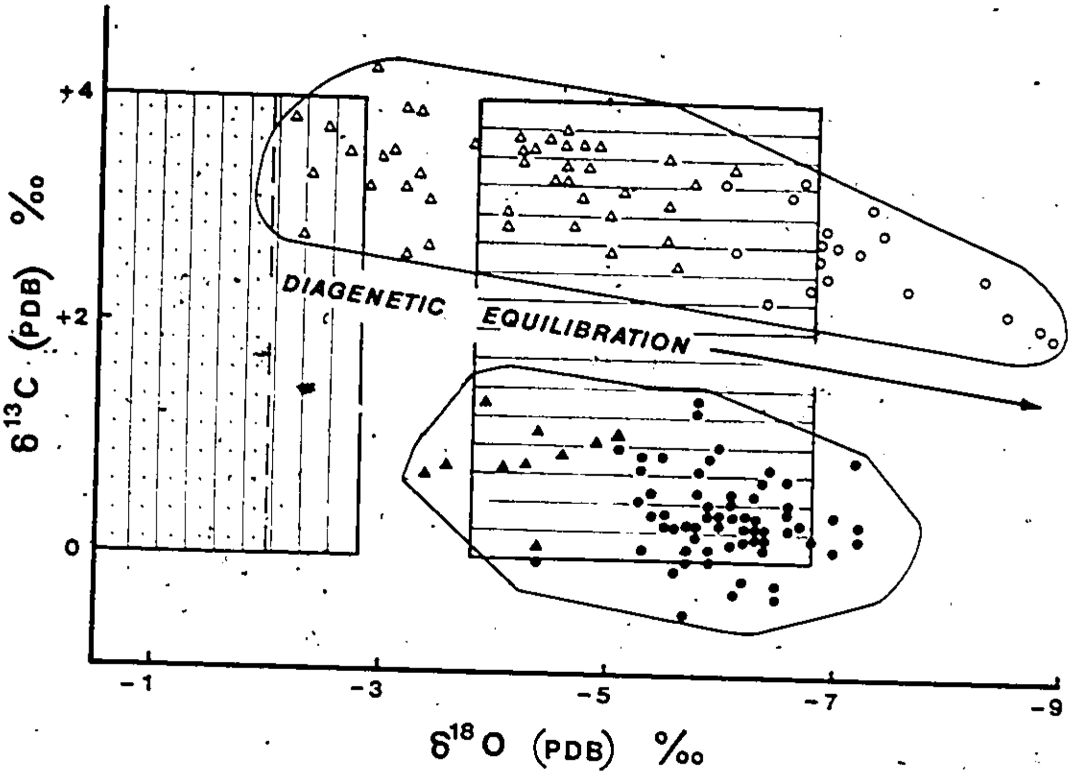


Fig. II-6. Summary scatter diagram of $\delta^{13}C$ vs. $\delta^{18}O$ for all studied samples. The Recent (▨), Mississippian (▥) and Upper Silurian (▤) fields are possible ranges for carbonates (HMC, A, LMC) in equilibrium with the postulated contemporaneous seawater (Gross, 1964; Keith & Weber, 1964). The ○ represents fossil and matrix samples from the Read Bay Formation at Goodsir Creek, Cornwallis Island. The ● represents the rest of the fossil and matrix samples from the Read Bay Formation of Cornwallis and Somerset Islands. The ▲ represents fossil and matrix samples from the Haight Creek Member of the Burlington Limestone. The △ represents the rest of the fossil and matrix samples from the Burlington Limestone.

mode of deposition (eg. skeletal - organic build ups, reefs or inorganic - "chemical precipitation") or perhaps (5) a combination of the above factors or at this time yet unspecified factors.

Possibility (1) on superficial examination seems a plausible explanation for the bimodal distribution since the heavy group is represented mostly by sparitic samples, whereas the light group is represented by micritic samples. However, this textural classification has a few flaws such as a) the association of micritic and sparitic samples also with the heavy- and light-^{13}C groups, respectively, and b) the fact that fossil components (brachiopods, crinoids, rugose corals) have $\delta^{13}C$ values similar to their enclosing matrix and as such are incorporated into both groups. This argues against a possible textural control over the bimodal ^{13}C distribution.

Alternative (2), the decomposition of organic matter will cause the precipitation of $CaCO_3$ in carbon isotopic disequilibrium with ambient seawater (Shinn, 1969; Land & Goreau, 1970; MacIntyre & Milliman, 1970). At this stage it is not known whether this process could cause a bimodal distribution of ^{13}C in $CaCO_3$.

Alternative (3) lately has received widespread attention. Methane - derived CO_2 in cement formation can be discounted because such a source results in either a <u>heavy</u> carbon group ($\delta^{13}C \sim +5$ to $+21$ ‰) formed in isotopic equilibrium between carbonate ion and methane, or a <u>light</u> carbon group ($\delta^{13}C \sim -2$ to -25 ‰) formed by disequilibrium between carbonate ion and methane (Murata <u>et al</u>., 1969, p. B1; Hathaway & Degens, 1969; Allen et al., 1969). This is clearly outside the range of $\delta^{13}C$ values observed in the present study.

On the other hand, meteoric cement would be characterized by low Mg and light $\delta^{13}C$ values and high Fe content (ferroan calcite cement) (Oldershaw & Scoffin, 1967; Hem, 1970; Scherer, 1977; Richter & Füchtbauer, 1978). The highest degree of Fe-staining and increase in sparite cement (2nd-generation cement) is observed in the samples with lowest Mg content, as predicted above, but contrary to predictions are low in Fe and heavy in $\delta^{13}C$ values (Table II-6 and Appendices II and III). This is unexpected since an increase in sparite cement will cause a depletion in ^{13}C (Magaritz, 1975). Those samples with high Fe content show no distinct staining and, in general, fall into the light-^{13}C group. Therefore, it seems highly unlikely that meteoric cement could cause the observed bimodal $\delta^{13}C$ distribution.

Marine cement has to be considered in conjunction with alternative (4), since its mineralogy and isotopic composition are closely linked to its mode of deposition. Aragonite and HMC cement studied in Recent skeletal environments of deposition (areas of organic build ups, reefs, areas of high concentration of skeletal debris) fall into the heavy $\delta^{13}C$ range of +2 to +4 ‰ (Shinn, 1969; Land & Goreau, 1970; Land, 1973; Deuser & Degens, 1969; Lowenstam & Epstein, 1957; Moore, 1973; Milliman & Baretto, 1975; Gross & Tracy, 1966; Buddemeier et al., 1975; Milliman & Müller, 1978), whereas A cement formed as a direct chemical precipitate from shallow seawater is light in ^{13}C

FORMATION Locality	biomicrite	biosparite	d. biomicrite	d. biosparite	equant	2-G,bladed-equant	syntaxial	non Fe-calcite	Fe-calcite I	Fe-calcite II	Fe-calcite III	averages (ppm) Fe	averages (ppm) Mg	averages (‰) $\delta^{13}C$
BURLINGTON														
Iowa														
Burlington		a			c	p	a	1	2-F	3		450	1300	-2.1*
Mediapolis		a		p	c		a	1	V			420	9800	-1.0
Missouri														
Columbia		a			c		a	1	2F	2F		600	1400	-2.8
Springfield		a			c		a	1	2			190	1300	-3.7
READ BAY														
Somerset Is.														
Garnier Bay	a				a	p		M				1500	10500	-0.4
Creswell Bay	a				a			M				1300	12600	-0.1
Fury Beach	a				a	p		M	F			1400	8300	-0.2
Cape Garry	a				a			M				1100	3400	-
Cornwallis Is.														
Goodsir Cr.		a	a		a		p	M	F			600	23000	-2.6
Depot Pt. Lake	a	c			a	c		M	F			800	6400	-0.3
Read Bay	c		a		a	c		M.	FV	D		1500	24000	-0.8
Cape Rescue			a		a	p		M	F	F	F	900	69000	-0.2

Table II-6. Fe-staining of cement/matrix and average Fe and Mg concentrations and $\delta^{13}C$ content of the samples from the localities studied.
(Note: a = abundant, c = common, p = present;
1 = 1st G-syntaxial cement, 2 = 2nd G-syntaxial cement,
3 = 3rd G-syntaxial cement; M = matrix, D = dolomite
V = vug filling spar, F = fracture filling spar).
* contains samples from the light-^{13}C (ave. 0.9 ‰) and the heavy-^{13}C (ave. 3.2 ‰) groups.

(-1 to +2 ‰) (Katz et al., 1977). Ancient analogues of the Recent heavy and light ^{13}C groups have been described by Davies (1974; 1977), Davies & Krouse (1975) and Keith & Weber (1964). A submarine origin for these cements has been postulated by Davies (1977), Schroeder (1972), Ginsburg & Schroeder (1973), Ginsburg & James (1976), James et al.,(1975), Goreau & Land (1974).

Milliman & Müller (1978, p. 663) suggested that A and HMC cements of the heavy-^{13}C group, precipitated in apparent disequilibrium with ambient seawater. This would agree with alternative (2) discussed earlier. However, this is questioned since the enclosed fossils (brachiopods, crinoids, rugose corals) are also enriched in ^{13}C (Fig. II-6). This also holds true for the material of the light-^{13}C group. It is possible that seawater, due to some biological control , in these environments of skeletal deposition was in disequilibrium with open ocean water, and this disequilibrium would be reflected by the cements, matrix and biological fossil components. In any case more studies are needed to define this disequilibrium phenomenon, the effect it has on organic and inorganic components and how it relates to those components forming in other environments of deposition.

In analogy with the above discussion the light-^{13}C group is interpretated as containing amounts of originally inorganically derived A muds (chapter one , Veizer et al., 1978) and cements and fossil components precipitated in carbon isotopic equilibrium with their ambient shallow seawater and submarine environment (Fig. II-7). This group comprises predominantly the micritic samples from the Read Bay Formation and samples from the Haight Creek Member of the Burlington Limestone.

The heavy-^{13}C group is interpreted as containing appreciable amounts of organically-derived originally HMC and A cements precipitated in carbon isotopic disequilibrium with ambient seawater and their submarine environment (Fig. II-6). All the remaining samples from the Burlington Limestone fall into this group. In addition samples from the Read Bay Formation at Goodsir Creek (representing reef-flank and reef-core samples, J.J. Packard, 1978, pers. comm.) make up the rest of this group

In summary, the Burlington Limestone (except for the Haight Creek Member samples) and the Read Bay Formation samples from Goodsir Creek were cemented by HMC and A cement in the submarine environment, and are typified by heavy-^{13}C values (Fig. II-6; Davies, 1977; Davies & Krouse, 1975). In addition, the marine-derived, 1st-generation, non-ferroan, syntaxial, calcite cement, in the Burlington Limestone samples, was followed by subsequent 2nd-generation ferroan-calcite cementation in the diagenetic meteoric phreatic environment (Table II-6, Fig. II-6; Richter & Füchtbauer, 1978)

The Haight Creek Member samples and the remainder of the Read Bay Formation samples were cemented by inorganically-derived originally A cement in the submarine environment or in the presence of marine-derived pore solutions and are light in ^{13}C (Fig. II-6; Katz _et al._, 1977).

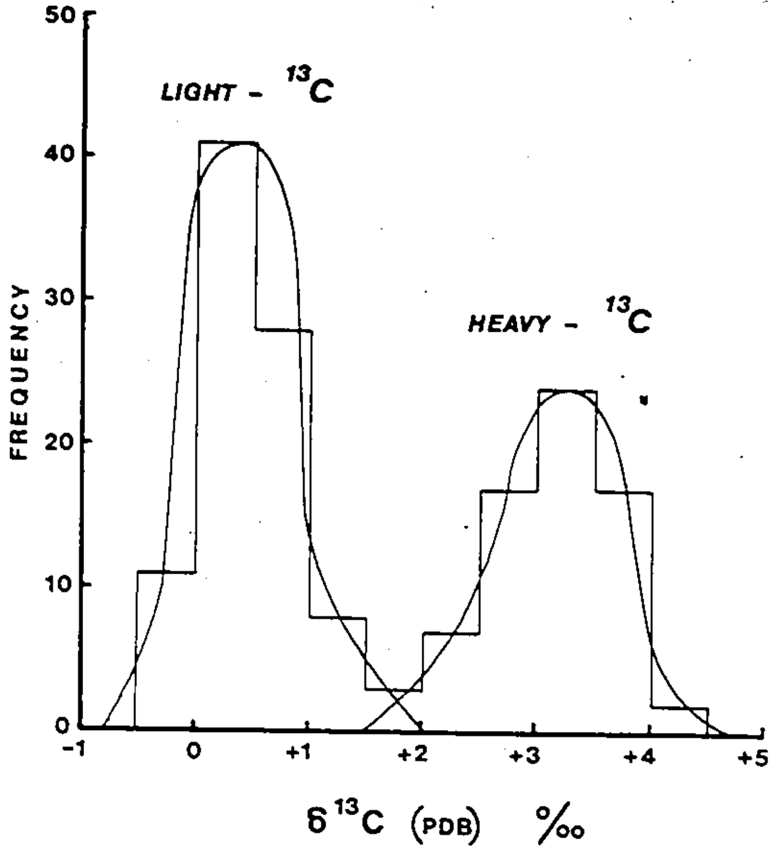


Fig. II-7. $\delta^{13}C$ distribution histogram. The mode of the light-^{13}C group is (+ 0.5 ± 0.4 ‰) and for the heavy-^{13}C group it is (+3.1 ± 0.7 ‰). See text for discussion.

CONCLUSIONS

The oxygen and carbon isotopic study of the Mississippian Burlington Limestone (Iowa and Missouri) and Upper Silurian Read Bay Formation (Arctic Canada) produced the following conclusions:

(1) Trace element and textural criteria (chapter one) show that the Burlington Limestone was subjected to stronger diagenetic equilibration with meteoric water than was the Read Bay Formation. The stable isotope data conform with this interpretation if the secular increase in ^{18}O of progressively younger seawater is accepted. In contrast, assumption of constant $\delta^{18}O$ of ancient oceans leads to the opposite interpretation. Such a conclusion is, however, at variance with all trace element and textural observations;

(2) Projection of isotope data into the "least" altered range indicates that ocean waters of the Mississippian and the Upper Silurian were about 1 ‰ and 5 ‰ lighter, respectively, than present day seawater;

(3) If the above estimates for Paleozoic seawater are correct, the average diagenetic shift in $\delta^{18}O$ of the Read Bay Formation (stabilized in a "partly closed" diagenetic system) was about -1 ‰, and of the Burlington Limestone (stabilized in an open diagenetic system) was about -3 ‰ PDB. Due to small ^{18}O fractionation between the original $CaCO_3$ components, the diagenetic path of all components (A, HMC, LMC) is similar, although LMC, due to its greater stability, shows a slightly smaller $\delta^{18}O$ shift than either HMC or A;

(4) If Mississippian seawater was about 1 ‰, and Upper Silurian seawater about 5 ‰ lighter in ^{18}O than present day ocean water, then calculated average temperatures (from LMC components) for the Mississippian of Iowa and Missouri and the Upper Silurian of Arctic Canada would be about 31 ± 4°C and 21 ± 2°C, respectively;

(5) Oxygen paleothermometer temperature calculation and comparison with results obtained from the brachiopods suggests that Paleozoic rugose corals, partly due to their different original mineralogy (LMC), and Paleozoic crinoids show no signs of biological fractionation such as has been observed in their Recent counterparts;

(6) The $\delta^{13}C$ of the studied samples is distributed bimodally with +0.5 and +3.1 ‰ as the modes of the two groups. The heavy-^{13}C group is associated with samples from organic build-ups or from areas of high concentrations of skeletal debris. They are cemented mostly by spar and pseudospar. The light-^{13}C group is typical for environments with subordinate skeletal contribution and high proportions of micritic matrix and/or cement;

(7) Comparison with Recent analogues indicates that the above bimodality is due to the type of cement involved. The heavy-^{13}C group is characteristic of organically derived originally HMC and A cement precipitated in carbon isotopic disequilibrium with ambient seawater, while the light-^{13}C group is characteristic of inorganically derived originally A mud matrix and/or cement precipitated in carbon isotopic

equilibrium with ambient seawater;

(8) Textural and isotopic criteria suggest that the Read Bay Formation limestones were cemented in the submarine environment, or cementation and lithification was achieved in the presence of marine-derived pore solutions. In contrast, the Burlington Limestone samples show two generations of cement; an initial stage of HMC and A submarine cementation followed by Mn-rich - LMC cementation in the diagenetic, meteoric, phreatic environment.

CHAPTER III

THE REDISTRIBUTION OF TRACE-ELEMENTS AND STABLE ISOTOPES DURING "DORAG" DOLOMITIZATION

ABSTRACT

Late diagenetic dolostones form as a replacement of stabilized low-Mg calcite limestones with average Sr values of about 450 ppm. This replacement takes place in the "Dorag" fresh-seawater mixing zone.

This transformation is selective for the matrix (30 to 300 microns), while the allochems are usually replaced by larger crystals, but only after the original matrix has been dolomitized.

Any possible original isotopic or chemical differences within or between precursor limestones are eradicated during "Dorag" dolomitization, since this diagenetic transformation proceeds in a more or less open system with respect to the bulk aquifer (pore) water.

This precludes the use of trace elements and isotopes as facies, paleoenvironmental or paleoflow indicators for "Dorag" dolostones, while at the same time differentiating this group of dolostones from the "early diagenetic" varieties described by other authors.

