BIOGEOCHEMISTRY OF PALEOZOIC BRACHIOPODS
FROM
NEW YORK STATE AND ONTARIO

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by

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©1989

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In Praise of Limestone

If it form the one landscape that we, the inconstant ones,
    Are consistently homesick for, this is chiefly
Because it dissolves in water.....

W.H. Auden, 1951.
Abstract

A comprehensive elemental, isotopic and microstructural analyses was undertaken of brachiopod calcites from the Hamilton Group (Middle Devonian), Clinton Group (Middle Silurian) and Middle to Upper Ordovician strata of Ontario and New York State. The majority of specimens were microstructurally and chemically preserved in a pristine state, although a number of specimens show some degree of post-depositional alteration. Brachiopod calcites from the Hamilton and Clinton Groups were altered by marine derived waters whereas Trenton Group (Middle Ordovician) brachiopods altered in meteorically derived fluids.

Analysis of the elemental and isotopic compositions of pristine Hamilton Group brachiopods indicates there are several chemical relationships inherent to brachiopod calcite. Taxonomic differentiation of Mg, Sr and Na contents was evident in three co-occuring species from the Hamilton Group. Mean Mg contents of pristine brachiopods were respectively *Athyris spiriferoides* (1309ppm), *Mucrospirifer mucronatus* (1035ppm) and *Mediospirifer audacula* (789ppm). Similarly, taxonomic differentiation of shell calcite compositions was observed in co-occuring brachiopods from the Clinton Group (Middle Silurian) and the Trenton Group (Middle Ordovician). The taxonomic control of elemental regulation into shell calcite is probably related to the slightly different physiological systems and secretory mechanisms.

A relationship was observed in Hamilton Group species between the depth of respective brachiopod communities and their Mg, Sr and Na contents. These elements were depleted in the shell calcites of deeper brachiopods compared to their counterparts in shallower reaches. Apparently shell calcite elemental composition is related to environmental conditions of the depositional setting, which may have controlled the secretory regime, mineral morphology of
shell calcite and precipitation rates of each species. Despite the change in Mg, Sr and Na contents between beds and formations in response to environmental conditions, the taxonomic differentiation of shell calcite composition is maintained. Thus, it may be possible to predict relative depth changes in paleoenvironmental reconstructions using brachiopod calcite. This relationship of brachiopod chemistry to depth was also tested within a transgressive-regressive (T-R) cycle in the Rochester Shale Formation (Middle Silurian). Decreasing Mg, Sr and Na contents were observed in the transition from the shallow carbonates of the Irondequoit Formation to the deeper shales of the lowest 2 m of Rochester Shale. However, no isotopic and elemental trends were observed within the entire T-R cycle which suggests that either the water conditions did not change significantly or that the cycle is illusory.

A similar relationship was observed between the Fe and Mn chemistries of shell calcite and redox/paleo-oxygen conditions. Hamilton Group brachiopods analysed from deeper areas of the shelf are enriched in Mn and Fe relative to those from shallow zones. The presence of black shales and dysaerobic faunas, during deposition of the Hamilton Group, suggests that the waters of the northern Appalachian Basin were stratified. The deeper brachiopods were marginally positioned above an oxycline and their shell calcites reflect periodic incursions of oxygen depleted water. Furthermore, analysis of Dalmanella from the black shales of the Collingwood Shale (Upper Ordovician) in comparison to those from the carbonates of the Verulam Formation (Middle Ordovician) confirm the relationship of Fe and Mn contents to periodic but not permanent incursions of low oxygen waters.

The isotopic compositions of brachiopod calcite found in Hamilton Group (δ¹³C; +2.5‰ to +5.5‰; δ¹⁸O -2.5‰ to -4.0‰) and Clinton Group (δ¹³C; +4.0‰ to +6.0; δ¹⁸O; -1.8‰ to -3.6‰) are heavier than previously reported.
Uncorrected paleotemperatures (assuming normal salinity, 0°/oo SMOW and no fractionation effects) derived from these isotopic values suggest that the Clinton sea temperature (Middle Silurian) ranged from 18°C to 28°C and Hamilton seas (Middle Devonian) ranged between 24°C and 29°C. In addition, the isotopic variation of brachiopod shell calcite is significant and is related to environmental conditions. Within a single time-correlative shell bed (the Demissa Bed; Hamilton Group) a positive isotopic shift of 2-2.5°/oo in δ13C compositions and a positive shift of 1.0-1.5°/oo in δ18O composition of shell calcite is observed, corresponding with a deepening of brachiopod habitats toward the axis of the Appalachian Basin. Moreover, a faunal succession from deeper Ambocoelia dominated brachiopod association to a shallow Tropidoleptus dominated association is reflected by isotopic shifts of 1.0-1.5°/oo. Although, other studies have emphasized the significance of ±2°/oo shifts in brachiopod isotopic compositions, the recognition of isotopic variability in brachiopod calcite within single beds and within depositional settings such as the Appalachian Basin has important implications for the interpretation of secular isotopic trends. A significant proportion of the variation observed isotopic distribution during the Paleozoic is related to environmental conditions within the depositional setting.
Table of Contents

ABSTRACT.................................................................i
LIST OF FIGURES..........................................................ix
LIST OF TABLES.............................................................xvi
INTRODUCTION.............................................................xviii

Chapter 1. Preliminary considerations and methodology

THEORETICAL CONSIDERATIONS.................................................1
DIAGENETIC CONSIDERATIONS..................................................5
GEOCHEMISTRY OF BRACHIOPOD SHELL CALCITE............................8
BRACHIOPOD ECOLOGY..........................................................10
METHODOLOGY
  Area of study...............................................................11
  Sampling procedure.........................................................15
  Sample preparation.........................................................15
  Trace and minor element analysis.......................................16
  Carbon and oxygen isotopic analysis...................................17
  Scanning electron microscopy.............................................17
  Thin section studies.......................................................18
  Statistical analysis of chemical data...................................18

Chapter 2. Primary and diagenetic microstructures of brachiopod
  shell calcite

INTRODUCTION........................................................................20
Chapter 3. Diagenetic and paleoenvironmental investigation of brachiopod shell calcite from the Middle Devonian Hamilton Group; New York State and Ontario.

INTRODUCTION ................................................................. 41

GENERAL GEOLOGY ......................................................... 45

RESULTS ................................................................. 48

Diagenetic trends ............................................................. 50

Diagenetic waters of the Hamilton Group ........................................... 56

Selection of best preserved material .............................................. 57

BRACHIOPOD SHELL CALCITE CHEMISTRY

Generic trends ................................................................. 61

Fractionation of Mg ........................................................... 61

Fractionation of Sr ............................................................. 64

Fractionation of Na ............................................................ 66

Relationship of shell chemistry to biofacies and environmental conditions ........................................... 67

Isotopic trends ................................................................. 70

PALEOENVIRONMENTAL ANALYSIS OF THE "DEMISSA " BED ........................................... 71

Chemical trends ................................................................. 73

Isotopic trends ................................................................. 76
Chapter 4. **Diagenetic and paleoenvironmental study of brachiopod shell calcite from the Clinton Group (Middle Silurian); New York State and Ontario.**

**INTRODUCTION** .................................................................................................................. 92

**GENERAL GEOLOGY** ........................................................................................................... 93

**RESULTS AND DISCUSSION**

Chemical trends .................................................................................................................. 95

Elemental fractionation and taxonomic trends ................................................................. 98

Isotopic trends ...................................................................................................................... 98

**DIAGENETIC EVALUATION OF CLINTON GROUP BRACHIPODS**

Merritton Formation ........................................................................................................... 101

Reynales Formation ............................................................................................................ 103

Irondequoit and Rochester Shale Formation diagenetic waters ......................................... 104

**PALEOENVIRONMENTAL ANALYSIS OF THE IRONDEQUOIT FORMATION** .................. 106

**PALEOENVIRONMENTAL ANALYSIS OF THE ROCHESTER SHALE FORMATION**

Introduction ........................................................................................................................... 110
| Chapter 5. | Diagenetic and paleoenvironmental study of brachiopod calcite from the Middle and Upper Ordovician; southern Ontario and Manitoulin Island. |
| INTRODUCTION | 133 |
| GENERAL GEOLOGY | 133 |
| RESULTS |  |
| Chemical trends | 137 |
| Isotopic trends | 141 |
| Lithology and preservation potential | 141 |
| Diagenetic waters of the Middle and Upper Ordovician | 144 |
| PALEOENVIRONMENTAL ANALYSIS OF MIDDLE TO UPPER ORDOVICIAN | 149 |
| Taxonomic differences in shell calcite composition | 150 |
| Relationship of depth to Mg, Sr, and Na compositions of brachiopod calcite | 150 |
| Brachiopod calcite and low oxygen conditions | 152 |
| Depositional waters | 154 |
| Isotope trends | 154 |
| CONCLUSIONS | 156 |

Chapter 6. **Secular trends of oxygen and carbon isotopes**
### List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1.1</td>
<td>Locality map of Middle and Upper Ordovician sampling sites</td>
<td>12</td>
</tr>
<tr>
<td>Figure 1.2</td>
<td>Locality map of Middle Silurian sampling sites in Ontario and New York State</td>
<td>13</td>
</tr>
<tr>
<td>Figure 1.3</td>
<td>Locality map of Hamilton Group (Middle Devonian) sampling sites</td>
<td>14</td>
</tr>
<tr>
<td>Figure 2.1</td>
<td>Generalized cross-section of an articulate brachiopod exoskeleton</td>
<td>21</td>
</tr>
<tr>
<td>Figure 2.2</td>
<td>S.E.M. micrograph of primary and secondary calcite layers of <em>Laqueus vancouverensis</em></td>
<td>23</td>
</tr>
<tr>
<td>Figure 2.3</td>
<td>S.E.M. micrograph cross section of foliated secondary shell layer around punctae</td>
<td>23</td>
</tr>
<tr>
<td>Figure 2.4</td>
<td>S.E.M. micrograph of the imbricate internal surface of <em>L. vancouverensis</em></td>
<td>27</td>
</tr>
<tr>
<td>Figure 2.5</td>
<td>S.E.M. micrograph of regularly-spaced punctal openings on the internal surface of a <em>L. vancouverensis</em> shell</td>
<td>27</td>
</tr>
<tr>
<td>Figure 2.6</td>
<td>S.E.M. micrograph close up of fibrous secondary shell layer</td>
<td>28</td>
</tr>
<tr>
<td>Figure 2.7</td>
<td>S.E.M. micrograph of the secondary layer of <em>Mediospirifer audacula</em> (#400; Hamilton Group)</td>
<td>28</td>
</tr>
<tr>
<td>Figure 2.8</td>
<td>S.E.M. micrograph of the secondary layer of <em>Mucrospirifer mucronatus</em> (#178; Hamilton Group)</td>
<td>30</td>
</tr>
<tr>
<td>Figure 2.9</td>
<td>S.E.M. micrograph of the secondary layer of <em>Eospirifer radiatus</em> (#2301; Lewiston Member, Middle Silurian, New York State)</td>
<td>30</td>
</tr>
<tr>
<td>Figure 2.10</td>
<td>S.E.M. micrograph of the imbricated internal valve surface of <em>Athyris spiriferoides</em> (#403, Wanakah Shale, New York State)</td>
<td>31</td>
</tr>
<tr>
<td>Figure 2.11</td>
<td>S.E.M. micrograph of the internal surface of an etched Athyris</td>
<td>31</td>
</tr>
</tbody>
</table>
Figure 2.12  S.E.M. micrograph of primary, secondary and tertiary layer shell calcite layers of *Mediospirifer audacula* (#71, Wanakah Shale)..................32

Figure 2.13  S.E.M. micrograph cross section of prismatic trabecular calcite morphology in *Whitfieldella nitida* valves (#2108, Irondequoit Formation)...............................................................32

Figure 2.14  S.E.M. micrograph of the internal surface of an etched *Tropidoleptus carinatus* (#409, Wanakah Shale, New York State)..................33

Figure 2.15  S.E.M. micrograph cross section of the secondary shell layer of *Tropidoleptus* (#409, Wanakah Shale, New York State)..................33

Figure 2.16  S.E.M. micrograph of the internal valve surface of *Rhipidomella vanuxemi* (#412, Wanakah Shale, New York State)..................35

Figure 2.17  S.E.M. micrograph of micropores on the internal valve surface of *Eospirifer radiatus* (#2195, Lewiston Member, New York)..................35

Figure 2.18  S.E.M. micrograph of the secondary fibrous shell layer of altered *Athyris spiriferoides* (#5, Wanakah Shale, Middle Devonian, New York)...................................................................................36

Figure 2.19  S.E.M. micrograph of the secondary fibrous shell layer of altered *Athyris spiriferoides* (#61, Wanakah Shale, Middle Devonian, New York)...................................................................................36

Figure 2.20  S.E.M. micrograph of recrystallized *Pentameroides* sp. from the Merriton Formation (#2007, Middle Silurian, Ontario).........................................................37

Figure 2.21  S.E.M. micrograph of laminar secondary shell structure of *Rafinesquina deltoidea* (#794, Verulam Formation, Ontario).........................................................37

Figure 2.22  S.E.M. micrograph of secondary shell structure of orthid *Dalmanella rogata* (#754, Verulam Formation, Ontario).........................................................39

Figure 2.23  S.E.M. micrograph of punctate brachiopod *Tropidoleptus* showing punctal filling cements (#409, Wanakah Shale, New York State)..................39
Figure 3.1  Generalized paleoecological model relating Hamilton Group biofacies to inferred gradients of depth-related parameters, turbidity and/or sedimentation rates and oxic conditions..........................43

Figure 3.2  Diagrammatic cross-section of the Upper Hamilton Group (Middle Devonian) across New York State...........................................................................44

Figure 3.3  Paleogeographic reconstruction of the Appalachian Basin during deposition of the Middle Devonian Hamilton Group.........................................................46

Figure 3.4  Generalized stratigraphic section of the Ludlowville and Moscow Formations of the Hamilton Group...........................................................................47

Figure 3.5  Scatter plot of Fe vs Mn for all Devonian brachiopods..........................................................52

Figure 3.6  Scatter diagram of Na vs Mg for brachiopods and matrix of the Hamilton Group (Middle Devonian).................................................................53

Figure 3.7  Scatter plot of Fe vs Mn for *Tropidoleptus* and *Rhipidomella* brachiopods from the Hamilton Group (Middle Devonian)........................................55

Figure 3.8  Scatter plot of Na vs Mg for *Tropidoleptus* and *Rhipidomella* brachiopods from the Hamilton Group........................................................................55

Figure 3.9  The mean and standard deviations of unaltered elemental chemistries of three Hamilton Group brachiopod species........................................63

Figure 3.10  Routes of elemental transport from the external environment toward the site of carbonate secretion.................................................................65

Figure 3.11  Mean and standard deviations of unaltered brachiopod elemental chemistries related to brachiopod biofacies and depth.................................68

Figure 3.12  Mean and standard deviation of unaltered chemistries; *Athyris* and *Mediospirifer* from the *Demissa* Bed across the Hamilton Shelf.................74

Figure 3.13  Isotopic compositions of *Athyris* and *Mediospirifer* brachiopods from the Hamilton Group.................................................................................77

Figure 3.14  Scatter plot of Fe vs Mn for Lower Windom brachiopods
from western New York State.................................................................80

Figure 3.15 Scatter diagram of Fe vs Mn contents of upper and lower Kashong Shale Member brachiopods (upper Hamilton Group).................................83

Figure 3.16 Scatter plot of Fe vs Mn for Mucrospirifer brachiopods from the Arkona, Hungry Hollow and Widder Formations (Middle Devonian)........85

Figure 3.17 Scatter plot of Na vs Mg for Mucrospirifer brachiopods from the Arkona, Hungry Hollow and Widder Formations (Middle Devonian).......87

Figure 4.1 Middle Silurian stratigraphy of southern Ontario and New York State.....94

Figure 4.2 Scatter plot of Fe vs Mn for all species from the Middle Silurian Clinton Group (Wenlockian)........................................................................97

Figure 4.3 Diagenetic trend of isotopic compositions of Middle Silurian Clinton Group brachiopods........................................................................100

Figure 4.4 Isotopic compositions of Eospirifer from Irondequoit, Rochester Reynales and Merritton Formations of the Middle Silurian Clinton Group........................................................................................................102

Figure 4.5 Scatter plot of Na vs Mg for all species from the Middle Silurian Clinton Group (Wenlockian).................................................................105

Figure 4.6 Rochester Shale/Irondequoit Formation brachiopod associations with reference to inferred gradients of depth-related parameters and turbidity and/or sedimentation rates.........................................................108

Figure 4.7 Diagenetic trend of Irondequoit Formation brachiopods (Middle Silurian)....................................................................................................109

Figure 4.8 Scatter plot of Na vs Mg contents of Irondequoit brachiopods illustrates two diagenetic trends.................................................................109

Figure 4.9 Rochester Shale stratigraphic section at Niagara Gorge.....................111

Figure 4.10 Facies map of the Rochester Shale across southern Ontario and western New York State.................................................................113
Figure 4.11 Scatter plot of Fe vs Mn for all species from the Lewiston Member of the Rochester Shale Formation

Figure 4.12 Na vs Mg scatter plot of Lewiston Member brachiopods

Figure 4.13 Plot of mean Sr, Mn and Fe contents of *Atrypa reticularis* and *Eospirifer radiatus* against height within the Lewiston Member section

Figure 4.14 Plot of mean Mg and Na contents of pristine *Atrypa reticularis* and *Eospirifer radiatus* height within the Lewiston Member section

Figure 4.15 Plot of mean Mg and Na contents of pristine *Atrypa reticularis* from the Lewiston Member subunits A and B

Figure 4.16 Mean isotopic composition (in per mil; PDB) of pristine *Eospirifer radiatus* from the Irondequoit Formation and Lewiston Member of western New York State (Clinton Group Middle Silurian)

Figure 4.17 Plot of oxygen isotopes versus Mg contents within pristine *Eospirifer radiatus* from the Irondequoit Formation and Lewiston Member (Clinton Group, Middle Silurian)

Figure 4.18 Burleigh Hill Member stratigraphic section at the type locality in St. Catharines, Ontario

Figure 4.19 Scatter plot of Fe vs Mn for all species from the Burleigh Hill Member (Clinton Group)

Figure 4.20 Scatter plot of Sr vs Mg for all brachiopod species of the Burleigh Hill Member (Clinton Group)

Figure 5.1 Generalized stratigraphic section of southern central Ontario

Figure 5.2 Middle and Upper Ordovician Stratigraphy of Manitoulin Island

Figure 5.3 Scatter plot of Fe vs Mn for all brachiopods from the Middle and Upper Ordovician of south Ontario and Manitoulin Island

Figure 5.4 Diagenetic trend of oxygen isotopic composition for Middle and
Upper Ordovician *Dalmanella rogata* and *Rafinesquina deltoidea* brachiopods of southern Ontario.......................................................... 142

Figure 5.5 Diagenetic trend of oxygen isotopic composition for Middle and Upper Ordovician *Dalmanella rogata* and *Rafinesquina deltoidea* brachiopods of southern Ontario and Manitoulin Island.......................................................... 142

Figure 5.6 Scatter plot of Sr vs Mn for *Dalmanella rogata*.......................................................... 143

Figure 5.7 Scatter plot of Sr vs Mn for *Sowerybella* sp.......................................................... 145

Figure 5.8 Scatter diagram of Na vs Mg for brachiopods from Manitoulin Island and from southern Ontario.......................................................... 147

Figure 5.9 Mean and standard deviation of unaltered chemistries of *Dalmanella rogata*, *Rafinesquina deltoidea* and *Sowerybella* sp. of the Verulam Formation.......................................................... 152

Figure 5.10 Scatter plot of Fe vs Mn for *Dalmanella rogata*.......................................................... 155

Figure 6.1 Secular trend of carbon isotopes during the Paleozoic.................................................. 161

Figure 6.2 Secular trend of oxygen isotopes during the Paleozoic.................................................. 161

Figure A-1 Stratigraphic section of Hamilton Group (Middle Devonian) units at Hungry Hollow Quarry.......................................................... 196

Figure A-2 Stratigraphic section of Wanakah and Windom Shale Members at Eighteen Mile Creek.......................................................... 197

Figure A-3 Stratigraphic section of Hamilton Group strata exposed at Penn Dixie Quarry.......................................................... 200

Figure A-4 Stratigraphic section of Hamilton Group strata exposed at Cazenovia Creek.......................................................... 202

Figure A-5 Section of Hamilton Group strata exposed at Murder Creek........................................... 205

Figure A-6 Section of Hamilton Group strata exposed at Jaycox Creek........................................... 208

Figure A-7 Stratigraphic section of Verulam Formation from the Bolsover roadcut.................................................. 219
Figure A-8  Stratigraphic section of Verulam Formation at Kirkfield Quarry...............220
Figure A-9  Stratigraphic section of Verulam Formation at Lakefield Quarry near
Peterborough........................................................................................................224
Figure A-10  Stratigraphic section of Verulam Formation outcropping along roadcuts
at the intersection of Highways 33 and 401..............................................................225
List of Tables

Table 3.1 Middle Devonian chemical data of all brachiopods and pristine brachiopods ................................................................. 49

Table 3.2 Comparison of microstructural preservation and chemical contents for selected brachiopods from the Middle Devonian Hamilton Group of western New York State and southern Ontario ........................................ 52

Table 3.3 T-test: Upper Hamilton Group unaltered brachiopods ............................................. 62

Table 3.4 T-test: Demissa bed (upper Wanakah Shale) unaltered brachiopod chemical data ................................................................. 62

Table 3.5 T-test: Demissa bed (Wanakah Shale) unaltered brachiopods ................................. 75

Table 4.1 Summary of chemical data for all Clinton Group brachiopods and for pristine specimens ................................................................. 96

Table 4.2 Comparison of microstructural preservation and chemistry for selected brachiopods, representing different species and lithologies ................................................................. 96

Table 4.3a Summary of pristine brachiopod calcites from the Rochester Shale and Irondequoit Formations ................................................................. 99

Table 4.3b Unpaired T-test: pristine brachiopod chemistry (Clinton Group) ................................................................. 99

Table 4.4 Unaltered brachiopod chemistries from locality 36 (Burleigh Hill Member) ......................... 128

Table 4.4 Unaltered brachiopod chemistries from locality 34 (Burleigh Hill Member) ......................... 128

Table 5.1 Geochemical data of Middle and Upper Ordovician brachiopods from Ontario and Manitoulin Island ................................................................. 138

Table 5.2 Comparison of microstructural preservation and chemistry for selected brachiopods, representing different species and lithologies ................................................................. 139

Table 5.3 T-test: Verulam Formation unaltered brachiopods ................................................................. 151

xvi
| Table A-1 | Factor analysis of Devonian brachiopod elemental chemistries | 249 |
| Table A-2 | Factor analysis of *Athyris spiriferoides* | 249 |
| Table A-3 | Factor analysis of *Mucrospirifer mucronatus* | 250 |
| Table A-4 | Factor analysis of *Mediospirifer audacula* | 250 |
| Table A-5 | Factor analysis of *Tropidoleptus carinatus* | 251 |
| Table A-6 | Factor analysis of *Rhipidomella vanuxemi* | 251 |
| Table A-7 | Factor analysis of Middle Devonian brachiopod elemental chemistries | 252 |
| Table A-8 | Factor analysis of Silurian brachiopod elemental chemistries | 252 |
| Table A-9 | Factor analysis of *Eospirifer radiatus* elemental chemistries | 253 |
| Table A-10 | Factor analysis of *Whitfieldella nitida* elemental chemistries | 253 |
| Table A-11 | Factor analysis of *Atrypa reticularis* elemental chemistries | 254 |
| Table A-12 | Factor analysis of Ordovician brachiopod elemental chemistries | 254 |
| Table A-13 | Factor analysis of *Dalmanella rogata* elemental chemistries | 255 |
| Table A-14 | Factor analysis of *Rafinesquina deltoidea* elemental chemistries | 255 |
| Table A-15 | Factor analysis of *Sowerybella* sp. elemental chemistries | 256 |
GENERAL INTRODUCTION

Articulate brachiopods were a common faunal element of Paleozoic shelf communities. Their abundance, and the fact that they secrete a low-Mg calcite shell that is quite resistant to diagenetic alteration makes them suitable for paleochemical investigations (Brand and Veizer, 1980; Popp et al., 1986a; Brand, 1982, 1983, 1989a). Brachiopods are generally assumed to incorporate stable isotopes in equilibrium with their external environment and shell calcite can provide a chemical record of changes in ocean and atmosphere chemistry during the Phanerozoic. As such, brachiopods have been used to investigate isotopic shifts at stratigraphic boundaries (e.g., Permo-Trias, Gruszczynski et al., 1989), extinction events (e.g., Frasnian-Famennian; Brand, 1989c) and the secular changes in isotopic compositions of Paleozoic oceans (Veizer 1985; Popp et al., 1986; Veizer et al., 1986; Brand, 1989a). For example, a post Devonian-Carboniferous change in brachiopod calcite δ¹⁸O compositions has been attributed to either global cooling (Kump, 1989a) or to a change in the isotopic composition of oceans (Veizer et al., 1986). A further use of brachiopod calcite may be in the paleoenvironmental reconstruction of depositional settings and conditions (e.g., Adlis, 1988).

Although brachiopods are used in isotopic investigation, there is at present, little empirical data on their chemical composition. The composition of brachiopod calcite has been assumed to be singularly uniform for the purpose of selecting chemically pristine specimens for use in isotopic interpretations (Veizer et al., 1986). However, fractionation of Mg and Na contents into shell calcite has been reported previously (Popp et al., 1986; Brand, 1989a) which indicates that the chemistry of their shell calcite is variable and needs further scrutiny. As yet there is no comparative study of the chemistry of co-occurring
brachiopod species within the context of strict paleoecological and stratigraphic criteria. The spatial distribution of brachiopods upon a shelf is in part controlled by the environmental conditions (e.g., depth, turbidity, nutrient supply; Fursich and Hurst, 1974), and if a relationship between brachiopod chemistry and environmental conditions can be determined, brachiopod calcite may be useful in paleoenvironmental reconstructions and constraining isotopic interpretations. It is therefore the purpose of this thesis to investigation the trace element and isotopic geochemistry of ancient brachiopods in the context of their paleoecologic and stratigraphic settings.

The objectives of this study are as follows;

1. Assess the microstructural preservation of articulate brachiopod shell calcites from the Middle Devonian (Hamilton Group), Middle Silurian (Clinton Group), and Middle and Upper Ordovician of Ontario and New York State and illustrate the textural changes in shell calcite accompanying post-depositional alteration.

2. Evaluate the chemical preservation of shell calcites and determine the degree and direction of alteration of brachiopod calcite.

3. Investigate the elemental and isotopic trends in co-occurring brachiopod species, in order to illustrate: i) elemental fractionation; ii) taxonomic differentiation of shell calcite compositions and; iii) the relationship of shell calcite chemistry to environmental conditions such as depth and low oxygen conditions.

4. Evaluate the isotopic trends in brachiopod shell calcite within: i) a single shell bed that deepens across a basin and; ii) a transgressive-regressive cycle.
5. Evaluate the isotopic compositions of pristine brachiopod shell calcites in context with secular variations of mean oceanic d13C and d18O compositions during the Paleozoic.
CHAPTER 1

Preliminary considerations and methodology
THEORETICAL CONSIDERATIONS

The precipitation of calcium carbonate can be described by six simple chemical equilibria (Bathurst, 1975). Overall the reaction can be written:

\[
\text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \leftrightarrow \text{Ca(HCO}_3\text{)}_2
\]  
(1)

Biogenic and inorganic carbonates contain other cations and anions beside Ca and the incorporation of minor and trace elements into calcium carbonate minerals can occur through five recognized processes (McIntire, 1963; Zemann, 1969; Veizer 1983a, b). These are:

1. Diadochic substitution of Ca\(^{2+}\) in the CaCO\(_3\) lattice by minor (Mg\(^{2+}\), Sr\(^{2+}\)) and trace elements (e.g., Fe\(^{2+}\), Mn\(^{2+}\), Zn\(^{2+}\), Cu\(^{2+}\)).
2. Incorporation interstitially between lattice planes;
3. Occupation of vacant lattice positions due to crystal structural defects (e.g., point, line defects);
4. Adsorption to lattice surfaces due to remanent ionic charges;
5. Presence of non-carbonate components within silicate impurities and fluid inclusions;

The theory of diadochic substitution for Ca\(^{2+}\) (factor 1) is reasonably well understood and is a general basis for fossil biogeochemical studies (Brand and Veizer, 1980; Al-aasm and Veizer, 1982; 1986a, b; Veizer et al., 1986). The influence of other factors on chemical distribution is less certain (Veizer, 1983 a, b). Divalent metallic ions, such as Cd\(^{2+}\), Cu\(^{2+}\), Mn\(^{2+}\) and Co\(^{2+}\), can be actively adsorbed onto the calcite lattice (Zachara et al., 1988) although this and the
influence of processes 2 to 4 are suggested to be random and negligible when compared to factor 1 (Veizer, 1983a). The fifth process, elemental leaching of Fe, Mn and Al from non-carbonate fractions, can be significant (Brand and Veizer, 1980; Boyle, 1981), but its contribution to the overall chemical composition can be minimized by refinements of the geochemical analysis, such as removal of all adhering matrix and the reduction of digestion times (Brand and Veizer, 1980; Veizer 1983a, 1983b; Morrison and Brand, 1986). Similarly, the presence of minute organic-rich fluid inclusions (1000Å or less in size) in biogenic carbonates may contribute to the analysis but these constitute less than 1% by volume (Bruni and Wenk, 1985; Gaffey, 1988). The significance of these chemical biases remain difficult to determine and quantify.

Carbonate mineralogy and crystal structure will partly determine the concentration of lattice bound minor and trace elements (Pingitore, 1976, 1978; Brand and Veizer, 1980; Veizer, 1983a, b; Morrison and Brand, 1986). Orthorhombic aragonite selectively incorporates larger cations (Sr$^{2+}$, Ba$^{2+}$, and Pb$^{2+}$) into lattice sites (Okumura and Kitano, 1986) whereas rhombohedral calcite favours smaller cations (Mg$^{2+}$, Fe$^{2+}$, Mn$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, and Cd$^{2+}$; Reeder, 1983).

The incorporation of minor and trace elements into the CaCO$_3$ lattice is governed by a distribution coefficient (D) between solution and the particular mineralogical phase. It is defined as (McIntire, 1963; Kinsman, 1969);

$$\frac{^{(m)}Me}{^{(m)}Ca} \text{ (s)} = D \frac{^{(m)}Me}{^{(m)}Ca} \text{ (aq)}$$

(2)

where ($^m$) indicates molar concentration, Me is trace/minor element concentration, D is the distribution coefficient and (s) and (aq) represent solid and aqueous phases of calcium carbonate, respectively. This relationship is
only valid when the system is at equilibrium (constant temperature and pressure) and there are no concentration gradients between the phases (Veizer, 1983a, b). If a gradient exists, a heterogenous distribution law applies (Gordon et al., 1959; Morrison and Brand, 1986),

\[ \log \left( \frac{m_{Me_i}}{m_{Me_f}} \right) = D \log \left( \frac{m_{Ca_i}}{m_{Ca_f}} \right) \]  

(3)

where \( i \) and \( f \) indicate initial and final concentrations of trace and minor elements and Ca in solution.

The trace and minor element distribution in carbonate, relative to the major elements Ca and Mg, will be governed by conditions of the distribution coefficient \( D \). When \( D \) is equal to 1, the carbonate will incorporate Me in equilibrium with the aqueous phase. If \( D \) is greater than 1, the solid phase will contain higher Me concentrations than the aqueous phase and when \( D \) is less than 1, the carbonate precipitate will contain lower Me concentrations than the aqueous phase. Experimentally derived distribution coefficients for most elements in aragonite and calcite are listed in Veizer (Table ?, 1983a). Equilibrium conditions (\( D = 1 \)) occur only when the amount of precipitate is minor compared to the volume of fluid (Veizer, 1983a). Partitioning of minor and trace elements into carbonates is dependant on certain physico-chemical conditions related to temperature (Bordine et al., 1965; Kinsman, 1969), coupled substitution (Mucci and Morse, 1983; Busenberg and Plummer, 1985), rate of precipitation (Lorens, 1981), and the nature of the overall reaction such as replacement, seeded growth or nucleation and growth (Reeder and Grams, 1987). For example, the partitioning of elements is less pronounced with increasing precipitation rates of carbonate (Lorens, 1981). The incorporation of Sr into non-lattice sites affects calculations of \( D_{sr} \) calcite at low Sr
concentrations (Pingitore and Eastman, 1985), and differential partitioning was observed in different crystal growth sectors of calcite cements (Reeder and Grams, 1987). Skeletal carbonates are assumed to incorporate Me in equilibrium with ambient conditions, however, biological fractionation occurs when the organism physiologically controls partitioning of elements into biogenic calcite. In molluscs and coral ectoderm, manipulation of extrapallial fluids by ionic regulation will be reflected in positively or negatively fractionated elemental contents of their carbonate.

The incorporation of oxygen and carbon isotopes into carbonate minerals is similarly governed by a fractionation factor (α);

\[
R_{(s.)} = \alpha_{(s.)-(aq.)} R_{(aq.)}
\]  

(4)

where R is the isotopic ratio \((^{18}\text{O}/^{16}\text{O}, ^{13}\text{C}/^{12}\text{C})\) in solid and liquid phases. Equilibrium isotopic fractionation in natural systems is significantly affected by kinetic factors, precipitation rates and temperature (Faure, 1986). Tarutani et al. (1969) have observed an \(^{18}\text{O}\) enrichment of about 0.6\(^{\circ}\) in aragonite compared to calcite during inorganic precipitation at 25\(^{\circ}\)C. Similarly, changes in salinity may influence incorporation of \(^{13}\text{C}\) and \(^{18}\text{O}\) into calcium carbonate and positive correlations of skeletal \(^{\delta^{13}}\text{C}\) and \(^{\delta^{18}}\text{O}\) with salinity (Mook, 1971). The fractionation factor for carbon isotopes is only slightly temperature sensitive (Veizer, 1983b). The fractionation factor of oxygen is temperature dependant (Faure, 1986) and paleotemperature determinations for calcite were derived by Urey et al. (1951). This equation is;

\[
T^\circ \ (\text{C}) = 16.9 - 4.14 \ (\delta_c - \delta_w) + 0.13 \ (\delta_c - \delta_w)^2
\]
where $\delta_c = \delta^{18}O$ value of CO$_2$ generated from carbonate samples at 25°C (relative to PDB) and $\delta_w = \delta^{18}O$ value of CO$_2$ in equilibrium with ambient seawater at 25°C (relative to SMOW).

Many organisms, such as bryozoa and gastropods, apparently secrete calcium carbonate in equilibrium with seawater conditions (Lowenstam, 1961; Veizer, 1983a; Morrison and Brand, 1986). However, the calcification process in some biogenic carbonates, such as corals and foraminifera, produces non-equilibrium isotopic fractionation (McConnaughey, 1989a). Isotopic deviation from equilibrium may be the result of 'metabolic' or 'kinetic' effects. There may be changes in the $\delta^{13}C$ of dissolved inorganic carbon (DIC) near calcification nucleation sites that result from photosynthetic or respiratory processes (Swart, 1983); respiration may decrease skeletal $\delta^{13}C$ by selective additions of metabolic $^{12}C$. Kinetic effects result in discrimination against heavy isotopes during the hydration and hydroxylation of CO$_2$ (McConnaughey, 1989a; 1989b). Strong kinetic disequilibrium occurs with rapid skeletal growth (Land et al., 1975) and there appears to be a convergence towards isotopic equilibrium with slower calcification rates (McConnaughey, 1989a; 1989b).

**DIAGENETIC CONSIDERATIONS**

Metastable aragonites, high-Mg and intermediate-Mg calcites on exposure to diagenetic waters, dissolve partially or fully, in response to chemical gradients (Veizer, 1983a, b) and surface reactivity (Walter, 1985). Trace and minor elements are repartitioned into a secondary, diagenetic low-Mg calcite product (dLMC) in single or multiple dissolution-reprecipitation events (Bathurst, 1975; Brand and Veizer, 1980). Low-Mg calcites are relatively resistant to alteration in the presence of diagenetic fluids (Veizer, 1983a, b) but
even this mineralogical phase will re-equilibrate with diagenetic waters (Al-
Aasm and Veizer, 1982; Veizer et al., 1986; Popp et al., 1986a; Brand, 1988).