RÉSUMÉ

Les dolomies diagénétiques tardives ont remplacé les calcaires stabilisés, à faible teneur en Mg, et dont la teneur en Sr est d'environ 450 ppm. Ce remplacement a lieu dans la zone "Dorag" où il y a mélange d'eau douce et d'eau de mer.

Cette transformation est sélective pour la matrice (30 à 300 microns) tandis que les allochèmes sont habituellement remplacés par des cristaux plus grands et cela seulement après

dolomitisation de la matrice originelle.

Les différences chimiques ou isotopiques originelle possibles à l'intérieur des ou entre les calcaires précurseurs ont été détruites au cours de la dolomitisation "Dorag", puisque cette transformation a lieu dans un systeme plus où moins ouvert par rapport à la masse d'eau météorique.

Cela met donc dans l'impossibilité l'emploi des oligo-éléments et des isotopes pour indiquer les faciès, les paléomilieux ou les paléocourantes des dolomies "Dorag", tout en permettant de distinguer ce groupe de dolomies des variétés "diagénétiques précoces" décrites par des autre auteurs.

ZUSAMMENFASSUNG

Spätdiagenetische Dolomite werden als eine Verdrängung der stabilisierten Tief-Mg Kalzitkalksteine mit Sr Mittelwerten von ungefähr 450 ppm gebildet. Diese Verdrängung findet in der "Dorag" Frisch-Meerwasser Mischungszone statt.

Diese Umwandlung ist für die Matrix (30 bis 300 mikrons) auswählend, während die Allochems meistens von grösseren Dolomitkristallen verdrängt werden, aber nur nachdem die ursprüngliche Matrix dolomitisiert ist.

Irgendwelche ursprüngliche Isotopen oder Spurenelement Erhaltungsunterschiede innerhalb und zwischen Kalksteinvorgänger wurden während der "Dorag" Dolomitisierung ausgelöscht, weil diese diagenetische Umwandlung in einem mehr oder weniger, offenen System mit dem Hauptteil des Grundwassers vor sich geht.

Dies schliesst den Gebrauch, von Isotopen und Spurenelemente als Fazies-, Palaoumwelt- oder Palaostrommesser für "Dorag" Dolomiten aus, während es zur gleichen Zeit diese Dolomitgruppe von der "frühdiagenetischen" Art, die von anderen Verfassern beschrieben ist, unterscheidet.

INTRODUCTION

The origins of "Primary" (Penecontemporaneous) and "Secondary" (= Dorag) dolostones have puzzled carbonate petrologists for a long time. This is due to the fact that dolomite is the most stable carbonate phase thermodynamically, and is prominent in the geologic record. Yet experimentalists have persistently failed to synthesize dolomite in the laboratory under earth surface or shallow subsurface conditions (Garrels, 1960; Hanshaw et al., 1971).

However, dolomite formation and dolomitization of other carbonate phases has been achieved under hydrothermal conditions (Graf & Goldsmith, 1956; Rosenberg & Holland, 1964; Rosenberg et al., 1967; Sureau, 1974; Katz & Matthews, 1977).

In the past twenty years several dolomitization models have been proposed (eg. Seepage reflux - Adams & Rhodes, 1960; Evaporative pumping - Friedman & Sanders, 1967; Hsü & Siegenthaler, 1969; Sabkha model - Illing et al., 1965; Kinsman, 1964; Bathurst, 1971; Schizohaline model - Folk & Siedlecka, 1974). These models can explain the formation of penecontemporaneous dolostone, but are incapable of explaining the textural character and volumetric occurrence of "Dorag" dolostones.

The enigma of the "secondary" (= late diagenetic; here termed "Dorag" dolostones, = Dd) persisted until the early 1970's. The "Dorag" model (Hanshaw et al., 1971; Land, 1973) may provide the answer for the formation of secondary dolostones. According to Badiozamani (1973, p. 979, p. 965) it "...has the advantage of being independent of extensive evaporation and high Mg/Ca ratios in solution..." and acts by "...mixing meteoric groundwaters with up to 30 % sea water which causes undersaturation with respect to calcite, whereas dolomite saturation increases continuously...".

However, the degree of dolomite saturation and calcite undersaturation is not just a factor of mixing seawater with meteoric water. For example, Plummer (1975) and Wigley & Plummer (1976) have shown that the saturation index is influenced by P_{CO_2} in an open and closed diagenetic system. This model is further complicated by observations of Veizer et al. (1978, p. 1457) that "... direct mixtures of sea and meteoric waters cannot precipitate dolomites with the whole range of the observed Sr concentrations, regardless of whether the high or low partition coefficients are accepted". This suggests that penecontemporaneous dolomite formation is possibly related to some diagenetic microenvironment, whereas "Dorag" - dolomitization is an equilibrium process (Katz et al., 1972; Katz & Matthews, 1977; Veizer, 1977; Veizer et al., 1978; chapter one, this thesis; for further discussion see page 120, this chapter).

This type of mixing is attained in the fresh - marine phreatic zone and if this zone is highly mobile, it possibly can account for the regional and substantial volumes of ancient dolostones (Hanshaw et al., 1971; Badiozamani, 1973; Land, 1973; Land et al., 1975; Veizer et al., 1978). The mobility of the "Dorag" zone can be achieved by numerous cycles of marine transgression-regression.

Limestone stabilization, which is believed to precede "Dorag" dolomitization (Veizer et al., 1978), was investigated in chapter one, with the following major conclusions:

1. Diagenetic mineralogical stabilization of limestones is generally accomplished in partly closed diagenetic environments termed "reaction zones". The "Messenger Film" of these zones is not in chemical equilibrium with the bulk aquifer (pore) water.

2. The progressive textural coarsening (maturity) of the rocks is accompanied by distinct trends in chemical composition, Sr decrease and Mn increase being the clearest examples.

3. The rate of this chemical and textural equilibration process is controlled by the stability and chemistry of the original carbonate phase. Except in the case of complete diagenetic equilibration, stabilization through the "reaction zone" microenvironment results in preservation of chemical gradients. These gradients, proportional to original chemical differences and thus to mineralogy, can be utilized to determine the original composition (mineralogy) of a phase.

The principal objectives of this study are (1) to ascertain whether an increasing degree of dolomitization leads to the evolution of distinct redistribution patterns of trace, minor and major elements and of stable isotopes, and if so, whether these changes are accompanied by textural evolution.

(2) To examine whether "Dorag" dolomitization proceeds via a dissolution - reprecipitation process in equilibrium with the bulk aquifer (pore) water or whether, in analogy to limestones, it is controlled by microequilibration in discrete "reaction zones".

(3) To evaluate whether the formation of "Dorag" dolomite (Dd) is accomplished by direct replacement of the original metastable $CaCO_3$ precursors or through an intermediate stable calcitic (dLMC, chapter one) phase.

PETROGRAPHY

The observed dolomitization can be subdivided into two easily distinguishable types, namely macrodolomitization, which is characterized by its crystal shape and size and non-staining by alizarin - red (Evamy, 1969; Lindholm & Finkelman, 1972) (Plate 6). These samples are classified as groups II and III diagenetic dolomites ("early to late") (Fritz & Jackson, 1972).

Among the allochems only crinoids are partially to completely dolomitized, with partial retention of their unit extinction characteristics. In contrast, brachiopods and rugose corals show no signs of dolomite replacement.

The other type is microdolomitization, distinguishable by its anhedral to subhedral dolomite crystals and size, which are restricted to crinoid ossicles and syntaxial overgrowth cement (cf. Lohmann & Meyers, 1977; Meyers & Lohmann, 1978).

In addition to the above noted features, the alizarin - red and potassium ferricyanide stained thin sections commonly have a spotted appearance. Under high magnification distinct dolomite crystals could seldom be resolved to account for this lack of stain. It is suggested that these spots (noticed in all thin sections from the Burlington Limestone and the Read Bay Formation) could possibly be centres of dolomite nucleation. This inferred incipient dolomite nucleation affects matrix and allochems equally, but the mechanism needs further study (Plates 3 and 4).

Macrodolomitization and silicification seem not to have occurred at the same time in particular samples. The timing and exact nature of this relationship are not resolved. However, dolomite preferentially replaces the matrix (dLMC) while silicification mostly affects the allochems (Marcher, 1964; Wilson, 1966; J. J. Packard, 1978, pers. comm.). On the other hand, dolomitization of the allochems proceeds only after the replacement of the matrix is more or less complete (Murray, 1960; Lucia, 1962; Carozzi & Soderman, 1962; Hanshaw _et al._, 1971; Renard, 1972; Fritz & Jackson, 1972) (Plates 1 and 6).

In general, the Burlington Limestone does not show any signs of macrodolomitization, except for two samples from the Haight Creek Member; otherwise only micro- (crinoid ossicles and syntaxial overgrowth cement) and incipient dolomitization were observed (Table III-1). Silicification (of the fossil allochems) is the dominant replacement process in these samples from the Burlington of Iowa (cf. chapter one) (Plate 1).

Only incipient- and some minor macrodolomitization and discrete silicification of the allochems were noted in the Read Bay Formation samples from Somerset Island (Plate 4). The whole spectrum of dolomitization was observed in the Read Bay Formation samples from Cornwallis Island (Table III-1). In this case the dolomitization process proceeds in the sequence: matrix/cement, impingment of fossil allochems and complete replacement of allochems (Murray, 1960; Carozzi & Soderman, 1962; Lucia, 1962; Hanshaw _et al._, 1971). A complete transition from biomicrite to dolomitic biomicrite to biodolosparite (ie. fossiliferous dolostone) is present in these samples (Plates 5 to 8).

FORMATION Locality	biomicrite	biosparite	dolo. biomicrite	dolo. biosparite	dolosparite	dolomite	micro-	incipient	(microns) 30 - 50	50 - 100	100 - 200	> 200	staining	silicification	fossil
BURLINGTON															
Iowa															
Burlington		a					a	a							a
Mediapolis		a		a			a	a	M				N		a
Missouri															
Columbia		a					a	a							p
Springfield		a					a	a							
READ BAY															
Somerset Is.															
Garnier Bay	a							a	m						c
Creswell Bay	a								m						
Fury Beach	a							a	m						
Cape Garry	a								m						
Cornwallis Is.															
Goodsir Cr.		p	c	a			p	a	M	M			N		
Depot Pt. Lake	a		p					a	M	M			N		
Read Bay			a	c				a	M	M			D		
Cape Rescue			a		a					M	M	A	N		

Table III-1. Petrographic description of the studied samples from the Read Bay Formation and Burlington Limestone. (Note: a = abundant, c = common, p = present; M = major part of matrix, m = minor part of matrix, A = fossil allochems; N = non-staining of dolomite matrix, D = dolomite Fe II-III).

THEORETICAL CONCEPTS

From studies of aquifer systems in Tertiary carbonates of Florida and the Yucatan Peninsula, Hanshaw et al. (1971) postulated that "late - diagenetic" dolomitization occurs in the brackish water, ie. phreatic fresh - seawater mixing zone, and is caused by circulation of groundwater with Mg/Ca ratio > 1 (Land, 1973). Badiozamani (1973) proposed the term "Dorag" for this mixing zone. Lately this model has been used to explain the extensive dolomite sequences in the Canadian Arctic on Devon Island (Land et al., 1975; Morrow & Kerr, 1977) and on Somerset and Prince of Wales Islands (Veizer et al., 1978).

The simplified reaction of limestone dolomitization:

$$2\ CaCO_3 + Mg^{2+} \rightleftharpoons Ca,Mg(CO_3)_2 + Ca^{2+} \qquad (III\text{-}1)$$

shows that, during this wet transformation process, Mg will extensively substitute for Ca in the calcium carbonate lattice (Bathurst, 1971, p. 528). According to Hanshaw et al., (1971, p. 721) this process "...given enough time and a sufficient magnesium ion supply..." (the latter coming from seawater, which acts as an external reservoir), will proceed until "ordered" stoichiometric dolomite is formed.

Trace elements with ionic radii similar to that of Mg (eg. Fe, Mn) will preferentially substitute in ordered dolomite, whereas those with larger radii (eg. Sr) will be incorporated to a lesser degree. For example, the partition coefficient of Sr in dolomite is either $K^{D}_{Sr} \sim 0.05$ (Behrens & Land, 1972; Jacobson & Usdowski, 1976) or ~ 0.025 (Katz & Matthews, 1977); both considerably lower than the partition coefficient accepted for calcite ($K^{c}_{Sr} = 0.14$, Kinsman, 1969) (see fig. I-3 for alternative partition coefficients).

Furthermore, the Sr/Ca ratio of the dolomitizing water and the water/rock ratio of the wet transformation process will be of considerable importance, but these parameters are as yet not well defined for the "Dorag" system. Veizer et al. (1978) postulated that "Dorag" dolomite (Dd) must have been formed in environments in which $CaCO_3$ phases with $\gtrsim$ 1500 ppm Sr (eg. high-Sr aragonite) were absent, either due to their diagenetic transformation into dLMC, or - less likely - due to their primary absence. Therefore, dolomite formation must either be preceded by dLMC with low - Sr values and/or by other low - Sr "intermediate" carbonate phases.

In an experimental study of dolomites at 252 - 295°C, Katz & Matthews (1977) were able to show the existance of "intermediate" carbonate phases, confirming earlier work by Rosenberg et al. (1967) and Sureau (1974). Katz & Matthews (1977, p. 309) found that replacement of LMC by dolomite "...involves dissolution of the reactants (and) precipitation, from the solution of an intermediate product phase", a HMC with approximately 35 mole % Mg. This intermediate phase is later dissolved and finally dolomite is precipitated (Katz & Matthews, 1977).

On the other hand, dolomitization of A according to Katz & Matthews (1977, p. 307)"...involves the growth and subsequent dissolution of two magnesian calcites, the first being a low magnesian (5.6 mole %) and the second a high magnesian (39.6 mole %) calcite ...". This mineralogical sequence of intermediate carbonate phases is complemented by their oxygen and chemical data (Katz & Matthews, 1977; Matthews & Katz, 1977).

According to Matthews & Katz (1977, p. 1431) there is a "... marked enrichment of ^{18}O in dolomite relative to calcite with which it is in equilibrium..." in a diagenetic environment at earth surface and shallow subsurface conditions. This enrichment ranges from +0.5 to +10 ‰ $\delta^{18}O$ (Epstein <u>et al</u>., 1964; Weber, 1964; Gross & Tracey, 1966; Fritz, 1967; Clayton <u>et al</u>., 1968; Pandey & Sharma, 1970; Sheppard & Schwarcz, 1970). The ^{18}O enrichment is about +5 to +7 ‰ for penecontemporaneous dolomites compared to syngenetic calcite (O'Neil & Epstein, 1966).

Isotopic fractionation of oxygen in the system dolomite-water and dolomite-bicarbonate is not well known at low temperatures, due to the already mentioned failure to synthesize dolomite at normal earth surface conditions (Fritz & Smith, 1970).

Small or nearly zero oxygen fractionations have been observed between synthetic hydrothermal dolomite and its precursor calcite (Matthews & Katz, 1977). In other words hydrothermal dolomites are not enriched in ^{18}O compared to syngenetic calcite.

In "Dorag" dolostones an ^{18}O enrichment between +0.5 to + 3.0 ‰ has been observed (Fritz & Smith, 1970). Fritz & Smith (1970, p. 1170-1172) discuss the discrepancy between the observed $\delta^{18}O$ values of "Dorag" dolostones and those values predicted from extrapolations of high temperature experiments (O'Neil & Epstein, 1966). They offer several reasons that may be the cause for the discrepancy, such as 1) changes in the temperature of the oceans, 2) changes in the isotopic composition of seawater with geologic time or 3) differences in the dolomite-water and protodolomite -water fractionation factors. The authors favour the latter alternative. For further discussion the reader is referred to Fritz & Smith (1970).

The exact nature of ^{13}C fractionation in "Dorag" dolomitization is not clear (Fritz & Smith, 1970; Fritz, 1967; Veizer <u>et</u> <u>al</u>., in prep.).

REGIONAL GEOLOGY

ORIGINAL COMPONENT MINERALOGY

The regional geology, description of localities and the petrological and mineralogical properties of the studied components were described in chapter one (this thesis). For additional information concerning localities see Appendix I.

ANALYTICAL TECHNIQUES

The analytical techniques and their accuracy and precision were reported in chapters one and two (this thesis), which also contain the statistical evaluation of the results. Note that all discussion of the chemical data is based on concentrations recalculated on a total (100 %) carbonate (insoluble residue-free) basis. In preparation of samples for isotopic analyses the reaction rates were varied according to their mineralogy (Walters _et_ _al_., 1972). The list of chemical and isotopic data is given in Appendix III. The correction for the dolomite acid fractionation has been applied.

EVALUATION OF TRACE ELEMENT DISTRIBUTION

General

In the previous chapters the distribution of trace elements and stable isotopes in $CaCO_3$ phases was discussed. This chapter will deal exclusively with "Dorag" dolomitization and the role it plays in trace element and stable isotope redistribution.

In all the studied samples, dolomitization is the second most important factor, with 28.1 percent of the total trace element variation (Table I-3, chapter one). The inverse relationship between Ca and Mg, and to a minor degree also between Sr, Mn and Fe is as predicted from theory. Since Sr-Mg gives the best resolution of the dolomitization trend, these parameters will be utilized in the subsequent discussion.

It is generally believed that dolomitization is texturally destructive (Bathurst, 1971). This can be confirmed, to some degree, since the preferential dolomitization of the matrix obliterates any depositional structures and textures. In crinoids, however, dolomitization follows the c-axis alignment of the precursor single and polycrystalline calcite crystals (Towe, 1967).

This textural and chemical trend is depicted by Figure III-1. Field 1 delineates the composition of the originally metastable precursors (upper part of field - A, middle part of field - HMC, lower part of field - LMC). Field 2 delineates non-dolomitized micrite matrix (and associated fossils) samples

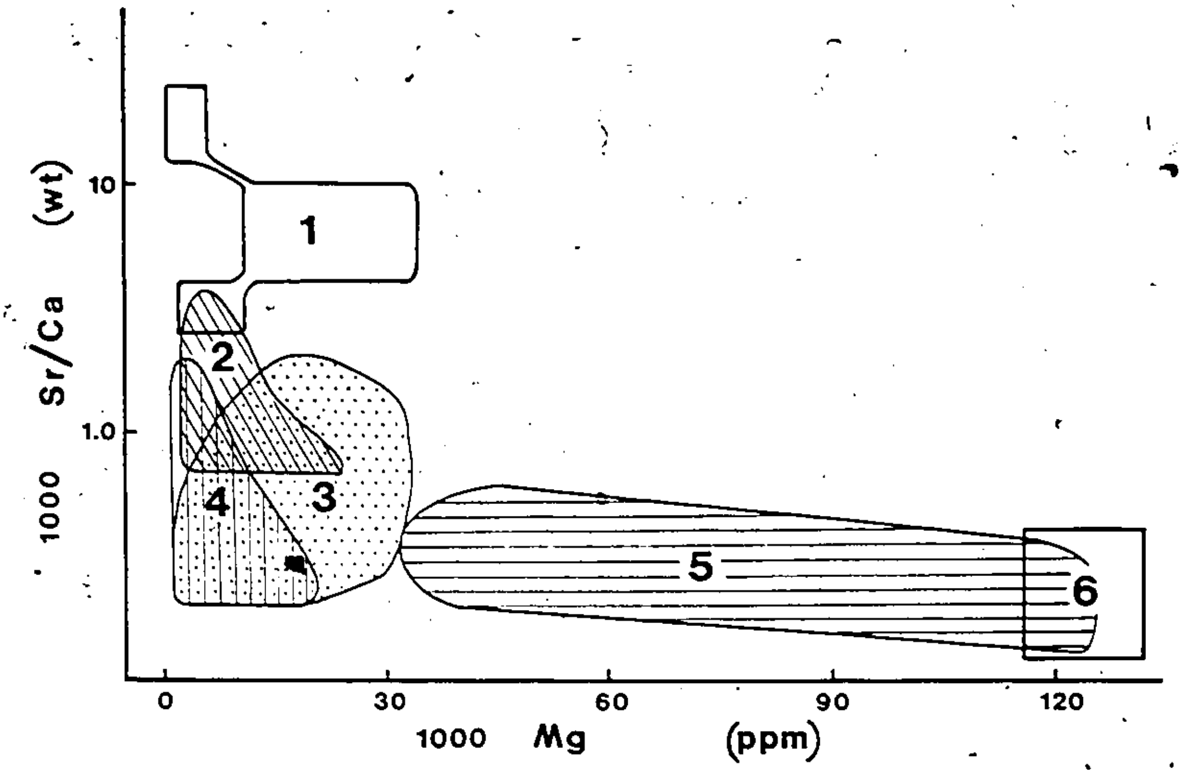


Fig. III-1. Textural and chemical variation of the different carbonate phases with increasing dolomitization. Field 1 represents the composition of the originally metastable precursors (cf. fig. I-4, chapter one). Field 2 represents Read Bay Formation samples from Somerset Island and field 3 represents Read Bay Formation samples from Depot Point Lake and Read Bay. Field 4 represents Burlington Limestone samples from Iowa and Missouri. Field 5 represents Read Bay Formation samples from Goodsir Creek and Cape Rescue. Field 6 represents the theoretical possible range of dolomite (Garrels & Christ, 1965; Katz & Matthews, 1977; Veizer & Demovič, 1974).

from the Read Bay Formation of Somerset Island, while field 3 comprises mostly micrite - microspar, allochems and some minor pseudospar and dolomite from the Read Bay Formation of Cornwallis Island. Field 4 depicts matrix and fossil samples from the Burlington Limestone, which contain microdolomite (cf. Lohmann & Meyers, 1977), incipient dolomite and some minor macrodolomite in the Dolbee Creek Member samples. Field 5 comprises the whole range from limestone to dolostone, with samples in the left part having only part of their micritic matrix dolomitized. The dolomite crystals fall into group II of Fritz & Jackson (1972) with average size of $\gtrsim$ 30 microns. The samples on the right side of field 5 are comparable to group III dolostones of Fritz & Jackson (1972). Usually two dolomite generations are present. In the matrix the average grain size is ~100 microns, while in the fossil allochems it is $\gtrsim$ 200 microns. The samples conform to the predicted chemical and textural covariance trend (micrite to microspar -and possibly spar - to dolomite) with increasing dolomitization.

High-Mg calcite

Factor analysis does not depict any variation due to dolomitization (Table I-4, chapter one), for only a few samples are partially or completely dolomitized (Fig. III-2). The majority of the rock samples in the process of diagenetic equilibration, rapidly lose their Sr as well as Mg (purification) (Lowenstam, 1961; previous section). These samples, in general, show microdolomite inclusions in the crinoids and syntaxial

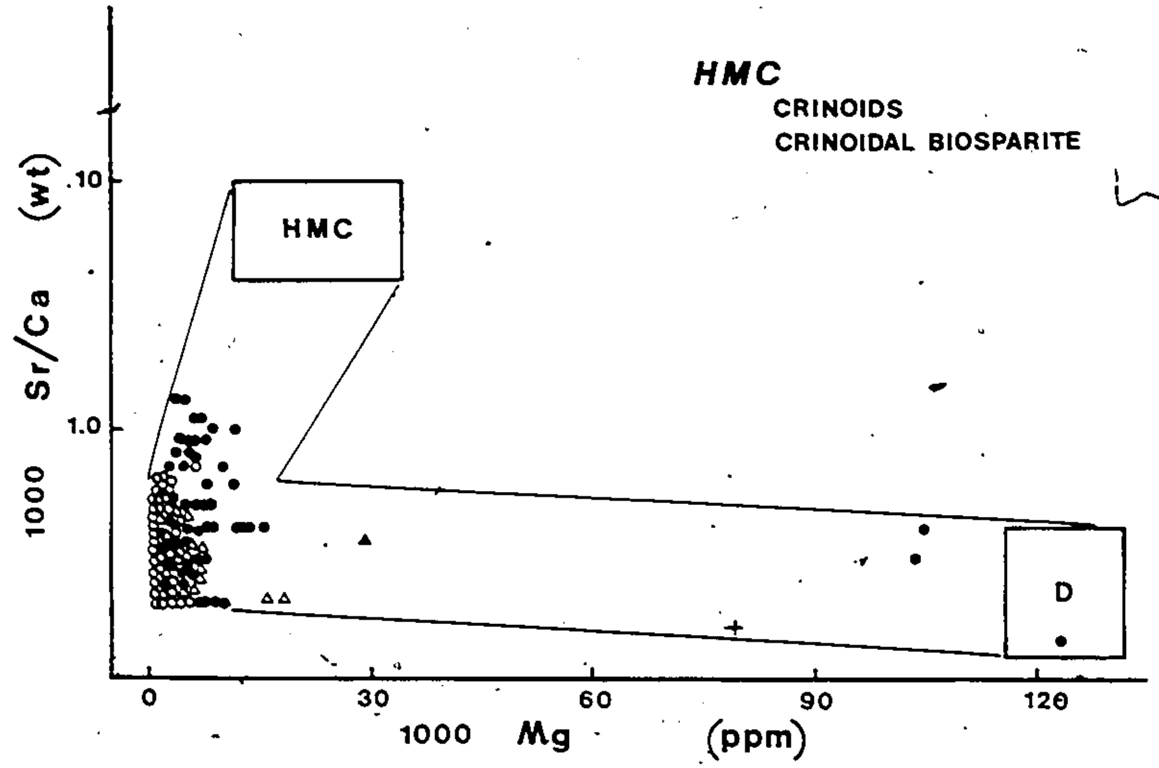


Fig. III-2. Sr distribution in the presumed originally HMC components in relation to stabilization and dolomitization in meteoric and "Dorag" waters. The HMC field is the observed possible range of HMC in equilibrium with present day seawater (Chave, 1954; Milliman, 1974). The D field as in fig. III-1 (field 6). The ● denotes crinoids from the Read Bay Formation of Somerset and Cornwallis Islands. The + represents a crinoid from the Read Bay Formation at Goodsir Creek, Cornwallis Island (A. Legun, 1979, pers.comm.). The ○ and △ represent crinoids and crinoidal biosparite, respectively, from the Burlington Limestone of Iowa and Missouri. The ▲ represents a crinoidal dolomitic biosparite from the Read Bay Formation at Goodsir Creek.

cement in the biosparite. A few samples from the Dolbee Creek Member of the Burlington Limestone show minor amounts of dolomite (group II, Table III-1). Otherwise, the few dolomitized crinoids are from the Read Bay Formation at Cape Rescue and one from Goodsir Creek (the latter was analysed by A. Legun, see Appendix III).

After the initial concomitant loss of Sr and Mg during the HMC → dLMC transition, the subsequent dolomitization only lowers the Sr content by another factor of 3-5. Non-stoichiometric Mg values are not indicative of disordered dolomite, but rather of coexisting calcite.

Aragonite

Factor analysis of the presumed originally A micrite (Table I-5, chapter one) shows that dolomitization (Factor 2) accounts for 42.2 percent of the total chemical variation. As predicted by theory (previous section) dolomitization is accompanied by decreases in Ca and Sr and increases in Mg and Na.

The samples with < 30000 ppm Mg have already been discussed in chapter one (Fig. I-6). After the initial decrease in the Sr content, due to diagenetic transformation of the metastable precursor, the subsequent dolomitization results in its further decrease by a factor of 3 (Fig. III-3). The latter decrease is similar in magnitude to the one observed for the HMC phase (Fig. III-2). However, this trend is not accompanied by a further increase in Mn (Fig. I-6, chapter one).

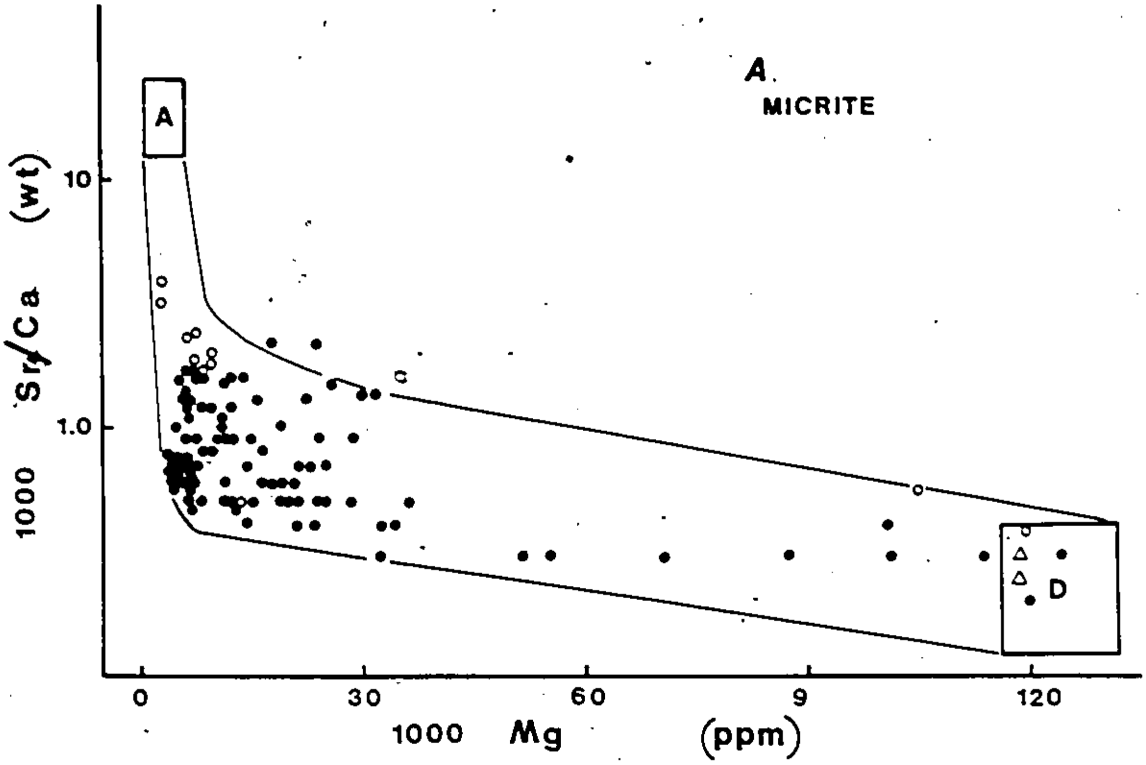


Fig. III-3. Sr distribution in the presumed originally aragonite (A) components in relation to stabilization and dolomitization in meteoric and "Dorag" waters. The A field is the observed possible range of A in inorganic equilibrium with present day seawater (Kinsman, 1969; Bathurst, 1971; Milliman, 1974). The D field as in fig. III-1 (field 6). The ● represents samples from the Read Bay Formation of Somerset and Cornwallis Islands. The ○ represents averages of analogous micritic facies from the Mesozoic of Czechoslovakia (Veizer & Demovič, 1974). The △ represent averages for dolomite samples of the Allen Bay and Lang River Formations of Arctic Canada (Veizer et al., 1978).

The transition from limestone to dolomitic limestone to dolostone is accompanied by an increase in crystal size (Table III-1). The mostly non-stoichiometric nature of these "Dorag" dolostones has been discussed previously by Veizer *et al.* (1978).

Low-Mg calcite

None of the sampled LMC components show any signs of either micro- or macrodolomitization.

Summary

The previously discussed trends for particular components are summarized in Fig. III-4. From this it is evident that "early" diagenetic stabilization (transformation into dLMC) will preserve some chemical differences of the initial components, while subsequent (dLMC → Dd) dolomitization, by "Dorag" waters, will lead to an assemblage where all internal components are in chemical equilibrium.

Renard (1972, fig. 2) proposed a similar model for "late diagenetic" (Dorag) dolomitization. However, examination of the chemical data shows that all his "dolomie" contain > 200 ppm Sr, which is clearly outside the postulated and observed Sr range for "Dorag" dolostones (Veizer & Demovič, 1974; Veizer *et al.*, 1978; Land *et al.*, 1975; this study, Fig. III-4). Furthermore, half of his samples are either poorly- or non-lithified marl, dolomite or lime mud, which is *not* common in "Dorag" dolostones. Also, if the samples are lithified, then the dolomite is usually < 20 microns in size (Renard, 1972,

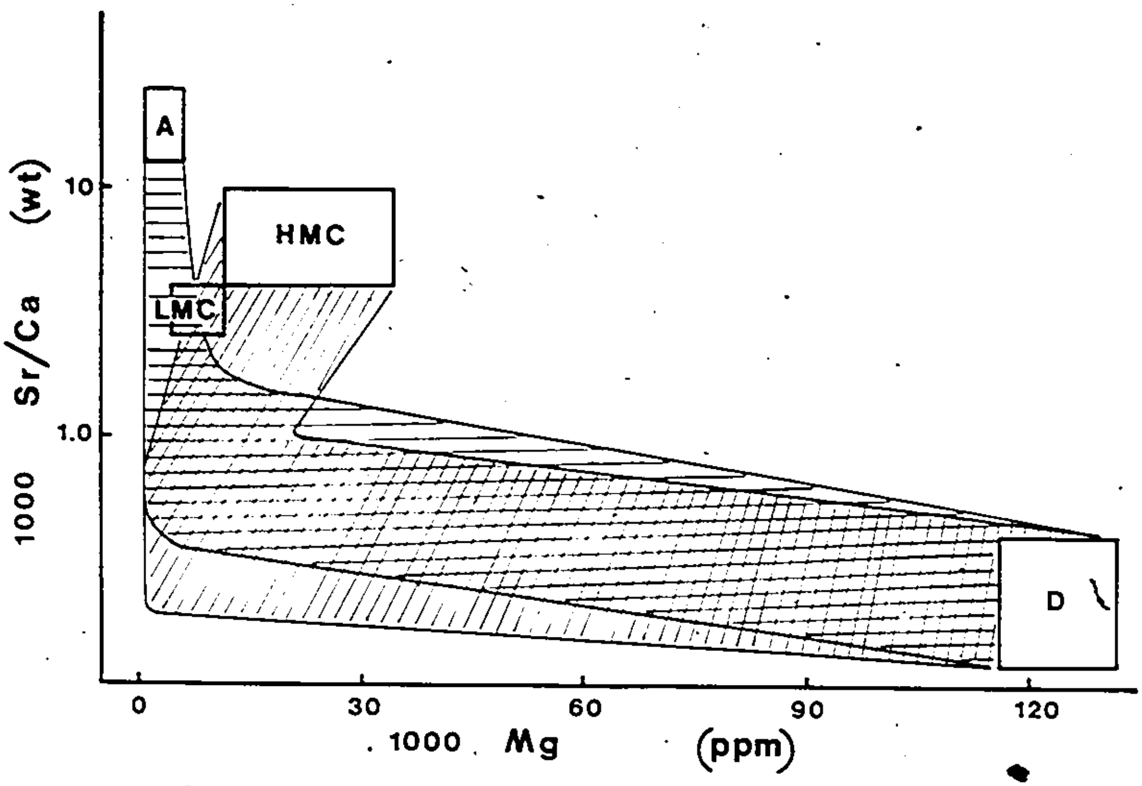


Fig. III-4. Summary of Sr redistribution trends due to diagenetic stabilization and dolomitization of the different original carbonate phases (HMC,A). For LMC see text. The A, HMC and D fields as defined in figs. III-1,2 and 3.

picture 1; table 1).