The rate and magnitude of alteration is influenced by a number of factors;

1. The partition coefficient (k). This is influenced by rates of precipitation,
kinetic, temperature effects and a mineralogical control (i.e. calcite
rhombohedra will more readily accept small cations, Mn$^{2+}$, Fe$^{2+}$, etc).
Depending on the deviation of a particular partition coefficient from unity,
the diagenetic product will be elementally or isotopically enriched or
depleted in the direction of equilibrium with diagenetic waters (Brand and
Veizer, 1980; Veizer, 1983a).

2. The chemistry of the diagenetic waters. Alteration below the permanent
water table occurs with waters of meteoric, mixed meteoric or marine
phreatic origin (Veizer, 1983a; James and Choquette, 1984). Chemistries
of any diagenetic product will reflect the complexities and compositional
differences of single or mixed sources (e.g., ionic strengths, redox
conditions; Veizer, 1983a). Isotopic repartitioning depends on
temperature and salinity, altitude, latitude, seasonal changes,
superimposed on pertinent global seawater isotopic secular variations

3. Rock-water ratios. Dissolution-reprecipitation across a messenger film
(Pingitore, 1976; 1978; Brand and Veizer, 1980) is partly a function of
host lithology and rock-water volume. Diffusion of ions is controlled by: i)
diffusion coefficients; ii) pore geometry and pathway between aquifer and
reaction zone; and iii) the concentration gradient between aquifer and
reaction zone (Pingitore, 1982). Furthermore, Pingitore (1982) correlates
an increase in dissolution rates to lithofacies in the following order of
mudstone < wackestones < grainstones. Variance of rock-water volumes will result in a spectrum of diagenetic products reflecting grain reaction-controlled dissolution-reprecipitation to fluid-controlled dissolution-reprecipitation (Brand and Veizer, 1980; Pingitore, 1978; 1982; Drever, 1982; Veizer, 1983a).

Diagnostic elements such as Sr$^{2+}$, Mn$^{2+}$, Fe$^{2+}$, Na$^{2+}$, and Mg$^{2+}$ are used to establish the degree and direction of diagenetic alteration within fossil allochems (Brand and Veizer, 1980; Brand 1989a, b). Textural indicators, such as microstructural preservation, may give support to these chemical trends. The bound and free water contents of skeletal carbonates is a potential indicator of diagenetic alteration especially in aragonite and high-Mg calcite, although even low-Mg calcite may lose free H$_2$O from fluid inclusions and possibly bound H$_2$O (Gaffey, 1988). Re-equilibration of biogenic carbonates with diagenetic waters may be reflected isotopically. Meteorically derived waters are generally enriched in light isotopes (Siegenthaler, 1979; Anderson and Arthur, 1983; Faure, 1986) and a diagenetic low-Mg calcite product will generally become depleted in $\delta^{13}$C and $\delta^{18}$O. Alteration in the presence of marine- or mixed-waters will reflect higher oceanic $\delta^{13}$C and $\delta^{18}$O values (Baker et al., 1982; Elderfield et al., 1982). Once a determination of the degree of post-depositional alteration of fossils is made, chemical distribution can be used to decipher paleoenvironments and possible changes in paleoocean chemistry (Veizer et al., 1986; Popp et al., 1986b; Morrison and Brand, 1988; Brand, 1988).
GEOCHEMISTRY OF BRACHIOPOD SHELL CALCITE

Calcite is subdivided into: low-Mg calcite (LMC) with approximately 0-5 mol% MgCO₃; intermediate-Mg calcite (IMC) with 5-8 mol% MgCO₃; and high-Mg calcite (HMC) with 8-28 mol% MgCO₃ (Milliman, 1974, p. ?). All articulate brachiopods secrete low-Mg calcite shells (Chave, 1954), with less than 5 mol% MgCO₃ and usually 3000-5000 ppm Mg (Morrison and Brand, 1986). Two exceptions to this are mentioned in the literature (Brand and Veizer, 1980; Morrison and Brand, 1987), but they are inarticulate species. The recent brachiopod Crania and the order Trimerellidae are possible exceptions to the above rule (Brand and Veizer, 1980; Morrison and Brand, 1986). The fossil Trimerellidae, may have secreted aragonite (Jaanusson, 1966), and Recent Crania are unusual inarticulate brachiopods (Laverack, 1987; Stricker and Reed, 1985; Gorjansky and Popov, 1986).

The application of partitioning theory to ancient biogenic carbonates gives indications of original water chemistries or diagenetic regimes (Brand, 1981a, 1983, 1987a, b). However, equilibrium physicochemical conditions for skeletal carbonates are complicated by possible physiological controls exerted by carbonate precipitating organisms. Biological fractionation appears to be ubiquitous to most taxa and is well documented for bivalves (Rosenberg, 1980), gastropods (Milliman, 1974; Bathurst, 1975), ammonites (Buchardt and Weiner, 1981) and other taxa (see Morrison and Brand 1986; Brand and Morrison, 1987a). Brachiopods fractionate Mg and Na with respect to inorganic low-Mg calcite precipitated in equilibrium with ambient conditions, discriminating against Mg and preferentially incorporating Na into shell calcite (Brand and Veizer, 1980; Brand, 1988). Sodium contents in brachiopod calcite are 5-10
times greater than in inorganic low-Mg calcite (White, 1977; Brand and Morrison, 1987a).

There may be other factors involved in the partitioning of elements into brachiopod calcite. Lowenstam (1961) suggested that Sr contents in brachiopod calcite reflect changes in salinity. In a subsequent paper, he proposed thatRecent and Pliocene to Mississippian brachiopods discriminate physiologically against Sr (Lowenstam, 1963). In addition, he also suggested that Mg contents increased proportionately with respect to salinity. Morrison and Brand (1984) and Popp et al., (1986) have observed potential taxonomic differences in Sr between spirifers and productids, and data from the latter study (Popp et al, 1986a, b) suggests that there may also be a taxonomic control of Mg. The fractionation of Mg contents in shell calcite may also be related to shell mineral morphology. In a few Recent (Stricker and Reed, 1985; Rowell and Grant, 1987; Hiller, 1988) and fossil brachiopods, primary prismatic layer calcite is enriched in Mg relative to secondary layer fibrous calcite (Foster, 1974). Differential pH, T° and/or metabolic activity at the mantle generative zone may be responsible for different secretory regimes, growth rates and differential partitioning between shell layers.

Isotopic disequilibria ("vital effects") are common in foraminifera (Grossman, 1984; 1987; Grossman et al., 1986) and corals (Land et al., 1975; Gonzalez and Lohmann, 1985; McConnaughey, 1989a; 1989b) but, empirical data concerning brachiopods is limited. A study on three specimens of *Argyrotheca bermudana* suggest that they discriminate against the incorporation of $^{13}$C by 4-5°/oo (Wefer, 1985) whereas extant brachiopods are observed to incorporate $^{18}$O in equilibrium with ambient conditions (Lowenstam, 1961; Wefer, 1985). The incorporation of oxygen isotopes is temperature dependant (Lowenstam, 1961) and has been used as a basis for
paleotemperature determinations and evaluation of secular trends of $\delta^{18}$O reservoirs.

**BRACHIOPOD ECOLOGY**

Ancient brachiopods were lophophorate suspension feeders (Rudwick, 1970; Tasch, 1973) and proliferated in a great variety of substrate and habitat settings on Paleozoic shelves. Areal and spatial distribution are related to physical and biological parameters of their environment, such as salinity, temperature, substrate, agitation, turbidity, fugacity of epiplanktic reproduction. Depth related brachiopod communities are recognized from the Ordovician (e.g., Lockley, 1983), Silurian (e.g., Zeigler, 1965; Cocks, 1967; Hancock et al., 1974), Devonian (e.g. Brett et al., 1986a; Miller, 1985). Fursich and Hurst (1974) suggest that food supply, lophophore surface area and morphological adaptations are factors controlling Silurian brachiopod community distribution. Brachiopods with thick shells and large pedicle openings may prefer more turbulent settings (e.g., *Pentamerus*). In contrast, brachiopods with either a) a fairly large, median sulcus; b) alae; or c) thin, smooth shells prefer quiet water environments. Since brachiopods are high level suspension feeders (Walker and Bambach, 1974), the direction of inhalent and exhalent currents (Jones, 1982) and the orientation and hydrodynamic stability of modern and ancient brachiopods may have determined substrate preferences (Alexander, 1975; LaBarbera, 1977; 1978, 1981a; Alexander, 1984, 1986). Modern species appear to tolerate a wide range of mud, sand or semi-cryptic substrates and physical conditions (Richardson, 1981a, b; Campbell and Fleming, 1981; Chapman and Richardson, 1981; Richardson and Mineur, 1981; Aldridge, 1981, Stewart, 1981; Witman and Cooper, 1983; Foster, 1989), which may be
partially related to pedicle structure (Richardson, 1981a). Articulate brachiopods have often been assumed as stenohaline (Rudwick, 1970; Tasch, 1973). However, Fursich and Hurst (1980) demonstrated that brachiopods as a taxon were able to tolerate both hypersaline and brackish conditions. Paleoecological study of brachiopod communities provides information about the physical and chemical conditions of their environment. Complementary information about their chemical environment is potentially discernible from brachiopod shell calcite.

**METHODOLOGY**

**Area of study**

A succession of Paleozoic limestones and shales, outcropping in Ontario and New York State, were sampled for this study. Middle Ordovician brachiopods were collected from Trenton Group carbonates of southern Ontario and Manitoulin Island (Fig. 1.1), whereas Upper Ordovician Whitby and Georgian Bay Formations were sampled from Manitoulin Island and along the shore of Georgian Bay (Fig. 1.1). Clinton Group (Middle Silurian) specimens were collected from the Merritton, Reynales, Irondequoit and Rochester Shale Formations, which outcrop along the Niagara Escarpment in Ontario and western New York State (Fig. 1.2). Brachiopods of Middle Devonian age were collected from shales of the Ludlowville and Moscow Formations (Hamilton Group, Givetian) exposed in western New York State. Additional material was obtained from the Arkona, Hungry Hollow and Widder Formations (Hamilton Group) in Ontario (Fig. 1.3).
Figure 1.2. Locality map of Middle Silurian sampling sites in Ontario and New York State. Localities are; 26. Stoney Creek; 27. Dewitt Road; 28. Vinemount; 29. Wolverton Road; 30. Beamers Falls; 31. 15 Mile Creek; 32. Rockway Falls; 33. Decew Falls; 34. Brock-Decew; 35. Highway 406; 36. Burleigh Hill; 37. Lock 5 Thorold; 38. Old Welland Canal; 39. Niagara Falls Gorge (Ontario); 40. Niagara Falls Gorge (Artpark); 41. Niagara Falls Gorge (Robert Moses Hydroelectric); 42. Bree Road; 43. Lockport; 44. Brewer Street Rochester; 45. Hydro Road Rochester; 46. Sodus Creek. Complete description of each section and sampling horizons, lithology and brachiopods is listed in Appendix I.
Sampling Procedure

Specific stratigraphic horizons and sampling localities were identified from a variety of sources (Liberty, 1969; Liberty and Bolton, 1971; Liberty, 1975; Barnes et al., 1978; Telford, 1978; Baird and Brett, 1981; Telford et al., 1981; Brett and Cottrell, 1982; Brett, 1983a, b; Grasso, 1983; Brett and Brookfield, 1984; Speyer and Brett, 1985, 1986; Grasso et al., 1986; Miller, 1986; Wygant, 1986; Brett et al., 1986a, b; Landing and Brett, 1987; Brookfield and Brett, 1988; Liebe and Grasso, 1988; Miller et al., 1988; Parsons et al., 1988). Where possible, entire bedding plane samples were collected for thin sectioning and taphonomic data, such as the state of articulation, corrasion, abrasion, and life position. Confirmation of brachiopod species identification was based on the relevant literature (e.g., Williams et al., 1965; Bolton, 1966; Shimer and Shrock, 1972; Sinclair, 1971; Cottrell and Brett, 1982; Brett, 1983a, 1989; Sinclair et al., 1984; Rowell and Grant, 1987; Brett et al., 1986a). A complete list of sampling localities, precise stratigraphic position of units and specific horizons, lithologies and dominant brachiopod species is compiled in Appendix I.

Sample Preparation

Individual brachiopods were separated from their enclosing matrix to reduce matrix and iron oxide contamination in chemical analysis. Brachiopods from shale, calcareous shales or calcisiltite lithologies were manually separated from most of the adhering matrix. In some instances, matrix was removed from brachiopod shells by cleaning in water and final rinsing with deionized water. Dental picks and a Dremel moto-tool drill were used to remove more resistant matrix from shell material and adhering epibionts were completely removed. While cleaning, brachiopods were periodically immersed in 10% (v/v) HCl solution for 30-45 seconds to aid in the cleaning process. The presence of
delicate costae in some taxa (e.g., *Mucrospirifer mucronatus*) necessitated the removal of shell material during cleaning to ensure removal of all matrix; similarly, cracks and borings (e.g., *Athyris spiriferoides*) required the drilling out of both matrix and surrounding shell material. After a final HCl rinse and followed by a deionized water rinse, the brachiopods were allowed to air dry.

Cleaning of some brachiopods from Middle Ordovician units presented additional problems. Trenton Group strophomenids, sampled from wackestones and packstones, were difficult to separate from their matrix. Exposed bachiopod shell surfaces (e.g., *Rafinesquina deltoidea*) were thoroughly cleaned with water and 10% HCl washes. Each brachiopod was washed with a final deionized water rinse and left to air dry. Shell material was then picked and drilled out of the sample and collected. Between drilling, the brachiopods were washed with HCl and deionized water and left to dry, in order to ensure that the drill had not passed through to the matrix beneath. The drill tool (steel alloy) was cleaned of powder after each sampling. These protracted cleaning processes assured that contamination by matrix and iron oxides were minimized.

**Trace and minor element analysis**

Six hundred and twenty six brachiopods, fifteen crinoids, fifteen matrix and eight cement samples were analysed for Ca, Mg, Sr, Mn, Na, Fe and Al by atomic absorption spectrophotometry (AAS) using a Varian 1475-HP 85. Shell fragments of each sample were separated for later S.E.M. study and individual brachiopod, matrix and cement samples were then carefully powdered. Approximately 0.1g of each sample was digested in 10mL of 5% (v/v) HCl for 70-80 minutes. Insoluble residue (I.R.) was determined gravimetrically by ashing the filter paper and residue at 800°C for 1 h. Mean insoluble residue
was less than 6%; data and discussions in the text are based on concentrations recalculated to 100% (insoluble residue-free; Brand and Veizer, 1980). Filtrates were analysed by AAS against reference standards and National Bureau of Standards solutions. Mean accuracy relative to N.B.S. 634 and 636 was Ca (4.0; 1.6); Mg (6.6; 3.9); Sr (2.5; 9.0); Mn (3.4; 4.3); Na (9.0; 4.2); Fe (10.5; 14.8); and Al (8.1; 14.9) percent respectively. Average precision was Ca (0.6); Mg (1.5); Sr (2.7); Mn (2.9); Na (1.8); Fe (3.0); and Al (4.8) percent. A compilation of chemical data is presented in Appendix III.

**Carbon and oxygen isotopic analysis**

Seventy-three brachiopod samples were analysed for stable isotopes. Analyses were performed on a 602 VG Micromass Spectrophotometer at the University of Waterloo. Approximately 10 mg of powdered sample was reacted with 100% phosphoric acid at 50°C for 30 min. The isotopic ratios are reported in the standard notation (δ) relative to the PDB standard in ‰. Reproducibility of results was (0.13‰) for δ¹⁸O and (0.25‰) for δ¹³C. The ¹⁷O correction was applied to the data (Craig, 1957) and isotopic data is reported relative to PDB (Epstein et al., 1953).

**Scanning Electron Microscopy**

The preservation of brachiopod skeletal calcite microstructure was investigated using an International Scientific Instruments scanning electron microscope (S.E.M.), and approximately 23% of all brachiopod specimens were analysed; representative of different species, lithologies and ages. Fractured shell material allowed cross-sectional views of primary and secondary shell calcite-layers and internal and external surfaces were examined for punctal and other biomineralization structures. Initially, fragments were cleaned in deionized
water and dried in an oven at 50°C, then after cooling in a dessicator, fragments were mounted on metal stubs and coated with gold/palladium prior to examination. Microstructures were identified and later compared to those reported by Williams (1968a, 1968b, 1971), Popp (1981), Brand (1981, 1983, 1987), Curry (1983b), Stricker and Reed (1985), Rowell and Grant (1987), and Hiller (1988).

**Thin section studies**

Petrography of each sampled horizon was studied by thin-section, which were stained in accordance with the procedures of Lindholm and Finkelman (1972). Folk's (1962) classification was used to denote the grain and matrix type and Dunham's (1962) classification is used to denote depositional texture.

**Statistical Analysis of Chemical Data**

Unpaired T-tests were used to compare the means of chemical populations. Trace element distribution in carbonates is log normally distributed (Veizer and Demovic, 1974; Brand, 1989), therefore chemical data were log transformed for factor analytic calculations. The recognition of chemical alteration in biogenic carbonates has been successfully confirmed by factor analysis of geochemical data (e.g., Brand and Veizer, 1980; Al-Aasm and Veizer, 1982; Waasenaar, 1986; Morrison, 1986; Veizer et al., 1986; Al-Aasm and Veizer, 1986a, b; Brand, 1989a, b.). Three controls of chemical distribution have been recognized; 1. the re-equilibration of skeletal carbonate with diagenetic waters (Mn, Fe); 2. biological fractionation (Sr, Na, Mg); and 3. leaching of aluminosilicates (I.R., Al). The distribution of elements in crystal lattices is dependant upon relatively few physicochemical parameters and may justify the original underlying factor analytic hypothesis of a small number of
factors (Temple, 1978). Computations were performed using the statistics program Statview 512™ on an Apple Macintosh microcomputer.
CHAPTER 2

Primary and diagenetic microstructures of brachiopod shell calcite
INTRODUCTION

The structural characteristics of articulate brachiopod valves has remained constant since the Cambrian (Rowell and Grant, 1987). Similarly, it can be assumed that the secretory mechanisms and the processes controlling calcification remain unchanged. As a consequence, a comparative analysis of modern and ancient brachiopod shell calcite can provide the basis for determining the preservation states and degree of post-depositional alteration of brachiopod calcite. As such, microstructural analysis can augment chemical and isotopic trends that are indicative of diagenetic alteration. The identification of pristine shell calcite and the elimination of altered material is essential to the investigation of ancient shell calcite compositions and paleoenvironmental reconstructions. Use of altered material can lead to misinterpretation of chemical data (Brand, 1989a).

This purpose of this chapter is to identify primary and diagenetic microstructures within brachiopod shell calcites collected from the Paleozoic of New York State and southern Ontario and illustrate the textural changes accompanying post-depositional alteration.

BRACHIOPOD SHELL SECRETION AND MICROSTRUCTURE

Modern brachiopods possess an exoskeleton composed of a thin outer proteinaceous layer, the periostracum, which is underlain by primary and secondary layers of calcite (Fig. 2.1; Rudwick, 1970; Tasch, 1973; Rowell and Grant, 1987). These foliated calcite layers are recognized in ancient brachiopods but the outer organic periostracum degrades quickly after death.
Figure 2.1. Generalized cross section of an articulate brachiopod exoskeleton. Modified from Rudwick (1970), Grant and Rowell (1987.).
and is not fossilized (Williams, 1966; 1968a, b; Rowell and Grant, 1987; Brand, 1988). Shell calcite secretion is controlled by epithelial cells within a generative zone close to each valves mantle edge (Fig. 2.1; Rowell and Grant, 1987). Initially these cells assemble a thin organic meshwork periostracum which is composed of conchiolin, a protein-polysaccharide complex (Rosenberg et al., 1988). The cells then switch to secretion of a thin calcitic primary shell layer, constructed of small fused prismatic crystallites, oriented tangentially to the shell surface: the primary layer is secreted without benefit of an organic matrix (Williams, 1968a).

The secretory regime changes once more as the epithelial cells moves further away from the generative zone and thick layers of foliated calcite are constructed as the secondary shell layer. In ancient brachiopods, differentiation of this layer into fibrous or laminar foliation is recognized. Fibrous shell layers consist of long calcite rods ensheathed in membranous organic matrices, oriented about 10° to the primary layer (Fig. 2.2). In contrast, laminar shell structure is constructed of thin platy laths of calcite fused to form individual separated lamina; orientation is roughly parallel to the shell surface. This type of structure is restricted to brachiopods of the order Strophomenida. Cells secreting the secondary layer may intermittently cease depositing an organic matrix causing layers or lenses of prismatic calcite, arranged normally to the mantle, to build up within the fibrous layer (Rowell and Grant, 1987). Alternately, some taxa secrete distinct tertiary layers of prismatic calcite, which may thicken and strengthen the valve in response to physiological, ontogenetic or environmental demands.

Growth lines, similar to those observed in bivalves, are recognized in modern (e.g., Terebratulina retusa; Curry, 1982) and ancient brachiopods
Figure 2.2. Scanning electron micrograph of the primary and secondary calcite layers of the modern brachiopod *Laqueus vancouverensis*. The primary shell layer is composed of small, stacked prismatic calcites oriented at 90° to the outer valve surface. The secondary layer is composed of rounded elongate calcite fibres. The organic matrix between each fibre is not visible. The shell structure is modified by punctal openings that terminate just below the prismatic layer upper surface. Crystallites on the internal surfaces of each punctae are fused.

Figure 2.3. S.E.M. micrograph cross section of foliated secondary shell layer around punctae. Individual calcite fibres are rounded, oblate and curve upward to meet punctal surface. (*Laqueus vancouverensis*).
Some modern species apparently dissolve portions of their inner shell in response to metabolic anaerobiosis, although this does not extend to the outer shell (Hughes et al., 1989). The Recent rhynchonellid *Notosaria nigricans* exhibits three types of recognizable growth lines, which result from cessation of shell growth in response to diurnal, seasonal and disturbance controls (Hiller, 1988). Growth increments in bivalves are the subject of numerous conflicting studies (e.g., Crenshaw, 1980; Carter, 1980; Brand et al., 1987; Rollins et al., 1987) which indicate that skeletal growth lines may be the result of either anaerobic or physiological processes. The Lutz and Rhoads (1977) theory of anaerobiosis explains growth increments as the result of cycles of aerobic calcite precipitation and anaerobic dissolution controlled by a complex interaction of physiological and environmental interactions (Crenshaw, 1980). Alternately, inherent cyclic protein and calcite deposition may be the cause for growth increments (see discussion by Rosenberg et al., 1988). Future ontogenetic and environmental analysis of brachiopod valves may be possible with the evolution of microprobe analysis and microsampling techniques.

Punctate brachiopods possess structural modifications of shell microstructure. In Recent articulate brachiopods, punctae are small cylindrical pores (15 μm diameter) within the primary and secondary layers, which are generally uniformly distributed over the surface of the shell (Kemyzys, 1965). They extend from the inner surface of the valve to just below the outer primary layer where growth of the mantle epithelial tissue (caeca) into the punctae connects with the periostracum via fine organic strands (Rowell and Grant, 1987). The majority of shell organic matter in modern species, *Liothyrella uva*, is located within the caeca (Peck et al., 1989) and it has been suggested that
caecal contents inhibit boring organisms and function in a nutrient storage capacity (Curry, 1983b). Several authors suggest that punctae have a respiratory function (Shumway, 1982; Curry, 1983a, 1983b) because they effectively communicate with the external environment (Thayer, 1986b). When the valves are closed, caecal respiratory needs can be meet by simple diffusion through the punctae. However, observations on closed *Liothyrella uva* have shown that internal tissues are not supplied by punctal diffusion and must rely on oxygen enclosed within the body cavity (Peck et al., 1986; 1989). Metabolic needs in mantle tissues are apparently switched from aerobic pathways to anaerobic pathways after prolonged oxygen deprivation of about 15 hours (Peck et al., 1986). Brachiopods have been described as oxygen "minimal organisms" (Thayer, 1986b) because they metabolize slowly and efficiently (LeBarbera, 1981b). Consequently ATP generation by anaerobiosis may enable them to survive extensive periods of oxygen deprivation (Hammen, 1977; Shumway, 1982). There are no long-term studies of oxygen deprivation and it is not known how or if oxygen depleted environments affect the ultimate viability of brachiopod communities. Tunnicliffe and Wilson (1988) observed that although modern *Terebratulina* survive prolonged periods of anoxia (20-35% of time) there is a slow retreat by the community from deeper, more persistent anoxic conditions. Absence of ancient and modern brachiopod populations from anaerobic and strongly dysaerobic facies, suggests that permanent low oxygen conditions were lethal to individual brachiopods and brachiopod communities.
MODERN BRACHIOPOD SHELL CALCITE MICROSTRUCTURE

SEM analysis of a Recent brachiopod *Laqueus vancouverensis* clearly illustrates the primary calcite layer of prismatic crystallites, which is oriented normally to the external surface (Fig. 2.2). Tangentially oriented calcite fibres of the secondary shell layer are also evident; each fibre is rounded and oblate in cross section (Fig. 2.3). Rounded and stacked calcite fibres of the secondary layer are exposed on internal surfaces of several Recent brachiopods, including *Laqueus vancouverensis*, (Fig. 2.4), rhynconellid *Notosaria nigricans* (Hiller, 1988, p. 180), terebratulids, *Waltonia* and *Liothyrella* (Rowell and Grant, 1986, p. 472) and this primary structural feature is informally termed "imbricate structure" here. Furthermore, observation of the protegulum of juvenile *Terebratalia transversa* indicates that this internal valve microstructure is present shortly after metamorphosis (Stricker and Reed, 1985, p. 297).

Punctae are recognized in many modern brachiopod species. In *Laqueus vancouverensis*, small regularly spaced punctal openings (Fig. 2.5) transverse the entire secondary fibrous layer into the primary layer, but terminate just below the upper surface of the primary layer (Fig. 2.6). Furthermore, strong foliation of secondary shell layers around each punctae is evident (Fig. 2.6).

PALEOZOIC BRACHIOPOD MICROSTRUCTURE

Primary structures

In general, excellent microstructural detail is preserved in the majority of Paleozoic brachiopods from New York State and southern Ontario. The foliated
Figure 2.4. S.E.M. micrograph of the imbricate internal surface of *L. vancouverensis*. Oblate and flattened calcite fibres of the secondary layer are exposed at the internal valve surface. Punctal openings are also common.

Figure 2.5. S.E.M. micrograph of regularly-spaced punctal openings on the internal surface of a *L. vancouverensis* shell. Openings are not filled and exposed fibres of the secondary layer can be seen.
Figure 2.6. S.E.M. micrograph close up of fibrous secondary shell layer. Ultrastructure of *Laqueus vancouverensis* shows stacked nature of secondary calcite fibres, which are elongate, rounded and oblate in section.

Figure 2.7. S.E.M. micrograph of the secondary layer of *Mediospirifer* (#400; Hamilton Group). Stacked nature of rounded, oblate calcite fibres is evident and separation between fibres is a few micrometres. Fractures in this layer are probably the result of sample preparation.
secondary layer is the most common feature observed by S.E.M. Comparisons between calcite fibres of modern brachiopods and many Paleozoic specimens offers no visible difference in their preservation state (compare Figs. 2.2, 2.3, with 2.7). Tangential and obliquely broken shell fragments of many Paleozoic specimens commonly display regularly stacked elongate fibres which are rounded and oblate with no dissolution features (Figs. 2.8, 2.9). Imbricate structure is present on the internal valve surfaces of Paleozoic specimens (e.g., *Athyris spiriferoides*; Figure 2.10; Middle Devonian, Hamilton Group). Furthermore, the internal stacked nature of secondary calcite fibres is evident in the majority of etched brachiopod valves (Figure 2.11).

The primary shell layer is rarely seen in Paleozoic brachiopods, which may reflect removal of outer shell layers by sample preparation, natural abrasion or superficial thickness. A thin, outer prismatic primary layer has been observed in *Mediospirifer audacula* (Hamilton Group; Middle Devonian) together with a second prismatic layer underlying the foliated secondary layer (Figure 2.12). Prismatic calcite fibre structure, termed trabecular calcite, is common to Recent and ancient brachiopods (e.g., Recent *Neothyris lenticularis* and Carboniferous *Neospirifer* sp., *Composita*, and *Spirifer gorei*; Brand, 1989). In valves of *Whitfieldella nitida* (Fig. 2.13; Clinton Group, Middle Silurian) trabecular structure may represent modification of prismatic shell calcite. Only along the mantle edge does this species exhibit the secondary fibrous-calcite layers.

Punctal structures are recognized in two species from the Middle Devonian Hamilton Group. Etched inner surfaces of *Tropidoleptus carinatus* reveal regularly spaced punctae (Fig. 2.14), which have dimensions similar to those seen in Recent specimens (Figs. 2.5). Foliation of the fibrous secondary
Figure 2.8. S.E.M. micrograph of the secondary layer of *Mucrospirifer mucronatus* (#178; Hamilton Group). Stacked calcite fibres do not show signs of dissolution or reprecipitation of pore-filling cements.

Figure 2.9. S.E.M. micrograph of the secondary layer of *Eospirifer radiatus* (#2301; Lewiston Member, Middle Silurian, New York State). Close up reveals rounded and elongate calcite fibres similar to those in Figure 2.3, 2.7 and 2.8.
Figure 2.10. S.E.M. micrograph of the imbricated internal valve surface of *Athyris spiriferoides* (#403, Wanakah Shale, New York State). This primary structure on the internal surfaces of ancient valves is also observed in Recent brachiopods and results from modification of oblate fibres oriented at ~10° by epithelial cells.

Figure 2.11. S.E.M. micrograph of the internal surface of an etched *Athyris spiriferoides*. Etching of inner surfaces reveals stacked calcite inclined at low angle from the surface (#445, Wanakah Shale, New York State).
Figure 2.12. S.E.M. micrograph of primary, secondary and tertiary layer shell calcite layers of *Mediospirifer audacula* (#71, Wanakah Shale).

Figure 2.13. S.E.M. micrograph cross section of prismatic trabecular calcite morphology in *Whitfieldella nitida* valves (#2108, Irondequoit Formation). Similar primary structure are reported by Brand (1981, 1983, 1989a).
Figure 2.14. S.E.M. micrograph of the internal surface of an etched *Tropidoleptus carinatus* (#409, Wanakah Shale, New York State). Numerous punctae are evident on the inner brachial valve although not regularly spaced as in some modern species (Kemyzs, 1965). Shallow pits are evident surrounding punctal openings, while the small punctal pores (a few micrometres in diameter) are partially filled with cements.

Figure 2.15. S.E.M. micrograph cross section of the secondary shell layer of *Tropidoleptus carinatus* (#409, Wanakah Shale, New York State). Foliation of secondary layer fibrous calcite is penetrated by small undulating punctal pores that pass completely through. The punctae do not appear to be significantly filled with secondary calcites. The upper oblique view of the internal valve surface shows the depressions surrounding the punctal openings.
layer around each punctae is still visible and are comparable to those seen in modern brachiopods (compare Figs. 2.15 with 2.2). In specimens of *Rhipidomella vanuxemi* regularly spaced punctae are visible and the stacked fibrous calcites of the secondary layer meet the inner valve surface at a low angle (Fig. 2.16).

An etched outer surface of an *Eospirifer radiatus* (Rochester Shale; Middle Silurian) valve reveals minute pore openings (Fig. 2.17). These pores are about 1 μm in diameter, are not filled and do not penetrate into the fibrous layer. Their function is unknown but they could be part of shell micro-ornamentation.

**Diagenetic structures**

Although brachiopods are composed of low-Mg calcite and are relatively stable in the presence of diagenetic fluids, microstructural alteration does occur and varying states of preservation are recognized in Paleozoic specimens. Alteration of the fibrous layers ranges from slight dissolution between calcite rods (Fig. 2.18, 2.19) to almost complete obliteration of any structural features (Fig. 2.20). Slight dissolution and subsequent calcite cement filling between fibres is evident (e.g., *Athyris spiriferoides* valve; Fig. 2.18). Dissolution, reprecipitation and fusing of calcite fibres progressively obscures microstructural detail (Fig. 2.19). In rare cases, the microstructures of a few valves of *Rhipidomella vanuxemi, Athyris spiriferoides, Resserella elegantula* are almost completely obliterated and are replaced by fine grained secondary calcites. Valves of *Pentameroides* sp. are invariably completely recrystallized (Fig. 2.22).
Figure 2.16. S.E.M. micrograph of the internal valve surface of *Rhipidomella vanuxemi* (#412, Wanakah Shale, New York State) Stacked oblate and flattened fibrous calcites meet the internal surface at low angles. Pits and depression are evident surrounding punctal openings which are partially filled with secondary calcites.

Figure 2.17 S.E.M. micrograph of micropores on the internal valve surface of *Eospirifer radiatus* (#2195, Lewiston Member, New York).
Figure 2.18. S.E.M. micrograph of the secondary fibrous shell layer of altered *Athyris spiriferoides* (#5, Wanakah Shale, Middle Devonian, New York). There is evidence of slight dissolution and fusing of fibres.

Figure 2.19. S.E.M. micrograph of the secondary fibrous shell layer of altered *Athyris spiriferoides* (#5, Wanakah Shale, Middle Devonian, New York). Progressed alteration has resulted in fusing and obscuring of secondary layer fibres and structure and significant dissolution and reprecipitation.
Figure 2.20. S.E.M. micrograph of recrystallized *Pentameroides* sp. from the Merritton Formation (#2007, Middle Silurian, Ontario). Recrystallization of primary or secondary shell layers is complete and original microstructures are replaced by calcite mosaic.

Figure 2.21. S.E.M. micrograph of laminar secondary shell structure of *Rafinesquina deltoidea* (#794, Verulam Formation, Ontario). The foliated secondary layer calcite laths are slightly fused.
Fused calcite laths apparently constitute the laminar shell layers of Strophomenids (Rowell and Grant, 1987), and as such makes it more difficult to identify pristine structure. The thin, flat valves of strophomenids *Sowerybella* sp., *Rafinesquina deltoidea* and *Coolinia subplana* are composed of fine laminar layers. Small calcite laths are recognized in some specimens (Fig. 2.21), but in most specimens the laminae appear fused (Fig. 2.22). It remains uncertain what degree of fusing can be ascribed to dissolution-reprecipitation events.

Although the punctae of *Tropidoleptus carinatus* and *Rhipidomella vanuxemi* are often open at the shell surface, the majority of punctal pores are partially filled with secondary calcites; many are filled with minute calcite cement rhombohedra (Fig. 2.23). The exposed face of an inner valve of *Tropidoleptus carinatus* reveals primary punctal pores but the openings are filled with pore cements (Fig. 2.14).

**CONCLUSIONS**

The results of S.E.M. study suggest that most brachiopod shell calcites of the Hamilton (Middle Devonian) and Clinton Groups (Middle Silurian) are essentially preserved in a pristine state. Brachiopod shell calcites from both these periods retain the original integrity of primary microstructural features, such as oblate calcite rod, shell foliation, and punctate structures. The termination of calcite fibres on internal surfaces of valves, here termed imbricate structure, is observed in modern and ancient specimens and indicative of the good degree of preservation.
Figure 2.22. S.E.M. micrograph of secondary shell structure of orthid *Dalmanella rogata* (#754, Verulam Formation, Ontario). The foliated calcite laths are slightly fused and there is some cement filling between laths.