Based on the above observations, Renard's (1972) "late diagenetic" dolomitization model is rejected. Instead his material could (and should) be re-interpreted as a scheme for penecontemporaneous dolostone formation. This would bring the chemical and petrographic (Renard, 1972) and isotopic observations (Fontes _et_ _al_., 1970) of the material into line with observations of other authors (cf. section, Theoretical Concepts).

The model proposed herein confirms the general belief that dolomitization is both texturally (Bathurst, 1971) and chemically destructive.

This open system behaviour (with respect to trace elements) of the "Dorag" - dolomitization process is probably a consequence of the slow rate of dLMC dissolution, as well as slow precipitation of the Dd. The latter process, being exceptionally slow (eg. Peterson _et_ _al_., 1963; 1966; Berner, 1971) is probably the rate-limiting step. Due to this slow reaction rate the water in a given "reaction zone" (cf. chapter one) microenvironment equilibrates to a considerable degree with the surrounding bulk aquifer (pore) water. This is in contrast to the A→dLMC, HMC→dLMC (and possibly A→D; as in early diagenetic dolomites; Veizer _et_ _al_., 1978) transformations, which are _relatively_ fast, thus enabling development of chemical gradients between "reaction zones" and bulk solutions.

EVALUATION OF STABLE ISOTOPE DISTRIBUTION

Carbon isotopes

Statistical evaluation of $\delta^{13}C$ variations shows that this parameter is not affected by dolomitization of the dLMC precursors (Tables II-1,2,3 and 4, chapter two). The observed bimodal $\delta^{13}C$ distribution has been fully discussed in chapter two (cf. carbon isotopes, Figs. II-6 and 7).

Oxygen isotopes

As discussed in the previous section, the distribution of $\delta^{18}O$ in the studied samples is controlled primarily by their age (Mississippian versus Silurian). Within a given age group the $\delta^{18}O$ becomes heavier with an increase in the degree of dolomitization. This ^{18}O enrichment will be discussed in detail in the subsequent sections.

High-Mg calcite

Factor analysis of the presumed originally HMC components of the Read Bay Formation shows that Fe, Na, Mg, $\delta^{18}O$ and Ca are all loaded on the dolomitization factor (Table II-2). On the other hand, the HMC components of the Burlington Limestone are controlled by the variation of Mg, Ca and $\delta^{13}C$, which is possibly dolomitization or Mg purification of the HMC phase (Table II-1, factor 3). These relationships are well depicted in Fig. II-6. However, the trend for the Burlington Limestone is incomplete, with the ^{18}O enrichment clear only in the material from the Arctic (Fig. III-5). Dolomitization appears

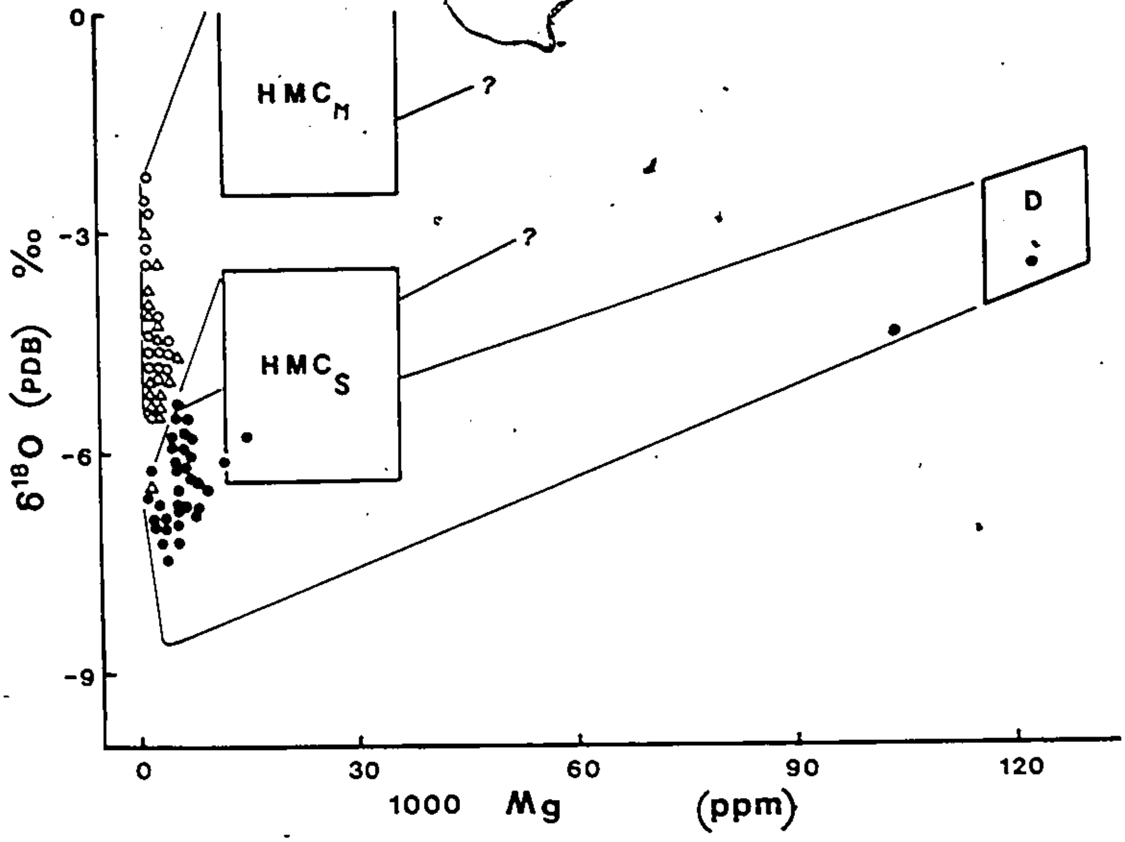


Fig. III-5. Scatter diagram of $\delta^{18}O$ vs. Mg for the presumed originally HMC components. The HMC fields are the postulated theoretical ranges of HMC in equilibrium with Mississippian (HMC$_M$) and Upper Silurian (HMC$_S$) seawater (Chave, 1954; Gross, 1964; Keith & Weber, 1964; Fritz, 1971; Veizer & Hoefs, 1976; chapter two, this thesis). The D field is the postulated range for Upper Silurian "Dorag" -dolomite (cf. "Theoretical Concepts"). The ● represent crinoids from the Read Bay Formation (Arctic Canada). The ○ and △ represent crinoids and biosparite, respectively, from the Burlington Limestone (Iowa and Missouri).

to be preceded by initial HMC → dLMC transformation, which lowers the $\delta^{18}O$ and Mg values. The two data fields of the Read Bay Formation samples could have developed by (1) two unrelated trends or (2) by one sequence. Veizer et al. (1978, p. 1458) pointed out that "...late diagenetic dolostones cannot be produced by dissolution of $CaCO_3$ phases with $\gtrsim$ 1500 ppm Sr...". They concluded that metastable A and HMC undergo a wet transformation into dLMC prior to dolomitization (aragonite → Mg-calcite → calcite → dolomite; Veizer et al., 1978, p. 1458-1459). Therefore, alternative two is accepted as the process represented here. Dolomitization of this stabilized phase (dLMC), is accompanied by ^{18}O enrichment. This is due to $\Delta^{18}O_{Dol-H_2O} > \Delta^{18}O_{CaCO_3-H_2O}$, which ranges from +0.5 to +10 ‰ (see Theoretical Concepts for discussion).

Aragonite

Factor analysis of the presumed originally A - micrite from the Read Bay Formation shows that dolomitization (Factor 2, Table II-3) accounts for 38.7 percent of the total chemical and isotopic variation.

The overall A trend is similar to the one for HMC (Figs. III-5 and III-6). However, in contrast to HMC, the initial diagenetic stabilization of A → dLMC step leads to ^{18}O depletion and slight Mg enrichment. This is due to the low Mg concentration in the original aragonite. By analogy with HMC, subsequent dolomitization of the dLMC phase (Veizer et al.,

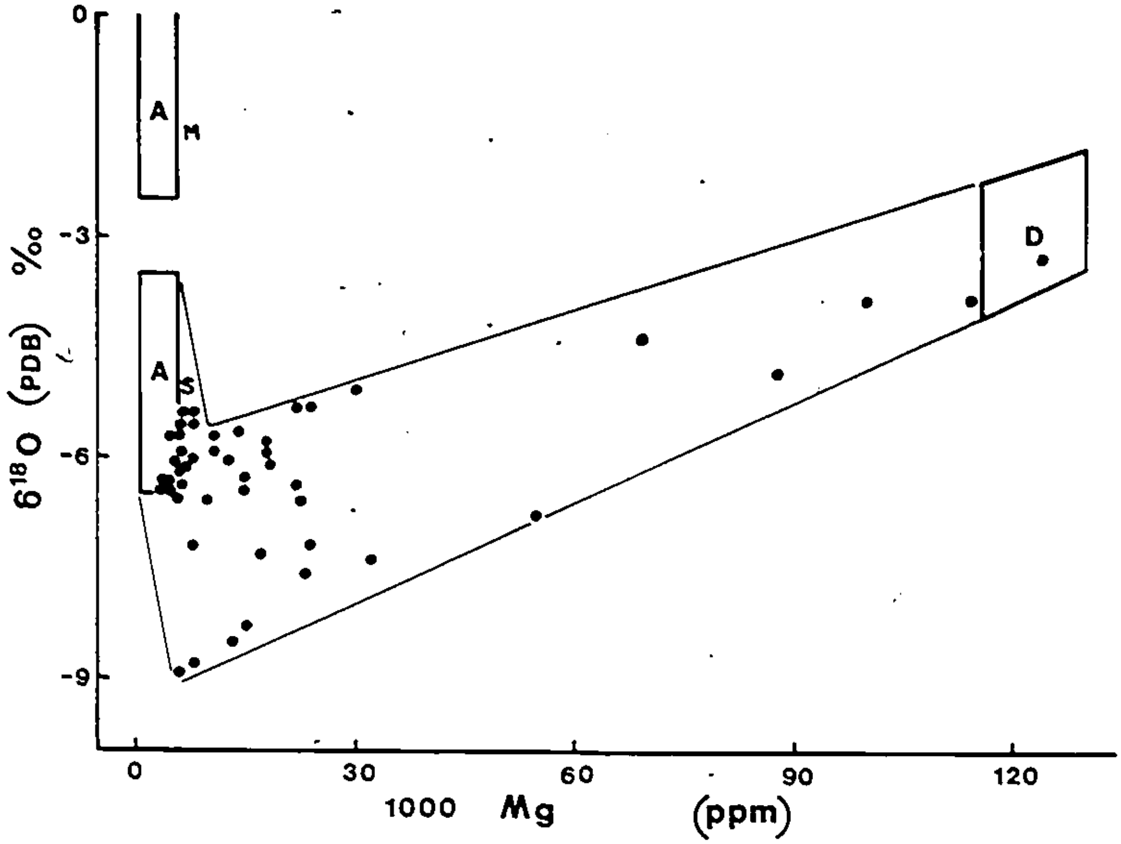


Fig. III-6. Scatter diagram of $\delta^{18}O$ vs. Mg for the presumed originally A (aragonite) components. The A fields represent the postulated theoretical ranges of A in equilibrium with Mississippian (A_M) and Upper Silurian (A_S) seawater (Kinsman, 1969; Milliman, 1974; Fritz, 1971; Veizer & Hoefs, 1976; chapter two, this thesis). The D field is the postulated range for Upper Silurian "Dorag" -dolomite (cf. "Theoretical Concepts"). The ● represents micrites and dolomitized micrites from the Read Bay Formation (Arctic Canada).

1978) results in heavier $\delta^{18}O$. Furthermore, the $\delta^{18}O$ data fall on the path (one sequence) regardless of the nature of the original metastable precursor.

Summary

The herein observed enrichment in $\delta^{18}O$ during "Dorag"-dolomitization is irrespective of secular variations and is as predicted by observations of other authors (cf. "Theoretical Concepts"). Furthermore, this enrichment is at variance with the trend predicted and observed for "hydrothermal" - dolomitization, which continually lowers the $\delta^{18}O$ values and proceeds via short-lived intermediate phases (Matthews & Katz, 1977). On the other hand, "Dorag" - dolomitization proceeds via dLMC instead of these "intermediate" phases.

CONCLUSIONS

Trace element, stable isotope and petrographic observations of dolomite samples interpreted as products of "Dorag" - dolomitization lead to the following conclusions:

(1) The textural variations of the precursor of dLMC limestones (micrite to sparite) are not reflected in the successor dolomites, which texturally belong to groups II ($\gtrsim$ 30 microns) and III (100 - 300 microns) of Fritz & Jackson (1972).

(2) Dolomitization is a selective process with preferential replacement of the matrix over allochems; the dolomite crystals of the allochems being usually larger (~ 200 microns) than those replacing the matrix (~ 100 microns).

(3) The formation of ("late-diagenetic") "Dorag" - dolostones proceeds through replacement of the diagenetically stabilized dLMC limestones containing, on average, ~ 450 ppm Sr.

(4) Any (elemental and isotopic) gradients (with the possible exception of $\delta^{13}C$), inherited by the stabilized dLMC phases from the original precursors are eradicated during the subsequent "Dorag" - dolomitization process.

(5) "Dorag" - dolomitization proceeds in an open diagenetic system in or near equilibrium with the bulk aquifer (pore) water. This may be a consequence of the slow dissolution rate of dLMC and in particular of slow Dd precipitation.

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APPENDIX I - LOCATIONS

The U.S. Standard Land Survey System is used for the locations in Iowa and Missouri. For the Arctic Canada locations the conventional latitude-longitude system is used. Samples are indicated by the numbers in brackets.

Burlington Limestone, Osagean (Mississippian)

Section 1: crinoidal biosparite (1A); Dolbee Creek Member; Burlington Limestone type section, Crapo Park, Burlington, Iowa; Des Moines County, Sec. 16, T 69 N, R 2 W.

Section 2: Platycrinites sp. and crinoidal biosparite (69-74); Triplophyllites sp. and Amplexus sp. and crinoidal biosparite (1070-1072); Haight Creek Member; Wever Quarry, north of Burlington, Iowa; Des Moines County, Sec. 25, T 72 N, R 2 W.

Section 3: Platycrinites sp. and crinoidal biosparite (1); Dictyoclostus sp. and crinoidal biosparite (1066); Haight Creek Member; Nelson Quarry, 10 km east of Mediapolis, Iowa; Des Moines County, Sec. 23, T 72 N, R 2 W.

Section 4: Platycrinites sp. and dolomitic crinoidal biosparite (3,4); Dolbee Creek Member; Dolbee Creek Quarry, 10 km east of Mediapolis, Iowa; Des Moines County, Sec. 23, T 72 N, R 2 W.

Section 5: Platycrinites sp. and crinoidal biosparite (61-66); Triplophyllites sp., Amplexus sp. and crinoidal biosparite (1068,1069); Dolbee Creek Member; Barb Creek, 2 km west of Augusta, Iowa; Des Moines County, Sec. 23, T 69 N, R 4 W.

Section 6: Platycrinites sp. and crinoidal biosparite (55-59); Columbia Quarry, Columbia, Missouri; Boone County, Sec. 18, T 48 N, R 12 W.

Section 7: Platycrinites sp. and crinoidal biosparite (50-52); U.S. Highway 63, 20 km north of Columbia, Missouri; Boone County, Sec. 24, T 51 N, R 13 W.

Section 8: Platycrinites sp. and crinoidal biosparite (1015, 1016); Dictyoclostus sp. and crinoidal biosparite (1067); Interstate 70, west of Stadium Blvd., Columbia, Missouri; Boone County, Sec. 12, T 48 N, R 13 W.

Section 9: Platycrinites sp. and crinoidal biosparite (76-80); Interstate 70, 1.6 km west of section 8; Boone County, Sec. 2, T 48 N, R 13 W.

Section 10: Platycrinites sp. and crinoidal biosparite (82-87); Interstate 70, 1.7 km west of section 8; Boone County, Sec. 11, T 48 N, R 13 W.

Section 11: Platycrinites sp. and crinoidal biosparite (1010-1014); Interstate 70, 1 km west of section 10; Boone County, Sec. 10, T 48 N, R 13 W.

Section 12: Platycrinites sp. and crinoidal biosparite (1001-1005); Interstate 70, exit to Blackwater, Missouri; Cooper County, Sec. 10, T 48 N, R 19 W.

Section 13: Platycrinites sp. and crinoidal biosparite (1017-1023); Interstate 70, 3.2 km east of section 12; Cooper County, Sec. 12, T 48 N, R 19 W.

Section 14: Platycrinites sp. and crinoidal biosparite (1006-1008); Interstate 70, 4 km east of section 12; Cooper County, Sec. 12, T 48 N, R 19 W.

Read Bay Formation, Ludlovian (Upper Silurian)

Section 15: Mucophyllum and biomicrite (101-105), new unidentified crinoid and biomicrite (106-110), Carpocrinus arcticus Frest & Strimple and biomicrite [illegible]11-115); Fury Beach, Somerset Island, 72° 53' N. lat., 92° 04' W. long.

Section 16: Mucophyllum and biomicrite (1050,1053,1058-1061, 1063-1065); Garnier Bay, Somerset Island, 73° 56' N. lat., 92° 10' W. long.

Section 17: Mucophyllum and biomicrite (1052, 1054-1057,1062); 10 km north of Creswell Bay, Somerset Island, 72° 52' N. lat., 93° 51' W. long.

Section 18: Mucophyllum sp. and biomicrite (1051); 20 km northwest of Cape Garry, Somerset Island, 72° 36' 30" N. lat., 93° 50' W. long.

Read Bay Formation, Member C, Ludlovian-Pridolian (Upper Silurian)

Section 19: New unidentified crinoid and dolomitic crinoidal biomicrite (917-961); Read Bay Formation, Member C type section; Read Bay, Cornwallis Island, 75° 5' N. lat., 93° 37' W. long.

Section 20: Mucophyllum sp. and biomicrite (1084, 1085); new unidentified crinoid, Carpocrinus arcticus Frest & Strimple and dolomitic biomicrite, crinoidal dolosparite (152-237); Cape Rescue, Cornwallis Island, 75° 17' N. lat., 93° 32' W. long.

Section 21: New unidentified crinoid and dolomitic crinoidal biosparite-micrite (712-776), and dolomitic crinoidal biomicrite (730, 734, 782); Goodsir Creek, Cornwallis Island, 74° 50' 5" N. lat., 93° 30' W. long.

Section 22: Carpocrinus arcticus Frest & Strimple and biomicrite (569-686); Depot Point Lake, Cornwallis Island, 74° 55' N. lat., 93° 26' W. long.

Burlington Limestone, Osagian (Mississippian)

Section 23: Triplophyllites sp., Amplexus sp. and crinoidal biosparite (1073,1074,1076,1078,1079,1081,1082), Dictyoclostus sp. and crinoidal biosparite (1075,1077,1080); Missouri Highway 13, 3.8 km north of Interstate 44, Springfield, Missouri; Greene County, Sec. 35, T 30 N, R 22 W.

Section 24: Dictyoclostus sp. and crinoidal biosparite (1083); Missouri Highway 13, 5.2 km north of Interstate 44, Springfield, Missouri; Greene County, Sec. 35, T 30 N, R 22 W.

APPENDIX II - PETROGRAPHIC DESCRIPTIONS

Petrographic descriptions of thin sections and hand specimens examined in this study. These are listed according to locality and identified by sample numbers (Appendix I).

Category headings and those that need additional explanations are listed below. (Note x denotes present, except where indicated otherwise).

1) Folk's classification (1959)
2) dolomitized
    biomicrite } 10 - 50 % diagenetic (dorag) dolomite
    biosparite }
   dolosparite > 50% diagenetic (dorag) dolomite
3) allochems (in percent)
4) bedding types
5) diagenetic fabrics (Orme & Brown, 1963; Bathurst, 1971)
6) diagenetic processes (Folk, 1965)
    dissolution - precipitation
    replacement
    neomorphism
7) constituents (in percent)
8) staining techniques (Lindholm & Finkelman, 1972)
    1 - 1 st. generation calcite
    2 - 2 nd. generation calcite
    3 - 3 rd. generation calcite
    F - fracture-filled calcite
    V - vug - filled calcite
    C - channel - filled calcite
    D - dolomite crystal
    M - minor staining of matrix
    PB - patchy gastropod-filled calcite
   thin sections stained with alizarin red and potassium ferricyanide
9) porosity classification (Choquette & Pray, 1970)
    (in percent)

10) replacement - dolomitization

incipient dolomite as defined in chapter III

Fritz & Jackson's dolomite classification (1972)

group	average crystal size (microns)	process-texture
I	< 20	"penecontemporaneous" uniform crystal size
II	20 - 50	"diagenetic" selective dolomitization of matrix
III	50 - 100	"diagenetic" dolomitization of fossils and matrix
IV	> 200	"hydrothermal" very coarse grained

11) compaction features

stylolites
- macro visible in hand specimen
- micro visible in thin section (Pseudostylolites, Shinn *et al.*, 1977)

12) pseudomorphs

13) silicification

14) fracturing

FORMATION Location sample	1						2										3			4
	micrite	biomicrite	pelsparite	biosparite	dolo. biomicrite	dolo. biosparite	dolosparite	algae	brachiopods	bryozoans	corals	crinoids	gastropods	ostracodes	pelecypods	pellets	trilobites	bedding	graded bedding	massive
BURLINGTON LST.																				
Iowa																				
sec. 1, 1A				x					1			99						x		x
2, 71				x						1		99						x		x
3, 1				x					7			90					3	x		x
4, 3						x						100						x		x
5, 62				x					10			90						x		
Missouri																				
sec. 6, 56				x								100						x		
7, 52				x						55		45						x		
8,1016				x					5			95						x		x
9, 78				x								100						x		x
10, 85				x								100						x		x
11,1010				x					7	8		85						x		x
1011				x					5			95								x
12,1005				x					5	10		80					5	x		x
13,1017				x					15		10	75								x
1020				x					20		10	70							x	x
14,1007				x					5	30		65						x		x
1008				x					15	25		60						x		x
23,1073				x					x		x	x								x
24,1083				x					x		x	x								x
READ BAY FM.																				
Somerset Is.																				
sec.15, 107		x							40	5	10	40					5	x		
109		x							5	30	20	20	10	10			5	x		
16,1064		x							25	10	20	40					5	x		
1065		x						10	20	5	10	30	10	5			10			
17,1055		x							x		x	x						x		
18,1051		x							x		x	x						x		

FORMATION Location sample			5			6									7				8
	syntaxial overgr.	equant	2G-bladed, equant	diss.-ppt.	neomorphism	replacement	allochems	micrite	spar	microspar	pseudospar	chert (diag)	qtz, mica (detrit)	opaques (FeO)	dolomite	non Fe-calcite	Fe-calcite I	Fe-calcite II	Fe-calcite III
BURLINGTON LST.																			
Iowa																			
sec. 1, 1A	x			x			40		55				1	2	2	1	2		
2, 71	x	x		x			57		40					2	1	1	F		
3, 1	x	x		x		x	50		45			1		1	3		V		
4, 3	x	x		x		x	60		20			10			10	M			
5, 62	x		x	x			50		48			1		1		1	2-3		
Missouri																			
sec. 6, 56	x	x		x			65		32					1	2	1	2		
7, 52	x	x		x	x?		70		29					1		1	2		
8, 1016	x	x		x	x		50		37	10		2		1		1	2		
9, 78	x	x		x	x		50		34	15				1		1	2-3		
10, 85	x	x		x			75		25							1		2	
11, 1010	x		x	x			70		29					1		1	2		
1011	x	x		x	x		70	5	24					1		C	C		
12, 1005	x	x		x	x		60		30	9				1		1	2	2	
13, 1017	x	x		x	x?		55	5	40							1	2		
1020	x		x	x	x		50	5	40	5						1	2	2	
14, 1007	x	x		x	x?		50		44	5?				1		1	2		
1008	x	x		x	x		50		39	10				1		1	F	F	
23, 1073	x			x			x		x					x					
24, 1083	x			x			x		x					x					
READ BAY FM.																			
Somerset Is.																			
sec. 15, 107		x	x	x	x	x	30	40	15	8			2		5	M	C-F		
109		x	x	x	x	x	35	40	15	4			2		4	1	2-F		
16, 1064	x	x	x	x	x	x	45	35	8	5			2		5	M			
1065	x	x	x	x	x	x	40	50	3	3			2		2	M			
17, 1055		x		x		x	x	x							x				
18, 1051		x		x		x	x	x							x				

FORMATION Location sample	9						10			11		12	13		14
	intraparticle	interparticle	intercrystal	channel	vug	fenestral	dolomite -fossil	-matrix	-incipient	stylolites -micro	-macro	pseudomorphs -gypsum	silicification -fossil	-matrix	fracturing
BURLINGTON LST.															
Iowa															
sec. 1, 1A	1	6						II	x	x	x				
2, 71	6	2							x						x
3, 1	1	4							x				x		x
4, 3		8						II	x				x		
5, 62	1	3							x				x		x
Missouri															
sec. 6, 56	2	6						II	x	x	x				x
7, 52		3							x						
8,1016	3	4							x				x		
9, 78	1	4							x						x
10, 85		5							x	x					x
11,1010	1	6							x						
1011	1	7							x						
12,1005	1	3							x						
13,1017	1	3			2				x						
1020		3			3				x						
14,1007	1	3							x	x	x				
1008	3	3							x	x					x
23,1073		x		x							x				
24,1083		x		x							x				
READ BAY FM.															
Somerset Is.															
sec.15, 107		1		1	2			III	x						x
109		1		2	1			II	x						x
16,1064				3	3			II	x				x		
1065				2	2			II	x				x		
17,1055		x		x							x				x
18,1051		x		x							x				x

FORMATION Location sample	1				2			3										4		
	micrite	biomicrite	pelmicrite	biosparite	dolo. biomicrite	dolo. biosparite	dolosparite	algae	brachiopods	bryozoans	corals	crinoids	gastropods	ostracodes	pelecypods	pellets	trilobites	bedding	graded bedding	massive
READ BAY FM.																				
Cornwallis Is																				
sec.19, 917						x			5	10	20	65						x		
920					x				15	10		65	5	5				x		
929					x			1	9	10	5	70	5					x		
939					x				15	5		69	5	5			1	x		
949						x			10	40	10	35	3	2				x		
sec.20, 152							x		10		20	70								x
200							x					100								x
212					x				20	10	10	45	5				10	x		x
223							x					100								x
224					x				20	30		35					15	x		x
1085					x				x	x	x	x						x		x
sec.21, 712						x			10		10	80								x
740						x			5			5[illegible]		5		35				x
749				x							5	95								x
773						x			10			85					5			x
775						x		5	10		10	75								x
730					x				5	20	9	65		1				x		
734					x				10	15	5	60		5			5	x		
782		x							10			80					10	x		
sec.22, 601		x										89		10		1		x		
672		x								25	50	20		5				x		
678		x							5			85		10				x		
684					x					10	40	50						x		
686		x							10		40	45					5	x		

	5			6			7									8			
FORMATION Location sample	syntaxial overgr.	equant	2G-bladed,equant	diss.-ppt.	neomorphism	replacement	allochems	micrite	spar	microspar	pseudospar	chert (diag)	qtz,mica (detrit)	opaques (FeO)	dolomite	non Fe-calcite	Fe-calcite I	Fe-calcite II	Fe-calcite III
READ BAY FM.																			
Cornwallis Is																			
sec.19, 917	x	x	x	x	x	x	65	5	9			1			20	M	F		
920		x	x	x	x	x	40	40	5						15	M	FV		
929			x	x		x	35	47				1	2		15	1	2		
939		x	x	x	x	x	50	35	5						10	M	FV		
949	x	x	x	x	x	x	50	5	8				2		35	1	2	D	
sec.20, 152		x				x	40								60	M	F		
200		x				x	40								60	1	2-2		
212	x	x	x	x	x	x	32	45	5	5		3			10	1	2	PB	
223		x				x	31								69	M			
224		x	x		x	x	20	56		10		4			10	M	F		
1085						x	x	x							x				
sec.21, 712	x	x			x	x	58	1		5				1	35	M		F	F
740	x	x			x	x	65	5		17			2	1	10	M	F		
749	x	x			x	x	60				10			1	9	M			
773	x	x	x	x	x	x	60		20						20	M			
775	x	x		x	x	x	50	5		5					40	M	F	F	
730	x	x	x	x	x	x	55	30	6					1	10	1	2		
734	x	x	x	x	x	x	45	35	9					1	10	M	M		
782	x	x	x		x	x	40	44		5	5			1	5	M	F	-F	
sec.22, 601	x	x	x	x	x		15	70		10	5					M	F		
672		x	x	x		x	40	50	4		1				5	1	2	F	
678	x	x			x	x	40	40	5	3	2			1	9	M	F		
684		x			x	x	30	30	15	10					15	M			
686		x	x	x	x	x	20	60	5	5	3	2			5	1	2-2		

FORMATION	9						10			11		12	13		14
Location-sample	intraparticle	interparticle	intercrystal	channel	vug	fenestral	dolomite -fossil	-matrix	-incipient	stylolites -micro	-macro	pseudomorphs -gypsum	silicification -fossil	-matrix	fracturing
READ BAY FM. Cornwallis Is.															
sec.19, 917		1	4					II	x	x			x		
920		3						II	x	x	x		x		x
929	1		3					III	x	x			x		
939		3	2					II	x	x					x
949			6					III	x	x					
sec.20, 152			3		3		IV	III		x	x				x
200			9				IV	III							
212			3		1		IV	III				x?	x		
223			6		3		IV	III		x					
224			3	3				II	x	x			x		x
1085	x	x									x				x
sec.[illegible], 712			3		2		III	III	x	x					x
740			3		3			III	x	x					x
749			6		3			III	x	x					x
773			9				III	III							
775			5				III	III	x	x					x
730	2		1					II	x	x					x
734	3		1					III	x	x					x
782	1		3					II	x	x					x
sec.22, 601	1				2			II	x	x					x
672	1			4				II	x	x			x		x
678	1	1			1	2		II	x	x			x		x
684			3	6				III	x				x		x
686		3	3					II	x				x		x

APPENDIX III - PLATES

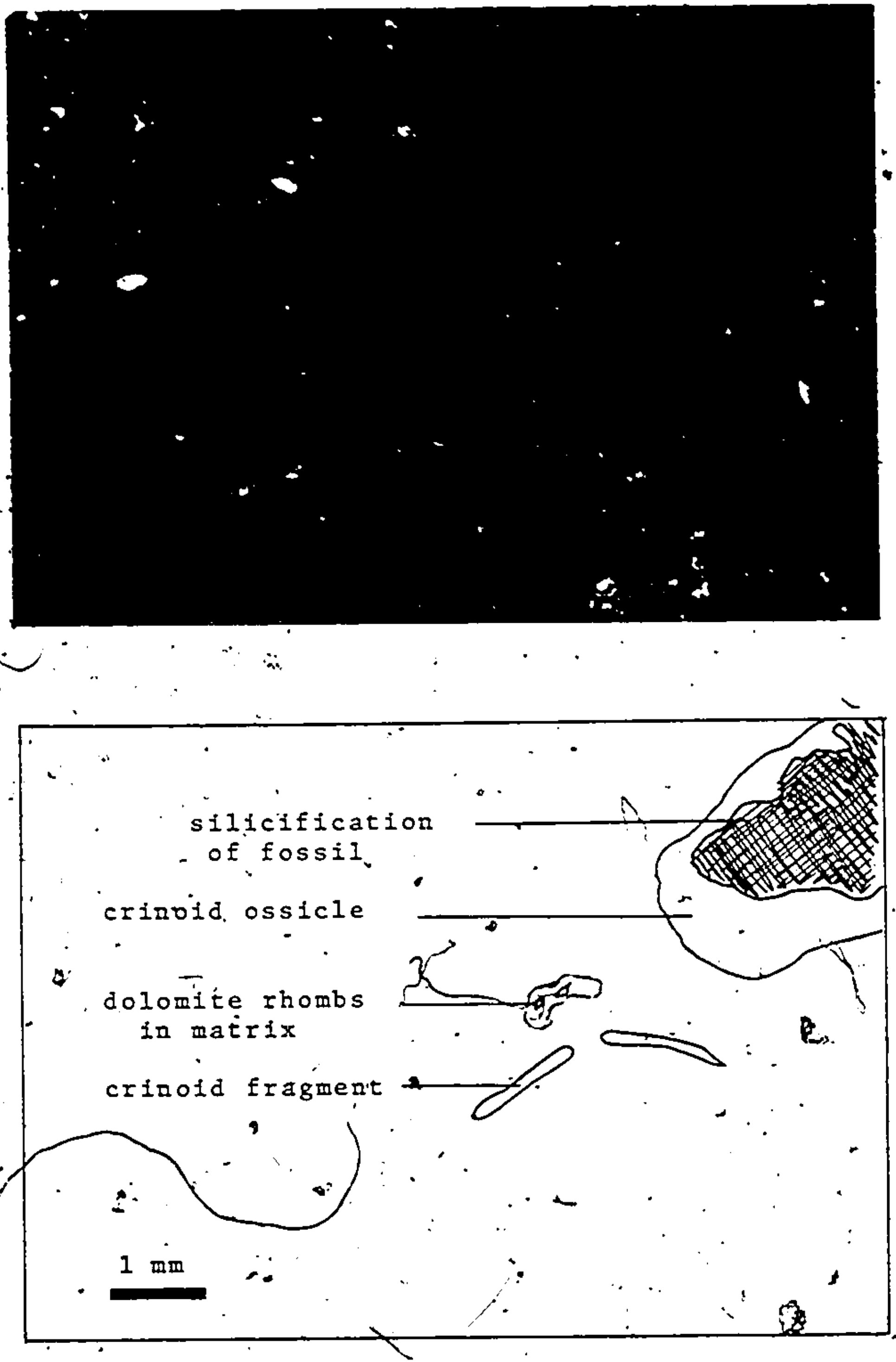


Plate 1. Photomicrograph of sample # 3 (plain light). Dolomitic crinoidal biosparite.