Figure 2.23. S.E.M. micrograph of punctate brachiopod *Tropidoleptus carinatus* showing punctal filling cements (#409, Wanakah Shale, New York State).
Post-depositional alteration of some specimens is indicated by fusing of calcite rods, loss of integrity of the foliated layers, progressive obscuring of microstructure and precipitation of cements between fibres. Complete obliteration of shell structure is rare and recrystallization is restricted to Pentamerid specimens. Moreover, the punctal canals of *Tropidoleptus carinatus* and *Rhipidomella vanuxemi* are invariably cement filled, although surrounding foliation is preserved. A spectrum of microstructural alteration is evident in brachiopod shell calcites analysed from Trenton Group (Middle Ordovician) limestones and Georgian Bay Formation (Upper Ordovician) shales.
CHAPTER 3

Diagenetic and paleoenvironmental investigation of brachiopod shell calcite from the Middle Devonian Hamilton Group; New York State and Ontario.
INTRODUCTION

The elemental and isotopic composition of brachiopod shell calcite is potentially a record of the chemical environment within which the carbonate was precipitated. The analysis of preserved brachiopod calcite has lead to the investigation of secular changes in the oceanic reservoirs of $^{18}\text{O}$ and $^{13}\text{C}$ and the establishment of carbon and oxygen isotopic curves for the Paleozoic (Popp et al., 1986; Veizer et al., 1986; Brand, 1989). However, it must be determined whether brachiopod low-Mg calcite has undergone chemical and microstructural changes with post-depositional alteration. Diagenetic alteration of calcite in either meteoric, marine or mixed settings will overprint primary elemental and isotopic compositions (Brand and Veizer, 1980, 1981; Baker et al., 1982; Al-aasm and Veizer, 1982; Veizer, 1983a, b). Manganese enriched contents of brachiopods (>100 ppm; Al-aasm and Veizer, 1982; Veizer et al., 1986) and the recognition of cathodoluminescent valves (Popp, 1981, 1986; Popp et al, 1986a, b; Adlis et al., 1989) have been used to eliminate altered brachiopods from geochemical interpretations. This approach is problematic, since Mn contents over 100 ppm may reflect primary compositions of shell calcite, rather than a diagenetic product (Brand, 1989a, b). It is assumed that brachiopods inhabited open marine, fully oxic conditions (Veizer et al., 1986) and as such, brachiopods of different ages, taxa and lithology are treated as a singularly uniform and chemically unvariable organism. However, recent studies suggest that ancient brachiopods had a wide range of environmental tolerances, especially of anoxia (Thayer, 1974, 1986a, b; Kammer et al., 1986; Thompson and Newton, 1987; Racki, 1989) and modern brachiopods are able to survive and function for prolonged periods with oxygen levels frequently below 0.1 mlL-1 (Tunnicliffe and Wilson, 1988). Previous investigations of
secular isotopic changes have not taken into consideration possible inherent chemical variability within co-occurring brachiopod species, nor possible isotopic/elemental differences within single beds that reflect depth changes, organic carbon content and temperature variability. Shifts of 1-3\(^o\) in \(\delta^{18}O\) and \(\delta^{13}C\) (Popp et al., 1986; Adlis et al., 1989) may not be overly significant if similar isotopic variability in one single shell bed can be explained as the response to a deepening basin and to local paleoenvironmental conditions.

During deposition of the Middle Devonian Hamilton Group in western New York State and southern Ontario, benthic habitats were occupied by diverse invertebrate fauna. These are the focus of recent paleoecologic and stratigraphic studies (e.g., Baird and Brett, 1981; Baird, 1983; 1985; Brett, 1986b; Brett and Cotrell, 1982; Brett and Baird, 1985; Brett et al., 1986; Dick and Brett, 1986; Savarese et al., 1986; Wygard, 1986; Baird and Brett, 1986; Brett et al., 1986a; Miller et al., 1988). Spatial distribution of brachiopods on the Hamilton Shelf can be defined within the context of idealized biofacies (Brett, et al., 1986b; Miller, 1986; Grasso, 1986), which represent groups of closely related intergrading fossil associations, the distribution of which are controlled by environmental parameters (e.g., depth, turbidity, oxic conditions; Fig. 3.1). Persistent brachiopod shell beds that deepen toward the basin centre can be traced across the shelf for tens of kilometers (Figure 3.2). These shell beds represent an ideal opportunity to investigate possible chemical and isotopic changes in brachiopod shell calcite reflecting taxonomic and environmental variability.

The purpose of this chapter is to investigate the diagenetic and depositional chemistries of brachiopods from Hamilton Group strata. Objectives are fourfold: i) to determine diagenetic trends within brachiopod calcite and select pristine specimens for further paleoenvironmental investigations; ii) to
Figure 3.1. Generalized paleoecological model relating Hamilton Group biofacies to inferred gradients of depth-related parameters, turbidity and/or sedimentation rates and oxic conditions. From Brett et al. (1986).
Figure 3.2. Diagrammatic cross-section of the Upper Hamilton Group (Middle Devonian) across western New York State. Vertical lines represent sections at sampling sites: numbers correspond to sampling localities listed in Appendix III. Lettering corresponds to prominent stratigraphic units and persistent shell beds. Modified from Baird (1979) and Brett and Cottrell (1982).
report the distinct chemical differences in shell carbonate between co-occurring brachiopod species; iii) evaluate the chemical and isotopic trends across a deepening basinwide shell bed, and; iv) investigate possible relationships between chemical and isotopic contents, biofacies and inferred paleoenvironmental conditions.

GENERAL GEOLOGY OF THE HAMILTON GROUP

During the Middle Devonian, reactivation of the Appalachian Basin and surrounding arches was initiated by the second tectonic phase of the Acadian Orogeny (Ettensohn, 1985a). Reconstruction of basin physiography suggests that a shallow tropical epicontinental sea occupied most of New York State and Pennsylvania (Fig. 3.3; Parsons et al., 1988). This semi-enclosed lobe of the Appalachian Basin lay south of the equator (Oliver, 1976; Heckel and Witzke, 1979; Kent, 1985; Miller, 1986; Vogel et al., 1987; Parsons et al., 1988) and, although basin waters were probably connected to the Rheic Ocean to the southwest, water exchange was apparently limited (Woodrow, 1985). Limestones and calcareous shales accumulated on the shallow shelf in the west (Fig. 3.2) whereas coarse siliciclastics, derived from the Acadian landmass, accumulated as the Catskill delta complex to the east (Woodrow, 1985; Parsons et al., 1988).

The Hamilton Group, which represents a time span of about 5-7 (±1-2) million years (Harland et al., 1982; Brett, 1986a), is subdivided into four formations: the Marcellus, Skaneateles, Ludlowville and Moscow (Fig. 3.4). These units are separated by thin but persistent carbonate beds (e.g., Tichenor, Michenor, Menteth Limestones), which represent the culmination of large-scale transgressive-regressive sequences within each formation, and superimposed
Figure 3.3. Paleogeographic reconstruction of the Appalachian Basin during deposition of the Middle Devonian Hamilton Group. Modified from Parsons et al. (1988).
Figure 3.4. Generalized stratigraphic section of the Ludlowville and Moscow Formations of the Hamilton Group (Middle Devonian) in Erie County and Genesee Valley. Shell beds and thin limestones that are widely traceable across western New York State are designated by letters A to J (see Fig. 3.2. for explanation). Modified from Brett et al. (1986).
smaller transgressive-regressive cycles of 1-3m (Brett and Baird, 1985; Brett and Baird, 1986a, b; Savarese et al., 1986; Landing and Brett, 1987). This vertical sequence of sediment deposition in western New York was controlled by the lateral movement of facies belts in northward or southward directions as a result of transgressive-regressive events (Brett and Baird, 1982; Brett et al., 1986b). An actively subsiding trough was centred around the Seneca and Cayuga Lakes region and during deposition of the Ludlowville Formation, grey shales of the Ledyard and Wanakah Shale Members were transitional with black shales of the basin depocentre (Baird, 1981, Brett et al, 1986a, b). The basin axis slowly moved westward toward the Genesee Valley during subsequent deposition of the Moscow Formation Deep Run and Kashong Shale Members (Miller, 1986). The west and eastward thinning of the facies may be the result of condensation, non-deposition, and submarine erosion (Miller, 1986; Brett and Baird, 1986a, b).

RESULTS

Five co-occurring brachiopod species (i.e., impunctate spiriferids *Athyris spiriferoides spiriferoides*, *Mediospirifer audacula audacula* and *Mucrospirifer mucronatus mucronatus* and punctate *Rhipidomella vanuxemi vanuxemi* and *Tropidoleptus carinatus carinatus*) were chemically analysed from the Ludlowville and Moscow Formations of the Hamilton Group (Table 3.1). The ranges of their shell calcite chemical composition are similar to those reported for modern (e.g., Milliman, 1974; Morrison and Brand, 1986; Brand, 1989a) and ancient brachiopods (Brand and Veizer, 1980; Brand, 1983; Popp et al., 1986b; Veizer et al., 1986; Brand and Morrison, 1987). Elemental contents are variable (e.g. *Athyris spiriferoides* Mn; range 10-1645 ppm), reflecting the influence of
Table 3.1. Middle Devonian chemical data of all brachiopods and pristine brachiopods

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<th>Mg</th>
<th>Sr</th>
<th>Mn</th>
<th>Na</th>
<th>Fe</th>
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<td></td>
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**PRISTINE CHEMISTRIES**

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<th>Fe</th>
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All elemental concentrations are in ppm.
two primary controls: 1) composition of the original precipitated shell calcite, regulated by the organism physiology and external chemical environment; and 2) the chemical changes associated with diagenetic re-equilibration of calcite in the presence of fluid(s).

**Diagenetic Trends**

The similarity of microstructure to modern brachiopods and the retention of the fabric integrity of most Hamilton Group brachiopod calcite indicates a high degree of chemical preservation (Figs. 2.6 to 2.8; 2.10). However, despite the stability of low-Mg calcite, a number of brachiopods were subjected to varying degrees of post-depositional alteration, resulting in textural changes (Figs. 2.18, 2.19) and the repartitioning of trace/secondary elements into diagenetic low-Mg calcite. Microstructural alteration is evident in those specimens where calcite fibres show signs of fusing, dissolution and precipitation of cements between fibres. Moreover, complementary chemical changes are observed with diagenesis; similar chemical trends accompanying microstructural alteration are demonstrated in previous studies of molluscs, crinoids, trilobites and brachiopods (Brand and Veizer, 1980; Al-Aasm and Veizer, 1982; Morrison and Brand, 1987; McAllister, 1989; McAllister and Brand, 1989; Brand 1989a, b). A representative suite of Hamilton Group brachiopod specimens of different species are compiled in Table 3.2, with microstructural preservation listed against respective Mg, Mn, and Fe contents. These three elements were chosen because they are the most diagnostic of chemical alteration. It is apparent that there is a corresponding increase in the degree of fusing with progressive chemical diagenesis. Graphically, the direction of alteration is toward coeval matrix samples, which show the greatest effect of post-depositional alteration (Figure 3.5; 3.6), and follows theoretical considerations such as partition
Table 3.2. Comparison of microstructural preservation and chemical contents for selected brachiopods from the Middle Devonian Hamilton Group of western New York State and southern Ontario. Lithology symbols denote (S= dark grey shale).
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<th>Sample Number</th>
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<th>Preservation State</th>
<th>Diagenetic features</th>
<th>Mg (ppm)</th>
<th>Mn (ppm)</th>
<th>Fe (ppm)</th>
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Figure 3.5. Scatter plot of Fe vs Mn for all Middle Devonian brachiopods. The LMC field represents the general categorization of microstructurally and chemically pristine brachiopods. The boundaries are loosely defined. A few Tropidoleptus specimens plot within this field but are deemed altered because of the presence of pore filling cements within punctae. Metastable high-Mg calcite crinoids from the Hamilton Group are extensively altered, plotting close to matrix values. The open meshwork structure, typical to crinoids (Bathurst, 1975; Brand and Morrison, 1987b; Brand, 1987) may have promoted fluid controlled reactions and multiple dissolution-reprecipitation events.
Figure 3.6. Scatter diagram of Na vs Mg for brachiopods and matrix of the Hamilton Group (Middle Devonian). The means and ranges of unaltered brachiopods are plotted amongst individual altered specimens.
coefficients, water chemistries and variable water-rock ratios (Brand and Veizer, 1980; Veizer, 1983a).

Factor analysis of chemical data supports the inference that diagenetic alteration can explain a significant percentage of variation observed in brachiopod calcite (Appendix IV, Tables A-1 to A-6.) and concurs with the observed chemical changes associated with diagenesis. Factor 1 is repeatedly loaded by Mg, Fe and Mn for brachiopods by species and by formation; similar confirmation of diagenetic trends is reported in other studies (e.g., Brand and Veizer, 1980; Al-Aasm and Veizer, 1982; 1986a, b; Veizer et al., 1986; Majid and Veizer, 1986; Brand 1989a, b).

The degree of brachiopod alteration is variable and reflects the composition of original shell calcite and diffusion or fluid controlled diagenesis (Veizer, 1983a; 1983b). The chemical equilibration process progresses by the dissolution of calcite fibres and subsequent reprecipitation of diagenetic low-Mg calcite cements into available pore spaces. Slightly altered specimens, which plot close to the pristine field (Fig. 3.5), have undergone diffusion controlled diagenesis and retain much of their original composition. Pore spaces between shell fibres are less than 1 μm wide (Figs. 2.7, 2.8), and as a consequence, alteration can be constrained by the minute dimensions of the reaction zone (Pingitore, 1976; 1978; Veizer, 1983, Brand, 1989).

The Mg, Fe and Mn contents of *Tropidoleptus carinatus* and *Rhipidomella vanuxemi* are significantly higher than co-occurring spirifers (Fig. 3.7, 3.8; Table 3.1) and reflects the presence of punctae in shell calcite. Although, the integrity of shell foliation is retained, the punctae are invariably filled with secondary calcite cements (Figs. 2.28, 2.30). The proportion of punctae may be small compared to the whole shell, but pore-filling cements
Figure 3.7. Scatter plot of Fe vs Mn for *Tropidoleptus* and *Rhipidomella* brachiopods from the Hamilton Group (Middle Devonian). The LMC field represents unaltered Hamilton Group brachiopods.

Figure 3.8. Scatter plot of Na vs Mg for *Tropidoleptus* and *Rhipidomella* of the Hamilton Group. Progressive enrichment in Mg may reflect increasing proportion of pore-filling cements within punctae.
contribute significantly to overall "averaged" calcite chemistry. Furthermore, the punctae may facilitate the passage of fluids through the shell calcite, and effectively increase the surface area available for diagenetic reaction. Magnesium contents reflect the extent of diagenetic re-equilibration and pore-filling cements. Altered *Tropidoleptus carinatus* specimens exhibit chemical ranges related to a whole spectrum of diffusion to fluid controlled alteration (Fig. 3.7). *Tropidoleptus carinatus* with low Mg contents reflect diffusion controlled reactions (Fig. 3.8), whereas those with higher Mg contents were altered in the presence of larger water volumes. The presence of pore-filling cements precludes the use of punctate brachiopods from paleoenvironmental investigation.

**Diagenetic waters of the Hamilton Group**

The alteration of Ludlowville and Moscow Formation brachiopod calcite resulted in progressive enrichment of Mg, Mn and Fe contents whereas Sr and Na contents were only slightly reduced. Retention of Sr and Na contents is not characteristic of meteoric diagenesis (Brand and Veizer, 1980; Veizer, 1983a, b), which suggests that the diagenetic fluids were essentially Mg, Sr and Na rich. The passage of marine- or mixed- waters is the most likely explanation, and it is possible that waters derived from the Upper Silurian Salina Group may have migrated through fracture planes; Salina Group fluids were probably highly ionic (O'Shea et al, 1988; Fritz et al, 1988). Alternately, *in situ* formation waters within this semi-enclosed basin may have been responsible for shell calcite alteration. The outcrop pattern in western New York State is essentially west to east and the passage direction of the diagenetic fluid(s) was impossible to decipher from this data set.
Selection of best preserved material

Previous workers have used trace and minor elemental compositions of brachiopod shell calcite to determine the best preserved material (e.g., Lowenstam, 1961; Brand and Veizer, 1980; Buchardt and Weiner, 1981; Al-Aasm and Veizer, 1982; Veizer et al., 1986; Brand, 1989). Low-Mg calcite precipitated in equilibrium with ambient seawater is expected to contain Mn contents averaging 5-50 ppm and Fe contents averaging 20-500 ppm (Brand and Veizer, 1980; Al-Aasm and Veizer, 1982; Morrison and Brand, 1987). Ordovician brachiopods from Anticosti Island with mean Mn contents of 150 ppm were deemed to be altered by as much as 20% by Al-Aasm and Veizer (1982) and Veizer et al. (1986). They suggested that shell calcites containing Mn contents over 70 ppm and Fe contents greater than 300 ppm are essentially altered.

In previous studies, brachiopods of different taxa and ages have been grouped together and deemed altered if they exceed a certain critical chemical value (i.e. >100 ppm Mn; <1200 ppm Na; <900 ppm Sr; Veizer et al., 1986). This oversimplification ignores the influence of inherent original variability of shell calcite between taxa, ionic regulation, and potentially different local chemical/physical environments. For example, although the Na and Mg chemical ranges of unaltered Athyris spiriferoides, Mediospirifer audacula and Mucrospirifer mucronatus overlap, there are distinct differences between species (Fig. 3.6; Table 3.1). Brachiopod shell calcite containing 1200 ppm Mg can be pristine or altered depending on whether it is an Athyris spiriferoides or a Mediospirifer audacula, the original composition controlling the chemistry of the diagenetic product. Therefore, careful evaluation of all elemental (i.e., Mn, Fe, Mg, Sr, Na, Al) and microstructural data must be used to establish pristine from altered specimens.
Similarly, cathodoluminescence in ancient brachiopods has been used by several workers to identify altered brachiopods (Popp, 1981; Popp et al., 1986a, 1986b; Adlis et al., 1989). For example, non-luminescing *Mucrospirifer mucronatus* valves from the Middle Devonian Hungry Hollow Formation were considered unaltered, whereas luminescent specimens from the Speeds and Beechwood Limestones were identified as altered (Popp, 1981; Popp et al., 1986b). In biogenic carbonates, cathodoluminescence results from the presence of Mn substituting for calcium within the crystal lattice (Meyers, 1974; Pierson, 1981; Frank and others., 1982), although other elements may serve as activators and sensitizers (Machel, 1985). The minimum Mn content required to produce luminescence ranges from 300 ppm (Frank et al., 1982) to as low as 15 ppm (Ten Have and Heijen, 1985) and is dependant on the presence or absence of other activators or quenchers; notably Fe acting as a quencher (Frank et al., 1982; Fairchild, 1983; Machel, 1985).

Both of these approaches to the selection of pristine shell calcite assume that brachiopods incorporated Mn and Fe in inorganic equilibrium with open marine seawaters. However, it is increasingly apparent that this may be an oversimplified assumption. Pristine, modern brachiopod calcite can contain as much as 300-450 ppm of Mn (Brand, 1989a), which is enough to activate luminescence. Similarly, ancient brachiopod calcite, by analogy, may reflect original compositions and the complexities of cation regulation by the organism and different chemical environments (e.g. redox conditions, temperature, salinity, precipitation rates). For example, Adlis et al. (1988) observed that the primary prismatic calcite shell-layer of a Pennsylvanian brachiopod *Crurithyris planoconvexa* are luminescent, whereas the secondary fibrous layers are non-luminescent. This may be related to the preferential alteration of the outer prismatic layer, but it may also represent inherent differences in the original
Mn/Fe compositions of both layers, which in turn may be partially related to such processes as biological fractionation and/or differential partitioning between the mineral morphologies.

The Fe and Mn chemistries of pristine Hamilton Group brachiopods are highly variable (5 to 200 ppm Mn and 70 to 650 ppm Fe) and many fall outside the compositional ranges observed in inorganic low-Mg calcite postulated to have precipitated in equilibrium with modern seawater (Table 3.1; Fig. 3.6). This divergence may be the result of a number of processes. The Mn and Fe contents of shell calcite may be partly controlled by soluble oxide coatings (Sherwood et al., 1987), or calcite metal fractions (Thomson et al., 1986), but these influences are generally restricted to deep water brachiopods (>1000 m). Alternately, the leaching of Mn and Fe from the aluminosilicate residue may contribute to chemical concentration in biogenic carbonates (Brand and Veizer, 1980; Boyle, 1981; Al-Aasm and Veizer, 1982; Veizer, 1983a). Significant leaching from the aluminosilicate fraction is indicated if factor analysis of data correlates Fe and Mn contents with I.R. and/or Al contents (Brand and Veizer, 1980; Al-aasm and Veizer, 1982; 1986a, b; Majid and Veizer, 1986; Veizer et al., 1986; Brand, 1989). However, the Mn, Fe and Mg contents of Hamilton Group brachiopod calcite do not correlate with I.R. or Al (Tables A-1 to A-6), which supports the assertion that they reflect primary chemical compositions. Moreover, Al contents are low (mean 40 ppm; range 0 to 330 ppm?), which is close to or below machine detection limits. Analytic methods and sample preparation apparently minimized contamination from aluminosilicates.

Alternately, the Mn compositions may reflect its active or passive incorporation into lattice or non-lattice positions within biogenic carbonates. Mn is apparently bound within pigments or is part of the mineralogical structure of carbonates (Rosenberg, 1980). Shen and Boyle (1988) observed that Mn, even
though ionically much smaller than calcium, is a chemical component of aragonite corals. They also suspect that reduction must take place in the coral ectoderm in order to incorporate Mn$^{2+}$ into the aragonite lattice. Mn apparently substitutes for Ca in the aragonite lattice of *Mya arenaria* (White et al., 1977) and within the calcite lattice of *Mytilus edulis* (Blanchard and Chasteen, 1976). Boyle (1983) observed that the Mn/Ca ratios of Foraminifera tests increase significantly below the manganese redox boundary. The amount of Mn incorporated into calcite decreases with increasing precipitation rates (Lorens, 1981; Major et al., 1988; Mucci, 1988; Pingitore et al., 1988). Since brachiopod metabolism and secretion rates are slow (Rosenberg et al., 1988), this may promote the incorporation of Mn. Furthermore, the presence of minute organic-rich fluid inclusions (Bruni and Wenk, 1985; Gaffey, 1988) may have contributed to the overall chemical composition of shell calcite.

A number of previous authors have demonstrated that Mn and Fe contents in biogenic carbonates are related to facies controls and redox conditions (e.g., Veizer and Demovic, 1974; Veizer, 1977; Brand, 1987a, b; 1988; 1989; Morrison and Brand, 1988). Brand (1987) concluded that high Mn and Fe contents of Carboniferous brachiopods are a response to redox conditions and/or high detrital inputs. Moreover, the limited data of Recent brachiopods indicates that Mn and Fe chemistries are extremely variable (Mn, 5-460 ppm; Fe, 20-610 ppm) within a range of depths, salinities and temperatures (Brand, 1989a). Most Hamilton Group brachiopods have pristine microstructure and it is probable that the incorporation of these elements was controlled in part by oxygen and redox conditions within their external chemical environment.
BRACHIOPOD SHELL CALCITE CHEMISTRY

Generic Trends

Evaluation of chemically pristine brachiopod calcite from the Ludlowville and Moscow Formations suggests that there are inherent chemical differences in shell calcite compositions (Table 3.1). Significant differences are observed in the Mg, Sr and Na contents of the species Mediospirifer audacula, Athyris spiriferoides and Mucrospirifer mucronatus (Table 3.3; t-test, p < 0.05). This chemical pattern is repeated in systematic analysis of single shell beds within formations. Taxonomic differentiation and biological fractionation may be explained by each species physiological control of trace and minor element incorporation into shell calcite.

Fractionation of Mg

The three co-occurring spiriferid species of this study selectively discriminated against the incorporation of Mg into shell calcite when compared with Mg contents of inorganically precipitated calcite. Moreover, it is apparent that there are distinct taxonomic differences in the fractionation of Mg into shell calcite. The mean Mg contents of Mediospirifer audacula (789 ppm), Mucrospirifer mucronatus (1035 ppm) and Athyris spiriferoides (1309 ppm) are significantly different (Table 3.1, 3.3; Fig. 3.9) and this heirarchical pattern is always present within each shell bed or horizon sampled. The taxonomic control of Mg by Hamilton Group spirifers may be explained by a number of processes. Molecular and cation transport occurs across the epithelial cell membranes of modern brachiopods (Doherty, 1981) and divalent ions readily replace Ca$^{2+}$ within Ca pumps (Rega, 1987). Substitute cations are delivered to the extracellular fluid which serves as the medium for carbonate secretion at
Table 3.3. T-test: Upper Hamilton Group unaltered brachiopods

<table>
<thead>
<tr>
<th>Element</th>
<th>Mucrospirifer</th>
<th>Mediospirifer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Athyris</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>$p&lt;0.05$ 1.315</td>
<td>$p&lt;0.05$ 0.246</td>
</tr>
<tr>
<td>Mg</td>
<td>$p&gt;0.05$ 4.950</td>
<td>$p&gt;0.05$ 11.371</td>
</tr>
<tr>
<td>Sr</td>
<td>$p&gt;0.05$ 6.129</td>
<td>$p&gt;0.05$ 2.796</td>
</tr>
<tr>
<td>Mn</td>
<td>$p&lt;0.05$ 0.070</td>
<td>$p&gt;0.05$ 2.183</td>
</tr>
<tr>
<td>Na</td>
<td>$p&gt;0.05$ 6.253</td>
<td>$p&gt;0.05$ 3.844</td>
</tr>
<tr>
<td>Fe</td>
<td>$p&gt;0.05$ 1.990</td>
<td>$p&lt;0.05$ 0.485</td>
</tr>
<tr>
<td>D.O.F.</td>
<td>(130)</td>
<td>(113)</td>
</tr>
<tr>
<td>Mediospirifer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>$p&lt;0.05$ 1.225</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>$p&gt;0.05$ 3.984</td>
<td></td>
</tr>
<tr>
<td>Sr</td>
<td>$p&gt;0.05$ 2.369</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>$p&gt;0.05$ 2.572</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>$p&gt;0.05$ 2.182</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>$p&gt;0.05$ 2.138</td>
<td></td>
</tr>
<tr>
<td>D.O.F.</td>
<td>(105)</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.4. T-test: Dimissa Bed (Wanakah Shale) unaltered brachiopods

<table>
<thead>
<tr>
<th>Element</th>
<th>Mucrospirifer</th>
<th>Mediospirifer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Athyris</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>$p&lt;0.05$ 0.074</td>
<td>$p&lt;0.05$ 0.482</td>
</tr>
<tr>
<td>Mg</td>
<td>$p&gt;0.05$ 3.694</td>
<td>$p&gt;0.05$ 4.340</td>
</tr>
<tr>
<td>Sr</td>
<td>$p&gt;0.05$ 6.045</td>
<td>$p&gt;0.05$ 0.797</td>
</tr>
<tr>
<td>Mn</td>
<td>$p&lt;0.05$ 1.057</td>
<td>$p&lt;0.05$ 0.688</td>
</tr>
<tr>
<td>Na</td>
<td>$p&gt;0.05$ 3.696</td>
<td>$p&lt;0.05$ 1.601</td>
</tr>
<tr>
<td>Fe</td>
<td>$p&gt;0.05$ 1.468</td>
<td>$p&lt;0.05$ 1.473</td>
</tr>
<tr>
<td>D.O.F.</td>
<td>(32)</td>
<td>(29)</td>
</tr>
<tr>
<td>Mediospirifer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>$p&lt;0.05$ 0.452</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>$p&gt;0.05$ 1.771</td>
<td></td>
</tr>
<tr>
<td>Sr</td>
<td>$p&gt;0.05$ 3.016</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>$p&lt;0.05$ 0.134</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>$p&lt;0.05$ 2.045</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>$p&lt;0.05$ 0.453</td>
<td></td>
</tr>
<tr>
<td>D.O.F.</td>
<td>(23)</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.9. The mean and standard deviations of unaltered elemental chemistries of three Hamilton Group brachiopod genera.
nucleation sites (Fig. 3.10; Simkiss, 1976; McConnaughey, 1989b). Slightly different physiological systems may have directly controlled Mg contents in extracellular fluids which in turn may influence the amount of Mg incorporated into shell calcite. Alternately, differential brachiopod growth rates, in association with changing partition coefficients of Mg, could conceivably have controlled the resultant incorporation of Mg from extracellular fluids.

Fractionation of Sr.

Inorganic low-Mg calcite precipitated in equilibrium with ambient seawater is postulated to contain about 1000ppm of Sr (Veizer, 1983a). Hamilton Group spirifers contain Sr contents close to apparent equilibrium conditions (means 850-980ppm Sr; Table 3.1), but there are significant differences between species. *Mucrospirifer mucronatus* incorporates more Sr compared to *Athyris spiriferoides* and *Mediospirifer audacula*. Consequently, this suggests there are taxonomic differences in the physiological or secretory regimes controlling Sr composition. Sr fractionation may be influenced by relative precipitation rates since the partition coefficient (D) of Sr increases with precipitation rates. Furthermore, there appears to be competition between Sr$^{2+}$ and Mn$^{2+}$ for lattice and non-lattice sites (Mucci, 1988). The Sr and Mn contents of Hamilton Group spirifers are inversely related which suggests that there is a fractionation relationship between these elements. Similar trends were seen in the chemistries of some aragonitic molluscs (Fig. 7; p. 152; Rosenberg, 1980). This has implications for the evaluation of Mn chemistries of any ancient brachiopod shell calcite. If Mn is preferentially fractionated by the organism for the purpose of incorporation as a structural component of shell calcite, Mn concentrations may not therefore, singularly represent redox conditions of the environment, diagenetic compositions or the presence of soluble iron oxides.
Figure 3.10. Routes of elemental transport from the external environment toward the site of carbonate secretion. The flux of Ca and minor/trace elements is controlled by a calcium pump in the epithelial membrane and the enzyme Calcium ATPase (Alberts et al., 1983; Rega, 1987). Na is osmo-regulatorily controlled by Na-K pumps, and Na incorporation into shell calcite is partly dependant on amount of crystal lattice defects present. Modified from McConnaughey (1989b).
Fractionation of Na

Sodium contents of inorganic low-Mg calcite, precipitated in equilibrium with ambient seawater, range from 100-300ppm (Milliman, 1974), whereas Na contents in modern brachiopods, range from 500 to 3600ppm (Brand, 1989a; Morrison and Brand, 1987). Mean Na contents of Hamilton Group brachiopods range from 1250ppm to 1560ppm, which is indicative of preferential incorporation of Na into brachiopod calcite. This concurs with the Brand and Veizer (1980) observation of biological Na fractionation in fossil brachiopods.

Taxonomic differences of Na content are evident in Hamilton Group brachiopods (Tables 3.1; 3.3; Fig. 3.9). Na incorporation into biogenic carbonates may be a function of either solid solution with the calcite lattice (Fritz and Katz, 1972; Land and Hopps, 1973; White, 1977); leaching from the aluminosilicate fraction; or in fluid inclusions (Al-Aasm and Veizer, 1986). Na contents in artificial calcites were smaller by factors of 20 than for biogenic calcites (White, 1978). The presence of organics may be responsible for the higher levels in biogenic carbonates (White, 1978) but Iskikawa and Ishikuni (1984) report similar Na levels between synthetic and biogenic calcites. However, the amount of Na may be dependant on the number of defects in the calcite lattice (Busenberg and Plummer, 1985). The number of defects increase with precipitation rate resulting from the substitution of Ca$^{2+}$ by other cations (Mucci, 1988). Skeletal carbonates contain minute fluid inclusions in amounts that range from a few tenths of a percent to 2-3% by weight (Gaffey, 1985). The number of fluid inclusions is higher in aragonite nacreous layers than the prismatic low-Mg calcite layers of molluscs (Towe and Thompson, 1972), and may partly explain the higher Na contents of aragonitic carbonate.

Although sodium pumps in epithelial membranes probably regulated Na contents in extracellular fluids (Fig. 3.10), taxonomic controls of Na may not
necessarily be a reflection of different extracellular fluid compositions between species. Differential growth rates, thus calcite precipitation rates, may have controlled the amounts of Na within shell calcite of Hamilton Group brachiopods. Higher growth rates may increase Na incorporation into shell calcite by increasing lattice defects.

**Relationship of shell chemistry to biofacies and environmental parameters**

Evaluation of pristine brachiopod calcites from the Wanakah Shale Member (Ludlowville Formation) in western Erie County (New York State) suggests that there may be a relationship between depth and the incorporation of Mg, Sr and Na into shell calcites (Fig. 3.11). The spatial distribution of Ludlowville Formation brachiopods and idealized biofacies can be related to environmental parameters such as relative depth and turbidity (Fig. 3.1; Brett and Baird, 1986). Several distinct brachiopod associations were sampled throughout the Wanakah Shale Member, representative of the various offshore (deepest) to nearshore (shallowest) biofacies. Among the horizons and shell beds sampled, brachiopods were analysed from the deepest *Ambocoelia* association (3A), the *Athyris spiriferoides* (4A) and *Mucrospirifer mucronatus* -chonetid (4B) associations and from the shallowest winnowed shell beds, containing a high diversity of brachiopods species belonging to the *Pseudoatrypa* (5A) or *Tropidoleptus carinatus* (5B) brachiopod associations.

Taxonomic differentiation of elemental fractionation is observed within single shell bed analysis of *Athyris spiriferoides*, *Mucrospirifer mucronatus* and *Mediospirifer audacula* calcites (Fig. 3.11), confirming earlier statements. Overprinting this taxonomic control is an environmental control on shell calcite composition. Chemically, *Athyris spiriferoides* calcite, from the shallow
Figure 3.11. Mean and standard deviations of unaltered brachiopod elemental chemistries related to brachiopod biofacies and depth (Brett et al., 1986). Brachiopods are sampled from the Wanakah Shale (Hamilton Group) of Erie County, New York State. Specific beds are listed in Fig. 3.4 and Appendix I whereas the relationship of biofacies associations to environmental parameters are identified in Fig. 3.1.
*Tropidoleptus carinatus* association (5B) contains significantly higher Mg, Sr and Na contents than *Athyris spiriferoides* calcites from the deeper *Athyris spiriferoides* association (4A), which in turn are higher than those from the deepest *Ambocoelia* -chonetid association (3A). This chemical trend is repeated for *Mucrospirifer mucronatus* and *Mediospirifer audacula*. Thus, the incorporation of Mg, Sr and Na into brachiopod calcite appears to be in part dependant upon depth. The cause of this relationship is difficult to determine, since there is no empirical data on chemical variations with depth within modern brachiopod populations. It may conceivably be a function of: different secretory regimes; the relationship between functional morphology, structural requirements and mineral morphology of the shell structure within any given habitat; growth and maturation rates; and physiological needs of the organism. Slower growth rates, for example, whether caused by a combination of depth, less particulate matter, cooler temperatures or oxic conditions, could result in reduced incorporation of Sr ($D_{Sr}$ increases with precipitation rates; Lorens, 1981; Mucci 1988). Moreover, there may have been more time for the organism to actively discriminate against Mg, either at nucleation sites or within the extracellular fluids. Furthermore, reduced precipitation rates of calcite may have decreased the percentage of lattice defects and, as a consequence, Na contents would presumably be lower. Tunnicliffe and Wilson (1988) report that populations of the modern brachiopod *Terebratulina*, in depths of over 80m and within a marginally aerobic environment, are significantly smaller than shallower populations (this presumably is the result of reduced metabolism and slower growth rates). Despite the uncertainty of its cause, this chemical relationship has implications for the use of brachiopod calcite in paleoenvironmental investigation, since it may be possible to predict relative depths from shell calcite chemistry. Further chemical and isotopic testing of
brachiopods within these beds and associations is required to confirm this scenario.

Isotopic Trends

The control of elemental contents in Hamilton Group spirifers may be related to growth rates. Similarly, growth rates may also influence the isotopic compositions of brachiopods, since "kinetic" disequilibrium is dependant on growth/calcification rates (McConnaughey, 1989a). There appears to be no significant difference between the isotopic values of pristine Mediospirifer audacula and Athyris spiriferoides shell calcites of the Hamilton Group (t-test, p>0.05, f=22). However, factor analysis correlates Mg, which is taxonomically controlled, with δ¹⁸O and δ¹³C (Factor 2; Table A-15), although this is not evident in the unrotated correlation matrix and may be an analytic artifact.

A potential vital effect of 4-5‰ was observed in δ¹³C for three specimens of a modern brachiopod Argyrotheca bermudana from the Bermuda Platform (Wefer, 1985). The analysed brachiopods were collected from Walsingham Pond and are isotopically light (-0.41‰, δ¹³C; p. 70) compared to waters and substrate (+1.9-2.1‰, δ¹³C and +3.6-4.4‰, δ¹³C; p. 18; Wefer, 1985). However, the water and substrate isotopic analyses come from Harrington Sound, Bermuda and these two inshore water settings are very different (for discussion of substrate, salinities, temperature see Morris et al., 1977; Barnes and Bodungen, 1978; Bodungen et al., 1982). Harrington Sound is an enclosed marine lagoon with a water residence time of about 150 days and coarse carbonate eolianite substrates. Seasonal temperature, oxygen and density stratifications occur annually (Morris et al., 1977). In contrast, Walsingham Pond, is an enclosed mangrove swamp, connected to Castle Harbour lagoon by only a small boat cut (Logan, 1975; pers. obs. 1986). The
Argyrotheca community is a relict population existing marginally within the landlocked Walsingham pond. Isotopically-light organic muds derived from mangrove decomposition, may explain the light $\delta^{13}C$ values observed in shell calcite by Wefer (1985). Isotopic analysis of coeval waters, substrate and brachiopods from Walsingham Pond, needs to be done to confirm this assertion. Moreover, in small brachiopods (< 5-7mm), 70-80% of the total organic matter is located within the shell (Peck et al., 1987) and the organic matrix may have significantly contributed to isotopic analysis of the diminutive Argyrotheca (<2mm; Logan, 1975; Sterrer, 1986).

Modern brachiopods appear to be oxygen minimal organisms (Thayer, 1981) which metabolize very slowly (Rosenberg et al., 1988). The calcification process is essentially a "kinetic" disequilibria process. However, slow precipitation rates reduce the isotopic displacement due to kinetic disequilibria since isotopic exchange can quickly equilibrate internal extracellular DIC with external DIC prior to calcification (McConnaughey, 1989a; 1989b). Assuming slow metabolic and precipitation rates for ancient brachiopods, it is likely that brachiopod shell-calcite was secreted in isotopic equilibrium with ambient conditions. Therefore, if altered specimens are eliminated from the analysis, shell calcite should reflect ambient physical and chemical parameters, such as temperature, salinity and composition of oceanic isotopic reservoir. The following discussion will assume that brachiopods incorporated isotopes essentially in equilibrium with ambient conditions.

**CHEMICAL TRENDS WITHIN THE "DEMissa ' BED**

Shell beds are recognized in the Hamilton Group and many are persistent across western New York State for tens of kilometres (Figs. 3.2, 3.4).
Detailed taphonomic analysis of these mudstone beds suggest they are the result of storm winnowing and episodically blanketed by rapid deposition of muds (Parsons et al., 1988). The shell beds may represent accumulations of long duration (10-1000 years) and many of these beds have complex internal geometries (e.g., Smoke Creek Bed, lower Windom Shale Member; Speyer and Brett, 1985). The "Demissa" Bed, an upper Wanakah shell bed, is recognized across western New York, from the Lake Erie to the Genessee Valley, a distance of 120-130 km. This complex shell bed (10-15cm thick) is an amalgamation of lenticular, simple shell beds separated by thin, grey bioturbated peloidal mudstones (Brett et al., 1986).

In Erie County, the bed contains a diverse brachiopod fauna (e.g., epibenthic spirifers Mediospirifer audacula, Mucrospirifer mucronatus, Athyris spiriferoides; Ambocoelia umbonata, Devonochonetes, Pseudoatrypa; Stropheodonta, reclining orthids Tropidoleptus carinatus, Rhipidomella vanuxemi) which correspond to the relatively shallow Pseudoatrypa association (5A; Fig. 3.1) of Brett and Baird (1986). Articulation ratios are high but variable between species. Many brachiopods are closed and show few signs of abrasion or corrosion. In the Genessee Valley, the bed is less fossiliferous and is dominated by Athyris spiriferoides and Mediospirifer audacula, comprising a deeper water assemblage (Athyris, 4A). Articulation ratios remain high and many individuals are found in life position. This bed may represent brachiopod patch communities across the shelf, which were episodically winnowed and buried by muds. The fact that articulation ratios are high, implies that there has been little or no transport within the "Demissa" Bed. This bed fits the criteria for an autochthonous (in place assemblage) or parautothothonous (sensu Aigner 1985) winnowed coquinite (Brett et al., 1986; Parsons et al., 1988). The depositional setting of this bed deepens west to east.
towards the basin depocentre, which is centred around Seneca and Cayuga Lakes. As such, it provides a time correlative model for testing elemental and isotopic trends across a deepening shelf.

**Chemical trends**

Pristine brachiopods of the "Demissa" Bed illustrate several inherent taxonomic and environmental differences. The Mg contents of shell calcite within this bed are taxonomically controlled (Table 3.4, 3.5; Fig. 3.12). Although Mg varies within this shell bed, *Athyris spiriferoides* shell calcite always contains more Mg than *Mucrospirifer mucronatus* calcite, which in turn contains more than *Mediospirifer audacula*. Similarly, *Mucrospirifer mucronatus* shell calcite always contains more Na and Sr than co-occurring *Athyris spiriferoides* calcite. The Na contents of *Mucrospirifer mucronatus* across the shelf are significantly greater than either *Athyris spiriferoides* or *Mediospirifer audacula*. It is apparent that *Mucrospirifer mucronatus* selectively incorporated Na when compared to other co-occurring species. However, it is difficult to ascertain whether this is related to either different physiological systems controlling the composition of the extracellular fluid, the mineral morphology and percentage of lattice defects or if Na is involved as structural component of shell calcite.

Previously, it was observed that the decreasing Mg, Sr and Na contents of *Athyris spiriferoides, Mediospirifer audacula* and *Mucrospirifer mucronatus* are related to increasing depth. The "Demissa" bed is essentially autochthonous and brachiopod shell calcite should reflect a significant deepening across the shelf. However, the Sr, Fe and Mn contents remain fairly constant across the shelf, while brachiopods from the deepest locality (20) are not depleted in Na or Mg. If we assume that the relationship of depth and incorporation of Mg, Sr and Na can be applied to this situation, the lack of
Figure 3.12. Mean and standard deviation of unaltered chemistries; *Athyris* and *Mucrospirifer* from the "Demissa" Bed across the Hamilton Group shelf. Locality data in Appendix III.
<table>
<thead>
<tr>
<th>Brachiopod species</th>
<th>Stat.</th>
<th>Ca</th>
<th>Mg</th>
<th>Sr</th>
<th>Mn</th>
<th>Na</th>
<th>Fe</th>
</tr>
</thead>
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<td>Mean</td>
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<td>171</td>
<td>1258</td>
<td>262</td>
</tr>
<tr>
<td>UNALTERED</td>
<td>Std. Dev.</td>
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<td>238</td>
<td>65</td>
<td>45</td>
<td>216</td>
<td>170</td>
</tr>
<tr>
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<td>246830</td>
<td>845</td>
<td>770</td>
<td>80</td>
<td>840</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>max</td>
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<td>1820</td>
<td>1035</td>
<td>250</td>
<td>1600</td>
<td>690</td>
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<tr>
<td><strong>Mucrospirifer</strong></td>
<td>Mean</td>
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<td>338</td>
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<tr>
<td>UNALTERED</td>
<td>Std. Dev.</td>
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<td>136</td>
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<td>240</td>
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</table>

All elemental concentrations are in ppm.
significant elemental trends suggests that either the depth changes were not
great, or that there are other unrecognized contributing factors. The chemical
changes recognized within the vertical Wanakah Shale sequence were related
to transitions from the deeper *Mucrospirifer* association (3A) to the shallow
*Tropidoleptus carinatus* association (5B). Within the "Demissa " Bed, the
environmental conditions controlling the distribution of the *Pseudoatrypa* (5A)
and *Athyris spiriferoides* (4A) associations may not be significantly different.
The chemical variation observed in "Demissa " bed brachiopods may reflect
slight changes in a number of inter-related factors such as temperature, salinity,
seawater composition, growth/calcification rates and inherent chemical
variability of a population.

The chemical variation observed within the shell bed may reflect a slight
salinity, temperature and ambient seawater elemental compositions may be
slightly different between sites. The Mg contents of Paleozoic brachiopods have
been attributed to different seawater chemistries (Brower, 1978). In molluscan
carbonate the incorporation of Sr and Mg is dependant on temperature (see
Rosenberg, 1980), while Sr contents of shell calcite may be directly controlled
by concentrations within external seawater (Rosenberg, 1980; Morrison and

**Isotopic trends**

An apparent deepening across the Hamilton shelf is reflected in the
isotopic values (Fig. 3.13). "Demissa " bed brachiopods close to the basin
depocentre (Genesse Valley) are heavy for carbon (+4.8‰, δ¹³C) and oxygen
(-3.0‰, δ¹⁸O) compared to those in the west (Erie County; +2.4-3.0‰, δ¹³C; -
3.5-4.6‰, δ¹⁸O). The isotopic depositional trends between depocentre and
shallower reaches of the basin are repeated for Jaycox, Deep Run and
Figure 3.13. Isotopic compositions of *Athyris* and *Mediospirifer* brachiopods from the Hamilton Group. Sample numbers are listed in Appendix III.
Kashong brachiopods (Fig. 3.13) and during deposition of these units the basin depocentre was located in the Genesee Valley region. If we assume there were no salinity changes across the shelf, this isotopic trend may indicate that the bottom waters were cooler and depleted in organic matter toward the basin centre (Genesee Valley) during the deposition of the shell bed. The "Demissa" bed bottom waters to the west were apparently warmer and contained more light carbon. Alternately, this isotopic trend may be related to other environmental conditions such as density, oxygen or temperature stratification of the basin waters. Transition of facies from grey to black shales toward the basin axis suggests that this semi-restricted basin may have been subject to temperature, salinity and oxygen stratification. There is evidently a large variation in isotopic values within the same bed (about 1.5-2.5‰, δ¹³C; and 0.5-1.5‰, δ¹⁸O). This has significant implications for interpretations of secular changes in Paleozoic oxygen and carbon reservoirs since many trends are based on smaller isotopic shifts (e.g., Adlis et al., 1988). If isotopic analyses are not constrained by sedimentological and paleoecological parameters, secular trends may only represent onshore-offshore isotopic trends. Isotopic variability throughout geologic time, must therefore, be evaluated with extreme care.

**PALEOENVIRONMENTAL ANALYSIS OF THE LOWER WINDOM SHALE**

Windom Shale brachiopods were sampled from the lowest two metres at Eighteen Mile Creek and Penn Dixie Quarry (localities 3, 6). At Eighteen Mile Creek, a thin sequence of dark-grey, *Ambocoelina* dominated shales overlie the calcarenite Tichenor Member. Associated with these pavements are small, juvenile, closed and articulated *Mucrospirifer mucronatus* and *Athyris*
Overlying these beds are the bioturbated coral-rich Bay View Bed mudstones. Supraadjacent shale beds correspond to a general deepening transition from the shallow coral-rich Bay View Bed, to calcareous shales of a complex shell bed (Smoke Creek Bed) to deeper dark-grey ambocoellid-chonetid dominated shales of the Middle Windom Member (Speyer and Brett, 1985). Laterally this sequence is restricted between Lake Erie and Cazenovia Creek, whereas the Smoke Creek Bed outcrops across western New York as far as Fall Brook Falls, Geneseo (Locality 19).

Chemical trends

Three separate fields of chemically pristine brachiopods, corresponding to different horizons, can be observed (Fig. 3.14) and may reflect potentially oxygen depleted, reducing conditions. Brachiopods from the ambocoellid dominated, dark shale plot with significantly higher Fe and Mn contents than those from the Bay View and Smoke Creek Beds (Fig. 3.14). These ambocoellid pavements are interpreted by Brett and co-workers to belong to a deeper and potentially more dysaerobic brachiopod biofacies (Ambocoelia - chonetid; 3A; Fig. 3.1; Brett et al., 1986; Miller, 1986; Grasso, 1986). The bioturbated Bay View Bed with a diverse association of brachiopods and corals represents a much shallower biofacies association (Fig. 3.1; Pseudoatrypa : 5A). The majority of Mediospirifer audacula and Pseudoatrypa are disarticulated, whereas Rhipidomella vanuxemi are commonly articulated. The Smoke Creek bed is a complex shell bed that may represent a rapid depositional event (Speyer and Brett, 1985; Parsons et al., 1988) and analysed brachiopods from subunit C are predominantly articulated and non-splayed. Chemically, the brachiopods reflect the apparent shallowing facies transition from lowest Windom dark ambocoellid shales into the Bay View Bed. Although these
Figure 3.14. Scatter plot of Fe vs Mn for Lower Windom brachiopods from western New York State.
brachiopod biofacies are generalized and transitional (Brett et al., 1986), the Mn and Fe chemical data supports the paleoecological inferences, particularly of brachiopod associations in potentially more oxygen depleted environments.

**Isotope trends of the Lower Windom Shale**

Brachiopods from the Bay View Bed are isotopically enriched in $^{13}$C (+3.70‰ $\delta^{13}$C) relative to those from the ambocoeliid pavements which are isotopically lighter (+1.93‰ $\delta^{13}$C). Strict interpretation of biofacies would suggest that the ambocoeliid dominated beds were probably deeper, cooler, and within bottom waters tending to dysaerobia. However, isotopic analysis suggests the opposite. Lighter carbon values in the ambocoeliid bed indicate that these beds were more organically rich, and organic content usually declines with depth (Fürsich and Hurst, 1980). Oxygen isotopic data is more negative in the ambocoeliid beds ($\delta^{18}$O; -3.97‰) than the Bay View Bed ($\delta^{18}$O; -3.01‰) and paleotemperature analysis suggests that the Bay View Bed waters (25-30°C) were much cooler than the ambocoeliid layer waters (30-35°C) and thus potentially deeper. This contradicts the physical parameters inferred from biofacies associations. Conceivably, the ambocoeliid brachiopod community at this site, may represent a shallower, warmer water association. However, the presence of oxygen depleted bottom waters may have allowed only the colonization of slight dysaerobia-tolerant brachiopods such as *Ambocoelia*, and limited growth of small spiriferids. Subsequently, cooler and less organic rich, but more aerobic bottom waters, may have promoted the colonization of a diverse faunal association found in Bay View Bed. The dysaerobic *Leiorhynchus* brachiopod communities recognized in the Middle Devonian sediments of New York State (Kammer et al., 1986; Thompson and Newton, 1986), may not be depth dependant *sensu strictu*, but anoxia bottom
water dependant. More study is required into the isotopic composition of brachiopods and the redox, depth relationships of ambient seawater.

PALEOENVIRONMENTAL ANALYSIS OF THE KASHONG SHALE

Two stratigraphic horizons within the Kashong Shale (Moscow Formation) were sampled to investigate possible chemical difference between them. Sparsely fossiliferous dark-grey fissile shales and thin wackestones of the Lower Kashong Shale are exposed at Eleven Mile Creek (Fig. 3.2; locality 13A) and are dominated by *Mediospirifer audacula* brachiopods in association with *Athyris spiriferoides*, *Ambocoelia* and *Strophomena* (4A biofacies; Fig. 3.1). Closed, unabraded brachiopods and articulated crinoid stems and trilobites (e.g., *Phacops rana*) attest to the quiet water habitat, minimal disturbance and autochthoneity of this fauna. Upper Kashong Shales outcrop at Retsof (Brett and Cottrell, 1982; locality 18) and consist of light grey shales with diverse crinoid, trilobite and brachiopod faunas dominated by *Tropidoleptus carinatus*. Articulation ratios are low and many valves show evidence of abrasion which suggests that they may have been transported. This brachiopod assemblage corresponds to a shallow water *Tropidoleptus carinatus* biofacies (5B; Fig. 3.1).

Elemental contents of biogenic calcites from the Kashong Shale are variable reflecting a range of chemically unaltered to altered specimens. Metastable high-Mg calcite crinoids are extensively altered and chemically similar to matrix compositions (Fig. 3.15). The open meshwork structure, typical to crinoids (Bathurst, 1975; Brand and Morrison, 1987b; Brand 1987), may have promoted fluid controlled reactions and extensive dissolution-reprecipitation events. The chemistry of altered brachiopods is variable and may be related to lithological availability of Fe and Mn in diagenetic waters, redox conditions of the diagenetic fluids and the pore geometry of the host lithology and shell.
Figure 3.15. Scatter diagram of Fe vs Mn contents of upper and lower Kashong Shale Member brachiopods (upper Hamilton Group). Each field represents pristine brachiopod compositions.
Punctae within the shell calcite of *Tropidoleptus carinatus* probably facilitated pore filling and chemical alteration.

Despite the similarity of Na and Mg chemistries within pristine brachiopod calcites, there are significant differences in Fe and Mn contents (Fig. 3.15). An apparent relationship is recognized between the depth controlled biofacies associations and concentrations of Fe and Mn. Enriched Mn and Fe contents of the Lower Kashong brachiopod calcite can be explained if there was increased availability of Fe and Mn for incorporation into shell calcite. These elements are redox controlled and potentially oxygen depleted bottom waters may have partially controlled shell calcite compositions. The semi-restricted Appalachian Basin was centred around the Genesee Valley area during deposition of the Kashong Shale. Marginally placed brachiopod communities, close to the oxycline- pycnocline, may have been periodically exposed to oxygen depleted waters. In contrast, the Fe and Mn contents of brachiopod shell calcites from the shallow, turbulent *Tropidoleptus carinatus* association (Upper Kashong) appear to reflect fully aerobic conditions.

**HUNGRY HOLLOW, WIDDER AND ARKONA FORMATIONS**

*Mucrospirifer mucronatus* were collected from the Hungry Hollow section at Arkona, southern Ontario (locality 1) and show clear alteration trends towards the chemistries of matrix and cement samples (Fig. 3.16). Samples within the general field represent Fe and Mn compositions of unaltered brachiopods. This data encompasses brachiopods collected from dark grey shales of the Arkona, Hungry Hollow and Widder Formation (Appendix I). Chemical evaluation of the unaltered field suggests that redox conditions may have controlled Fe and Mn distribution in *Mucrospirifer mucronatus*. Specimens from the light grey calcareous shales of the Widder Formation plot with the lowest Fe and Mn
Figure 3.16. Scatter plot of Fe vs Mn for *Mucrospirifer* brachiopods from the Arkona, Hungry Hollow and Widder Formations (Middle Devonian). Unaltered *Mucrospirifer* fields are denoted by A (Arkona Fm.); H (Hungry Hollow Fm.); and W (Widder Fm.). *Mucrospirifer* plotting outside these fields, show evidence of minor dissolution and reprecipitation of cements. Alteration of brachiopods becomes progressively more fluid-controlled toward matrix and cement chemistries. Additional data from Popp et al., (1986b) and L. Wassenaar (1986; unpublished data)
contents, whereas brachiopods from the grey shales of the Hungry Hollow and Arkona Formations have higher Fe contents. The upper Arkona Formation is interpreted as a marginally aerobic to dysaerobic setting (Landing and Brett, 1987) because of the presence of syngenetic pyrite and the lateral transition of the Arkona grey claystones into the dark grey/black shales of the Appalachian Basin. At Hungry Hollow, *Mucrospirifer mucronatus* are predominantly articulated perhaps indicative of quiet, deeper soft substrates of the Upper Arkona. The divergence of Fe and Mn chemistry in *Mucrospirifer mucronatus* may reflect the Eh of the depositional waters.

Individual specimens of *Mucrospirifer mucronatus* falling just outside this unaltered field have slightly elevated Mn and Fe contents although their Sr, Mg and Na chemistries are not concurrently depleted (Figure 3.16, 3.17). Shell calcites may have either undergone slight alteration, contain soluble iron oxide coatings or the Fe/Mn compositions reflect depositional conditions. *Mucrospirifer mucronatus* sampled from a thin skeletal-packstone limestone bed, of the lower Arkona Formation, have significantly different chemistries compared with *Mucrospirifer mucronatus* sampled from shales. Brachiopods in these thin, episodic tempestites (Landing and Brett, 1987) are monotypically *Mucrospirifer mucronatus*, disarticulate and abraded. The magnitude of re-equilibration and reaction toward cement and matrix chemistry indicates a fluid-controlled diagenetic regime. Therefore, grain size and pore geometry (see discussion Pingitore, 1976, 1982) has significantly influenced the potential of brachiopod LMC to resist alteration.

**Brachiopods and lower oxygen conditions**

Recent studies of modern brachiopod metabolism, secretory mechanisms and environmental tolerances (Doherty, 1981; Curry, 1982;
Figure 3.17. Scatter plot of Na vs Mg for *Mucrospirifer* brachiopods from the Arkona, Hungry Hollow and Widder Formations (Middle Devonian). Unaltered *Mucrospirifer* fields are denoted by A (Arkona Fm.); H (Hungry Hollow Fm.); and W (Widder Fm.). *Mucrospirifer* plotting outside these fields, show evidence of minor dissolution and reprecipitation of cements. Additional data from L. Wassenaar (1986; unpublished data)
Shumway, 1982; Thayer, 1986a, b; Peck et al., 1987; Rosenberg et al., 1988; Hiller, 1988) augment our understanding of chemical and isotopic trends observed in ancient brachiopod shell calcite. The increased Mn and Fe contents of Hamilton Group shell calcites from the deeper parts of the basin may reflect periodic oxygen-deficient conditions in the Appalachian Basin.

Brachiopods have very low rates of oxygen extraction (0.76 mL·h⁻¹) when compared to bivalves (Doherty, 1981). They have a low pumping ability but are either oriented toward or can actively orient themselves toward currents (LeBarbera, 1977; 1978; 1981b; Richardson, 1981c). Furthermore, some modern species are capable of anaerobic metabolism (Hammen, 1977; Peck et al., 1989) and can function with depressed metabolic rates for considerable lengths of time (Shumway, 1982). Moreover, several modern brachiopod species thrive in areas where dissolved oxygen levels are periodically below 0.1 mL·L⁻¹ (Saanich Inlet; Tunnicliffe and Wilson, 1988) and under potentially reduced water conditions (Nissenbaum et al., 1972; Presley et al., 1972). Thus these species are able to survive within dysaerobic environments as defined by Rhoads and Morse (1971) and modified by Thompson et al. (1985). In the Appalachian Basin, during deposition of the Hamilton Group, a number of species (e.g. Leoirhynchus and Ambocoelia) inhabited relatively shallow (50-100 m depth; Brett and Baird, 1986a) dysaerobic black shale environments (Thompson and Newton, 1986; Kammer et al., 1986; Miller, 1986). Many of the deeper brachiopod biofacies are transitional with these permanent dysaerobic communities. The presence of black shales and semi-restricted circulation suggests that the basin waters were probably stratified (Kammer et al., 1986; Witzke, 1987). The development of a relatively shallow oxycline/pycnocline, as the result of organic decay (anoxia can develop within depths of only 10-15 metres; Devils Hole; Morris et al., 1977) and/or surface biological productivity
(Demaison and Moore, 1980) is indicated. Many of the brachiopod communities were marginally placed to these oxygen-depleted waters and it is conceivable that fluctuation of the oxycline may have periodically pushed low-oxygen waters into shallower habitats. As with modern brachiopod populations (Tunnicliffe and Wilson, 1988), the community structure and depth patterns of Hamilton Group brachiopods (evidenced by the vertical and lateral faunal successions of *Leiorhynchus* to *Ambocoelia* to *Mucrospirifer mucronatus* dominated associations etc.) may have changed in response to longer-term shifts in oxic conditions.

The chemical composition of shell calcite is 'time-averaged' and as such encompasses potentially variable external conditions within a lifespan of 5-10 years (Paine, 1969). If we assume that Mn and Fe contents in shell calcites reflect "time-averaged" redox conditions, brachiopod calcite will reflect episodes of oxygen-deficiency, despite the lack of permanent anoxic conditions. Brachiopods would have continued to metabolize during low oxygen conditions and transport divalent ions (e.g. reduced Mn and Fe) across epithelial membranes to nucleation sites of shell calcite. Further study of modern brachiopods within marginally dysaerobic environments (e.g., *Terebratulina*, Saanich Inlet) and of ancient faunal successions in black shales (e.g., *Leiorhynchus* in Geneseo Shale, central New York State) is required to confirm a redox and low oxygen control of Mn and Fe contents in shell calcite.

**CONCLUSIONS**

The majority of brachiopod shell calcites of the Hamilton Group are microstructurally and chemically well preserved. A few altered specimens re-equilibrated in the presence of meteoric-mixed waters. Analysis of pristine calcites from three co-occurring spiriferid species suggests that Mg, Na, Sr
contents were fractionated into shell calcite. Moreover, an inherent taxonomic difference in Mg contents is observed between *Athyris spiriferoides*, *Mucrospirifer mucronatus* and *Mediospirifer audacula*. This hierarchical differentiation of elemental contents into shell calcite is repeated in each shell bed or mudstone horizon studied. Similarly, a taxonomic control of Sr and Na is observed and may reflect complexities of slightly different physiological systems, secretory mechanisms and mineral morphologies. Furthermore, analysis of these brachiopods from different biofacies associations in the Wanakah Shale indicates that there is an inverse relationship of Mg, Sr and Na incorporation into shell calcite with relative depth of the brachiopod habitat. This chemical relationship is potentially related to slower calcification rates in deeper waters promoting the active discrimination against Mg and Sr and reducing Na incorporation into lattice defects.

Analysis of *Athyris spiriferoides* and *Mediospirifer audacula* from a persistent Wanakah Shale shell bed indicates that there is large variation in isotopic values within a single bed. Isotopic values from deeper basinal brachiopod calcites are more positive by 1.5-2.50/oo d18O and 0.5-1.50/oo d13C than calcites of shallower brachiopods. Similarly, shifts in isotopic values of brachiopods from the Lower Windom Shale also reflects changes in environmental conditions between suprajacent depth controlled brachiopod associations. A significant proportion of secular variation of 18O and 13C isotopes through time may reflect unrecognized depth-controlled onshore-offshore trends.

Analysis of pristine brachiopods from the Windom, Kashong, Widder, Arkona and Hungry Hollow Formations indicates that Mn and Fe contents are not a result of diagenetic alteration but a reflection of possible fractionation and complex chemical environments. Brachiopod calcites analysed from deeper
and apparently dysaerobia-tolerant communities contain elevated Mn and Fe contents compared to brachiopods in shallower habitats. Fluctuation of the oxycline and incursions of low oxygen waters in the semi-restricted stratified basin may have influenced marginally positioned communities, controlling faunal succession and the incorporation of redox controlled elements.
CHAPTER 4

Diagenetic and paleoenvironmental study of brachiopod calcite from the Clinton Group (Middle Silurian); western New York State and southern Ontario.
INTRODUCTION

Ancient brachiopods are assumed to have incorporated oxygen and carbon isotopes into shell calcite in equilibrium with ambient external conditions (Lowenstam, 1963; Veizer et al., 1986; Popp et al., 1986a; Brand, 1989a). Moreover, since the fractionation of oxygen isotopes into biogenic carbonates is reported to be temperature and salinity dependant (Epstein et al., 1953; Faure, 1983), chemically pristine shell calcite can potentially be used to retrieve information about salinity, temperature and depth changes within specific environments. Recently, brachiopod calcite of Crurithyris was analysed from two Pennsylvanian cyclothsms in the Midland Basin, Texas, and isotopic shifts were suggested by Adlis et al. (1988) to be the result of relative depth changes of approximately 70m. Similar changes within recognized transgressive-regressive cycles should be recorded in other brachiopod shell calcite.

In Middle Silurian strata of western New York State and Ontario, a transgressive-regressive cycle is sedimentologically and paleoecologically reported in the Lewiston Member of the Rochester Shale Formation (Brett, 1983a). The Rochester Shale contains some of the best taphonomically preserved fossils in North America (Brett, 1983) and the abundance of brachiopods (notably Eospirifer radiatus) throughout the section allows the study of elemental and isotopic changes within this vertical sequence. Furthermore, previous studies have indicated that the Silurian oceans were depleted in $^{18}O$ by about 5.5‰ (Brand and Veizer, 1981; Veizer et al., 1986; O'Shea et al., 1988). Therefore isotopic analysis of Eospirifer radiatus and other brachiopods will verify possible secular variation of oceanic $^{18}O$ during the Middle Silurian.
The purpose of this chapter is to investigate: i) the diagenetic and depositional chemistries of brachiopod shell calcite from Clinton Group (Middle Silurian) sediments in western New York State and southern Ontario; ii) the isotopic and elemental trends within brachiopod calcites collected from a transgressive-regressive cycle.

GENERAL GEOLOGY

During the Wenlockian, Clinton Group strata accumulated within the shallow northern Appalachian Basin and intervening arch/platform areas (Brett, 1983a; Droste and Shaver, 1987). Paleogeographic reconstructions of the Middle Silurian in North America suggest that the basin, extending across Ontario, New York State and Pennsylvania, was close to the equator (Zeigler et al., 1977). Clinton Group siliciclastic and carbonate deposition was probably controlled by movements of the Algonguin Arch to the northwest (Sanford et al., 1985; Johnson, 1987) and uplift of a Taconic landmass to the southeast (Brett, 1983a). In southern Ontario and western New York State, a sequence of shallow marine limestones and shales of the Merritton, Neagha and Reynales Formations (Fig. 4.1; Grasso, 1983; Liebe and Grasso, 1986) accumulated on a Upper Ordovician to early Middle Silurian clastic wedge (Queenston, Grimsby and Thorold Formations; Grasso, 1983; Faill, 1985). Between the Reynales and Irondequoit Formations, a non-depositional erosional surface of several million years is present in Ontario (Brett, pers. comm. 1988), whereas in western New York State, these units are separated by the Sodus Shale and Williamson Shale Formations (Liebe and Grasso, 1986). Crinoidal biosparites and biomicrites of the Irondequoit Formation were deposited within crinoidal shoal banks on the platform areas overlying the Algonguin-Findlay Arch. Presumed
Figure 4.1. Middle Silurian stratigraphy of southern Ontario and New York State. The Williamson and Sodus Shales are present between the Reynales and Irondequoit Formation in western New York State. Sources and ages from Telford, 1978; Grasso, 1983; Brett, 1983a, b; Liebe and Grasso, 1986.
deepening of the basin and arch, resulted in accumulation of grey calcareous mudstones of the Rochester Shale Formation, where complex lithofacies and faunal distributions have been attributed to the north-south migration of facies belts (Brett, 1983a). Toward the northwest, the Rochester Shale thins and merges with the platform carbonate sediments of the Wiarton-Amabel Group and to the south, thickens towards the Appalachian Trough in central New York State and Pennsylvania (Brett, 1983a). Brachiopods were collected from these Middle Silurian formations (localities listed in Appendix I and Fig. 1.2). Recent research on the stratigraphical, sedimentological and paleoecological aspects of the Clinton Group (Thusu, 1972; Brett, 1983a, 1983b, 1989; Grasso, 1983; Liebe and Grasso, 1986) provides a framework for evaluating the diagenetic and depositional chemical trends within these units.

RESULTS AND DISCUSSIONS

Chemical trends

The trace and minor element data of Clinton Group brachiopods (Table 4.1) are comparable to the chemical ranges of other Paleozoic brachiopods (Brand and Veizer, 1980; Al-Aasm and Veizer, 1982; Veizer et al., 1986; Brand and Morrison, 1987). Chemical and microstructural evaluation of shell calcite indicates that the majority of specimens are pristine (e.g. Figs. 2.9, 2.13), although post-depositional alteration of some brachiopod calcite has occurred (e.g. Fig. 2.20). The valves of *Eospirifer radiatus*, *Atrypa reticularis* and *Whitifieldella* which show signs of dissolution and calcite layer fusion, are also significantly enriched in Mn, Fe and Mg (Fig. 4.2; Table 4.2); indicating that a significant degree of diagenetic alteration has taken place. Further confirmation of this diagenetic trend is provided by factor analysis of the data (Tables A-7 to
Table 4.1. Summary of chemical data for all Clinton Group brachiopods and for pristine specimens.

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<td></td>
<td>min.</td>
<td>282990</td>
<td>1150</td>
<td>855</td>
<td>35</td>
<td>905</td>
<td>70</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>max</td>
<td>446840</td>
<td>22020</td>
<td>1560</td>
<td>1390</td>
<td>1830</td>
<td>2230</td>
<td>190</td>
<td></td>
</tr>
</tbody>
</table>

All elemental concentrations are in ppm.

Table 4.2. Comparison of microstructural preservation and chemistry for selected brachiopods, representing different species, and lithologies. Lithology symbols denote (S= dark grey shale; CM= calcareous mudstones; ML= micritic limestones; W= wackestones; P= packstones; CG= crinoidal grainstones)

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Species</th>
<th>Age</th>
<th>Lithology</th>
<th>State</th>
<th>Preservation features</th>
<th>Diagenetic Mg (ppm)</th>
<th>Mn (ppm)</th>
<th>Fe (ppm)</th>
<th>Figured</th>
</tr>
</thead>
<tbody>
<tr>
<td>2602</td>
<td>Pentameroides</td>
<td>Rey.</td>
<td>CG</td>
<td>Poor</td>
<td>Recrystallized</td>
<td>3900</td>
<td>370</td>
<td>1235</td>
<td>2.20</td>
</tr>
<tr>
<td>2007</td>
<td>Pentameroides</td>
<td>Mer.</td>
<td>ML</td>
<td>Poor</td>
<td>Recrystallized</td>
<td>12330</td>
<td>300</td>
<td>870</td>
<td>2.20</td>
</tr>
<tr>
<td>2193</td>
<td><em>A. reticularis</em></td>
<td>Low.</td>
<td>CM</td>
<td>Good</td>
<td>None</td>
<td>2970</td>
<td>115</td>
<td>225</td>
<td>2.20</td>
</tr>
<tr>
<td>2308</td>
<td><em>A. reticularis</em></td>
<td>Low.</td>
<td>CM</td>
<td>Poor</td>
<td>Dissolution</td>
<td>3975</td>
<td>220</td>
<td>320</td>
<td>2.20</td>
</tr>
<tr>
<td>2306</td>
<td><em>A. reticularis</em></td>
<td>Low.</td>
<td>CM</td>
<td>Fair</td>
<td>Slight diss.</td>
<td>5160</td>
<td>215</td>
<td>375</td>
<td>2.20</td>
</tr>
<tr>
<td>2108</td>
<td>W. nitida</td>
<td>Low.</td>
<td>CG</td>
<td>Good</td>
<td>None</td>
<td>2120</td>
<td>75</td>
<td>230</td>
<td>2.13</td>
</tr>
<tr>
<td>2190</td>
<td>W. nitida</td>
<td>Low.</td>
<td>CM</td>
<td>Good</td>
<td>None</td>
<td>1320</td>
<td>80</td>
<td>90</td>
<td>2.13</td>
</tr>
<tr>
<td>2132</td>
<td>W. nitida</td>
<td>Iro.</td>
<td>CG</td>
<td>Good</td>
<td>None</td>
<td>4050</td>
<td>220</td>
<td>385</td>
<td>2.13</td>
</tr>
<tr>
<td>2182</td>
<td>W. nitida</td>
<td>Low.</td>
<td>CM</td>
<td>Poor</td>
<td>Recrystallized</td>
<td>15550</td>
<td>930</td>
<td>1280</td>
<td>2.13</td>
</tr>
<tr>
<td>2100</td>
<td>E. radiatus</td>
<td>Low.</td>
<td>CG</td>
<td>Good</td>
<td>None</td>
<td>1090</td>
<td>20</td>
<td>130</td>
<td>2.13</td>
</tr>
<tr>
<td>2301</td>
<td>E. radiatus</td>
<td>Low.</td>
<td>CM</td>
<td>Good</td>
<td>None</td>
<td>3240</td>
<td>90</td>
<td>150</td>
<td>2.13</td>
</tr>
<tr>
<td>2195</td>
<td>E. radiatus</td>
<td>Low.</td>
<td>CM</td>
<td>Good</td>
<td>None</td>
<td>2860</td>
<td>120</td>
<td>210</td>
<td>2.17</td>
</tr>
<tr>
<td>2193</td>
<td>E. radiatus</td>
<td>Low.</td>
<td>CM</td>
<td>Good</td>
<td>None</td>
<td>2970</td>
<td>115</td>
<td>225</td>
<td>2.17</td>
</tr>
<tr>
<td>2104</td>
<td>E. radiatus</td>
<td>Low.</td>
<td>CG</td>
<td>Good</td>
<td>None</td>
<td>3080</td>
<td>165</td>
<td>295</td>
<td>2.17</td>
</tr>
<tr>
<td>3018</td>
<td>Dalejina</td>
<td>BH.</td>
<td>CM</td>
<td>Good</td>
<td>None</td>
<td>3390</td>
<td>120</td>
<td>660</td>
<td>2.17</td>
</tr>
<tr>
<td>3011</td>
<td>Dalejina</td>
<td>BH.</td>
<td>CM</td>
<td>Good</td>
<td>None</td>
<td>3610</td>
<td>180</td>
<td>470</td>
<td>2.17</td>
</tr>
<tr>
<td>3025</td>
<td>Dalejina</td>
<td>BH.</td>
<td>CM</td>
<td>Good</td>
<td>None</td>
<td>4410</td>
<td>130</td>
<td>720</td>
<td>2.17</td>
</tr>
<tr>
<td>3036</td>
<td>Dalejina</td>
<td>BH.</td>
<td>CM</td>
<td>Good</td>
<td>None</td>
<td>3170</td>
<td>180</td>
<td>695</td>
<td>2.17</td>
</tr>
<tr>
<td>3014</td>
<td>R. elegantula</td>
<td>BH.</td>
<td>CM</td>
<td>Good</td>
<td>None</td>
<td>4960</td>
<td>175</td>
<td>610</td>
<td>2.17</td>
</tr>
<tr>
<td>3016</td>
<td>R. elegantula</td>
<td>BH.</td>
<td>CM</td>
<td>Good</td>
<td>None</td>
<td>5400</td>
<td>190</td>
<td>790</td>
<td>2.17</td>
</tr>
<tr>
<td>3015</td>
<td>R. elegantula</td>
<td>BH.</td>
<td>CM</td>
<td>Poor</td>
<td>Recrystallized</td>
<td>8470</td>
<td>265</td>
<td>930</td>
<td>2.17</td>
</tr>
</tbody>
</table>

96
Figure 4.2. Scatter plot of Fe vs Mn for all genera from the Middle Silurian Clinton Group (Wenlockian). The diagenetic trend shows an increase of Mn and Fe contents with progressive diagenesis. The dashed fields define the approximate unaltered brachiopod of each species. W denotes pristine Whitfieldella; E denotes pristine Eospirifer and A denotes pristine Atrypa.
A-10). Diagenetic re-equilibration has not significantly depleted Na and Sr contents of shell calcite, which suggests that Na and Sr rich fluids were involved in the alteration process.