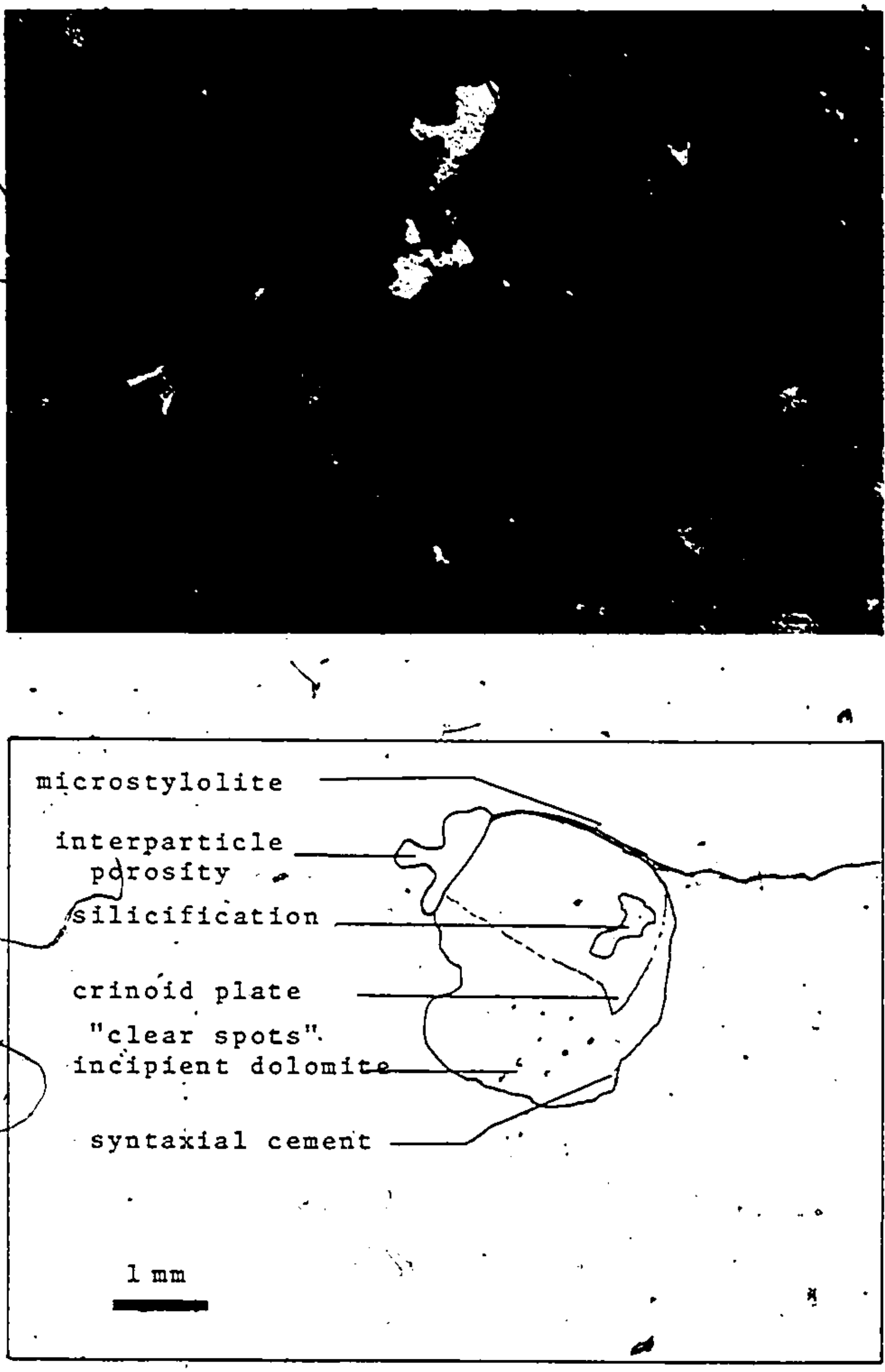


Plate 2. Photomicrograph of sample # 1016 (plain light). Crinoidal biosparite.

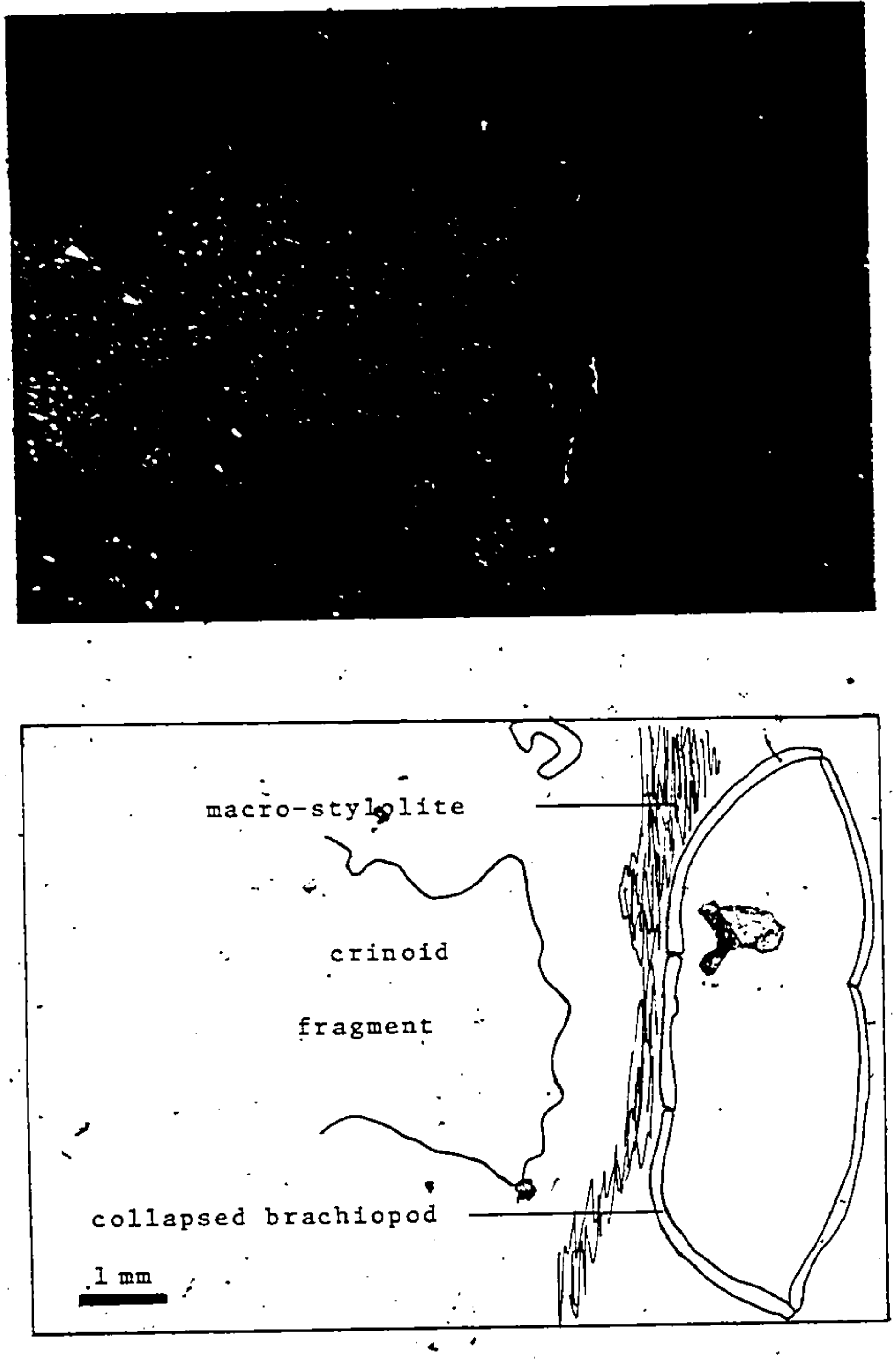


Plate 3. Photomicrograph of sample # 1020 (plain light).
Crinoidal-brachiopod biosparite.

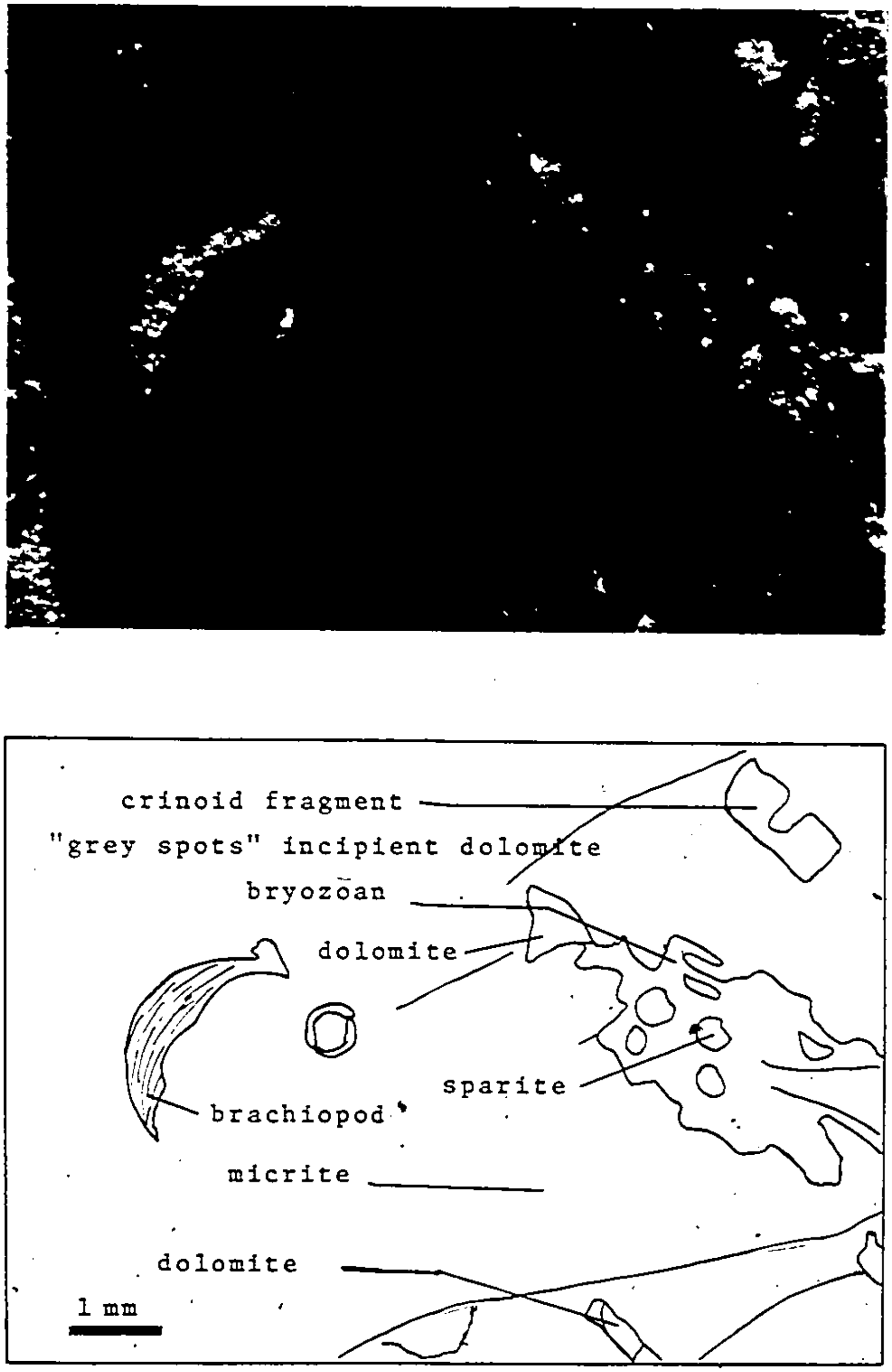
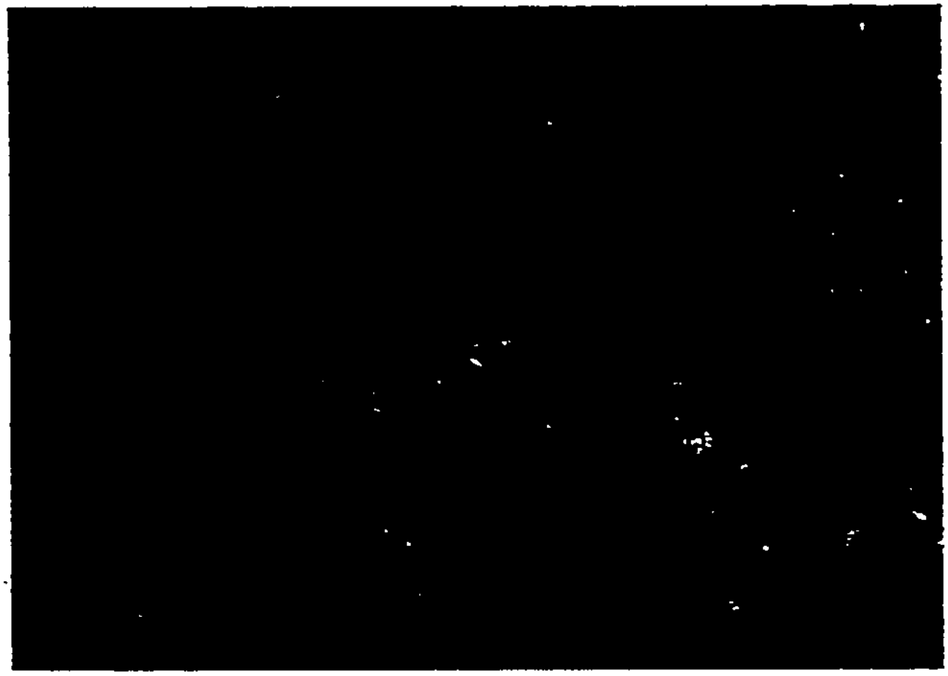


Plate 4. Photomicrograph of sample # 107 (plain light). Brachiopod-crinoidal biomicrite.



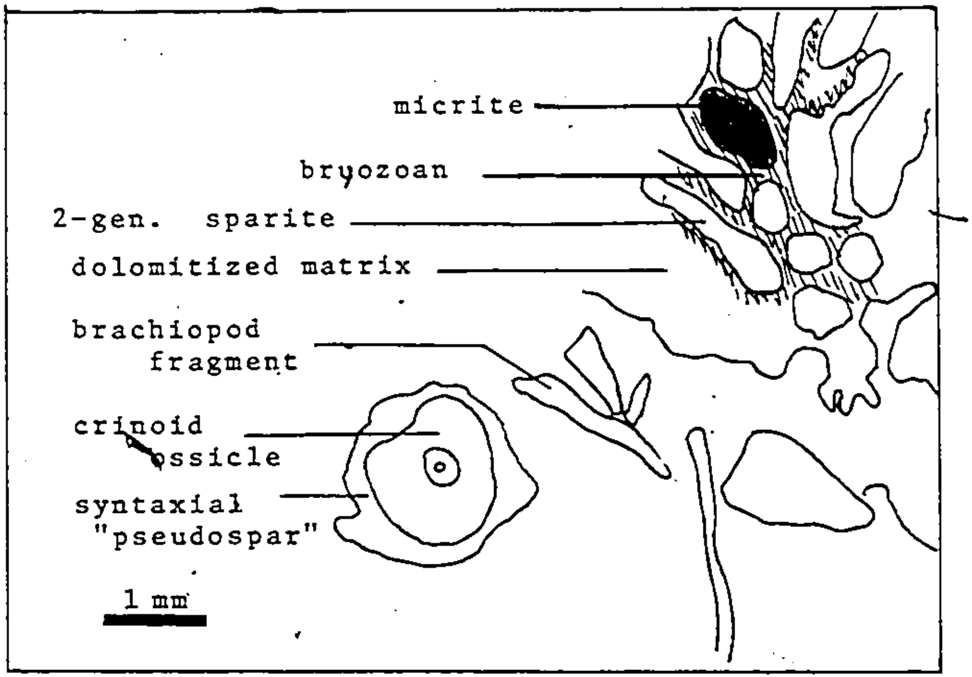


Plate 5. Photomicrograph of sample # 949 (plain light). Dolomitic bryozoan biosparite.