**Elemental fractionation and taxonomic trends**

Ancient brachiopods fractionate Mg and Na (Brand and Veizer, 1980; Morrison and Brand, 1987) when compared to low-Mg calcites precipitated in inorganic equilibrium with ambient conditions. Chemical data of pristine Clinton Group shell calcites suggests that these brachiopods also fractionated Mg and Na. They discriminated against Mg and preferentially incorporated Na into shell calcite. Furthermore, comparisons between three co-occurring species *Whitfieldella nitida*, *Eospirifer radiatus* and *Atrypa reticularis*, indicates that the incorporation of Na and to a lesser extent Mg, Mn, and Fe, was taxonomically controlled (Table 4.1). *Atrypa reticularis* calcite contains significantly higher Na and Mg contents than co-occurring *Whitfieldella nitida* and *Eospirifer radiatus* calcite (Table 4.3; unpaired t-test, p > 0.05, f > 66). Taxonomic differentiation is likely to be determined by physiological factors, dissimilar growth rates (calcification rates) and/or the mineral morphology/structural requirements of their shells. Sr appears to be randomly distributed between the studied species.

**Isotopic trends**

The majority of brachiopod calcite analysed from the Irondequoit and Rochester Shale Formations represent pristine isotopic compositions. In several specimens isotopic re-equilibration of shell calcite with diagenetic waters is indicated by the fact that increasing Mn, Fe and Mg contents correspond with more negative δ¹⁸O and δ¹³C values (Fig. 4.3). Valves of *Pentameroides* from the Reynales and Merriton Formations are chemically and microstructurally the
Table 4.3a. Summary of pristine brachiopods calcites from the Rochester Shale and Irondequiot Formations.

<table>
<thead>
<tr>
<th>Brachiopod species</th>
<th>Stat.</th>
<th>Ca</th>
<th>Mg</th>
<th>Sr</th>
<th>Mn</th>
<th>Na</th>
<th>Fe</th>
<th>Al</th>
<th>I.R.</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Eospirifer</em></td>
<td>Mean</td>
<td>377550</td>
<td>2406</td>
<td>1230</td>
<td>103</td>
<td>1311</td>
<td>192</td>
<td>91</td>
<td>6.9</td>
</tr>
<tr>
<td>(n=23)</td>
<td>Std. Dev.</td>
<td>26400</td>
<td>670</td>
<td>72</td>
<td>41</td>
<td>99</td>
<td>69</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>min</td>
<td>318340</td>
<td>1090</td>
<td>1070</td>
<td>19</td>
<td>1140</td>
<td>30</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>max</td>
<td>416460</td>
<td>3800</td>
<td>1360</td>
<td>190</td>
<td>1545</td>
<td>295</td>
<td>190</td>
<td></td>
</tr>
<tr>
<td><em>Whitfieldella</em></td>
<td>Mean</td>
<td>388034</td>
<td>2061</td>
<td>1215</td>
<td>64</td>
<td>1027</td>
<td>133</td>
<td>77</td>
<td>5.5</td>
</tr>
<tr>
<td>(n=31)</td>
<td>Std. Dev.</td>
<td>32574</td>
<td>513</td>
<td>121</td>
<td>48</td>
<td>214</td>
<td>80</td>
<td>53</td>
<td></td>
</tr>
<tr>
<td></td>
<td>min</td>
<td>283730</td>
<td>1160</td>
<td>830</td>
<td>1</td>
<td>750</td>
<td>50</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>max</td>
<td>441070</td>
<td>3605</td>
<td>1625</td>
<td>215</td>
<td>1500</td>
<td>385</td>
<td>260</td>
<td></td>
</tr>
<tr>
<td><em>Atrypa</em></td>
<td>Mean</td>
<td>387567</td>
<td>3545</td>
<td>1222</td>
<td>181</td>
<td>1466</td>
<td>305</td>
<td>97</td>
<td>7.1</td>
</tr>
<tr>
<td>(n=45)</td>
<td>Std. Dev.</td>
<td>35613</td>
<td>205</td>
<td>128</td>
<td>79</td>
<td>187</td>
<td>92</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td></td>
<td>min</td>
<td>282990</td>
<td>1150</td>
<td>855</td>
<td>35</td>
<td>905</td>
<td>70</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>max</td>
<td>446840</td>
<td>4020</td>
<td>1560</td>
<td>370</td>
<td>1830</td>
<td>560</td>
<td>190</td>
<td></td>
</tr>
</tbody>
</table>

All elemental concentrations are in ppm.

Table 4.3b. Unpaired T-test: pristine brachiopod chemistry (Clinton Group).

<table>
<thead>
<tr>
<th>Element</th>
<th><em>Whitfieldella</em></th>
<th><em>Atrypa</em></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><em>Eospirifer</em></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td><em>t</em> (53) = 1.115, <em>p</em> &lt; 0.05</td>
<td><em>t</em> (66) = 1.315, <em>p</em> &lt; 0.05</td>
</tr>
<tr>
<td>Mg</td>
<td><em>t</em> (53) = 0.957, <em>p</em> &lt; 0.05</td>
<td><em>t</em> (66) = 5.698, <em>p</em> &gt; 0.05</td>
</tr>
<tr>
<td>Sr</td>
<td><em>t</em> (53) = 1.831, <em>p</em> &lt; 0.05</td>
<td><em>t</em> (66) = 0.087, <em>p</em> &lt; 0.05</td>
</tr>
<tr>
<td>Mn</td>
<td><em>t</em> (53) = 1.067, <em>p</em> &lt; 0.05</td>
<td><em>t</em> (66) = 4.109, <em>p</em> &gt; 0.05</td>
</tr>
<tr>
<td>Na</td>
<td><em>t</em> (53) = 6.849, <em>p</em> &gt; 0.05</td>
<td><em>t</em> (66) = 4.040, <em>p</em> &gt; 0.05</td>
</tr>
<tr>
<td>Fe</td>
<td><em>t</em> (53) = 0.622, <em>p</em> &lt; 0.05</td>
<td><em>t</em> (66) = 5.191, <em>p</em> &gt; 0.05</td>
</tr>
<tr>
<td></td>
<td><em>Atrypa</em></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td><em>t</em> (75) = 0.255, <em>p</em> &lt; 0.05</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td><em>t</em> (75) = 1.392, <em>p</em> &lt; 0.05</td>
<td></td>
</tr>
<tr>
<td>Sr</td>
<td><em>t</em> (75) = 1.806, <em>p</em> &lt; 0.05</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td><em>t</em> (75) = 0.772, <em>p</em> &lt; 0.05</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td><em>t</em> (75) = 10.979, <em>p</em> &gt; 0.05</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td><em>t</em> (75) = 2.042, <em>p</em> &gt; 0.05</td>
<td></td>
</tr>
</tbody>
</table>

n.b. Populations which are significantly different at the 95% confidence level are underlined.
Figure 4.3. Diagenetic trend of isotopic composition of Middle Silurian Clinton Group brachiopods. ◦ denotes altered; † denotes unaltered
most altered and show considerable diagenetic displacement of isotopic compositions.

In addition, significant differences of oxygen and carbon isotopes are evident between Irondequoit/Lewiston Member and Burleigh Hill Member pristine brachiopods (t-test, p > 0.05; f = 24; Fig. 4.4). Oxygen isotopic differences may be attributed to changes in salinity, temperature, paleodepth, and oceanic δ¹⁸O composition, whereas carbon is influenced by the δ¹³C of ambient dissolved inorganic carbon (DIC) of the seawater (Anderson and Scholle, 1983).

**DIAGENETIC EVALUATION OF CLINTON GROUP BRACHIOPODS**

**Merritton Formation**

Large, disarticulated *Pentameroides* brachiopods were collected from the dense green-grey calcareous mudstones of the Merritton Formation (Lower Clinton Group). The upper surface (3-4 cm deep) of this unit is a heavily phosphatized, pyritized hardground. Specimens from the hardground and underlying micrites were physically abraded and corroded, with little retention of original shell microstructure. Chemically, these brachiopods have high Mn, Fe and Mg contents, which are indicative of extensive dissolution and recrystallization (Fig. 4.2); Sr and Na contents are also retained in the diagenetic product. Meteoric diagenesis tends to significantly deplete Sr and Na (Brand and Veizer, 1980), therefore Merritton Formation diagenetic waters must have contained higher Sr and Na contents than surficially-derived meteoric waters. The hardground may represent an omission surface produced by a slowdown in sedimentation rates and during submarine lithification and early cementation, marine-derived waters may have contributed to the post-
Figure 4.4. Isotopic compositions of *Eospirifer* from Irondequoit, Rochester, Reynales and Merritton Formations of the Middle Silurian Clinton Group. ◇ denotes altered; ● denotes unaltered
depositional alteration of *Pentameroides* calcite. However, there are no chemical distinctions between shell calcite from the hardground or the micrites beneath. The micritic limestone matrix is partially dolomitized which suggests the post-depositional passage of mixed waters, since dolomitization is restricted to the matrix and probably postdates brachiopod alteration.

**Reynales Formation**

The Reynales Formation consists of 6m of grey, crystalline limestones and dolomitic limestones with thin shaly partings (Liebe and Grasso, 1986). In the Genesee river gorge at Rochester (Locality 44), *Pentameroides* sp. were collected from biostrome beds of the Wallington sub-member of the Reynales Formation, which was deposited in shallow shoal to subtidal marine settings (Grasso, 1983). Although the matrix is predominantly calcite biomicrite, fine euhedral rhombs of dolomite have replaced about 5-15% of the matrix. *Pentameroides* sp. shell valves exhibit physical evidence of extensive corrosion and dissolution, and poor microstructural preservation is complemented by chemical alteration. Dissolution and reprecipitation steps toward equilibration with diagenetic waters is suggested by enrichments of Fe, Mn and Mg and significant depletion of Sr and Na (Fig. 4.2); similar trends are exhibited in other studies of brachiopod diagenesis (Brand and Veizer, 1980). By comparison to the Merritton Formation, this chemical trend suggests that meteoric-derived waters were responsible for alteration of brachiopod calcite. Dolomitization of the matrix has left the brachiopod specimens unaffected, indicating that the passage of Mg-rich fluids probably postdates equilibration of shell calcite.
Irondequoit and Rochester Shale Formation diagenetic waters

Enrichments of Mg with alteration in Irondequoit and Lewiston brachiopods are significant but, by contrast, there is no significant depletion of Sr and Na contents with alteration (Fig. 4.5). Thus despite alteration of Irondequoit and Lewiston brachiopods, Sr and Na contents have been retained at similar values to original unaltered compositions, suggesting the influence of relatively marine-dominated waters in the diagenetic process. There are taxonomic and environmental controls of original chemistries and resultant diagenetic reaction directions are constrained by these initial compositions. Many *Eospirifer radiatus*, *Atrypa reticularis*, *Striispirifer niagarense* and *Resserella elegantula* from the Irondequoit and Rochester Formations show progressive increases of Mg with alteration, the direction of which is constrained by their original elemental contents (Trend A; Fig. 4.5). The average Na contents of pristine *Eospirifer radiatus* and *Atrypa reticularis* are about 1300-1400 ppm which is retained in altered specimens. In contrast, pristine *Whitfieldella nitida* contain Na compositions of 850-1000 ppm and the alteration direction is similarly constrained by original shell calcite composition (Trend B; Fig. 4.5). The Irondequoit crinoidal biosparite is pervasely dolomitized, which has selectively replaced the matrix but left brachiopods unaffected. Alteration appears to be diffusion controlled because the diagenetic product retains much of the original chemistry; only two specimens appear to be partially dolomitized. Similarly, dolomitization of the Lewiston and Burleigh Hill members is quite pervasive. The grey mudstone, calcisiltite and calcarenite beds are partially dolomitized; replaced by fine-grained euhedral dolomite rhombs. The brachiopods are unaffected by the dolomitization process. At least two phases of diagenetic alteration are suggested by these observations. The
Figure 4.5. Scatter plot of Na vs Mg for all species from the Middle Silurian Clinton Group (Wenlockian). The diagenetic trend shows an increase of Mg contents with progressive diagenesis. The dashed fields define the approximate unaltered brachiopod of each species. W denotes pristine *Whitfieldella*; E denotes pristine *Eospirifer* and A denotes pristine *Atrypa*. 
first was a post-depositional alteration of brachiopods (and matrix?) in the presence of relatively marine dominated mixed waters followed by the passage of the dolomitizing fluids. Marine formation waters may have been the brachiopod-altering diagenetic fluids. The origin of the Mg rich fluids may be related to mixed water processes (Brand, pers. comm. 1989).

PALEOENVIRONMENTAL ANALYSIS OF THE IRONDEQUOIT FORMATION

The Irondequoit Formation varies from dolomitic grainstones in the east (Lockport, N.Y.) to dolosparites in the west (Hamilton, Ontario) and represents a crinoidal bank facies deposited under normal, open marine conditions (Brett, 1983a). Between St. Catharines, Ontario and Lewiston, New York State, the Irondequoit is less pervasively dolomitized and brachiopods are commonly preserved. In the Niagara Gorge (locality 40), the lower and middle Irondequoit consists of thick-bedded crinoidal grainstones which possess a low diversity brachiopod fauna dominated by *Whitfieldella nitida*. Most bioclasts are comminuted and disarticulated valves of *Whitfieldella nitida* are abraded and corroded, suggesting prolonged exposure and erosion. Winnowing of fines from these biosparites suggest these brachiopods occupied a moderate to high energy environment within the shallowest part of the crinoid shoal. The upper 20cm of the Irondequoit Formation is dominated by large brachiopods such as *Leptaena rhomboidalis*, *Atrypa reticularis*, *Whitfieldella nitida* and *Eospirifer radiatus* in varying states of disarticulation. The presence of micrite in these crinoidal biosparites suggests a reduction in the winnowing of fines or the influx of muddy siliciclastics prior to the deepening of the basin. Both faunal
associations are assigned by Brett (1989) to a shallow-water *Atrypa reticularis*-*Whitfieldella nitida* brachiopod association (Fig. 4.6).

Several chemical trends are evident from the data. The generally low Fe and Mn contents of pristine brachiopod calcite suggests that the shallow-waters of these Irondequoit crinoidal bank were well oxygenated, supporting the paleoecological and taphonomic assertions (Brett, 1983a; 1989). Differences between species in re-equilibration with diagenetic waters are evident in Fe and Mn plots of Irondequoit brachiopod data (Fig. 4.7). Pristine *Whitfieldella nitida* has significantly lower Mn and Fe contents than unaltered *Atrypa reticularis* and *Eospirifer radiatus* (Table 4.1; Fig. 4.2). The variable enrichments in Mn and Fe are a response to re-equilibration with diagenetic waters controlled by diffusion- or fluid- reactions; increasing enrichments representing increased control by fluids on the chemistry of the alteration product (Fig. 4.7). Diagenetic trends are also constrained by the original shell calcite composition. *Eospirifer radiatus* and *Atrypa reticularis* preferentially incorporate more Na compared to *Whitfieldella*, and the enrichment trend of Mg is dependant on this phenomena (Fig. 4.8). Although there is no change in lithology, the Na and Mg chemistries of pristine *Whitfieldella nitida* specimens are significantly higher in the upper Irondequoit than in the lower and middle. This may be due to shallower more turbulent conditions and fresh waters introduced by storms may have created slightly brackish conditions thereby reducing Na and Mg incorporation into shell calcite. Alternately, if the relationship between depth and Mg, Na contents observed in the Hamilton Group (this study) is applicable to these brachiopods, this may indicate slightly deeper waters within the upper biosparites of the Irondequoit Formation. The presence of large, thickened shells within the uppermost Irondequoit may be a
Figure 4.6. Rochester Shale/Irondequoit Formation brachiopods associations with reference to inferred gradients of depth-related parameters and turbidity and/or sedimentation rates. Source from Brett (1989).
Figure 4.7. Diagenetic trend of Irondequoit Formation brachiopods (Middle Silurian). Field W is unaltered *Whitfieldella* specimens and field EA represents is unaltered *Eospirifer* and *Atrypa*. Matrix data from Milinkovich (1986).

Figure 4.8. Scatter plot of Na vs Mg contents of Irondequoit brachiopods illustrates two diagenetic trends. Lower trend is from middle Irondequoit Formation (localities 40v, 40iv) and upper trend are brachiopods from upper 20cm of the Irondequoit (localities 40iii, 40ii). Key as in Figure 4.6. Matrix data from Milinkovich (1986).
morphological adaptation to a more turbulent (and presumably shallower?) environment (Fursich and Hurst, 1974).

PALEOENVIRONMENTAL ANALYSIS OF THE ROCHESTER SHALE FORMATION

Introduction

Medium to dark grey calcareous mudstones and thin limestones of the Rochester Shale conformably overlie the crinoidal Irondequoit Formation and are in turn overlain gradationally by the dolostones of the Lockport Formation (Thasu, 1972; Brett, 1983b). The Rochester Shale can be subdivided into the lower Lewiston Member and the upper Burleigh Hill Member between Brockport, New York State, and Grimsby, Ontario; to the east, the formation becomes undifferentiated (Brett, 1983a). West of Grimsby, the Burleigh Hill member grades into argillaceous dolostones of the Stoney Creek Member, which northwest of Hamilton Ontario, quickly pinch out. Brachiopods were collected from Lewiston Member type locality in the Niagara Gorge, New York, the Burleigh Hill Member type locality in St. Catharines, Ontario (Fig. 4.9), and from several additional localities in western New York and the Niagara peninsula (Fig. 1.2).

Stratigraphic setting of the Lewiston Member

Several recent studies have defined recurring and cyclical faunal associations within the Rochester Shale (Brett, 1983a; 1989). Sedimentologically and paleoecologically the entire Rochester Shale Formation has been interpreted as a transgressive-regressive cycle (Brett, 1983a; 1989; Tetrault, 1987) which is a result of the migration of facies belts in a
Figure 4.9. Rochester Shale stratigraphic section at Niagara Gorge. Numbers refer to sampling horizons listed in Appendix I.
north-south direction (Fig. 4.10). Superimposed upon this, the Lewiston Member, divided into 5 subunits (Brett, 1983b), records a smaller scale deepening (subunits A to C) and shallowing subcycle (subunits C to E). The sub-unit A is a brachiopod-dominated, argillaceous grey mudstone sequence which has a gradational contact with the Irondequoit Formation. In the Niagara Gorge, a large bryozoan bioherm at the Irondequoit/Rochester Shale contact interfingers with and extends into the subunit A. The uppermost Irondequoit Formation and lowest 20-30 cm of the subunit A is characterized by an association of large disarticulated brachiopods (*Leptaena rhomboidalis rhomboidalis*, *Atrypa reticularis reticularis*, *Whitfieldella nitida nitida*, *Eospirifer radiatus radiatus*, *Dicoelosia biloba*) which have been assigned to a *Atrypa reticularis*-*Whitfieldella nitida* community by Brett (1989) and may represent shallow, turbulent waters within crinoidal banks (Fig. 4.6). The middle and upper parts of subunit A are characterized by a diversity of brachiopod species (*Dicoelosia biloba, Atrypa reticularis reticularis, Whitfieldella nitida nitida, Leptaena rhomboidalis rhomboidalis, Coolinia subplana subplana, Plectodonta transversa, Eospirifer radiatus radiatus, Howellella crispa*) that have been assigned to the deeper *Atrypa reticularis*-*Leptaena rhomboidalis* community (Brett, 1989). This sequence of thin graded calcarenite and calcisiltite beds (2-6cm thick), interbedded with grey mudstones, contain an abundance of articulated brachiopods.

Subunit B consists of light grey mudstones interbedded with thin fossiliferous calcisiltites and calcarenites which have been interpreted as medial and distal storm deposits (Brett, 1983a). Subunit C consists of a sequences of grey mudstones interbedded with thin fossiliferous shales and calcisiltite beds (distal storm deposits). The presence of fossiliferous horizons with articulate crinoids, complete trilobites and graptolites suggests these beds
Figure 4.10. Facies map of the Rochester Shale across southern Ontario and western New York State. North/south migrations of facies belts produced transgressive-regressive sequence in Lewiston Member. Modified from Brett (1983a).
were quickly blanketed by muds and deposited in low-energy settings (Brett and Eckert, 1982). The brachiopod fauna, including *Striispirifer niagarenseniagarensis, Eospirifer radiatus* and *Atrypa reticularis*, which are commonly articulate and in life position, has been assigned to the *Striispirifer niagarensen* community and has been interpreted by Brett (1983a; 1989) as having occupied quiet, deeper shelf environments, that were episodically disturbed by storms.

Subunit D, of the Lewiston Member, resembles the subunit B lithologically and paleoecologically. The frequency of calcisitite and calcarenite beds increases from subunits C to E and represents a general shallowing upward sequence, culminating in the shallow bryozoan communities of the upper subunit E. There are abundant brachiopod faunas in association with these subunit E bryozoa beds (*Howellella, Atrypa reticularis, Whitfieldella nitida, Resserella, Dicoelosia, Plectodonta* are common) assigned to a *PlectAtrypa reticularis-Howellella-fenestrate* bryozoan community by Brett (1989). Overlying subunit E are barren dark grey shales of the Burleigh Hill Member. A disconformity between the Lewiston subunit E and the Burleigh Hill Member is represented by a thin heavily pyritized hardground (Fig. 4.8, locality 41). The Burleigh Hill Member records a shallowing upwards sequence (Brett, 1983a), and may represent a punctuated aggradational cycle of Goodwin and Anderson (1985).

**Chemical trends**

Most shell beds of the Lewiston Member are essentially autochthonous and transport, if any, was minimal. Therefore, the elemental and isotopic trends reflect depositional conditions at this locality during the transgressive-regressive cycle. The majority of brachiopods from the Lewiston Member are
microstructurally and chemically well preserved, but a few altered specimens were significantly enriched in Mg, Mn and Fe (Fig. 4.11) while retaining their Sr and Na contents (Fig. 4.12). Although brachiopods were analysed from a variety of lithofacies such as grey mudstones, calcisiltites and graded calcarenites, there was no systematic variation in brachiopod alteration between these beds. Specimens of *Resserella elegantula* from the uppermost pyritized hardground of the E subunit contain much higher Mg contents (5750-12860 ppm) than brachiopods in underlying Lewiston beds which may be a reflection of hardground cementation.

Once these altered specimens were eliminated from the data set, investigation of systematic changes in trace and minor element chemistries could continue. Within the transgressive-regressive cycle of the Lewiston Member, redox-controlled elements such as Mn and Fe varied between 10 and 180ppm but there was no significant difference between shallow (subunits A, E) and deeper facies (subunit C). Bottom waters of the Lewiston sea may therefore have alternated between aerobic and slightly dysaerobic conditions but this is not related to stratigraphic trends (Fig. 4.13).

Mg incorporation into brachiopod calcite was observed by Lowenstam (1961) to be dependant on salinity and related to the effect of greater ion concentrations on the physiology of the organism. Similarly, Na contents in biogenic carbonates have been used to determine paleosalinities (Veizer and Demovic, 1974; Veizer et al., 1978), but Ishikawa and Ichikuni (1984) suggest that Na contents in biogenic carbonates are not proportional to salinities over 10 ppt. Analysis of pristine brachiopods from the Hamilton Group suggests that Mg, Na and Sr contents are inversely proportional to depth (cf. Chapter 3) but analysis of Lewiston Member brachiopod calcites cannot confirm this finding. The concentrations of Sr and Na within shell calcite remains fairly constant.
Figure 4.11. Scatter plot of Fe vs Mn for all species from the Lewiston Member of the Rochester Shale Formation. The diagenetic trend shows an increase of Mn and Fe contents with progressive diagenesis. The fields define the approximate unaltered brachiopod of each species. W denotes \textit{Whitfieldella}, E denotes \textit{Eospirifer}; and A denote \textit{Atrypa}.

Figure 4.12. Na vs Mg scatter plot of Lewiston Member brachiopods. The fields define approximate unaltered chemistries of each species; W denotes \textit{Whitfieldella}; E denotes \textit{Eospirifer}; and A denote \textit{Atrypa}. In general the Na contents of \textit{Eospirifer} and \textit{Atrypa} are higher than \textit{Whitfieldella}; Mg contents are significantly higher in \textit{Atrypa} than \textit{Eospirifer} and \textit{Whitfieldella}.
Figure 4.13. Plot of mean Sr, Mn and Fe contents of *Atrypa* and *Eospirifer* against height within Lewiston Member section.
throughout the section (Sr 1050-1200 ppm; Fig. 4.13: Na 1200-1600 ppm; Fig. 4.14), and there are significant differences between shallow and deep facies of the Lewiston Member (Fig. 4.14, 4.15). Mg contents of *Atrypa reticularis* calcite do decrease from the base of the Lewiston to the middle of subunit B, but whether this is related to depth cannot be confirmed because the Mg contents of *Atrypa reticularis* in subunits C to E reflect chemically altered calcites.

Rochester Shale *Eospirifer radiatus*, *Atrypa reticularis* and *Whitfieldella nitida* biologically fractionated Mg and Na, discriminating against Mg and preferentially incorporating Na (Tables 4.1, 4.3). This fractionation is also taxonomically controlled because each species has significantly different Mg and Na contents. This phenomena is complicated by the fact that *Atrypa reticularis* incorporates Mg and Na differently from bed to bed in proportion, presumably, to concentrations determined by an environmental or physiological control. Analysis of pristine *Atrypa reticularis* from a number of horizons in subunits A and B, suggests that Mg and Na incorporation is inversely related; higher Mg contents correspond to lower Na contents and vice versa (Fig. 4.15). Growth rates may determine the amount of Na incorporated into shell calcite as a substitute for Mg and this may be determined by slight variation in environmental conditions such as salinity and temperature. This Na/Mg relationship does not correlate with the apparent transgressive-regressive cycle. Furthermore, *Atrypa reticularis* may have preferentially fractionated Mn and Fe, when compared to *Eospirifer radiatus* and *Whitfieldella nitida* (Table 4.1 and 4.3).

**Isotope trends**

Oxygen and carbon isotopes can reflect deepening events associated with trasgressive-regressive processes. A 5°C decrease in water temperature
Figure 4.14. Plot of mean Mg and Na contents of pristine *Atrypa* and *Eospirifer* against height within Lewiston Member section.
Figure 4.15. Plot of mean Na and Mg contents of pristine *Atrypa* from the Lewiston Member subunits A and B. Incorporation of Na and Mg into shell calcite is inversely related.
can cause a $1^\circ/_{oo}$ increase in $\delta^{18}$O (Epstein et al., 1953; Rye and Sommer, 1980). Adlis et al. (1989) have attributed slight shifts in $\delta^{13}$C and $\delta^{18}$O within the brachiopod shell calcite of *Planoconvexa crurithyris* to deepening within a Pennsylvanian cyclothem sequence. A $\delta^{18}$O increase of 0.6$^\circ/_{oo}$ has been ascribed to a cooling and depth change of 70m, associated with marine transgression and glacial dilution of the Pennsylvanian $\delta^{18}$O oceanic reservoir (Adlis et al., 1989). Similarly, changes in the $\delta^{13}$C have been attributed to deepening below the photic zone, stagnation, and increased influence of pore-water carbon derived from organic matter (Adlis et al., 1988). These authors assume no salinity effects associated with the transition from shallow marine limestones to deeper marine phosphatized gondolellid shales. Furthermore, these cyclothems were deposited in the semi-enclosed Midland basin, and isotopic variation caused by changing patterns of fresh water influx and salinity during transgression-regression may have contributed to the slight shifts in $\delta^{18}$O.

Specimens of *Eospirifer radiatus* were analysed isotopically through the Lewiston Member sequence, because they are present in many horizons. The analysis of a single species eliminated any potential isotopic differences between species and *Eospirifer radiatus* was assumed to incorporate isotopes in equilibrium with ambient conditions. Although only a limited number were analysed, several distinct observations can be made. Average $\delta^{13}$C composition of the brachiopods was $+5.0^\circ/_{oo}$ ($+4.6^\circ/_{oo}$ to $+5.7^\circ/_{oo}$), which suggests that the ambient bottom waters were relatively enriched in $^{13}$C. Average shell calcite $\delta^{18}$O composition was $-3.2^\circ/_{oo}$ (range $-1.7^\circ/_{oo}$ to $-3.9^\circ/_{oo}$). This corresponds to paleotemperatures of 26-31°C if the Wenlockian seas had the same $\delta^{18}$O composition as the modern ocean (Broecker, 1974). These time-averaged (brachiopod life span) temperatures are reasonable, considering that
southern Ontario was within 10-15° south of the paleoequator during the Middle Silurian (Scotese et al., 1979). This finding does not support the assertion that Silurian oceans were depleted in $^{18}$O by 5-6°/oo (Brand and Veizer, 1981; Veizer et al., 1986). Indeed, no correction of isotopic data from this study is necessary and it is therefore pre-emptive to assume that throughout the Silurian, mean oceanic $\delta^{18}$O compositions were depleted by 5.5°/oo (O'Shea et al., 1988). Conditions within the Michigan basin during deposition of the Upper Silurian Salina Group may indeed reflect depletion of $^{18}$O at that particular time within a restricted basin (O'Shea et al., 1988). The previously reported brachiopod isotopic data on brachiopod calcite may simply reflect the influence of post depositional alteration, salinity and temperature effects, glacial dilution, local environmental conditions and physiography of epicontinental oceans.

The isotope stratigraphy of the Lewiston Member is illustrated for the Niagara Gorge section in Fig. 4.16. There appears to be no significant trends in $\delta^{13}$C and $\delta^{18}$O in relation to the apparent deepening and subsequent shallowing observed within the Lewiston Member. Lowenstam (1961) observed that Mg contents in brachiopods were related to temperature and $\delta^{18}$O values; increasing $\delta^{18}$O is related to cooling associated with deepening. However, within the Lewiston sequence, there is no correlation between Mg and $\delta^{18}$O values (Fig. 4.17; hence temperature). Isotopically, *Eospirifer radiatus* from the deepest Lewiston C beds (*Striispirifer* community) are similar to those from the shallowest Lewiston A and E subunits. Furthermore, *Eospirifer radiatus* from the shallow crinoidal banks of the underlying Irondequoit Formation are not significantly different from *Eospirifer radiatus* in the Lewiston Member. The variation of $\delta^{18}$O is about 0.5°/oo (~3°C) and $\delta^{13}$C is approximately 0.7°/oo. The more negative $\delta^{18}$O values and hence slightly warmer paleotemperatures (~2-3°C) occur in the deeper Lewiston subunits B and C Members; contradictory to
Figure 4.16. Mean isotopic composition (in per mil; PDB) of pristine *Eospirifer* from the Irondequoit Formation and Lewiston Member of western New York State (Clinton Group; Middle Silurian). Interpretation of transgressive-regressive cycle from Brett (1983a).
Figure 4.17. Plot of oxygen isotopes versus Mg contents within pristine *Eospirifer* calcites from the Irondequoit Formation and Lewiston Member (Clinton Group, Middle Silurian).
paleoecologic interpretation (Brett, 1983a; 1989). There may be several possible explanations for these observations. Transgressions associated with glacio-eustatic changes, may decrease mean oceanic $\delta^{18}O$ composition by $1^\circ/_{oo}$ (Shackleton, 1967; 1974; Adlis et al., 1989). If the Lewiston cycle is assumed to be the result of glacio-eustatic changes, then the slightly more negative $\delta^{18}O$ values from the middle Lewiston may be explained by changes in the mean oceanic $\delta^{18}O$ composition. Alternately, salinity changes associated with cyclonic depressions that swept across the region may explain the slight $\delta^{18}O$ variations observed for this sequence. In tropical latitudes, seawater $\delta^{18}O$ can decrease by 0.1$^\circ/_{oo}$ per $^\circ/_{oo}$ salinity change (Craig and Gordon, 1965).

The Lewiston Member isotopic and elemental data does not support any temperature gradient associated with depth changes in this transgressive-regressive cycle. There may be a number of explanations for this. The cycle may not have involved major fluctuations in relative seawater and bottom water conditions may not have changed significantly. Depth changes need not have been great to produce significant lateral movements of facies and faunal associations. The slight differences observed in $\delta^{13}C$, $\delta^{18}O$ and elemental contents may represent the natural variations inherent to shell biomineralization and small fluctuations in the temperature, salinity, redox conditions, dissolved inorganic carbon, mean oceanic and localized oxygen compositions (Fig. 4.11).

Geochemistry of brachiopods from the Burleigh Hill Member

The lowest 6m of the Burleigh Hill Member consist of dark grey shales punctuated by a few thin but persistent calcisiltite lenses (Fig. 4.18). Few macrofossils are present (notably Coolinia subplana). About 5.7 m above the basal contact with the subunit E is a shell bed, informally termed the "Coolinia subplana" Bed, which contains abundant disarticulated and fragmented
Figure 4.18. Burleigh Hill Member stratigraphic section at the type locality in St. Catharines, Ontario. Numbers refer to locality and sampling interval identified in Appendix I.
brachiopods, including *Dalejina*, *Resserella elegantula*, *Leptaena rhomboidalis* and *Coolinia subplana* and trilobites *Dalmanites limulurus* and *Trimerus* sp. In the type section at Burleigh Hill (locality 36), this shell bed consists of several thin (5-7 cm) discrete calcisiltite beds, whereas westward, at Decew Falls, this shell bed is present as a thin amalgamated bed about 10 cm thick. The "*Coolinia subplana* " bed may represent winnowed distal storm beds deposited well below the fair weather wave base and below all but the deepest storm waves (Brett, 1989). The fauna within this bed can be assigned to the *Coolinia subplana*-*Dalejina* community of Brett (1983a; 1989) occupying higher energy environments.

Four brachiopod species were analysed from the Coolinia subplana Bed; *Resserella elegantula elegantula*, *Coolinia subplana subplana*, *Leptaena rhomboidalis rhomboidalis* and *Dalejina*. Microstructurally, most brachiopod calcite appear to be in a good preservation state, although post-depositional alteration is evident in the remaining specimens (Fig. 4.19; 4.20). There are significant difference in brachiopod calcite compositions between the Rochester and Irondoquoit Formations (Tables 4.2 and 4.4). The Mn and Fe contents are significantly higher in the Burleigh Hill brachiopods than those from the Lewiston Member or the Irondoquoit Formation. This could be the result of significant leaching of Fe and Mn from aluminosilicates. However, these brachiopods may simply have precipitated shell calcite in depleted oxygen conditions that facilitated the incorporation of Mn and Fe. Differences between Mn/Fe contents are seen between the strophomenids *Coolinia subplana* /*Leptaena rhomboidalis* and the orthids *Resserella elegantula* and *Dalejina*. The higher Mn/Fe contents of the strophomenids may, in part, be a function of laminar secondary-layer calcite secretion.
### Table 4.4. Unaltered brachiopod chemistries from locality 36 (Burleigh Hill Member)

<table>
<thead>
<tr>
<th>Brachiopod species</th>
<th>Stat.</th>
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<th>Sr</th>
<th>Mn</th>
<th>Na</th>
<th>Fe</th>
<th>Sr/Ca 1000</th>
</tr>
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<tbody>
<tr>
<td>Atrypa</td>
<td>mean</td>
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<td>3920</td>
<td>2111</td>
<td>122</td>
<td>1526</td>
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</tr>
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<td>370</td>
<td>670</td>
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<td>83</td>
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<td>70</td>
<td>1075</td>
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<td>39</td>
<td>118</td>
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<td>3765</td>
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<td>140</td>
<td>1280</td>
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<td>1060</td>
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<td>1600</td>
<td>1605</td>
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All elemental concentrations are in ppm

### Table 4.5. Unaltered brachiopod chemistries from locality 34 (Burleigh Hill Member)

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<th>Brachiopod species</th>
<th>Stat.</th>
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<th>Sr</th>
<th>Mn</th>
<th>Na</th>
<th>Fe</th>
<th>Sr/Ca 1000</th>
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<td></td>
<td>min</td>
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<td>3170</td>
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<td>160</td>
<td>1310</td>
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<td>930</td>
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All elemental concentrations are in ppm
Figure 4.19. Scatter plot of Fe vs Mn for all species from the Burleigh Hill Member (Clinton Group). The diagenetic trend shows an increase of Mn and Fe contents with progressive diagenesis. The field represents pristine brachiopods.
Figure 4.20. Scatter plot of Sr vs Mg for all brachiopod species of the Burleigh Hill Member (Clinton Group). The diagenetic trend shows a decrease of Sr with progressive alteration and an increase in Mg contents with partial dolomitization. The field represents pristine brachiopods.
Sr contents are unusually high for all four species, falling well outside the range of chemistries recorded in this study and other Silurian brachiopods previously (Brand and Morrison, 1987). It is uncertain whether this is a physiological phenomena or a reflection of originally high Sr content of the local depositional waters. Sr contents in brachiopods from the Lewiston Member (~1200 ppm) and the overlying Burleigh Hill Member (~2300 ppm) are significantly different. This twofold increase in Sr contents occurs in *Resserella elegantula, Atrypa reticularis* and *Whitfieldella nitida*. The concentration of Sr in modern oceans is quite uniform, and mean oceanic Sr composition has apparently remained fairly constant throughout the Phanerozoic (Holland, 1978, 1984; Brand and Morrison, 1987; Brand, 1988). Consequently, this observed increase may represent a regional influx of Sr-rich waters; the source of which is difficult to determine. Strontium derived from weathering of the Appalachian landmass to the east may explain the lateral east-west decline of Sr contents in the "*Coolinia subplana*" Bed.

**Conclusions**

Articulate brachiopods collected from the Middle Silurian Clinton Group are in general chemically and microstructurally well preserved. However, post-depositional alteration of some brachiopod shell calcite has resulted in Mg, Mn and Fe enrichments while the retention of Na and Sr contents suggests that the diagenetic waters were probably of marine- or mixed-water derivation. Subsequent, Mg-rich dolomitizing fluids selectively replaced matrices leaving brachiopods generally unaffected.

Clinton Group brachiopods apparently fractionated Mg and Na, which has been demonstrated previously in studies of other Paleozoic brachiopods (Brand and Veizer, 1980; Popp et al., 1986b; this study). The incorporation of
Mg and Na into the shell calcites of *Atrypa reticularis*, *Eospirifer radiatus* and *Whitfieldella nitida* was apparently taxonomically controlled. In contrast, Sr contents in brachiopod shell calcite were largely determined by the ambient concentrations of Sr in seawater. No significant isotopic and elemental trends were observed corresponding to a transgressive-regressive cycle is recognized in the Lewiston Member. This cycle may be illusory because the seawater conditions remained fairly constant during this vertical sequence. Slight variations in elemental contents and isotopic values may have been determined by inherent physiological variability and random temperature, salinity and growth rate fluctuations. Minor depth changes may have caused the migration of facies belts, explaining the lithological and paleoecological changes. Isotopic analysis of *Eospirifer radiatus* and other brachiopods from the Rochester and Irondequoit Formations averaged $-3.3^\circ/_{oo}$ for $\delta^{18}O$. Paleotemperatures calculated from pristine shell calcites ranged from $18^\circ C-32^\circ C$, which is in accordance with a postulated equatorial position of their habitats. The mid-Wenlockian ocean situated within the northern Appalachian Basin had oceanic $\delta^{18}O$ values similar to that observed in modern oceans. Uncorrected $\delta^{18}O$ contents of brachiopod calcite from this study do not support the assertion that Silurian oceans were depleted in $\delta^{18}O$ by 5-6$^\circ/_{oo}$ (Brand and Veizer, 1981; Veizer et al., 1986; O'Shea et al., 1988).
CHAPTER 5

Diagenetic and paleoenvironmental study of brachiopod calcite from the Middle and Upper Ordovician; southern Ontario and Manitoulin Island.
INTRODUCTION

Marine sediments of the Middle and Upper Ordovician of Ontario were deposited in apparently warm water, shallow-marine seas close to the equatorial belt (Scotese et al., 1979; Brookfield and Brett, 1988) and contain a diverse fauna including brachiopods, coralgal colonies, nautiloids, crinoids and trilobites. Brachiopods are common to the complex limestone facies of the Trenton Group which represents a carbonate sequence deposited on a transgressed shelf (Brookfield and Brett, 1988). Similarly, brachiopods are also present within basal sections of the Collingwood Formation (Whitby Formation) black shales which were deposited within a shallow anoxic epicontinental sea (Johnson and Rong, 1989).

The purpose of this chapter is to evaluate the degree of chemical preservation of three commonly occurring brachiopods within shales and limestones of the Middle and Upper Ordovician. If brachiopod calcites are unaltered, investigation of elemental and isotopic trends in shell calcites, associated with transgressed carbonate facies and anoxic environments, will proceed.

GENERAL GEOLOGY

Paleozoic sedimentary accumulation within southern Ontario and New York State was probably controlled by plate motions and orogenic processes affecting the stable Precambrian North American craton (Sanford et al., 1985). Sedimentary deposition was constrained by the relative uplift or subsidence of two depositional basins, the Michigan and Appalachian, and the arch that separated them (Algonquin-Findlay). Uplift during the Lower Ordovician,
resulted in the subaerial exposure of strata in southern Ontario (Telford, 1978; Sanford et al., 1985). By early Middle Ordovician, the regional subsidence of the arch, associated with the Taconic Orogeny (Rodgers, 1971), created a broad ramp that extended across southern Ontario, into New York State and as far as West Virginia and Maryland (Titus 1986; Carter et al., 1988; Brookfield and Brett, 1988). The ramp deepened to the west and a shelf break was present in central New York State (Cisne et al., 1982). The resultant transgression of the shelf spanned in age the mid-Blackriveran to earliest Maysvillian (Barnes et al., 1978; Ludvigsen, 1978) and resulted in the sequential deposition of supratidal/tidal flat clastics and carbonates (Gull River Formation), lagoonal/shoal bar carbonates (Bobcaygeon Formation), and shallow to deep shelf carbonates (Verulam and Cobourg Formations), in southern Ontario (Fig. 5.1). The ramp and basin were influenced by gentle crustal upwarping (Titus and Cameron, 1976; Titus, 1986) and facies distribution was controlled by emergent carbonate shoals and Precambrian Shield islands (Brookfield and Brett, 1988). Marine sedimentation on a Precambrian (Lorraine Quartzite) rocky shore occurred in the Manitoulin Island area (Johnson and Rong, 1989) where the Basal Beds were succeeded by the Swift Current, Cloche Island, Verulam and Cobourg Formations (Fig. 5.2).

At the beginning of the Upper Ordovician, subsidence of the Appalachian basin associated with the Taconic Orogeny, buried the carbonate sediments of southern Ontario with grey/black shales of the Whitby Formation. Trenton Group limestones in Virginia and West Maryland were similarly replaced by clastics of the Martinsburg and Reedsville Shales (Kreisa, 1981; Carter et al., 1988). Suprajacent calcareous shales and carbonates of the Georgian Bay Formation are deposited in southern Ontario. In Manitoulin Island, rapid transgression resulted in the deposition of Collingwood Formation (Whitby Formation) black
Figure 5.1. Generalized stratigraphic section of southern central Ontario. Ages from Rickard (1975); Sweet and Bergstrom (1976); Ludvigsen and Odin (1978); Brookfield and Brett (1988).
Figure 5.2. Middle and Upper Ordovician stratigraphy of Manitoulin Island. Stratigraphic information and ages are from Barnes et al., 1978; Telford (1978), Sanford and Mosher, (1978), Telford et al. (1981), Johnson and Rong (1989).
RESULTS AND DISCUSSIONS

Chemical trends

Three brachiopod species, *Dalmanella rogata*, *Rafinesquina eltoidea* and *Sowerybella* sp., were analysed from shale and limestone units of southern Ontario and Manitoulin Island (Table 5.1). SEM analysis of shell calcites from these species indicates that preservation states are variable. Good microstructure is observed in a number of specimens primarily from the Trenton Group and Whitby Formation. However, the majority of shell calcites appear to have undergone some degree of postdepositional alteration. Although primary foliation is generally retained, there is considerable fusing of calcite laths/rods and minor reprecipitation of cements between fibres. Correspondingly, chemical alteration is apparent in a greater number of shell calcites (Table 5.2). Many specimens contain elevated Mn and Fe contents, and are reciprocally depleted in Sr and Na, which is diagnostic of partial re-equilibration of brachiopod calcite with diagenetic waters (Fig. 5.3; Brand and Veizer, 1980; Al-Aasm and Veizer, 1982; Brand, 1989). Furthermore, factor analysis supports this observation because Fe and Mn are significantly loaded together (Factor 1, Tables A-15 to A-18).
Table 5.1. Geochemical data of Middle and Upper Ordovician brachiopods from southern Ontario and Manitoulin Island.

<table>
<thead>
<tr>
<th>Brachiopod species</th>
<th>Stat. Ca</th>
<th>Mg</th>
<th>Sr</th>
<th>Mn</th>
<th>Na</th>
<th>Fe</th>
<th>Al</th>
<th>l.R.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dalmanella (ALL; N=45) Mean</td>
<td>377217</td>
<td>5847</td>
<td>754</td>
<td>222</td>
<td>1046</td>
<td>1561</td>
<td>137</td>
<td>11.8</td>
</tr>
<tr>
<td>S. Dev.</td>
<td>55589</td>
<td>5079</td>
<td>249</td>
<td>178</td>
<td>247</td>
<td>588</td>
<td>147</td>
<td></td>
</tr>
<tr>
<td>min</td>
<td>215150</td>
<td>1135</td>
<td>370</td>
<td>70</td>
<td>345</td>
<td>90</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>max</td>
<td>621040</td>
<td>19670</td>
<td>1395</td>
<td>610</td>
<td>3565</td>
<td>6700</td>
<td>740</td>
<td></td>
</tr>
<tr>
<td>Rafinesquina. (ALL; N=64) Mean</td>
<td>377249</td>
<td>4137</td>
<td>965</td>
<td>260</td>
<td>1143</td>
<td>640</td>
<td>118</td>
<td>7.6</td>
</tr>
<tr>
<td>S. Dev.</td>
<td>19906</td>
<td>1558</td>
<td>222</td>
<td>243</td>
<td>456</td>
<td>380</td>
<td>185</td>
<td></td>
</tr>
<tr>
<td>min</td>
<td>317000</td>
<td>2490</td>
<td>490</td>
<td>45</td>
<td>215</td>
<td>135</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>max</td>
<td>440450</td>
<td>11100</td>
<td>1485</td>
<td>1160</td>
<td>2370</td>
<td>2300</td>
<td>1300</td>
<td></td>
</tr>
<tr>
<td>Sowerybella (ALL; N=21) Mean</td>
<td>386786</td>
<td>3069</td>
<td>792</td>
<td>118</td>
<td>1108</td>
<td>402</td>
<td>154</td>
<td>7.3</td>
</tr>
<tr>
<td>S. Dev.</td>
<td>24265</td>
<td>646</td>
<td>206</td>
<td>61</td>
<td>340</td>
<td>238</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td>min</td>
<td>303810</td>
<td>1510</td>
<td>310</td>
<td>40</td>
<td>100</td>
<td>50</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>max</td>
<td>413690</td>
<td>4850</td>
<td>1100</td>
<td>270</td>
<td>1525</td>
<td>790</td>
<td>420</td>
<td></td>
</tr>
<tr>
<td>Dalmanella Unaltered (VERULAM) (N=9) Mean</td>
<td>384387</td>
<td>3132</td>
<td>835</td>
<td>100</td>
<td>973</td>
<td>149</td>
<td>105</td>
<td>5.4</td>
</tr>
<tr>
<td>S. Dev.</td>
<td>16498</td>
<td>551</td>
<td>138</td>
<td>28</td>
<td>320</td>
<td>49</td>
<td>77</td>
<td></td>
</tr>
<tr>
<td>min</td>
<td>360090</td>
<td>1935</td>
<td>685</td>
<td>35</td>
<td>540</td>
<td>90</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>max</td>
<td>403820</td>
<td>3675</td>
<td>1135</td>
<td>135</td>
<td>1620</td>
<td>230</td>
<td>290</td>
<td></td>
</tr>
<tr>
<td>Rafinesquina Unaltered (VERULAM) (N=17) Mean</td>
<td>358731</td>
<td>3470</td>
<td>1073</td>
<td>94</td>
<td>1244</td>
<td>456</td>
<td>110</td>
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</tr>
<tr>
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<td>104</td>
<td>39</td>
<td>216</td>
<td>119</td>
<td>112</td>
<td></td>
</tr>
<tr>
<td>min</td>
<td>346390</td>
<td>2740</td>
<td>955</td>
<td>70</td>
<td>955</td>
<td>335</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>max</td>
<td>376400</td>
<td>4560</td>
<td>1270</td>
<td>160</td>
<td>1580</td>
<td>620</td>
<td>260</td>
<td></td>
</tr>
<tr>
<td>Sowerybella Unaltered (VERULAM) (N=16) Mean</td>
<td>388634</td>
<td>3050</td>
<td>843</td>
<td>106</td>
<td>1189</td>
<td>387</td>
<td>156</td>
<td>7.1</td>
</tr>
<tr>
<td>S. Dev.</td>
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<td>400</td>
<td>150</td>
<td>458</td>
<td>179</td>
<td>241</td>
<td>99</td>
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<td>55</td>
<td></td>
</tr>
<tr>
<td>max</td>
<td>413690</td>
<td>4270</td>
<td>1100</td>
<td>205</td>
<td>1525</td>
<td>790</td>
<td>420</td>
<td></td>
</tr>
</tbody>
</table>

All elemental concentrations are in ppm.
Table 5.2. Comparison of microstructural preservation and chemistry for selected brachiopods, representing different species, and lithologies. Lithology symbols denote (S = dark grey shale; CM = calcareous mudstones; ML = micritic limestones; W = wackestones; P = packstones; CG = crinoidal grainstones)

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Species</th>
<th>Age</th>
<th>Lithology</th>
<th>Preservation State</th>
<th>Diagenetic features</th>
<th>Mg (ppm)</th>
<th>Mn (ppm)</th>
<th>Fe (ppm)</th>
<th>Figured</th>
</tr>
</thead>
<tbody>
<tr>
<td>835</td>
<td>Sowerybella</td>
<td>Ver.</td>
<td>W</td>
<td>Good</td>
<td>No</td>
<td>2975</td>
<td>40</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>798</td>
<td>Sowerybella</td>
<td>Ver.</td>
<td>W</td>
<td>Fair</td>
<td>Slight diss.</td>
<td>3240</td>
<td>100</td>
<td>310</td>
<td></td>
</tr>
<tr>
<td>797</td>
<td>Sowerybella</td>
<td>Ver.</td>
<td>P</td>
<td>Fair</td>
<td>Slight diss.</td>
<td>3570</td>
<td>160</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>765</td>
<td>Sowerybella</td>
<td>Ver.</td>
<td>P</td>
<td>Fair</td>
<td>Slight diss.</td>
<td>4270</td>
<td>205</td>
<td>680</td>
<td></td>
</tr>
<tr>
<td>773</td>
<td>Dalmanella</td>
<td>Ver.</td>
<td>CG</td>
<td>Good</td>
<td>Slight diss.</td>
<td>3185</td>
<td>130</td>
<td>120</td>
<td>2.22</td>
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<tr>
<td>736</td>
<td>Dalmanella</td>
<td>G.B.</td>
<td>S</td>
<td>Poor</td>
<td>Dissolution</td>
<td>13030</td>
<td>510</td>
<td>3900</td>
<td></td>
</tr>
<tr>
<td>776</td>
<td>Dalmanella</td>
<td>Ver.</td>
<td>P</td>
<td>Poor</td>
<td>Dissolution</td>
<td>3990</td>
<td>150</td>
<td>130</td>
<td></td>
</tr>
<tr>
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<td>Dalmanella</td>
<td>Ver.</td>
<td>CG</td>
<td>Good</td>
<td>Slight diss.</td>
<td>3350</td>
<td>110</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>899</td>
<td>Dalmanella</td>
<td>Whit.</td>
<td>S</td>
<td>Good</td>
<td>Slight diss.</td>
<td>4810</td>
<td>70</td>
<td>550</td>
<td></td>
</tr>
<tr>
<td>794</td>
<td>Rafinesquina</td>
<td>Ver.</td>
<td>P</td>
<td>Good</td>
<td>None</td>
<td>3790</td>
<td>115</td>
<td>665</td>
<td></td>
</tr>
<tr>
<td>825</td>
<td>Rafinesquina</td>
<td>Ver.</td>
<td>CG</td>
<td>Poor</td>
<td>Yes</td>
<td>4295</td>
<td>300</td>
<td>700</td>
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<tr>
<td>764</td>
<td>Rafinesquina</td>
<td>Ver.</td>
<td>P</td>
<td>Poor</td>
<td>Yes</td>
<td>3810</td>
<td>160</td>
<td>520</td>
<td>2.21</td>
</tr>
<tr>
<td>827</td>
<td>Rafinesquina</td>
<td>Ver.</td>
<td>CG</td>
<td>Poor</td>
<td>Yes</td>
<td>3945</td>
<td>255</td>
<td>430</td>
<td></td>
</tr>
<tr>
<td>822</td>
<td>Rafinesquina</td>
<td>Ver.</td>
<td>P</td>
<td>Good</td>
<td>No</td>
<td>3160</td>
<td>50</td>
<td>495</td>
<td></td>
</tr>
</tbody>
</table>

All elemental values are in ppm.
Figure 5.3. Scatter plot of Fe vs Mn for all brachiopods from the Middle and Upper Ordovician of southern Ontario and Manitoulin Island. Open symbols denote unaltered specimens and closed symbols denote altered material. Altered specimens that plot with low Mn contents (~40-75ppm) are partially silicified.
Isotopic trends

Covariances of $\delta^{13}C$ and $\delta^{18}O$ contents with diagenetic re-equilibration of shell calcite is observed in specimens from the Middle and Upper Ordovician Ontario. For example, Mn and $\delta^{18}O$ contents of brachiopods show complementary diagenetic trends (Figure 5.4) and altered brachiopods are significantly more negative in $\delta^{13}C$ and $\delta^{18}O$ (Figure 5.5). The best preserved brachiopod shell calcites of *Dalmanella rogata* and *Rafinesquina deltoidea* have an average $\delta^{13}C$ of $+1.2^{\circ}/_{oo}$ (range $0.5^{\circ}/_{oo}$ to $1.7^{\circ}/_{oo}$) and contain an average value $\delta^{18}O$ of $-5.7^{\circ}/_{oo}$ (range $-6.8^{\circ}/_{oo}$ to $-4.5^{\circ}/_{oo}$). In contrast, altered calcite have a more negative average $\delta^{13}C$ of $-0.2^{\circ}/_{oo}$ (range $-0.8^{\circ}/_{oo}$ to $0.6^{\circ}/_{oo}$) and $\delta^{18}O$ of $-5.7^{\circ}/_{oo}$ (range $-6.8^{\circ}/_{oo}$ to $-4.5^{\circ}/_{oo}$). It is apparent that all the Upper Ordovician brachiopods analysed are post-depositionally altered, whereas Trenton Group shell calcites are the least altered.

Lithology and preservation potential

Lithologic control of chemical alteration of carbonates is reported by Pingitore (1978, 1982). In this study, the preservation of brachiopod low-Mg calcite appears also to be directly dependant upon lithology and pore geometries. Brachiopods analysed from limestone facies (i.e. wackestones) have divergent diagenetic trends to those analysed from shale facies (Figure 5.6). The relative enrichment or depletions of elemental contents is dependant on a number of factors. The Mn and Fe contents of a diagenetic product will depend upon fluid compositions and the Eh of the diagenetic microenvironment. Meteorically-derived fluids are compositionally enriched in Mn and Fe relative to marine waters (Drever, 1982) only if they exist in lower oxidation states within a reducing phreatic zone (James and Choquette, 1984); reduced divalent ions are more readily available for incorporation into
Figure 5.3. Diagenetic trend of oxygen isotopic composition for Middle and Upper Ordovician Dalmanella and Rafinesquina brachiopods of southern Ontario. Symbols denote; ◊ altered, ◦ least-altered.

Figure 5.5. Diagenetic trend of isotopic compositions of Dalmanella and Rafinesquina brachiopods from the Middle and Upper Ordovician of southern Ontario and Manitoulin Island. Symbols as in Figure 5.4.
Figure 5.6. Scatter plot of Sr vs Mn for shell calcites of Dalmanella rogata. Fields define range of pristine brachiopods and arrows depict direction of alteration for brachiopod calcite in shales and limestones. □ Verulam (locality 63i); ● Verulam (63ii); ■ Wekwenikongsing (51); ◊ Sheguiandah (50); □ Verulam (65); □ Bobcaygeon (66A); ▲ Verulam (66B); △ Collingwood beds; Whitby Fm. (59i). Dalmanella in the Verulam Formation are from mudstones and wackestones with the exception of locality 66B. Dalmanella calcites from the uppermost metre of cross laminated and bedded skeletal grainstone and packstone beds at Kirkfield Quarry (locality 65) are the most altered. Bioclasts are predominantly well sorted coarse crinoid columnals with brachiopod, bivalves and gastropods. Pore filling equant sparite is common. Thus pore geometries may have constrained diagenetic alteration and preservation potential.
diagenetic low-Mg calcite. The divergence of diagenetic trends observed here can be directly attributed to the lithological availability of Fe and Mn in shales compared to limestones. In addition, altered brachiopod calcites reflect the more "open", fluid controlled diagenesis of wackestone/packstone lithologies compared to diffusion controlled reactions in shale.

The control of lithology on potential preservation and magnitude of elemental repartitioning is also evident within brachiopod calcites of *Dalmanella rogata* and *Sowerybella* (Figure 5.7). The Na, Sr and Mg contents of *Dalmanella rogata* from the Verulam Formation are not significantly different between localities with the exception of those from the crinoidal grainstones at the Kirkfield road cut (locality 66B). Mn contents are elevated (Figure 5.6) and Na and Sr contents are significantly lower. Similarly, shell calcites of *Sowerybella* from a Verulam Formation wackestone bed from the County Road 6 Kirkfield exposure (locality 66b) are the least altered (Fig. 5.7). Specimens from skeletal packstones at Lakefield Quarry (locality 75) are increasingly altered, while those calcites from crinoidal grainstones (skeletal biosparites from localities 78, 79, 68) show the greatest effect of post-depositional alteration (Fig. 5.7). These crinoidal grainstones are pore filled with equant sparite cement. A spectrum of diffusion to fluid controlled diagenetic alteration appears to be directly controlled by lithology and pore geometries.

**Diagenetic waters of the Middle and Upper Ordovician**

Brachiopods altered in an essentially meteoric environment usually show a depletion of Sr and Na in association with Mn and Fe enrichments (Brand and Veizer, 1980; Al-Aasm and Veizer, 1982; Viezer 1983a) whereas the magnitudes of trace element diagenetic shifts are dampened in the presence of diagenetic waters of marine parentage (Veizer, 1983a). The concentration of
Figure 5.7. Scatter plot of Sr vs Mn for Sowerybella sp. Symbols denote lithology; ◆ wackestones (locality 66B), ◆ packstones (localities 78i); and ◆ grainstones (68, 77, 78i, 80). Sowerybella specimens show varying degrees of alteration which is controlled by lithology and pore geometry. A few of the crinoidal grainstone beds were graded and Sowerybella were in varying states of taphonomic preservation.
ionic species is that much greater (i.e. Na, Sr and Mg contents; Drever, 1982) and altered shell calcites retain high Sr and Na contents and enriched $\delta^{13}$C and $\delta^{18}$O compositions. Furthermore, Mg-depleted biogenic carbonates can gain Mg during recrystallization with marine derived waters (Baker et al., 1982).

Examination of chemical data for Trenton Group and Whitby Formation brachiopods of southern Ontario and Manitoulin Island suggests that there are different diagenetic fluids involved in brachiopod alteration (Figure 5.8). A plot of Na vs Mg for all brachiopods clearly illustrates these trends. Those brachiopods collected from southern Ontario show depletion of Na and Sr (not shown) with diagenesis, while Mg contents remain close to their original compositions. This chemical trend is characteristic of meteoric diagenesis described by previous authors (Brand and Veizer, 1980; AL-Aasm and Veizer, 1982; Veizer, 1983a; 1983b). In contrast, brachiopods analysed from the shales and carbonates of Manitoulin Island become progressively enriched in Mg with chemical alteration and do not show characteristic co-variant depletions of Sr and Na. The retention of Na, Sr and the enrichment of Mg suggests that the diagenetic waters responsible for alteration of shell calcites had significant ionic strength and were of marine parentage (Veizer, 1983a, b). These divergent diagenetic trends were observed in shell calcites of *Dalmanella rogata*, *Sowerybella*, *Rafinesquina deltoidea* and small rhyconellids (*Rhynchotrema* sp.) from the Trenton and Whitby Formations. Moreover, analysis of brachiopods just from the Verulam Formation also revealed a similar diagenetic divergence between southern Ontario and Manitoulin Island, despite the fact that the lithologies of both areas are very similar; thin to medium (4-15 cm thick), irregularly bedded skeletal packstones and grainstones interbedded with thin grey green shales (Sanford and Mosher, 1978).
Figure 5.8. Scatter plot of Mn vs Fe for *Dalmanella rogata*. Symbols denote Verulam (locality 63); Verulam (63ii); Wekwemikongsing (51); Sheguiandah (50); Verulam (65); Bobcaygeon (66A); Verulam (66B); Collingwood beds; Whitby Fm. (59). Fields represent chemically pristine brachiopods. Brachiopods from the Bobcaygeon Formation are partially silicified. *Dalmanella* brachiopods were collected from a shell pavement (6-8cm) within the upper sequence of grey shales belonging to the Sheguiandah Member in Manitoulin Island (Whitby Formation). This bed was composed exclusively of articulate *Dalmanella* coated with limonite. Their shell calcites are chemically altered, with elevated Mn, Fe and Mg contents (Fig. 5.7) and reciprocal depletion of Sr, Na, d13C and d18O contents. Similarly, *Dalmanella* collected from grey shales of the Wekwemikongsing Member in Manitoulin are also extensively altered.
The chemistries of the diagenetic fluids responsible for alteration can be estimated from the chemical contents and appropriate partition coefficients (Veizer 1983a, b; Brand, 1989b). Calculated molar ratios of the diagenetic fluids from southern Ontario suggests that the fluids were close to surface water compositions i.e. meteorically-derived. Furthermore, calculation of diagenetic waters from Manitoulin Island suggests that marine or marine-derived fluids were responsible for brachiopod alteration. However, experimental partition coefficients are variable and altered brachiopod calcite may not have fully equilibrated with diagenetic fluids. The limited isotopic data cannot confirm these diagenetic trends. Shell calcites from southern Ontario and those from Manitoulin Island show depletions of $\delta^{13}C$ and $\delta^{18}O$ with alteration, characteristic of meteoric derived waters (Veizer, 1983a; 1983b). Additional isotopic testing of brachiopods, cements and matrix from Manitoulin Island may help determine the waters involved in brachiopod alteration.

An explanation for these divergent diagenetic waters of the Trenton Group is at best speculative. The Algonguin Arch trending through southern Ontario was rejuvenated during Middle Ordovician times (Sanford et al., 1985) and the carbonate platform may have been emergent during Trentonian times (Telford, 1978; Sanford et al., 1985; Brookfield and Brett, 1988). Trenton carbonate deposition is often around Precambrian inliers (Liberty, 1969; Brookfield and Brett, 1988) and hardgrounds may or may not be evidence of aerial exposure of the platform (Brett and Brookfield, 1984). Dolomitization is widespread in the Middle Ordovician carbonates deposited basinward on the Findlay Arch. Sanford et al., (1985) suggests that dolomitizing fluids were either derived from Cambrian sandstones or from meteoric waters during a hiatus at the close of the Middle Ordovician. Conceivably, exposure of Trenton Group carbonates in southern Ontario may have resulted in the build-up of surficially
derived meteoric waters that were responsible for brachiopod alteration. In this scenario, brachiopods would have been close to the presumed recharge zone on the Algonquin Arch high and undergone alteration in gradients driven by these surficially derived fluids. In Manitoulin Island, there was an apparent hiatus before rapid transgression and deposition of the Upper Ordovician Collingwood Formation (Copper, 1978). Since this region was on the flank of the arch, there may not have been exposure of Trenton carbonates and alteration of brachiopod calcite could have proceeded within a phreatic mixing zone or marine phreatic zone.

PALEOENVIRONMENTAL ANALYSIS OF MIDDLE TO UPPER ORDOVICIAN

The least altered brachiopods were selected by evaluating elemental concentrations of Fe, Mn, Mg, Sr and Na in combination with microstructural preservation. Unaltered brachiopod calcites were recognized primarily from the Verulam and Collingwood Formations. As a preliminary caveat to further discussions, it must be stated that strict interpretations about *Sowerybella* and *Rafinesquina deltoidea* chemistry are constrained by the fact that the slightly fused nature of these strophomenid shell calcites, recognized as a primary structure by other authors (Rowell and Grant, 1987), may indeed be a diagenetic structure. Despite this, covariances of elemental contents will give a good indication of degree of chemical alteration and altered specimens are eliminated from further discussion. A number of potentially environmentally controlled chemical trends are evident in the best preserved material.
Taxonomic differences in shell calcite composition

Within the best preserved material of the Verulam Formation, there appears to be a significant difference in Fe contents between the strophomenids *Rafinesquina deltoidea* and *Sowerybella* with the orthid *Dalmanella rogata* (Table 5.3; t-test, p < 0.05, f=31). This may reflect either unrecognized diagenetic alteration, the Eh and potential reducing conditions of the depositional setting or a physiological/mineralogical difference between these species. Alternately it may due to differences in habitat/substrate preference between each species.

Relationship of depth to Mg, Sr and Na compositions of brachiopod calcite

In a previous chapter, a possible relationship between Mg, Sr, Na contents and environmental factors (i.e., depth) was observed in Hamilton Group brachiopod species. A similar relationship is observed between the three species analysed from the Verulam Formation. Lithofacies distribution of Verulam sediments deposited on the Trenton platform range from shallow high energy shoal-bar facies to quieter, potentially deeper shoal margin and open marine facies (Brett and Brookfield, 1984). In general, distribution of brachiopods is restricted to various lithotypes and presumed energy environments (Brookfield and Brett, 1988). *Dalmanella rogata* and *Sowerybella* were collected from mudstone and wackestone sequences that may represent quiet-water, low to moderate energy environments whereas *Rafinesquina deltoidea* were sampled from presumably shallower, shoal-bar crinoidal grainstones and packstones. Mg, Sr and Na contents of *Rafinesquina deltoidea* shell calcite are correspondingly higher compared to *Dalmanella rogata* and *Sowerybella* (Fig. 5.9). Although there is the potential for diagenetic bias, this
Table 5.3. T-test: Verulam Formation

<table>
<thead>
<tr>
<th>Element</th>
<th>Rafinesquina</th>
<th>Sowerybella</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Signif.</td>
<td>T-stat</td>
</tr>
<tr>
<td>Dalmanella</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>$p&gt;0.05$</td>
<td>0.127</td>
</tr>
<tr>
<td>Mg</td>
<td>$p&lt;0.05$</td>
<td>2.860</td>
</tr>
<tr>
<td>Sr</td>
<td>$p&gt;0.05$</td>
<td>1.085</td>
</tr>
<tr>
<td>Mn</td>
<td>$p&gt;0.05$</td>
<td>0.333</td>
</tr>
<tr>
<td>Na</td>
<td>$p&gt;0.05$</td>
<td>2.258</td>
</tr>
<tr>
<td>Fe</td>
<td>$p&lt;0.05$</td>
<td>2.902</td>
</tr>
<tr>
<td>D.O.F.</td>
<td>(25)</td>
<td></td>
</tr>
<tr>
<td>Sowerybella</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>$p&lt;0.05$</td>
<td>0.386</td>
</tr>
<tr>
<td>Mg</td>
<td>$p&lt;0.05$</td>
<td>3.131</td>
</tr>
<tr>
<td>Sr</td>
<td>$p&gt;0.05$</td>
<td>1.166</td>
</tr>
<tr>
<td>Mn</td>
<td>$p&gt;0.05$</td>
<td>0.404</td>
</tr>
<tr>
<td>Na</td>
<td>$p&gt;0.05$</td>
<td>0.904</td>
</tr>
<tr>
<td>Fe</td>
<td>$p&gt;0.05$</td>
<td>1.340</td>
</tr>
<tr>
<td>D.O.F.</td>
<td>(33)</td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.9. Mean and standard deviation of unaltered chemistries of Dalmanella, Rafinesquina and Sowerybella from the Verulam Formation. There are differences in Mg, Sr and Na chemistries between the shallow water Rafinesquina and slightly deeper Dalmanella and Sowerybella. Sowerybella and Dalmanella were collected from sequences of thin nodular wackestones and mudstones. Sowerybella brachiopods were often found in shell pavements on the upper surfaces of medium bedded, nodular mudstones and wackestones. Taphonomic preservation was good, with articulated valves and lack of fragmentation common. Dalmanella were present within thin (3-5 cm thick) irregular, hummocky mudstones and wackestones, interbedded with occasional packstones (crinoidal biosparites) and thin partings of dark grey claystones. Their shells were commonly articulated and there was little evidence of abrasion, encrustation or fragmentation of valves. This suggests that there was minimal reworking and transport of these brachiopods. They may have inhabited deeper parts of the shoal margins or depressions, close to the storm wavebase (Brookfield and Brett 1988).

Disarticulated Rafinesquina deltoidea were collected from thin to thick (5 cm-25 cm thick) planar or irregular bedded, graded packstone and grainstone beds. These grainstones often contain low-angle cross lamination and are composed of well rounded crinoidal stems and other bioclasts with Rafinesquina as the dominant brachiopod. Graded grainstone beds often contain disarticulate and abraded Rafinesquina in lower part of bed and articulated Sowerybella on the upper surface (e.g., Lakefield quarry; Trenton). It is uncertain if this represents ecologic succession within the bed or size sorting of storm beds (Westrop, 1986). Rafinesquina collected from these low-angle cross-laminated grainstones are interpreted by Brett and Brookfield (1984) as representing sediments deposited on a shallow shoal bar facies, within the fairweather wavebase.
chemical relationship may reflect environmental/physical conditions (i.e., depth, turbidity and energy of environment) and substrate preferences which controlled precipitation rates and shell calcite compositions.

**Brachiopod calcite and low oxygen conditions**

Articulated *Dalmanella rogata* were analysed from the dark grey shales of the lower Whitby Formation, which overlie the Cobourg Formation (locality 59). The lowest couple of metres of the Whitby is composed of a sequence of dark grey shales separated by thin shell pavement beds (0.5-1.5cm thick). *Dalmanella rogata* brachiopods are the dominant fauna within these winnowed shell beds. Preservation is variable, with a spectrum of articulated valves to disarticulated, abraded and fragmented specimens. Significant reworking, and postmortem transport indicate a position above storm wave base. Overlying these basal beds are black fissile shales that contain abundant *Pseudogygites* trilobites in varying states of articulation. The lack of bioturbation, petroliferous nature of the dark shales, and presence of abundant pyrite suggests a high input of organics and a potentially anoxic/reducing environment.