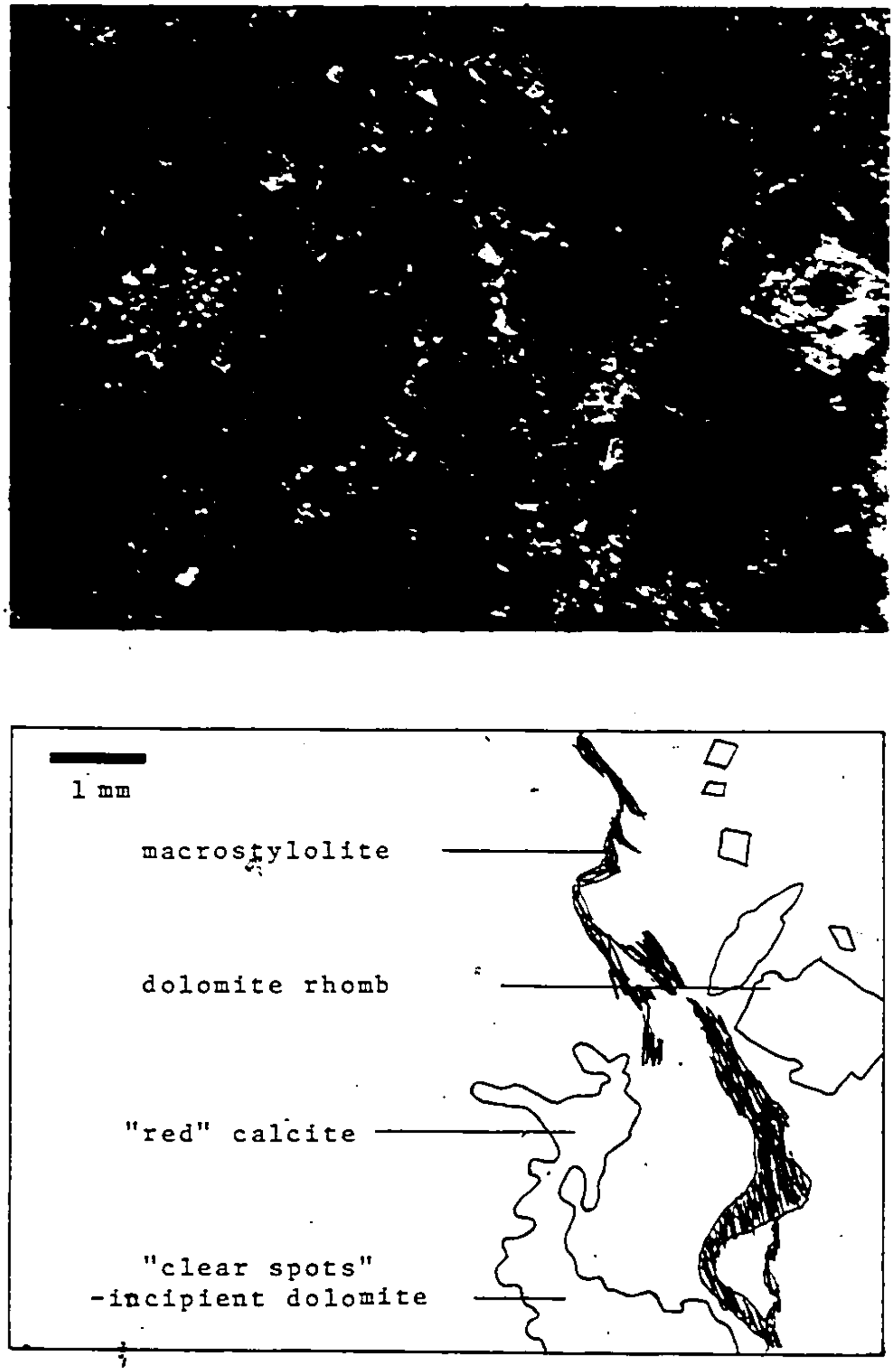


Plate 6. Photomicrograph of sample # 152 (plain light).

Crinoidal dolosparite.

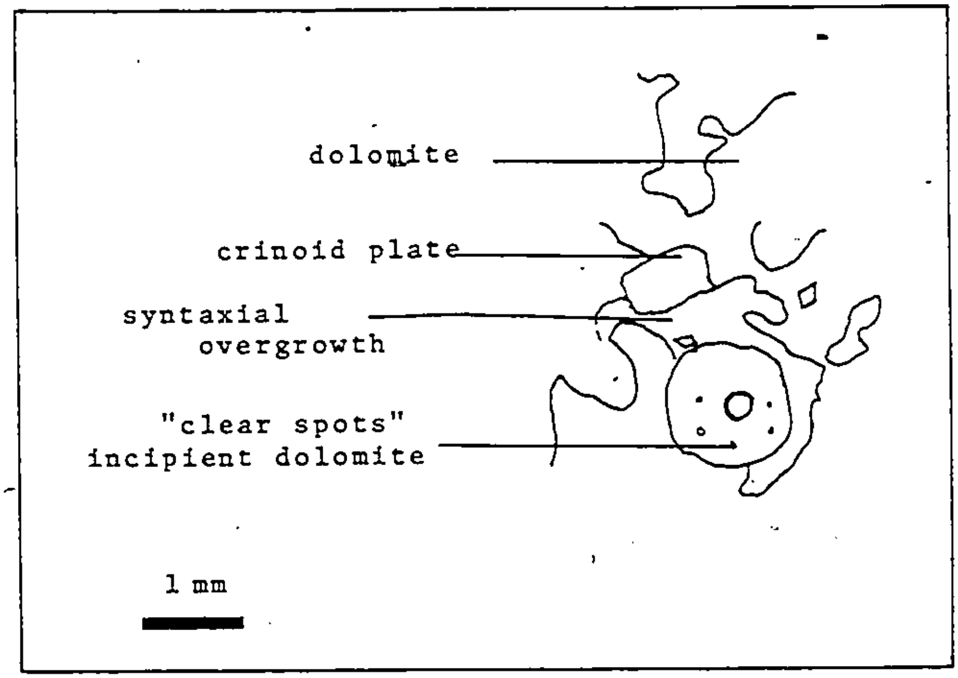


Plate 7. Photomicrograph of sample # 712 (plain light). Dolomitic crinoidal biosparite.

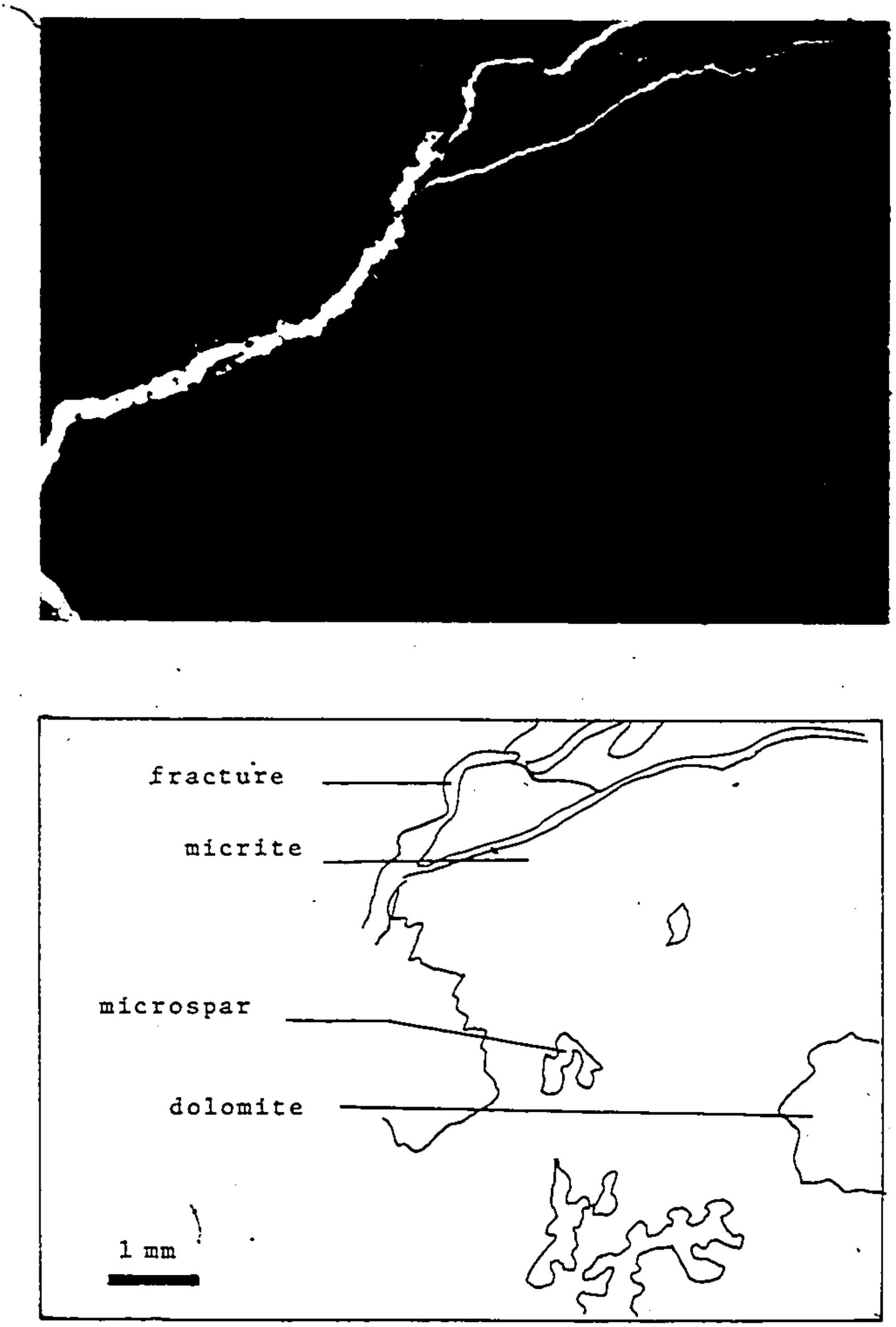


Plate 8. Photomicrograph of sample # 684 (plain light). Dolomitic crinoidal-coral biomicrite.

APPENDIX IV - CHEMICAL DATA

Chemical data are concentrations re-calculated on total carbonate (I.R.-free) basis. Ca and I.R. are in %; Sr, Mn, Na, Fe, Al and Mg are in ppm; $\delta^{18}O$ and $\delta^{13}C$ are in ‰ (PDB). Sample numbers are fossil specimens, those with "a" suffixed are their corresponding enclosing matrix.

Sample	I.R.	Sr	Mn	Na	Fe	Al	Mg	Ca	$\delta^{18}O$	$\delta^{13}C$
Brachiopods, corals and crinoids from Iowa:										
69	71.3	140	540	440	430	620	1180	39.4		
71	62.2	140	440	220	470	550	1380	39.9	-4.4	+1.7
73	41.7	130	400	70	290	100	1090	32.7		
74	41.0	230	440	340	350	50	2850	31.4	-5.0	+4.1
1070	46.1	110	560	70	580	140	1940	38.0	-4.1	+0.8
1071	9.6	90	450	40	440	50	830	38.5	-4.4	+0.1
1072	18.7	110	490	70	520	50	740	38.2	-5.1	+1.1
1	38.6	80	340	350	300	80	990	37.0	-3.4	+2.7
1066	49.8	530	160	760	250	110	600	38.2	-2.3	+2.8
3	45.9	70	400	130	220	130	1130	39.2		
4	51.1	70	410	150	290	240	1700	35.5		
61	53.4	100	600	90	430	250	1200	31.2		
62	53.3	130	450	120	430	220	1640	36.0		
63	58.8	100	610	110	490	150	1310	38.4	-2.7	+3.5
64	40.9	100	490	70	200	80	1290	39.6	-2.5	+3.7
66	38.5	110	460	320	230	120	1530	37.5	-2.2	+3.8
1068	7.3	80	690	80	680	60	1290	34.7	-4.1	+2.9
1069	35.7	90	690	80	600	100	1510	33.8	-3.2	+2.6
Crinoidal biosparite from Iowa:										
69a	4.5	110	460	70	370	70	1170	38.3		
71a	4.4	140	410	70	290	50	1050	38.8	-4.4	+1.1
73a	9.2	120	410	70	470	60	1010	31.8		
74a	3.6	220	400	90	370	50	2920	37.9	-4.3	+0.8
1070a	6.8	110	560	120	430	170	1280	39.1	-3.6	+0.8
1071a	4.1	90	480	50	360	70	860	34.2	-4.9	+1.0
1072a	3.6	100	470	50	380	60	850	32.9	-4.6	+0.9
1a	4.9	100	430	80	210	20	1100	39.7	-3.9	+1.2
1066a	7.5	170	540	80	440	90	1700	35.0	-3.4	+0.7

Sample	I.R.	Sr	Mn	Na	Fe	Al	Mg	Ca	$\delta^{18}O$	$\delta^{13}C$
3a	15.4	60	480	310	510	90	18440	37.7		
4a	16.6	70	480	160	500	80	17810	34.2		
61a	10.9	90	530	90	360	50	1050	35.9		
62a	3.8	100	480	70	400	60	1150	37.8		
63a	6.3	90	750	110	470	110	1090	38.8	-3.9	+1.2
64a	9.2	100	520	50	420	50	1120	38.0	-3.3	+3.3
66a	12.1	90	600	130	680	50	1650	38.1	-4.1	+3.0
1068a	9.0	90	700	80	670	70	1400	35.7	-3.4	+3.1
1069a	9.4	80	730	80	600	70	1240	38.0	-3.2	+3.2

Brachiopods, corals and crinoids from Missouri:

Sample	I.R.	Sr	Mn	Na	Fe	Al	Mg	Ca	$\delta^{18}O$	$\delta^{13}C$
55	2.9	60	130	150	140	30	1240	34.5		
56	3.1	80	280	140	200	30	1580	39.5		
59	4.1	90	200	160	130	30	1300	38.6	-3.2	+3.9
50	4.4	180	510	80	310	60	1830	39.2	-4.6	+3.4
52	5.2	140	470	120	420	30	2080	40.9		
1015	3.9	140	230	180	170	30	1380	38.6		
1016	2.8	130	240	70	140	20	1410	39.2		
1067	11.4	480	160	640	560	20	840	33.2	-4.2	+3.7
76	3.5	180	240	90	150	30	2130	40.8		
77	3.7	170	290	340	200	40	1430	39.8	-4.8	+3.6
78	3.4	210	340	180	160	30	1300	34.1		
79	3.4	170	270	230	230	40	1520	40.1	-4.8	+3.4
80	3.1	190	250	220	260	40	1840	36.2		
82	4.1	160	350	300	340	70	1800	35.5		
83	3.0	140	400	140	330	30	2690	36.0		
85	5.2	210	350	140	280	30	1890	37.8		
86	3.2	210	270	70	140	40	1420	37.2		
87	2.7	210	290	60	140	30	1450	36.8	-4.6	+3.6
1010	3.3	120	330	210	290	30	2110	36.3	-5.5	+3.5
1011	3.5	190	300	230	270	40	1880	38.8		
1014	3.4	160	320	220	310	40	1640	39.2		
1001	3.1	210	320	210	220	40	1540	39.6	-4.5	+3.3
1003	3.9	200	350	110	200	40	1660	39.3	-4.6	+3.7
1004	3.0	230	320	120	270	30	1830	38.7		
1005	3.4	170	360	160	380	50	2470	40.2		
1017	2.4	230	330	210	190	30	1470	39.1	-4.2	+3.6
1018	3.6	180	420	120	210	20	1320	37.1		
1019	3.6	180	360	120	390	30	1540	38.4		
1020	2.7	140	250	100	310	20	1930	40.3		
1022	2.5	200	280	130	230	30	1920	40.1		
1023	3.0	220	270	110	200	20	1600	37.2		

Sample	I.R.	Sr	Mn	Na	Fe	Al	Mg	Ca	$\delta^{18}O$	$\delta^{13}C$
1006	2.9	140	320	130	170	30	1450	38.0		
1007	6.3	190	220	230	250	20	1860	39.1	-4.6	+3.4
1008	3.2	180	220	140	160	20	1360	38.1		
1074	2.7	250	140	70	100	20	2100	37.3	-4.4	+3.7
1075	1.9	660	70	600	60	20	1040	34.0	-3.4	+3.9
1076	2.6	240	230	60	100	10	1900	32.4	-2.9	+4.3
1077	1.5	590	60	560	80	10	710	31.9		
1078	2.7	250	170	60	190	40	1710	35.3		
1079	1.8	220	180	40	160	40	1620	32.7		
1080	2.1	620	70	550	80	20	320	36.8		
1081	1.9	290	130	30	110	20	1360	37.7	-5.0	+3.7
1082	1.9	190	210	30	140	20	1080	34.9	-4.3	+3.7
1083	1.8	320	150	300	80	50	450	36.2	-4.8	+3.2
Crinoidal biosparite from Missouri:										
55a	2.7	90	240	130	500	20	3570	39.1		
5[illegible]a	2.1	90	290	60	750	30	5080	38.1		
59a	3.4	90	270	80	270	40	1070	37.4	-3.8	+3.6
50a	5.3	180	590	180	610	220	1270	38.6	-4.7	+2.9
52a	4.8	120	700	40	1180	160	1050	39.3		
1015a	2.9	190	280	140	340	40	1380	38.1		
1016a	4.2	120	280	90	460	30	1280	37.6		
1067a	3.4	90	350	130	650	40	1430	36.2	-4.2	+3.5
76a	2.3	200	300	150	270	40	1260	39.1		
77a	3.4	190	340	110	400	60	1240	40.5	-5.5	+3.1
78a	3.3	170	350	350	440	50	1320	37.5		
79a	2.2	180	330	210	470	50	1340	38.1	-5.5	+2.8
80a	2.9	170	340	210	520	100	1350	39.6		
82a	4.7	160	320	230	460	150	1430	36.8		
83a	3.6	170	420	100	380	50	1340	38.4		
85a	3.1	180	310	100	410	50	1140	38.7		
86a	3.9	190	420	90	520	100	1330	38.3		
87a	2.9	210	460	160	400	70	1370	38.6	-5.1	+3.2
1010a	3.1	150	400	130	520	60	1470	38.5	-6.5	+1.8
1011a	3.1	190	340	130	580	70	1260	39.3		
1014a	3.0	180	330	130	560	60	1310	38.8		
1001a	3.8	160	380	160	760	110	1190	39.7	-5.0	+2.7
1003a	3.0	170	410	210	680	60	1310	39.9	-5.0	+3.0
1004a	3.7	150	400	300	780	60	1220	39.1		
1005a	2.9	180	440	80	830	50	1000	37.1		