*Whitby* Formation *Dalmanella rogata* are microstructurally preserved and have Mn contents similar to *Dalmanella rogata* from mudstones and wackestones of the Verulam Formation. However, Fe contents are significantly higher (Fe; 575-880ppm; Fig. 5.10) which is possibly explained by a difference in redox conditions between the shallow turbid shoal-margin facies of the Verulam and the black shale facies of the Whitby Formation. In Manitoulin Island, the black shale facies of the Collingwood Formation has been interpreted to be the result of a thermocline, developed just below the normal wavebase (Johnson and Rong, 1989). Emplacement of the thermocline is modelled on the periodic influx of brackish waters into an epicontinental sea.
The presence of an oxycline/pycnocline close to shallow marginally placed *Dalmanella rogata* populations may have caused the periodic impingement of dysaerobic and potentially more reducing water conditions into bottom waters surrounding *Dalmanella rogata*. As previously discussed, these ancient brachiopods probably could survive periods of dysaerobia and as such will reflect time-averaged incorporation of redox controlled elements.

The chemical compositions of *Dalmanella rogata* brachiopods from the Verulam Formation appear to be related to type of facies. *Dalmanella rogata* from the distal shoal margin mudstones and wackestones at the Bolsover roadcut (locality 63iii; Figure 5.10) have generally higher Mn and Fe contents than *Dalmanella rogata* from the shoal bar facies (locality 66B; Figure 5.10). Slight differences in oxic conditions between these environments may have similarly affected the availability of Fe and Mn for incorporation into *Dalmanella rogata* shell calcite.

**Depositional waters**

Previous authors have used elemental compositions of ancient pristine molluscan carbonate and experimentally derived partition coefficients to determine the chemistry of depositional waters (Brand, 1986, 1987, 1989b). This study has indicated that there is fractionation of Mg, Sr, Na and possibly Mn by varying degrees within brachiopod species of the Hamilton Group (Middle Devonian) and Clinton Group (Middle Silurian). Trenton Group brachiopod shell calcite appears to reflect a complex interaction of taxonomic regulation and possible environmental controls. Partition coefficients are derived from inorganic calcites, and biological regulation of shell calcite
Figure 5.10. Scatter diagram of Na vs Mg for brachiopods from Manitoulin Island and from southern Ontario. Specimens collected from the Trenton Group, Sheguiandah and Wekwemikongsing Members in Manitoulin Island were altered in the presence of Sr, Mg and Na rich water (i.e. of marine derivation). Brachiopods from the Trenton Group in southern Ontario were altered in the presence of meteoric type waters. These divergent diagenetic trends are observed for *Dalmanella* and *Sowerybella* brachiopods. Field indicates ranges of unaltered specimens. Silicification trend occurs in Bobcaygeon Formation brachiopods.
composition does not allow the unequivocal retrieval of information about original depositional waters from brachiopod calcites.

**Isotope trends**

Paleogeographic reconstructions of the Trenton platform suggests that carbonates were precipitated from warm, shallow-marine waters within the equatorial belt (Scotese et al., 1984; Brookfield and Brett, 1988). Salinities were probably within normal ranges and disturbed only by episodic climatic depressions contributing fresh waters to surficial marine environments. Changes in the isotopic compositions of brachiopod shell calcites, associated with the marine transgression in Ontario, are not evident with data from this study. Slight differences in the δ¹⁸O contents of pristine brachiopods calcites may be related to natural isotopic variability of shell calcite, localized water temperature and salinity changes or unrecognized diagenetic effects. The δ¹³C contents of Trenton Group brachiopods become more negative by 1‰ (PDB) from the Bobcaygeon to Cobourg Formations, although the isotopic data is limited. Brachiopods from the shallow shoal facies are the most positive in δ¹³C whereas those specimens from the deeper shoal margin proximal facies are slightly enriched in ¹²C. Further isotopic testing needs to be done to confirm whether there is significance to this trend.

**CONCLUSIONS**

Many of the brachiopod shell calcites analysed from limestones and shales of the Middle and Upper Ordovician are chemically altered and a relationship between the degree of chemical alteration and lithology is observed. Divergent diagenetic trends are apparent between altered
brachiopods analysed from southern Ontario and those from Manitoulin Island. Brachiopod calcites analysed from southern Ontario appear to have altered in meteorically derived waters which may have resulted from exposure of Trenton carbonates at the end of the Middle Ordovician. In contrast, brachiopod calcites in Manitoulin Island altered in the presence of diagenetic fluids of marine parentage.

Verulam Formation *Rafinesquina deltoidea*, analysed from shallow shoal bar facies, are elevated in Mg, Sr and Na contents compared to *Sowerybella* and *Dalmanella rogata rogata*, which inhabited deeper shoal margin environments. This trend confirms a previous relationship of brachiopod calcite composition with depth observed for Hamilton Group brachiopods (this study). The Fe chemistry of unaltered *Dalmanella rogata* calcite appears to be related to ancient seawater conditions. Marginally positioned *Dalmanella rogata* populations, which presumably lived above a thermocline developed during deposition of the Collingwood Formation, may reflect periodic incursions of oxygen deficient waters into shallower areas of the shelf.
CHAPTER 6

Secular trends of oxygen and carbon isotopes
INTRODUCTION

Marine sediments have provided a means for investigating the isotopic and elemental changes in ocean-atmosphere chemistry during the Phanerozoic (e.g., Holland, 1978, 1984; Veizer, 1985). Modelling of the long term changes in carbon, atmospheric O$_2$ and CO$_2$ levels, and climate have been focused on the isotopic compositions of marine carbonates (Kump, 1988; 1989a, b; Kasting, 1989; Popp et al., 1989; Lasaga, 1989). Furthermore, analysis of chemical sediments has provided a means of isotopically resolving stratigraphic correlations and investigating anoxic ocean events (e.g., Arthur et al., 1985a, b; Holser et al., 1986; Magaritz et al., 1986; Aharon et al., 1987; Arthur et al., 1989; Brasier and Magaritz, 1989). However, the vulnerability of chemical sediments to post-depositional alteration has led to the increasing use of biogenic carbonates for paleochemical investigation (e.g., Holser, 1984; Veizer et al., 1986; Popp et al., 1986; Holser et al., 1989; Grussczynski et al., 1989; Brand, 1989a, c), since chemical trends derived from matrix carbonate will tend to reflect polymineralic compositions and varying degrees of diagenetic re-equilibration (Popp et al., 1986). Thus brachiopods, composed of low-Mg calcite which is stable in most diagenetic settings, can be used since they record the ambient isotopic compositions of their depositional environment. Kinetic fractionation in biogenic carbonates is dependant on calcification rates; the faster growth rates the greater the apparent isotopic disequilibria (McConnaughey, 1989a). Since brachiopod metabolism is slow, it is likely that $^{13}$C and $^{18}$O were indeed in equilibrium with ambient conditions. Moreover, brachiopod calcites and preserved aragonitic molluscs from the Boggy and other Carboniferous formations have similar $\delta^{13}$C values, reflecting depositional conditions rather than isotopic fractionation (Brand, 1987, 1989).
Carbon isotopes

The variation in $^{13}$C$_{carb.}$ during the Paleozoic has been interpreted in terms of changes in the geochemical cycles of sulphur and carbon (Berner et al., 1983; Lasaga et al., 1985; Kump and Garrelts, 1986; Berner, 1987) and changes in sedimentation and burial rates of organic and inorganic carbon (Berner, 1989; Berner and Canfield, 1989). Positive shifts in $\delta^{13}$C are related to increased burial rates of organic carbon (Brand, 1988; Delaney, 1989). The distribution of carbon between carbonate and $^{13}$C depleted organic carbon sedimentary reservoirs controls the average oceanic carbon isotopic ratio and a change in the balance of these geological cycles by increased or reduced rates of C$_{org.}$ burial will result in complementary changes in mean oceanic $\delta^{13}$C values (Delaney, 1989). Similarly, carbon isotopes can reflect oceanic primary productivity such that a increase in $\delta^{13}$C may correspond to a reduction in primary productivity and enrichment in the dissolved inorganic carbon of deep bottom waters. Gruszczynski et al., (1989) report a positive carbon isotopic spike recorded in brachiopod calcite close to the Permo-Trias boundary, which they attribute to increased oxidation of organic carbon. This is suggested to have drastically affected oceanic nutrients and atmosphere oxygen levels sufficiently to result in mass extinctions of fauna.

A number of previous authors have reported gradual increases in $\delta^{13}$C$_{carb.}$ spanning the Ordovician to Permian (Veizer et al., 1980; Holser, 1984; Popp et al., 1986; Veizer et al., 1986; Popp et al, 1989). A positive shift in brachiopod $\delta^{13}$C from Middle Devonian to Permian, has been attributed to a greater burial of organic carbon and the expansion of the terrestrial biomass during the late Devonian (Brand, 1989a, c). The secular variation of $\delta^{13}$C$_{carb.}$ during the Paleozoic has been inversely correlated with variation of $\delta^{34}$S values.
in sulphate minerals (Veizer et al., 1986). This isotopic relationship of sulphur and carbon has been attributed to the redox balance of oxygen and carbon exogenic cycles (Berner et al., 1983; Veizer et al., 1986). The coupling of carbon and sulphur was modelled by Garrels and Lerman (1981) to predict changes in $\delta^{13}C_{\text{carb}}$ during the Devonian, and they suggest that the $\delta^{13}C$ of seawater should have been heavier in Middle Devonian (> +1‰) compared to Early and Late Devonian (< -1‰). However, Veizer et al. (1986) reported that the $\delta^{13}C$ compositions of Devonian brachiopods averaged about -1‰ and they postulated that the lack of correlation with the Garrels and Lerman (1981) model was due to deterioration of the carbon-sulphur coupling.

Isotopic analyses of brachiopod calcites from this study indicate that the $\delta^{13}C$ composition of shell calcite is much heavier (+2.5‰ to +6.0‰; Fig. 6.1) than previously reported for brachiopods of Devonian or Silurian age (~ -1‰ to +1‰; Popp et al., 1986a, b; Veizer et al., 1986; Brand, 1989a). The $\delta^{13}C$ composition of Devonian brachiopods is reported to vary between -1‰ to +1‰ (Popp et al., 1986a; Veizer et al. 1986). Similarly, the $\delta^{13}C$ compositions of late Silurian brachiopod calcites vary between -1.0‰ and +2.8‰ (Popp et al., 1986a; Veizer et al. 1986). In contrast, the isotopic compositions of pristine Hamilton Group (Middle Devonian) brachiopod calcite shifts range between ~+2.0‰ to ~+5.5‰ while the $\delta^{13}C$ values of Middle Silurian shell calcites range between +4.5‰ and +6.0‰. Furthermore, isotopic variation within a single shell bed is observed to be 2-2.5‰ and reflects changes in depositional waters with deepening toward the basin centre. These heavy $\delta^{13}C$ values may reflect greater burial rates and fluctuations in the marine biomass during these times. The absence of vascular plants prior to the Late Silurian (Niklas et al., 1985; Knoll and James, 1986; Berner, 1989) negates a terrestrial influence of carbon. Comparison of these new isotopic data to sulphate curves in Holland.
Figure 6.1. Secular variation curve of carbonate carbon isotopes with geologic age. Curves from Popp et al. (1986); open diamond; and Brand (1988); closed diamond. Data from this study is plotted as the mean and range of unaltered brachiopod material (open square). Approximate ages are from Harland et al. (1982).

Figure 6.2. Secular variation curve of carbonate oxygen isotopes with geologic age. Curves from Popp et al. (1986); open diamond; and Brand (1988); closed diamond. Data from this study is plotted as the mean and range of unaltered brachiopod material (open square). Approximate ages are from Harland et al. (1982).
(1984; Fig. 9.12, source Claypool et al. 1980), Veizer et al. (1986) and Kump, (1989a) suggests that the carbon isotopic compositions of brachiopods from the Middle Devonian and Middle Silurian are in accordance with the postulated values modelled by the C-S coupling during the Paleozoic (Garrels and Lerman, 1981; Veizer et al., 1986). However, extrapolation of these isotopic data to secular variation of δ^{13}C is problematic. The stratigraphic resolution and intervals of sampling is limited. Therefore the significance of trends within the basin is difficult to relate to global cycling of oxygen, carbon and sulphur during the Middle Devonian and Middle Silurian and requires further isotopic testing. Furthermore, the isotopic compositions of brachiopod calcites are only specifically pertinent to depositional waters of the Appalachian Basin reflecting environmental controls within the basin of δ^{13}C. Similarly, all the δ^{13}C carbonate values reported previously are from epicontinental basins (Veizer et al., 1986; Popp et al., 1986; Brand, 1989a). If we assume that epicontinental basin waters are uniform with mean ocean compositions then a direct extrapolation of data is possible. However, variation of 2.5-3.0‰ δ^{13}C within the *Demissa* bed illustrates the potential of the depositional environment to control shell calcite composition.

**Oxygen Isotopes**

A trend of decreasing δ^{18}O values with increasing age has been recognized in marine chemical sediments (e.g., Perry and Tan, 1972; Knauth and Epstein, 1976; Veizer and Hoefs, 1976). Similarly, a shift in δ^{18}O values of brachiopod calcites in the late Paleozoic has been reported (Veizer et al., 1986; Popp et al., 1986a; Brand 1989a). This trend has been attributed to either the post-depositional equilibration of brachiopod calcite, higher Paleozoic temperatures, or changes in the oxygen isotopic composition of seawater over
time (Veizer et al., 1986). Veizer et al. (1986) reported that the most positive \( ^{18}O \) values for Ordovician to Devonian brachiopod samples were -4.0/00 PDB; Ordovician samples (n=21) averaging -4.5/00 to -5.5/00; Silurian-Devonian samples (n=54; n=178) ranging from -5/00 to -7/00. Paleothermometry of these isotopic values suggests that marine temperatures, if brachiopods are assumed to incorporate \( ^{18}O \) in equilibrium with ambient conditions, were well over 40°C in Paleozoic tropical oceans. Veizer et al (1986), and Brand (1989a) suggest that these temperature ranges were greater than the thermal tolerances of marine metazoans, although the precise upper limit is debatable (38°C -50°C; Brock, 1985; Valentine, 1985). As an alternative, Veizer et al., (1986) propose that the isotopic composition of Paleozoic oceans has changed during geologic time. The cause of an enrichment in mean oceanic \( ^{18}O \) compositions is suggested by Veizer et al. (1986) to be due to "a substantial enhancement in the rate of high temperature oxygen isotopic exchange (plutonism, deep ocean ridge circulation, etc.) relative to low-temperature processes (e.g., shallow ridge circulation, submarine weathering)". Again this argument is unequivocal, since fluid inclusion analyses report \( \delta^{18}O \) values similar to present day \( \delta^{18}O \) values as far back as the Silurian (Knauth, 1985 et al; Knauth and Beeunas, 1986). Furthermore, the alteration of oceanic metabasalts with seawater and the buffering of \( \delta^{18}O \) at 0/00 by reaction with silicates of oceanic crust (Muehlenbachs and Clayton, 1976) may have maintained Paleozoic ocean \( \delta^{18}O \) isotopic compositions close to 0/00 (SMOW) (Veizer et al., 1986).

Isotopic analysis of brachiopods from this study indicate that Middle Ordovician isotopic values range from -4.5/00 to -6.0/00, which is in agreement with previous studies (Fig. 6.2). However, Middle Silurian and Middle Devonian brachiopod isotope values are considerably heavier than previously reported (Popp et al., 1986a; Veizer et al., 1986; Brand, 1989a). Middle Silurian values
range from 1.8%0 to -3.6%0 and Middle Devonian range from -2.5%0 to -4.0%0. Uncorrected paleotemperatures (assuming normal salinity, 0%0/00 SMOW and no fractionation effects) derived from these isotopic values suggest that the Clinton sea temperature (Middle Silurian) ranged from 18°C to 28°C and Hamilton seas (Middle Devonian) ranged between 24°C and 29°C. If a non-glacial correction of -1%00 SMOW is applied to the data, the temperatures decrease by 4-5°C (Berger, 1979). Paleogeographical reconstructions place these respective seas close to the equator (within 5-15°), whereby the paleotemperatures are well within the climatic ranges expected. Clearly, these temperatures cannot be reconciled with high Paleozoic ocean temperatures, which have been suggested by a number of authors (Knauth and Epstein, 1976; Karhu and Epstein, 1986), or reconciled with the general shift in δ18O during the late Paleozoic (Fig. 6.2; Popp et al., 1986a; Veizer et al., 1986; Brand, 1989a). These isotopic values suggest that Hamilton and Clinton Group waters were probably compositionally close to 0o/00 (SMOW). A unidirectional trend in mean oceanic 18O composition may not be an unequivocal explanation for isotopic shifts.

Diagenetic alteration of biogenic carbonate tends to result in more negative oxygen isotopes (Veizer and Fritz, 1976; Brand and Veizer, 1981) which reflect interactions with isotopically-light surficial and meteoric waters (Siegenthaler, 1979). Unrecognized post-depositional alteration may provide an explanation for the more negative values, reported by the other authors. Alternately, the scatter in isotopic values may represent brachiopod calcites sampling from a wide spectrum of different depositional and environmental settings. Significant variation in circulation patterns, glacio-eustatic conditions, temperature, salinity, fresh water input to the shelf and basin stratification may have controlled brachiopod calcite isotopic compositions. Hamilton and Clinton
Group brachiopods reflect conditions within an epicontinental sea that occupied the Appalachian Basin during the Middle Devonian and Middle Silurian. Similarly, the majority of brachiopod isotopic data reported elsewhere reflect the composition of waters within specific epicontinental basins (Brand and Veizer, 1981; Brand, 1981, 1983; Veizer et al., 1986; Popp et al., 1986a; Brand 1989a). Processes controlling isotopic compositions within these epicontinental seas may have been more manifold and complicated than previously realized. Thus, the variation in isotopic values of brachiopods shell calcites may reflect significantly different localized conditions and not per se, mean oceanic isotopic compositions. Isotopic trends may therefore have to be constrained by deep/shallow trends and environmental conditions within each sampled bed. Extrapolation of isotopic data into secular shifts may be pre-emptive, since the stratigraphic resolution and spatial distribution of sampling is so limited. However, it may ultimately be possible to relate isotopic changes to flux or perturbations in atmospheric O2 (Kump and Garells, 1984) as outlined in Brand (1989a), or to tectonically controlled cycles of oxygen exchange between seawater and the silicate crust (Veizer, 1985; Veizer et al., 1986).

CONCLUSIONS

The δ¹³C and δ¹⁸O compositions of brachiopod calcites from the Middle Devonian and Middle Silurian of New York State and Ontario are enriched relative to values previously reported. Variability of isotopic compositions within beds suggests that the isotopic compositions of brachiopod calcite are strongly influenced by the depositional conditions. Therefore the significance of secular isotopic shifts has to be interpreted in relation to environmental controls (i.e., basin type, depth) and within the context and confines of available paleoecologic, stratigraphic, and sedimentologic information.
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175


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192


Appendix 1

Locality and stratigraphic information
1A. Hungry Hollow Area

**Widder Formation.** (Fig. A-1)
Abandoned brick pit on north side of the Ausable River, 3.5 km east of Arkona, Ontario. Shales exposed in new diggings on west side of quarry.

i) Widder Formation. Calcareous dark grey fissile shales with scattered *Devonochoonetes, Mucrospirifer mucronatus,* and *M. thedfordensis.* Brachiopods are predominantly articulated and not deformed. Fine disseminated pyrite is common often coating valves. *Greenops boothi* and *Phacops rana* are commonly articulated. Sampled from the metre interval above base of the Widder Formation.

1B. Hungry Hollow Area

**Hungry Hollow and Arkona Formations.** (Fig. A-1)
Hamilton Group outcropping along the south bank of the Ausable River, 500 m west of the Hungry Hollow brick pit, 3.0 km east of Arkona, Ontario.

ii) Hungry Hollow Formation. Light grey claystone with abundant favositid corals and disarticulated *Mucrospirifer mucronatus.* From shale interval 50 cm above encrusted crinoidal grainstone hardground (see Landing and Brett 1987).

iii) Arkona Formation. Light grey claystone with abundant articulated and disarticulated *Mucrospirifer mucronatus* and *Devonochoonetes.* Shale interval 0.75-1.0 m below the base of Hungry Hollow Formation grainstone.

iv) Arkona Formation. Thin (4 cm), lenticular brachiopod and crinoid dominated packstone. A winnowed fossil hash bed approximately 5-6 m below the base of the Hungry Hollow Formation. Alate and disarticulate *Mucrospirifer arkonensis* are abundant. The bed may represent a winnowed *Mucrospirifer* patch community?

2. Lake Erie shoreline bluffs

**Ludlowville Formation** (Fig. A-2)
10-12 m outcrop along Lake Erie near mouth of Eighteen Mile Creek. Approximately 600 m northwest along creek north of abandoned Lakeshore Boulevard bridge. Wanakah, Erie Co., New York State.

i) Lower Wanakah Shale. Grey mudstone 15 cm-30 cm above Murder Creek Trilobite Bed (Miller et al., 1988). Collected over 15 cm interval. Abundant articulated *Athyris spiriferoides,* and *Rhipidomella vanuxemi; Mediospirifer audacula* and *Spinocyrtia granulosa* predominantly disarticulated and fragmented.

ii) Lower Wanakah Shale. Prominent shell layer (5-10 cm thick) within sequence of calcareous grey mudstones, 60 cm below base of "Murder Creek Trilobite Bed". Many brachiopods are in life position and still articulated. *Mediospirifer audacula, Athyris spiriferoides* dominant. Large *Spinocyrtia* are commonly encrusted.

iii) "*Pleurodictyum*" Bed (Grabau, 1899) or Darien Coral Bed (Miller et al., 1988). Lower Wanakah Shale. Scattered brachiopods from grey calcareous shales approximately 1.5 m below "Murder Creek Trilobite Bed". 40 cm above Lakeview (Nautilus) Bed. *Athyris, Mucrospirifer, Spinocyrtia, Rhipidomella,* and *Stropheodonta* sp. are abundant. Most are articulated and *Athyris* are commonly in life position.

195
Figure A-1. Stratigraphic section of Hamilton Group (Middle Devonian) units at Hungry Hollow Quarry. Numbers refer to sampling intervals listed in Appendix I. Modified from Landing and Brett (1987).
Figure A-2. Stratigraphic section of Wanakah and Windom Shale Members at Eighteen Mile Creek. Numbering refers to sampling horizons listed in Appendix I.
3. Eighteen Mile Creek

**Ludlowville Formation and Moscow Formation** (Fig. A-2)

Exposure on west bank of Eighteen Mile Creek; 100 m south of abandoned Lakeshore Boulevard bridge. Wanakah, Erie Co., New York State. 7-8 m vertical face with 10m talus slope. Middle Wanakah outcrops at base of talus slope.

i) Lowest Windom Shale Member. Calcareous grey mudstones 30-50 cm above Tichenor Limestone with abundant small, juvenile *Athyris spiriferoides, Mucrospirifer mucronatus* and *Ambocoelia umbonata*. Between this bed and the Tichenor Limestone are dark grey shales dominated by thin pavements of small *Ambocoelia umbonata*. Overlying is the Bay View Bed with abundant corals and diverse brachiopods.

ii) "Dimissa” Bed. Upper Wanakah Shale Member. Grey shales, approximately 0.8-1.0 m below Tichenor Limestone. Prominant shell layer with abundant disarticulated brachiopods *Athyris spiriferoides, Mediospirifer audacula, Rhipidomella vanuxemi*, and *Mucrospirifer mucronatus*. Fragments of *Phacops rana* are also common.

iii) Middle Wanakah Shale. Dark-grey calcareous fissile mudstones containing scattered *Ambocoelia* and small *Athyris spiriferoides, Mucrospirifer mucronatus*, orthids. Approximately 5-6 m below Tichenor Limestone.

4. Athol Springs

**Ludlowville Formation.**

Shoreline exposure along Lake Erie. 300 m south of Big Tree Road and Lakeshore Road junction. 3m outcrop below bar parking lot. Wanakah, Erie Co., New York State.

i) Wanakah Shale Member. Dark-grey calcareous fissile mudstones with rare disarticulated *Ambocoelia umbonata*.

5. Big Tree Road shale pit

**Ludlowville Formation.**

100m east of railway bridge and 100 m south of Big Tree Road. Small unnamed creek south of pit. Blasdell, Erie Co., New York State. 0.6-1.0 m outcrop of dark-grey Wanakah Shale.

6A. Penn Dixie quarry

**Moscow Formation.** (Fig. A-3)

South side of abandoned Penn Dixie quarry, 500 m northwest of intersection of Big Tree Road and Bay View Road, Blasdell, Erie Co., New York State. Exposure of Penn Dixie Bed forms a small escarpment (0.5 m) along the quarry floor.

i) "Penn Dixie Bed", Windom Shale. Dark-grey, pyritic mudstones containing abundant *Ambocoelia umbonata* and small, juvenile articulated *Athyris spiriferoides*. Disarticulated trilobites *Greenops boothi* and *Phacops rana* are common.

6B. Penn Dixie quarry

**Moscow Formation.** (Fig. A-3)

North part of quarry, 300 m north of locality 5A. Blasdell, Erie Co., New York State. Exposures of lower Windom Shale in sides of shale pits.
ii) "Smoke Creek Bed". Lower Windom Shale. Fissile, grey, calcareous mudstone containing abundant *Mucrospirifer mucronatus*, *Mediospirifer audacula* and *Rhipidomella vanuxemi*. The Smoke Creek Bed is subdivided into three subunits (Speyer and Brett, 1985). A lower subunit A of bioturbated, fossiliferous mudstones. Subunit B is a thin poorly defined bedding plane that yields articulated and clustered trilobites. Sampling was from subunit C, a platy, calcareous mudstone.

iii) "Bay View Bed". Lower Windom Shale. Grey calcareous mudstones between the Smoke Creek Bed and the Tichenor Limestone below. Diverse brachiopods assemblage, containing *Pseudoatrypa* sp., *Strophodonta* sp., *Mucrospirifer mucronatus*, *Athyris spiriferoides*, and *Mediospirifer audacula* amongst others.

iv) Tichenor Limestone. Brown calcarenite. Rare *Mediospirifer audacula* present on upper erosion surface.

6C. **Penn Dixie quarry**

**Ludlowville Formation.** (Fig. A-3)
Small creek, flowing northwards out of quarry, towards Rush Creek. 150 m northeast of locality 6B, Blasdell, Erie Co., New York State. The Tichenor limestone forms the cap to a small 1m waterfall, a feature common to most exposures of the uppermost Wanakah Shale.

v) "*Dimissa*" Bed. Upper Wanakah Shale. Grey shales with prominent shell layer approximately 0.8-0.9 m below Tichenor Limestone. Epibions attached to some brachiopod valves. Contains abundant *Athyris spiriferoides*, *Mediospirifer audacula*, *Pseudoatrypa* sp. *Mucrospirifer mucronatus*, *Rhipidomella vanuxemi*, *Tropidoleptus* sp.

vi) "Concretion Bed". Upper Wanakah Shale. Large calcareous concretions (15-35 cm thick) occur as distinct horizons within generally fissile grey mudstones. *Athyris spiriferoides* sampled directly from the second main concretion horizon, approximately 3.0-3.5 m below the Tichenor Limestone.

vii) Middle Wanakah Shale. *Athyris spiriferoides* and *Mucrospirifer mucronatus* sampled from grey shales approximately 1.0-1.3 m below second "Concretion Bed".

viii) Middle Wanakah Shale. *Devonochoonetes* and *Mucrospirifer mucronatus* sampled from grey shales approximately 2.5-2.8 m below second "Concretion Bed".

7A. **Smoke Creek.**

**Ludlowville Formation.**
Small waterfall over Tichenor Limestone, 100 m south of Mile Strip Road and 150 m east of Abbott Road/Mile Strip Road intersection. Upper 2 m of Wanakah Shale exposed in shale banks on both sides of creek.

i) "*Dimissa*" bed. Upper Wanakah Shale. Grey shales with an abundant brachiopod bearing horizon 0.9 to 1.0 m below the base of the Tichenor Limestone.

7B. **Smoke Creek.**

**Ludlowville Formation.**
2 m outcrop along small tributary of Smoke Creek South Branch (west side). Along California Road, 170 m east of Abbott Road and 650 m north of Mile Strip Road, Orchard Park, Erie Co., New York State.
Figure A-3. Stratigraphic section of Hamilton Group strat exposed at Penn Dixie Quarry. Numbers refer to sampling intervals listed in Appendix I.
ii) Middle Wanakah Shale. 20-35 cm sampling interval from grey calcareous shales, containing scattered *Mucrospirifer mucronatus, Athyris spiriferoides, Mediospirifer audacula, Rhipidomella vanuxemi, Pseudoatrypa* sp., *Stropheodonta, Spinocyrtia* sp., approximately 1.4-1.6 m above creek bed. 25-30 cm beneath a minor concretion horizon and approximately 2.5-3.0 m below Tichenor Limestone.

7C. Smoke Creek. Buffalo S.E. Quadrangle

**Ludlowville Formation**
5-6 m bank exposure on east side of Smoke Creek South Branch. 100 m west of Abbott Road, behind the Fire Station. 550 m north of Mile Strip Road, Orchard Park, Erie Co., New York State.

iii) Middle Wanakah Shale. Sampling from dark grey fissile shales approximately 1.5-2.5 m above creek bed and between two prominent concretion horizons. *Mucrospirifer mucronatus* is the only common brachiopod, with *Devonochoenetes* present.

8A. Cazenovia Creek. Orchard Park Quadrangle

**Ludlowville Formation** (Fig. A-4)
Small falls over Tichenor Limestone in Cazenovia Creek, 50 m east of Northup Road, Spring Brook, Erie Co., New York State.

i) Moscow Formation. Tichenor and Michenor limestone are separated by a thin dark grey calcareous shale. This represents the most easterly outcrop of the condensed Jaycox and Deep Run Shales. The Tichenor is a crinoidal packstone with scattered disarticulated *Mediospirifer audacula* valves. Large colonial corals are common to the Michenor upper surface.

ii) Upper Wanakah Shale. *Mucrospirifer mucronatus, Athyris spiriferoides, Mediospirifer audacula, Rhipidomella vanuxemi* sampled from grey mudstones 10 cm below Tichenor Limestone.

iii) "Dimissa Bed". Upper Wanakah Shale. Fissile, grey mudstones and thin lenticular limestones. Sampled from grey mudstones approximately 0.8 m below Tichenor Limestone. Diverse brachiopod assemblage of *Mucrospirifer mucronatus, Athyris spiriferoides, Pseudoatrypa* sp. *Mediospirifer audacula, Rhipidomella vanuxemi, Spinocyrtia* sp. *Tropidoleptus and Rhipidomella vanuxemi* are all articulated. Articulation ratio of other species is variable, but some *Athyris* appear to be in life position.

8B. Cazenovia Creek. Orchard Park Quadrangle

**Moscow Formation.**
Bank exposure along Cazenovia Creek, approximately 700 m east of Northup Road, Spring Brook, Erie Co., New York State. Over 10 m of Windom Shale.

iv) Windom Shale. Dark calcareous mudstones
Approximately 1.5-1.8 m above Tichenor Limestone.
Small *Ambocoelia umbonata*

9. Tributary of Buffalo Creek. Orchard Park Quadrangle

**Ludlowville Formation.**
Small, unnamed creek flowing north into Buffalo Creek. Immediately north of Bullis Road and 1.1 km east of Pound Road and Bullis Road intersection. Spring Brook Station, Erie Co., New York State.

201
Figure A-4. Stratigraphic section of Hamilton Group strata exposed at Cazenovia Creek. Numbers refer to sampling intervals listed in Appendix I.
i) Lower Wanakah Shale (above "Pleurodictyum" and "Murder Creek Trilobite Bed"). *Mucrospirifer mucronatus*, *Athyris spiriferoides*, and *Mediospirifer audacula* collected.

10. **Girdle Road, Buffalo Creek.**

*Ludlowville Formation.*

Low bank (4.5 m outcrop) of Buffalo Creek, immediately below Girdle Road bridge. Elma, Erie Co., New York State.

i) Upper Ledyard Shale. Medium grey calcareous mudstones 50 cm above base of outcrop dominated by scattered *Athyris spiriferoides* and *Mediospirifer audacula*.


11. **Bowen Road, Buffalo Creek.**

*Ludlowville Formation.*

South bank of Buffalo Creek, 200 m east of Bowen Road. Elma, Erie Co., New York State.

i) Lower Wanakah Shale. Sampling of *Athyris spiriferoides*, *Mucrospirifer mucronatus*, *Mediospirifer audacula*, *Rhipidomella vanuxemi* from shales in sequence of medium grey fissile shales and thin lenticular limestones. Approximately 60 to 120 cm above prominent Murder Creek Trilobite Bed.

12. **Bullis Road, Buffalo Creek.**

*Moscow Formation.*

Banks of Buffalo Creek, 150 m south of the abandoned Old Bullis Road bridge. Elma, Erie Co., New York State. 3-5 m outcrop from top with 5-7 m talus slope to creek floor.


13A. **Eleven Mile Creek**

*Moscow Formation.*


i) Lower Kashong Shale. 20 cm interval of dark grey calcareous mudstones approximately 0.5-1.0 m above Tichenor Limestone. *Mediospirifer audacula*, *Athyris spiriferoides*.

13B. **Eleven Mile Creek**

*Ludlowville Formation.*

Small waterfall over Tichenor Limestone in bed of Eleven Mile Creek, 25 m south of U.S. Highway 20. Genesee Co., New York State. 5 metre outcrop of Wanakah Shale below Tichenor and Michenor Limestones. Thin (15 cm) condensed highly calcareous Deep Run Shale between these limestones not sampled.
"Dimisa Bed". Upper Wanakah Shale. Medium grey to dark grey calcareous mudstones. Brachiopod horizon approximately 0.85-1.0 m below the Tichenor Limestone. Many *Athyris* brachiopods are in life position. Less diverse brachiopod community than "Dimissa" Beds outcropping to the west. *Athyris spiriferoides, Mediospirifer audacula*.

14. **Spring Creek**

**Ludlowville Formation.**
Banks of Spring Creek, 1.2 km south of Alden Municipal Park. Alden, Genesee Co., New York State.

i) **Middle Ledyard Shale.** Very fissile, dark grey shales approximately 1.0-1.5 m below Alden Pyrite beds. *Mucrospirifer mucronatus* is the only common brachiopod.

15A. **Murder Creek**

**Kashong Shale Fm.** (Fig. A-5)
Shale bank along west branch of Murder Creek. 650 m south of U.S. Highway 20, Darien, Genesee Co., New York State. 3 m outcrop.

i) **Kashong Shale.** 75 cm sampling interval from dark grey fissile shales, 1.0 m above base of creek. Dominated by articulated and pyritized *Mucrospirifer mucronatus, Devonochonetes* and crinoids.

15B. **Murder Creek**

**Moscow Formation.** (Fig. A-5)
Small waterfall (1 metre high) along west branch of Murder Creek. Beneath wooden footbridge, 350-400 m north of U.S. Highway 20, Darien, Genesee Co., New York State. Outcrop of Jaycox Shale between Tichenor and Michenor Limestones. Deep Run Shale found between Michenor Limestone and upper Menteth limestone bed.

ii) **Menteth Limestone.** Grey brown crinoidal calcarenite (25-30 cm thick)

iii) **Deep Run Shale.** Dark grey, highly calcareous mudstones. 50 cm thick condensed section of Deep Run Shale between limestones. Low brachiopod diversity i.e. *Mucrospirifer mucronatus*

iv) **Michenor Limestone.** 65 cm thick limestone bed. *Mediospirifer audacula*.

v) **Jaycox Shale.** 45 cm thick condensed section of highly calcareous mudstones.

vi) **Tichenor Limestone.** 45-50 cm thick limestone bed. *Mediospirifer audacula*.

15C. **Murder Creek**

**Ludlowville Formation.** (Fig. A-5)
Shale bank along west branch of Murder Creek. Approximately 750-850 m north of U.S. Highway 20 and 750 m south of Sharrack Road. Darien, Genesee Co., New York State. 3.5 m outcrop on east side of creek.

vii) **Upper Wanakah Shale.** Medium grey calcareous mudstones 50 cm interval, 2.0-2.5 m above base of exposure. Possibly approximately 1.5-2.0 m below base of Tichenor Limestone. *Athyris spiriferoides, Mucrospirifer mucronatus, Mediospirifer audacula*. 
Figure A-5. Stratigraphic section of Hamilton Group strata exposed at Murder Creek. Numbers refer to sampling intervals listed in Appendix I.
viii) Upper Wanakah Shale. Medium grey calcareous mudstones. Base of exposure, 30-35 cm sampling interval and approximately 3.5-4.5 m below Tichenor Limestone. *Athyris spiriferoides, Mucrospirifer mucronatus.*

16. **Bowen Creek**

**Ludlowville Formation.**
Banks of west branch of Bowen Creek, 0.4 km south of Walker Road and 0.6 km west of Gilate Road, Alexander, Genesee Co., New York State. Dark grey Wanakah Shale in creekbed.