Sample	I.R.	Sr	Mn	Na	Fe	Al	Mg	Ca	$\delta^{18}O$	$\delta^{13}C$
1017a	3.5	150	360	60	810	120	880	39.4	-5.5	+2.0
1018a	3.2	140	520	60	990	90	980	38.1		
1019a	3.6	200	360	150	590	90	1090	38.6		
1020a	2.9	180	380	100	680	70	1100	39.2		
1022a	3.0	230	360	200	520	60	1300	40.0		
1023a	3.1	180	390	70	730	60	1070	38.6		
1006a	3.7	160	400	210	670	90	1070	38.3		
1007a	3.4	150	440	70	780	120	950	38.6	-5.0	+1.9
1008a	4.2	180	340	240	680	110	1140	37.5		
1073a	1.7	200	280	100	190	20	1620	34.1		
1074a	2.0	200	230	110	220	30	1690	31.9	-6.1	+3.4
1075a	2.1	260	200	120	190	40	1830	34.2	-5.2	+3.8
1076a	1.6	240	200	120	180	30	1360	34.3	-5.2	+3.8
1077a	1.8	230	190	120	190	40	1170	34.2		
1078a	2.1	240	190	130	210	50	1500	34.2		
1079a	1.9	210	190	120	160	30	1500	34.0		
1080a	2.0	210	190	80	170	40	880	36.1		
1081a	1.7	270	190	110	190	30	870	32.1	-5.2	+3.8
1082a	1.8	140	240	40	200	30	870	36.2	-5.7	+3.3
1083a	2.9	110	180	130	70	40	780	34.4	-3.5	+3.8
Corals and crinoids from Somerset Island:										
101	27.0	1360	30	100	210	60	5180	39.1	-5.3	+0.9
102	10.7	920	40	60	170	60	4150	38.8		
103	25.2	840	50	60	250	50	4060	38.6		
104	14.3	840	50	70	320	60	4360	38.4	-5.9	+0.5
105	2.6	550	40	40	200	30	3290	38.0		
106	4.4	260	60	130	400	90	5620	37.8		
107	3.4	290	50	60	220	60	4410	37.8	-5.9	+0.5
108	4.4	270	80	60	370	80	6110	36.9	-5.9	+0.4
109	7.5	290	100	70	450	130	5560	36.7		
110	30.8	410	100	110	380	120	6330	36.8	-5.7	+0.0
111	5.7	350	80	50	330	40	4790	38.2	-5.8	+0.3
112	7.4	330	80	70	420	130	5170	36.7	-6.1	+0.1
113	6.6	340	80	80	630	210	6310	37.0	-5.8	+0.5
114	6.9	500	70	70	330	50	4370	37.8		
115	6.4	500	80	70	400	100	4980	37.7	-5.5	+0.4
1050	18.4	580	30	90	150	60	5740	37.5		
1053	5.4	960	40	40	80	20	3700	37.7	-6.1	+0.6
1058	25.2	1400	30	110	240	40	6200	38.0	-5.8	+1.3
1059	2.5	760	40	70	120	20	4800	37.6	-5.8	+0.8
1060	2.4	820	20	40	120	20	4930	38.0	-6.4	+0.7
1061	38.9	1190	30	100	390	160	5540	38.3	-6.3	+0.6
1063	14.5	650	40	80	170	50	5590	38.1	-5.8	+1.4
1064	6.0	580	50	60	210	40	5080	38.2		
1065	10.0	830	50	50	120	30	5080	37.9	-6.6	+0.7

Sample	I.R.	Sr.	Mn	Na	Fe	Al	Mg	Ca	$\delta^{18}O$	$\delta^{13}C$
1052	29.0	760	30	110	150	80	5170	36.9		
1054	47.1	670	60	100	300	160	4230	38.7		
1055	16.6	640	50	120	140	30	3930	38.0		
1056	17.7	540	50	100	130	30	2920	38.1	-6.2	+0.2
1057	9.1	670	40	100	90	30	3780	38.7	-6.0	+0.4
1062	22.2	630	40	100	230	90	4730	38.3	-5.9	+0.5
1051	3.4	470	60	80	160	40	3450	37.4		

Biomicrite from Somerset Island:

101a	10.9	320	120	150	1750	460	15260	36.5	-6.2	+0.4
102a	8.2	320	120	140	1370	330	12490	36.6		
103a	13.7	640	90	130	1020	470	8130	37.6		
104a	14.2	620	100	140	1210	650	8450	37.6	-6.0	+0.4
105a	7.7	340	100	130	1290	330	11850	36.8		
106a	15.5	330	110	120	1540	670	7740	37.7		
107a	13.9	350	120	160	1760	760	10840	37.0	-5.7	-0.5
108a	11.3	440	120	130	1070	460	6250	36.9	-5.7	+0.1
109a	17.1	430	120	120	1890	780	12490	35.5		
110a	13.5	460	120	130	1510	930	6640	35.7	-5.9	+0.1
111a	14.2	580	110	120	1180	590	6270	37.3	-5.6	+0.3
112a	10.0	630	100	130	900	250	8100	35.4	-5.4	+0.6
113a	14.2	590	110	140	1350	760	5520	37.3	-5.7	+0.3
114a	15.0	550	120	160	1730	700	11430	37.3		
115a	13.6	600	120	170	1540	910	7520	37.0	-5.5	+0.3
1050a	15.5	290	130	140	1440	290	9760	37.3		
1053a	14.5	500	190	110	850	220	6750	37.9	-6.4	+0.1
1058a	12.5	580	140	170	1550	600	14130	36.2	-5.6	-0.1
1059a	13.7	240	170	150	3480	1270	24800	34.8	-7.2	+0.9
1060a	12.5	380	120	150	1050	650	5350	37.9	-6.4	+0.8
1061a	13.4	460	150	180	1450	800	9740	37.3	-6.6	+0.5
1063a	15.7	400	130	120	800	250	6620	37.8	-6.1	+0.5
1064a	8.8	310	120	180	1150	540	9310	38.1		
1065a	11.3	440	190	160	1380	770	8230	37.5	-7.2	+0.2
1052a	15.1	390	100	160	1960	2070	11160	36.2		
1054a	15.2	370	140	150	1730	980	19190	35.9		
1055a	21.5	320	110	130	1060	910	6020	37.6		
1056a	16.4	240	120	140	1550	740	21800	35.5	-6.4	-0.2
1057a	8.7	500	80	150	500	350	6360	38.2	-5.4	+0.4
1062a	13.2	320	90	260	1080	490	11310	37.2	-5.9	+0.0
1051a	12.4	270	120	90	1090	1200	3420	37.2		

Sample	I.R.	Sr	Mn	Na	Fe	Al	Mg	Ca	$\delta^{18}O$	$\delta^{13}C$
Corals and crinoids from Cornwallis Island:										
917	3.3	170	40	150	310	70	6630	37.0	-5.5	+0.9
920	3.1	170	40	70	320	90	6290	37.9		
929	4.0	210	40	90	590	120	12290	37.3		
930	4.3	150	40	100	620	160	13590	36.7		
939	4.1	240	50	80	430	100	10380	37.2		
940	3.1	400	50	60	430	80	8840	37.9		
942	3.8	410	40	100	290	70	7440	38.1	-6.0	+1.0
945	3.2	70	40	130	480	50	6490	37.4	-6.1	+0.5
949	3.6	150	40	100	350	50	7050	37.3		
953	3.4	320	40	120	400	60	8070	35.7		
961	4.1	180	60	80	390	90	5970	37.8	-5.3	+0.5
dolomitic biomicrite and dolosparite from Cornwallis Island:										
917a	8.4	320	70	200	1350	460	23960	35.6	-5.3	+0.8
920a	14.2	300	80	210	1710	600	29030	35.1		
929a	18.5	460	90	230	2030	1100	32140	34.1		
930a	6.9	190	60	130	1290	290	24180	35.6		
939a	16.1	530	90	230	1580	770	25910	34.9		
940a	15.2	770	90	230	1670	960	23790	34.9		
942a	21.1	450	100	220	2380	1160	30590	33.1	-5.2	+1.0
945a	11.2	220	80	220	1300	640	17780	35.6	-5.8	+0.6
949a	6.4	220	70	150	1220	280	20620	35.4		
953a	9.4	450	70	200	990	500	16090	35.8		
961a	12.1	760	80	190	1330	690	18000	35.1	-5.9	+0.9
Corals and crinoids from Cornwallis Island:										
152	3.0	100	70	130	160	80	5370	36.9	-6.5	-0.2
160	3.5	100	70	100	150	100	4870	37.1		
164	3.3	140	80	150	200	100	12080	35.8		
170	2.5	70	130	190	140	50	7420	36.7	-6.3	+0.0
180	5.4	90	70	120	110	90	3860	38.0		
200	4.1	90	130	200	1180	220	105740	24.5		
203	3.3	130	100	130	280	110	15530	36.5	-5.8	+0.2
212	2.8	90	60	120	150	60	4930	37.5		
223	2.6	30	110	210	480	90	123760	21.1	-3.8	+0.3
224	3.6	380	100	80	190	60	12600	37.3	-6.1	-0.3
235	3.3	60	120	260	670	100	104300	23.7	-4.8	+0.2
237	3.8	70	60	110	140	60	9400	36.8	-6.5	-0.2
1084	12.8	590	60	110	460	70	7730	32.1	-6.1	-0.3
1085	5.2	640	30	80	80	20	4010	35.1	-5.7	+0.3

Sample	I.R.	Sr	Mn	Na	Fe	Al	Mg	Ca	$\delta^{18}O$	$\delta^{13}C$
Dolosparite and dolomitic biomicrite from Cornwallis Island:										
152a	6.8	80	120	190	1220	460	70370	27.4	-4.3	+0.5
160a	8.8	190	120	150	570	560	13090	36.3		
164a	4.5	40	120	240	930	250	119510	21.6		
170a	5.1	190	130	110	490	320	18900	35.7	-6.1	+0.4
180a	5.4	170	100	120	440	250	21310	35.0		
200a	7.4	100	130	210	1430	520	101790	24.8		
203a	6.1	80	140	270	1010	340	87630	26.3	-4.4	+0.0
212a	7.2	130	90	150	810	310	34650	33.3		
223a	8.3	60	120	320	1120	560	124350	23.1	-3.3	+0.4
224a	5.3	480	80	160	440	190	22820	36.1	-5.3	+0.1
235a	9.3	70	120	230	1040	500	114060	22.6	-4.0	+0.0
237a	9.1	90	120	310	1020	580	101540	27.8	-3.9	+0.2
1084a	8.0	320	190	190	1010	190	12310	31.6	-5.3	-0.1
1085a	5.8	370	120	180	410	140	10280	33.1	-5.3	+0.3
Crinoids from Cornwallis Island:										
730	3.1	160	150	160	230	50	5030	36.0	-7.2	+2.7
734	2.9	190	100	110	470	50	8710	37.6	-6.7	+3.2
782	3.6	230	240	120	280	50	7800	38.4	-6.4	+2.3
712	3.1	100	60	130	160	30	7990	37.0	-6.8	+2.4
714	2.5	110	50	80	150	20	6240	37.0		
716	2.2	130	50	70	120	20	5350	37.1	-7.0	+2.8
717	3.1	140	60	50	150	30	8230	36.4		
729	2.5	120	50	100	120	40	5370	37.3		
737	2.6	110	50	110	160	40	5600	36.0	-6.9	+2.9
740	2.3	200	50	140	120	40	5340	37.6		
741	2.5	160	60	200	90	40	4250	38.4		
746	2.7	120	50	110	100	40	4070	37.4		
749	2.8	120	40	170	130	50	5580	37.5		
750	3.5	120	40	90	100	50	4650	37.2		
755	2.6	120	50	90	100	40	3830	37.4		
772	5.0	120	50	130	80	20	3250	37.8	-6.9	+2.8
773	3.3	120	50	120	120	50	5630	36.9		
775	3.0	140	50	160	140	20	5490	37.3	-6.1	+2.7
776	2.9	140	50	90	110	20	5480	37.5	-6.8	+2.7
731	2.5	300	40	160	90	30	5710	36.7	-6.9	+2.8
735	2.6	140	50	120	120	20	3480	35.8		
Biomicrite and dolomitic biomicrite from Cornwallis Island:										
730a	7.5	250	180	140	1460	360	23140	35.3	-6.6	+3.2
734a	5.2	230	260	120	1660	160	17520	36.7	-7.3	+3.1
782a	7.4	590	160	210	750	350	12670	37.3	-6.0	+3.3

Sample	L.R.	Sr	Mn	Na	Fe	Al	Mg	Ca	$\delta^{18}O$	$\delta^{13}C$
712a	3.3	90	140	140	1040	90	55210	30.4	-7.1	+2.5
714a	3.0	130	120	90	560	80	20910	35.4		
716a	4.7	190	130	160	380	50	12970	35.8	-8.5	+2.2
717a	4.2	100	130	150	930	60	51560	31.3		
729a	3.4	110	120	100	740	50	32350	33.5		
737a	4.0	150	130	110	900	100	32080	35.3	-7.5	+2.9
740a	4.2	280	120	130	390	110	16080	36.7		
741a	3.3	220	90	140	370	110	18330	37.3		
746a	3.8	200	130	100	410	50	11040	36.6		
749a	3.3	190	90	130	270	60	8080	37.2		
750a	3.5	170	140	90	600	50	20900	36.0		
755a	2.8	170	140	80	680	60	24830	34.6		
772a	3.4	190	110	90	240	50	6280	36.6	-8.9	+2.0
773a	3.1	170	100	140	440	80	28820	34.2		
775a	3.0	150	110	120	560	60	23400	35.3	-7.6	+2.4
776a	3.6	170	100	90	230	50	7530	36.9	-8.8	+2.1
731a	3.5	260	110	100	430	60	14420	35.7	-8.3	+2.5
735a	3.7	170	140	130	1000	60	36710	32.8		
Crinoids from Cornwallis Island:										
569	3.5	100	90	160	130	10	1800	38.0	-6.3	+0.4
573	2.7	90	90	70	170	50	1840	37.7		
574	3.0	90	80	60	180	70	1330	37.8		
579	2.9	100	200	60	230	40	2480	37.9	-6.2	+0.3
583	3.0	100	70	80	170	50	2290	38.2		
589	2.9	90	60	80	140	50	1150	37.9	-6.4	+0.2
592	3.3	110	70	70	180	70	2670	37.5		
601	2.8	130	80	160	130	50	2070	37.8		
609	3.3	120	80	70	160	40	1960	37.8		
611	3.0	110	140	80	240	60	2580	37.9		
613	3.4	110	110	100	240	60	3130	37.7	-6.0	+0.4
615	3.6	100	160	80	210	80	2540	38.0		
628	3.1	180	100	80	220	70	3000	38.7	-6.3	+0.3
630	3.6	130	100	80	160	80	2660	38.0	-6.6	+0.3
631	3.4	180	140	70	250	90	3370	36.4		
672	3.1	110	90	70	150	40	2290	38.1	-6.3	+0.3
678	3.4	130	90	80	240	90	3600	37.8		
684	3.2	160	70	60	170	60	3060	38.1		
686	2.8	190	110	160	140	30	3050	37.7		
Crinoidal biomicrite from Cornwallis Island:										
569a	4.2	160	120	120	760	100	14860	36.3	-6.3	+0.4
573a	7.9	160	120	70	1100	210	15410	35.6		
574a	7.8	210	110	90	400	290	4130	36.6		
579a	12.1	240	120	110	890	480	5670	34.5	-6.2	+0.3
583a	6.0	230	130	140	610	310	6200	39.7		
589a	6.4	280	100	110	590	390	4110	37.7	-6.4	+0.2
592a	10.7	270	100	110	950	630	6360	36.9		

Sample	I.R.	Sr	Mn	Na	Fe	Al	Mg	Ca	$\delta^{18}O$	$\delta^{13}C$
601a	8.2	230	110	110	810	400	6060	37.2		
609a	5.6	220	120	80	580	210	7600	37.1		
611a	7.9	220	120	110	680	500	3560	38.2		
613a	8.7	250	90	100	840	590	5360	37.7	-6.0	+0.4
615a	9.6	270	130	90	840	600	6310	36.7		
628a	7.2	270	120	100	540	340	3410	38.0	-6.3	+0.3
630a	10.9	230	90	110	900	520	5630	37.4	-6.6	+0.3
631a	11.1	240	90	130	750	450	4490	37.6		
672a	9.2	260	100	110	650	390	4710	37.0	-6.3	+0.3
678a	9.8	250	100	120	890	770	5370	36.5		
684a	11.6	270	100	100	840	540	6580	37.3		
686a	9.8	240	130	100	770	440	6070	37.1		

Crinoid from the Read Bay Formation at Goodsir Creek (analysis by A. Legun, Dept. of Geology, Univ. of Ottawa):

12s	2.3	40	90	-	490	-	78500	-