17. **Bethany railcut**

**Ludlowville Formation**
Railroad cut along the abandoned Erie-Lackawanna line, just east of Francis Road. 2.5km north of U.S. Highway 20, Bethany, Genesee Co., New York State. North cut of railroad. Talus slope, 6-7m vertically. Francis Road pyrite in lower part of section (Dick and Brett, 1986).

i) Middle Wanakah Shale. Brachiopods collected from a 50 cm interval. *Athyris spiriferoides,* and rare *Mediospirifer audacula.* Fresh outcrop dug out from talus debris at 5.5m up slope.

ii) Middle Wanakah Shale. Fresh outcrop dug out from talus debris at 4.5m up slope. Brachiopods collected from a 40 cm interval of dark grey, pyritized mudstones. *Athyris spiriferoides,* and rare *Mediospirifer audacula.*

18. **Retsof**

**Moscow Formation.**
Railroad cut and shale dumps beside the International Salt Company mine, 400 m south of N.Y. Route 63, Retsof, Livingston Co., New York State.

i) Upper Kashong Shale Member. Macrofossils sampled from dark grey calcareous mudstones. This outcrop represents the upper Kashong Shale (Brett and Cottrell, 1982). *Tropidoleptus carinatus, Mucrospirifer mucronatus,* crinoids, and rare *Athyris spiriferoides* are present.

19A. **Fall Brook**

**Moscow Formation.**
Shale banks of Fall Brook Creek, just below Fall Brook Falls. Locality is 650 m north of 18A along Fall Brook Creek, Geneseo, Livingston Co., New York State. 18-20 m outcrop and 10m talus slope. Smoke Creek Bed exposed at base of falls.

i) Windom Shale Member. Brachiopods sampled from base of Windom outcrop. *Mediospirifer audacula* is most common brachiopod.

19B. **Fall Brook**

**Moscow Formation.**
Shale bank of Fall Brook Creek, 150 m east of N.Y. Route 39. 1.1 km south of N.Y. Route 63 and 39 intersection and 2.6 km south of Geneseo, Livingston Co., New York State. 3.5m outcrop.
j) Kashong Shale Member. Sampling from lowest metre of grey calcareous mudstones. *Tropidoleptus carinatus* is common brachiopod, and *Mucrospirifer mucronatus* is present.

20A. **Jaycox Creek**

**Moscow Formation.** (Fig. A-6)
Shale banks of Jaycox Creek, above small waterfall (3.0 m) over Tichenor Limestone. 850 m west of N.Y. Route 39, near horse farm and 3.5 km north of Geneseo, Livingston Co., New York State. 3 m outcrop.

i) Deep Run Shale Member. Approximately 2 m of dark, fissile calcareous mudstones with scattered articulated and disarticulated brachiopods are scattered. *Mediospirifer audacula* sampled from lowest 50-75 cm of Deep Run Shale and are predominantly

20B. **Jaycox Creek**

**Moscow Formation.** (Fig. A-6)
Shale banks of Jaycox Creek, below first waterfall over Tichenor Limestone. 100 m west of locality 19A, Geneseo, Livingston Co., New York State. 2.5 m outcrop.

ii) Jaycox Shale Member. Approximately 2.5 m outcrop of medium grey mudstones and occasional thin nodular limestones. Corals are abundant in lowest metre of Jaycox. Brachiopods sampled from lower metre interval of Jaycox Shale *Mediospirifer audacula, Tropidoleptus carinatus*.

20C. **Jaycox Creek**

**Ludlowville Formation.** (Fig. A.6)
Shale banks of Jaycox Creek, below second waterfall (4.0-4.5 m), 150 m west of locality 19B, Geneseo, Livingston Co., New York State.

iii) "Dimisa Bed". Upper Wanakah Shale. Dark fissile calcareous mudstones with concretion horizons beginning several metres below Michenor Limestone. *Mediospirifer audacula, Athyris spini-feroides, Mucrospirifer mucronatus* are abundant in Dimissa Bed approximately 0.9-1.0 m below the Michenor Limestone.

21. **Wheelers Gully**

**Moscow Formation.**
Shale bank of Wheelers Gully, 150m west of N.Y. Route 39, 4.8 km north of Geneseo, Livingston Co., New York State. 3.5 m outcrop.

i) Kashong Shale Member, *Mediospirifer audacula, Tropidoleptus carinatus*, crinoids collected from a 50 cm interval of sparsely fossiliferous dark grey calcareous mudstones within 50 cm interval, 1.5 m above creek floor. Minor pyritization of matrix present.

22A. **Menteth Gully**

**Moscow Formation.**
Shale banks upstream of high waterfalls (15-17 m), along Menteth Creek, 350 m west of West Lake Road, west side of Canandaigua Lake, Ontario Co., New York State.
Figure A-6. Stratigraphic section of Hamilton Group strata exposed at Jaycox Creek. Numbers refer to sampling intervals listed in Appendix I.
i) Kashong Shale Member. Shale bank 3.5 m high, east side of creek, just above falls. *Tropidoleptus carinatus* is dominant brachiopod in medium grey fissile, calcareous mudstones. Position in unit unknown.

22B. **Menteth Gully**

**Moscow Formation.**
Shale banks downstream of high waterfalls (15-17 m), along Menteth Creek, 250 m west of West Lake Road, west side of Canandaigua Lake, Ontario Co., New York State.

i) Kashong Shale Member. *Tropidoleptus carinatus, Mucrospirifer mucronatus* are sampled from base of waterfall, 9-10 m below top of falls.

23. **Kashong Creek**

**Ludlowville Formation.**
Shale banks of Kashong Creek, 500 m west of N.Y. Route 14, south of Geneva, Ontario Co., New York State.


24. **Indian Creek**

**Moscow Formation.**
Shale banks along north side of Indian Creek, 150 m west of N.Y. Route 96A and 3.5 km north of Willard, Ontario Co., New York State. 3.5 m outcrop.

i) Kashong Shale Member. Dark grey, highly fissile calcareous mudstones. Thin pavements with abundant *Ambocoelia umbonata* are sampled 30-50 cm above creek floor.

25. **Big Hollow Creek**

**Ludlowville Formation.**
Shale banks of Big Hollow Creek, east of Swick Road and 3.5 km north of Hayt Corners, Seneca Co., New York State.

i) King Ferry Shale Member. Lateral equivalent of the Wanakah Shale Member (Brett and Cortrell, 1982). Dark fissile calcareous mudstones with scattered *Mucrospirifer mucronatus.*

26. **Stoney Creek**

**Rochester Shale Formation**
Stoney Creek Member. Road cut, 1 km east of King Street East. Lateral equivalent of the Burleigh Hill Member of the Rochester Shale. Fine grained and thin bedded shaley dolostones of Stoney Creek Member.

27. **Dewitt Road, Stoney Creek.**

**Rochester Shale Formation.**
Thin bedded, shaley dolostones of Stoney Creek Member exposed.
28. **Vinemount**
   
   **Rochester Shale Formation.**
   Road cut, 2.4 km west of Winona. Fine grained dolostones of Stoney Creek member exposed.

29. **Wolverton Mountain Road,** Grimsby.
   
   **Rochester Shale Formation.**
   2 km west of Grimsby, a reduced section of Rochester Shale. A 1.2-1.6 m outcrop is exposed above Irondequoit Formation. Dark grey calcareous mudstones and several thin micritic limestones.

30. **Beamers Falls,** Grimsby.
   
   **Rochester Shale Formation.**
   Stream cut on 40 Mile Creek, 1 km south of Grimsby. Upper 3 m of Burleigh Hill member exposed in east face of gorge below upper waterfall. This sequence of dark gray fissile calcareous shale is essentially barren of macrofossils. Articulated *Atrypa reticularis* were collected from Lewiston E Member in exposure further down gorge towards Grimsby.

31. **15 Mile Creek.**
   
   **Rochester Shale Formation.**
   Stream cut at top of escarpment, 5 km southwest of St. Catharines. Exposes upper 2-3m of Burleigh Hill member. Grey calcareous shales, thin micrite limestones and thin shaley dolostones are essentially unfossiliferous. Single *Coolinia subplana* found in lowest calcareous shales.

32. **Rockway Falls.**
   
   **Rochester Shale Formation.**
   3.5 km southwest of St. Catharines along Highway 69. Complete section of Lewiston and Burleigh Hill members exposed. Here Lewiston Member is essentially a sequence of dark grey fissile calcareous mudstones, thin bedded calcisiltites and micritic limestone (bryozoan common). Burleigh Hill Member consists of dark grey barren mudstones, which in upper part of unit grade into thin bedded dolostones of the Decew Formation.

33. **Decew Falls.**
   
   **Rochester Shale Formation.**
   1 km southwest of Brock University, St. Catharines. Complete section of Lewiston and Burleigh Hill members.

   i) "*Coolinia subplana*" horizon. Burleigh Hill Member. This horizon is a 10-15 cm fossiliferous amalgamated calcarenite layer, within a sequence of barren grey calcareous mudstones.

34. **Brock-Decew,** St. Catharines.
   
   **Rochester Shale Formation.** (Fig. 4.18)
   Hydro road cut to Power House Dam, 0.5 km west of Brock University. Grey calcareous shales and thin-bedded dolostones of the upper Burleigh Hill member.

   i) "*Coolinia subplana*" horizon. Burleigh Hill Member. Brachiopods collected from two calcarenite layers (15 cm thick), approximately 2.5-3.0 m below beginning of gradational...
contact of Burleigh Hill shaley dolostones with the Decew Dolostone. This is the laterally equivalent horizon to that seen in the Burleigh Hill, Decew Falls and Old Welland Canal sections. Disarticulate Dalejina and Resserella elegantula valves are common.

35. Highway 406 stream cut, St. Catharines. Ontario

**Rochester Shale Formation.**
150 m east of the 406 highway, on the escarpment between Burleigh Hill and Sanatorium Hill. Middle and upper Burleigh Hill calcareous shales exposed. Disarticulated Dalejina and Whitfieldella valves were common.


**Burleigh Hill Member** (Fig. 4.18)
Road section along Burleigh Hill Road, 1 km south of St. Catharines, exposing the complete Burleigh Hill member.

6.5 m outcrop of the Burleigh Hill Member. (type locality) with gradational upper contact with the dolomitic Decew Dolostone. Coolinia subplana was the only brachiopod collected in the calcareous shales above and below the "Coolinia subplana" horizon.

i) "Coolinia subplana" horizon. Burleigh Hill Member.
Fossils sampled from eroded calcareous shale horizon, 40-50 cm thick, 5.2-5.4 m above base of Burleigh Hill Formation and approximately 2.2-5 m below beginning of gradational contact of Burleigh Hill shaley dolostones with the Decew Dolostone. Here this collecting horizon represents 3 and/or 4 separate storm bed layers. Brachiopods collected were Dalejina, Whitfieldella nitida, Resserella elegantula, strophomenids Leptaena rhomboidalis, Coolinia subplana, a few fragments of Atrypa reticularis. Other fossils collected were Dalmanites limulurus and Naticonema niagarense.


**Merritton Formation.**
Railway cut exposure, approximately 300 m west of Welland Canal Lock 5. 5-6 m outcrop of Clinton Group limestones and shales.

i) Merritton Formation. Pentameroides sp. brachiopods sampled from uppermost Merritton phosphatized hardground (2-3 cm thick) to 15 cm below top of unit. Valves are abraded, disarticulate and corroded.


**Rochester Shale Formation.**
Cliff section, behind abandoned power station dam. At the junction of the old Welland Canal and the St. Lawrence Seaway Haulage Road, 1.2 km south of the General Motors Plant.

i) "Coolinia subplana" horizon. Dark grey calcareous shales of the Burleigh Hill Member.
Section destroyed by percolating leachate from dump along escarpment.

39. Niagara Falls Gorge

**Rochester Shale Formation.**
Hydro road cut along Niagara gorge. Upper calcareous shale section of Burleigh Hill member. Essentially barren, except for a few fragments of Coolinia subplana.
Clinton Group. (Fig. 4.9)

Excised block on east side of gorge along old railway line, approximately 800 m south of the Artpark complex.

i) Lewiston A Member.
Thin calcisiltite beds 10-15 cm above base of Lewiston A. Abundant *Atrypa reticularis*, *Eospirifer radiatus*, *Whitfieldella nitida* and *W. obleta*, *Coolinia subplana*, *Eoplectodonta transversalis*, large *Leptaena*.

ii) Irondequoit Formation.
Uppermost 5 cm pink crinoidal biosparite with *Atrypa reticularis*, *Whitfieldella nitida*, *Eospirifer radiatus*.

iii) Irondequoit Formation.
Sampling interval from 5-15 cm below top of formation. Brachiopod dominated crinoidal biosparite. *Whitfieldella nitida*, *Eospirifer radiatus*, *Atrypa reticularis*.

iv) Irondequoit Formation.
1 m below upper contact with *Whitfieldella nitida*, *Eospirifer radiatus*, *Atrypa reticularis*. Sampled from crinoidal wackestones and packstones.

v) Irondequoit Formation.
2.0-2.4 m below upper contact. Disarticulate *Whitfieldella nitida*, and articulated *Eospirifer radiatus*, *Atrypa reticularis* are present. *Whitfieldella* are dominant, and commonly abraded.

Rochester Shale Formation. (Fig. 4.9)

Vertical exposures on east side of gorge along an abandoned railway line. Below the Robert Moses Parkway, close to the Hydroelectric facility and directly opposite the Sir Adam Beck Hydroelectric Station. Exposure of Upper Queenston (Upper Ordovician), Medina Group, Clinton Group and Lockport Group. The upper contact of the Rochester Shale with the Decew Formation is a gradational transition from dolomitic gray shales to thin bedded argillaceous dolostones to massive fine grained dolostone.

Burleigh Hill Member/Lewiston E Member.

i) 9.20 m above basal Rochester Shale contact. Pyritized hardground 8 cm thick containing abundant *Resserella elegantula*, *Whitfieldella nitida* and *Coolinia subplana*.

Lewiston E Member.

ii) 9.0 m above basal Rochester Shale contact. *Whitfieldella nitida* and *Eospirifer radiatus*.

iii) 8.20 to 8.28 m above contact. *Eospirifer radiatus*.

iv) 7.72 to 7.82 m above contact. *Eospirifer radiatus*.

Lewiston D Member.

v) 7.00 m above contact. *Eospirifer radiatus*.

vi) 6.60 to 6.70 m above contact. *Eospirifer radiatus*.

Lewiston C member.

vii) 4.0 m above contact. *Eospirifer radiatus*.
viii) 3.70-3.81 m above contact. Calcisiltite bed with Striispirifer niagarense, Whitfieldella nitida, Eospirifer radiatus.
ix) 3.55 to 3.59 m above contact. Thin calcisiltite bed Atrypa reticularis, Eospirifer radiatus, Striispirifer niagarense, Whitfieldella nitida.
x) 3.40 to 3.45 m above contact. Calcisiltite bed Whitfieldella nitida, Eospirifer radiatus, Striispirifer niagarense.

Lewiston B member.

xi) 2.32 to 2.35 m above contact. Atrypa reticularis.

xii) 2.01 to 2.02 m above contact. Atrypa reticularis.

xiii) 1.72 to 1.75 m above contact. Atrypa reticularis, Eospirifer radiatus.

xiv) 1.47 to 1.58 m above contact. Atrypa reticularis, Eospirifer radiatus.

xv) 1.25 m above contact. Atrypa reticularis, Whitfieldella nitida.

xvi) 1.00 to 1.25 m above contact. Atrypa reticularis, Whitfieldella nitida.

Lewiston A Member.

xvii) 0.90 m above contact. Atrypa reticularis, Eospirifer radiatus.

xviii) 0.80 to 1.00 m above contact. Atrypa reticularis, Eospirifer radiatus. Leptaena rhomboidalis occurs from this horizon into the Lewiston B member.

xix) 0.70 to 0.75 m above contact. Atrypa reticularis, Whitfieldella nitida and Eospirifer radiatus. Coolinia subplana occurs from this horizon into the Lewiston B member.

xx) 0.40 to 0.50 m above contact. Atrypa reticularis, Whitfieldella nitida.

xxi) 0.25-0.35 m above contact. Atrypa reticularis, Whitfieldella nitida and Eospirifer radiatus.

xxii) 0.20 to 0.25 m above contact. Atrypa reticularis, Whitfieldella nitida and Eospirifer radiatus.

xxiii) 0.10 to 0.25 m above contact. Atrypa reticularis, Whitfieldella nitida and Eospirifer radiatus.

xxiv) 0 to 0.10 m above Irondequoit contact. Atrypa reticularis, Whitfieldella nitida and Eospirifer radiatus.

42. Bree Road, Cambria County New York State.

Irondequoit Formation.
Road cut along Bree Road. Outcrop 1.5 m. Dolomitized wackestones with visibly altered brachiopods.

43. Canal Road, Lockport New York State.

Rochester Shale Formation.
Road cut along canal running through Lockport city centre. Burleigh Hill Member and Upper Lewiston member units exposed.

i) Lewiston E Member. Brachiopods collected from thin and slightly nodular calcarenite and calcisiltite beds within a generally unfossiliferous grey calcareous mudstone sequence. The abundance of bryozoa within these "storm bed" layers in addition to Coolinia subplana, Atrypa reticularis, Eospirifer radiatus, Resserella elegantula suggests these beds to be Lewiston E in character.

44. Brewer Street, Rochester New York State.

Rochester Shale Formation.
Overhanging cliff exposure, excised by the Genesee River on east side of gorge. Directly below the west end of Brewer Street and church.
i) The Rochester Shale exposed here is undifferentiated into its separate members recognized further west along the Niagara Escarpment. Brachiopods collected from a horizon approximately 5.5 m above Genesee River waterline. The poor condition of the exposure did not enable further collecting. *Coolinia subplana*, *Resserella elegantula*, and *Whitfieldella nitida*.

45. **Hydro Road**, Rochester

**Reynales Formation.**
Exposure along access road to the R.G. & E. Power Station, 350 m south of the junction of Seth Green Drive and Norton Street, Rochester.

i) Wallington Limestone Member. Thin beds of light grey crystalline limestone with shale partings containing abundant *Pentameroides* sp.

46. **Sodus Creek**

**Rochester Shale Formation.**
Sodus Creek exposure of the bryozoa Lewiston E member beds. *Atrypa reticularis*, *Eospirifer radiatus*, and *Howellella* from collection of D. Tetrault (University of Rochester, N.Y.)

47A. **Goat Island**

**Verulam Formation.**
An old railway cutting on the west side of Goat Island, just south of Highway 6 exposes Verulam Formation (about 5-6 m). Thin bedded, fossiliferous, nodular wackestones, packstones and calcareous mudstones with thin shale partings. These limestones are dominated by strophomenid brachiopods.

i) *Verulam Formation*. *Rafinesquina* sp. (*deltoidea*?) and *Dalmanella rogata*. collected from nodular skeletal grainstone beds (crinoidal biosparites; 5-10 cm thick) at base of exposure. These crinoidal grainstones are partially dolomitized (fine grained euhedral dolomite) and can be tentatively interpreted as shoal edge facies (cf. Brookfield and Brett, 1988).

47B. **Goat Island**

**Cobourg Formation.**
Cobourg formation is exposed along an abandoned railway cutting on the northeast side of Goat Island. Take a dirt track off Highway 6, just north of Little Current swing bridge. A 4-5m exposure is seen.

i) *Cobourg Formation*. Sequence consists of greenish grey shales interbedded with skeletal wackestones and calcareous mudstones. The upper part consists of greyish brown nodular packstones and wackestones with thin greenish grey shale partings. Dominated by small articulate rhyonconellid and large strophomenid brachiopods (notably *Rafinesquina deltoidea*). Trilobite fragments are common. Sampling of *Rafinesquina* from partially dolomitized wackestones.

48. **Little Current**

**Cobourg Formation.**
Just south of Little Current swing bridge on Highway 6 are old railway cuttings, exposing Cobourg Formation. 3.5 to 4 m exposures seen on both sides of road.
i) Cobourg Formation. Greenish grey nodular calcareous mudstones, wackestones and occasional packestones (biomicrites, biopelsparites and biosparites; 5-15 cm thick) are interbedded with thin green shales. Trilobite fragments, corals and small rhynconellid brachiopods are common in some of the thicker wackestone beds.

49. Little Current Manitoulin Island.

Cobourg Formation.
Along Harbour Road East, 250 m east of Little Current Harbour, a 4.5 m exposure of Cobourg Formation is seen.

i) Cobourg Formation. Greenish grey, nodular calcareous mudstones and wackestones (both biomicrites and crinoidal biosparites; 5-15 cm thick) are interbedded with thin green shales. Small articulated rhynconellids are very abundant, whereas strophomenids are rare. Large orthocone nautiloids (5-8 cm) are present with small solitary corals and trilobite fragments (possibly Isotelus sp.). Sampling was from upper 1.5 m of section.

50. South of Little Current Manitoulin Island.

Whitby Formation.
Low banks of small creek, approximately 5 km south of Little Current along Highway 6. 1.5 to 2 m of dark grey, fissile shales exposed.

i) Sheguiandah Member. These shales are essentially barren of macrofossils except for a 25-30 cm thick sequence of brachiopod pavements at top of exposure. Very abundant layers of predominantly articulated Dalmanella sp (roigata ?). Most are coated by iron oxides, limonite crusts.

51. South of Little Current Manitoulin Island.

Georgian Bay Formation.
Approximately 250 m south of locality 50 is a 5 to 6 m outcrop of weathered shale on the west side of Highway 6.

i) Wikwemikongsing Member. Light grey, green and brown shales. Brachiopods (predominantly Dalmanella rogata), crinoids, bryozoans and gastropods are weathered in relief.

52. Sheguiandah Manitoulin Island.

Cobourg Formation.
Cobourg Formation unconformably overlies Precambrian Lorraine Quartzite along Highway 6; section about 10 km south of Little Current. Boulders (up to 1.5 m size) of Lorraine Quartzite are incorporated into lowest 1.0 to 1.5 m of Cobourg Formation. At this section, Cobourg Formation is a light brown, medium bedded dolostone. Karstic? porosity is evident.

53. Sheguiandah Manitoulin Island.

Whitby Formation.
Black shales assigned to the Collingwood Member of the Whitby Formation overly Cobourg Formation in road section 100 m south of locality 52 along Highway 68. Shales here are essentially devoid of macrofossils.
54. Sheguiandah Manitoulin Island.

**Georgian Bay Formation.**
Road section along Highway 6 as it climbs escarpment overlooking Sheguiandah Bay. 1.5 km north of Ten Mile Point. 3-4 m exposed on both sides of road.

i) Meaford Member. Thin bedded greenish gray calcareous mudstones and wackestones with abundant but scattered small articulated rhyconellids.

55. High Falls Manitoulin Island.

**Georgian Bay Formation.**
About 30 km south of Little Current along Highway 6, a waterfall over the escarpment on the east side of road exposes approximately 10 m of the Kagawong Member.

56. Kagawong Village Manitoulin Island.

**Georgian Bay Formation.**
A 14-15 m outcrop at Bridal Veil Falls exposes the uppermost Wikwemikongsing Member (1.5 m) and the Meaford Member (12.5-13.5 m).

i) Meaford Member. A sequence of grey medium-bedded (5 to 15 cm thick) fossiliferous calcareous mudstones and skeletal wackestones (biomicrites). Interbedded with thin greenish grey shaley partings in lowest 3 m of Meaford. Beds close to base of section are extremely fossiliferous (almost "coquinite" packstones) consisting of predominantly single valves of *Sowerybella* sp. These brachiopods are however silicified and coated with thick layer of iron oxides (1-2 mm).

ii) Wikwemikongsing Member. A sequence of dark grey shales with hard, thinly bedded (1-2 cm) calcareous mudstones. Large *Sowerybella* sp. brachiopods from both the shales and calcareous mudstones (hard biomicrites) are silicified and oxide coated.

57. Keppel Township Bruce Peninsula.

**Georgian Bay Formation.**
18 km north of Owen Sound town centre, along County road 26 that fringes Owen Sound. On the waterline of the Keppel Township Park, 1 m of Georgian Bay Formation is exposed.

i) Georgian Bay Formation. Medium bedded (10-15 cm thick) greenish grey packstones, wackestones and calcareous mudstones are extremely fossiliferous, but singular in diversity, dominated by strophomenid brachiopods (notably *Rafinesquina* sp.) and coral fragments. Many of these beds are almost coquinite packstones (biomicrites). Sampling of *Rafinesquina* sp. from planar pelloidal wackestones (biopelsmicrites; 5-8 cm thick).

58. East Meaford Creek Bruce Peninsula.

**Georgian Bay Formation.**
Exposures of Georgian Bay Formation are seen along East Meaford Creek, just north of Highway 26, 3 km east of Meaford.

i) Upper Georgian Bay Formation. Sampling from upper section at East Meaford Creek that comprises of sequences of grey to greenish grey thin to thick bedded (4-20 cm) wackestones and calcareous mudstones (biomicrites) interbedded with thin green and grey shales. Fossiliferous wackestones are often singularly dominated by *Rafinesquina deltoidea*. Sampling of *Rafinesquina* restricted to planar wackestones (8 to 10 cm thick).
59. Craigleith

Whitby Formation
The Collingwood Beds of the Whitby Formation are exposed 1 km east of Craigleith Provincial Park, along the shoreline of Nottawasaga Bay.

i) Collingwood Member. From the waterline the first metre of Whitby Formation is characterized by thin (1-3 cm), fissile, fossiliferous (brachiopod pavements), dark grey calcareous mudstones interbedded with thin black shales (1-5 cm thick). The brachiopod pavements are dominated by *Dalmanella* sp. in a wide range of taphonomic conditions, from articulated to disarticulated to abraded to shell hash. Geochemical sampling was restricted to the best taphonomically preserved specimens. The majority of very thin calcareous mudstones (<1 cm thick) are a shell hash. The thin black shales are generally devoid of brachiopods but contain trilobites, especially large disarticulate *Isotelus gigas* and *Pseudogygites canadensis*.

ii) Collingwood Member. Lower grey calcareous mudstones and shales, of the Collingwood grade into predominantly fissile black shales with a few very thin shell hash layers. Trilobite faunas dominate these black shales.

60. Collingwood

Cobourg Formation.
A 6 metre exposure of Cobourg Formation is seen in an abandoned quarry along Lakefield Avenue, just off Highway 26, close to the Batteaux River.

i) Cobourg Formation. Sequence consists of thin to thick bedded (5-15 cm) skeletal wackestones and calcareous mudstones (biomicrites). The lower part consists of greyish brown nodular packstones with thin greenish grey shale partings and grades upwards into predominantly barren hard, calcareous mudstones. Brachiopod fauna is restricted to small *rhynchonellids*.

61. Beaverton

Cobourg Formation.
Cobourg outcrops at the intersection of Highway 12/48 and Thorah Line 4, as road cuts through Cobourg escarpment. 2.5 m outcrop.

i) Cobourg Formation. Planar bedded grey, crinoidal packstones, grainstones (5-10 cm) and thin calcareous mudstones with thin shale partings. Strophomenids dominate, *Rafinesquina deltoidea* and are sampled from crinoidal grainstones (coarse crinoidal biosparites).

62. Mara Quarry

Verulam Formation.
11 m section in Mara limestone quarry, 300 m west of Highway 12 in Gamebridge. Sequence of grey grainstones, pelloidal mudstones and hard, calcareous mudstones, irregularly bedded with thin grey shale partings. This section has been assigned to the lower Verulam Formation (Liberty, 1969) and is interpreted by Brookfield and Brett (1988) as a proximal to distal shoal lithofacies.

i) Verulam Formation. Sequence of light grey, thin, irregularly bedded skeletal wackestones, packstones and calcareous mudstones (5-10 cm thick) commonly with greenish grey thin shale partings. Brachiopods are sampled from crinoidal packstones (biomicrites). Single valved strophomenid brachiopods predominate within the basal parts.
of these beds i.e. Rafinesquina deltioidea and Sowerybella sp. Commonly Dalmanella rogata cluster on upper surfaces.

63. **Bolsover**

**Verulam Formation.** (Fig. A-7)

Road cut along Highway 48, 2 km south of Bolsover. 2 m section on either side of road. Brookfield and Brett (1988) have interpreted this outcrop as representative of a distal shoal cycle. Tentatively interpreted as Upper Verulam Formation.

i/ii) Verulam Formation. Sequence of thin grey shaley beds with thin calcareous mudstones weathering to rubbly brown. Sampling horizons are referred to in Fig. A.7. Articulate brachiopods i.e. predominantly Dalmanella rogata are common to these shaley and mudstone beds (Beds A and D). Outcrop has five thin, irregularly bedded, grey crinoidal wackestones and hard, nodular mudstones (3-10 cm thick) within two metre section (Beds B, C and E). Dalmanella rogata is present in uppermost wackestone bed (crinoidal biomicrite). This bed is an irregular and undulating hardground.

64. **Dalrymple**

**Bobcaygeon Formation.**

Road cut along Highway 503 south of Dalrymple. Weathered dark grey section of thinly bedded calcareous mudstones with single valved brachiopods present often at tops of beds. Predominantly Dalmanella rogata sampled from thin planar wackestones (skeletal biomicrites). Brachiopods are partially silicified.

65. **Kirkfield Quarry**

**Verulam Formation.** (Fig. A-8)

Abandoned quarry north of Kirkfield. Take first eastward dirt road just north of the Trent Canal lock. Quarry is water filled and only the lower Verulam Formation is exposed (2.5 m thick). The contact between Bobcaygeon and Verulam Formations is at the waterline.

i) Lower Verulam Formation. Thick to thin bedded crinoidal grainstones and packstones (5-20 cm thick) and pelloidal mudstones interbedded with rare shale partings. Some beds exhibit graded fabric. The lowermost beds are cross-laminated. Articulate Dalmanella sp. and crinoids are abundant in uppermost 20 cm of quarry section (from a crinoidal biosparite with minor micrite. These beds are interpreted by Brookfield and Brett (1988) to be shoal-edge lithofacies.

ii) Upper Bobcaygeon Formation. Uppermost half metre of thick, cross-bedded (20-25 cm thick) grey crinoidal packstones, wackestones and calcareous mudstones.

66A. **Trent Canal Lock**

**Bobcaygeon Formation.**

North of Kirkfield, 100m south of Trent Canal Lock along County Road 503. Road section exposes 2.5 m of weathered dark grey calcareous mudstones with thin lenses of crinoidal grainstones and packstones. Articulate Dalmanella rogata are common but are variably silicified.

i) Bobcaygeon Formation. Thin bedded (3-6 cm thick), grey, planar calcareous mudstones (biomicrites) and pelloidal wackestones (fine biopelsparite). Dalmanella rogata sampled from upper 50 cm of section (biomicrites).
Figure A-7. Stratigraphic section of Verulam Formation from the Bover roadcut. Numbers refer to sampling intervals listed in Appendix I. Modified from Brookfield and Brett, 1988.
Figure A-8. Stratigraphic section of Verulam Formation at Kirkfield Quarry.
66B. *North of Kirkfield*  

**Verulam Formation**  
North of Kirkfield, 250 m south of the Trent Canal Lock along County Road 503. Road section exposes 1.8 m of lower Verulam Formation.

67. *Kirkfield*  

**Verulam Formation.**  

i) **Verulam Formation.** 1.8 m outcrop in ditch of thick bedded, low angle cross-bedded crinoidal packstones (i.e. crinoidal biosparites)

68. *Glenarm*  

**Cobourg Formation.**  
Road cut 5.5 km south of Kirkfield along County Road 6. Liberty's (1969) S6 locality.  


ii) **Verulam Formation.** 500 m north of Cobourg Formation outcrop. Cross-bedded crinoidal grainstones outcropping in ditch. Can be tentatively interpreted as Upper Verulam Formation and in accordance with Brookfield and Brett (1988) part of shoal edge lithofacies.

69. *Eldon Hill*  

**Cobourg Formation.**  
6.5 km south of Kirkfield along County Road 6. Liberty’s (1969) H1 locality.

i) **Cobourg Formation.** Greenish grey, nodular skeletal packstones and wackestones, with pelloidal mudstones. Appears in this section to be sparsely fossiliferous. *Rafinesquina* sp sampled from medium bedded, planar, coarse pelloidal grainstones (coarse biopelsparite).

70. *Fenelon Falls*  

**Bobcaygeon Formation.**  
8.5 m outcrop at Fenelon Falls below the Trent Canal locks.  

i) Upper Bobcaygeon Formation. Five metre sequence of thin bedded brown wackestones with thin blue grey calcareous mudstones. Brachiopods are rare and limited to lowermost interval. *Dalmanella rogata* and *Onniella* sp. are present.  

ii) Lower Verulam Formation. Upper part of section dominated by thin to medium bedded planar crinoidal packstones and calcareous mudstones (biomicrites) with thin greenish grey shale partings.
71. **County Road 21**  

**Verulam Formation.**  
4 km southwest of Cameron, along County Road 21. 1.5m exposure at east side of road.  

i) Upper Verulam Formation. Thin to medium bedded planar crinoidal packstones and wackestones (crinoidal biosparites).

72. **Lindsay**  

**Cobourg Formation.**  
Road cut 4 km north of Lindsay along Highway 35/115. Section through Cobourg escarpment exposes 5-6m.  

i) Cobourg Formation. Grey, medium, planar bedded crinoidal grainstones and packstones (i.e. crinoidal biosparites). Low-angle cross lamination often developed in thicker beds.

73. **Dunsford**  

**Trenton Group.**  
2.5 km southwest of Dunsford along Highway 36. 10 m section cuts through Cobourg escarpment. Contact between Cobourg and Verulam Formations hidden beneath talus slope.  

i) Lower Cobourg Formation. Coarse pelloidal packstones (biopelsparites; 5-10 cm thick) with fine skeletal fragments of gastropods, bivalves and trilobites. Interbedded with nodular calcareous mudstones.  

ii) Upper Verulam Formation. Medium bedded, planar, grey coarse crinoidal biosparite, grainstones and packstones.

74. **Cedar Glen Road**  

**Verulam Formation.**  
Four outcrops of Verulam Formation along Cedar Glen Road between Highway 36 and Sturgeon Lake.  

i) Lower Verulam Formation. At waterfront of Sturgeon Lake.  

ii) Verulam Formation. 250 m from waterfront along Cedar Glen Road.  

iii) Verulam Formation. 100 m north of County Road 24.  

iv) Verulam Formation. At the intersection of Cedar Glen Road and Highway 36.

75A. **Dunsford**  

**Verulam Formation.**  
1.5 km north of Dunsford along Highway 36.  

i) Verulam Formation. Sequence of thin planar grey calcareous mudstones with thin grey shaley partings.

75B. **Bobcaygeon**  

**Bobcaygeon Formation.**  
3/4 km south of the town of Bobcaygeon. Highway close to Little Bob quarry.
76A. **County Road 7**

**Cobourg Formation.**
Road section 4 km north of Downeyville along County Road 7 between Downeyville and Dunsford.

i) Cobourg Formation. Coarse, planar pelloidal wackestone and packstone beds (coarse biopelsparite; 5-10 cm thick) with fine skeletal fragments of gastropods, bivalves and trilobites. Interbedded with nodular calcareous mudstones (fine biomicrites).

76B. **Highway 17.**

**Bobcaygeon Formation**
6km south of Bobcaygeon, along Highway 17. Cross-bedded grey crinoidal packstones and wackestones in ditch exposure.

77. **Lakefield Quarry**

**Verulam Formation.** (Fig. A-9)
Abandoned quarry west of Lakefield. 1.5 km east of Highway 28. Approximately 9m of grey medium bedded planar bioperalite grainstones, wackestones and packstones interbedded with thin biomicrite mudstones and grey shale partings. Dominated by *Rafinesquina deltoidea* and *Sowerybella* sp. Interpreted by Brookfield and Brett (1988) as part of a proximal shoal lithofacies.

i) Verulam Formation. Thick crinoidal grainstone bed. Abundant strophomenid brachiopods, and trilobite fragments.

ii) Verulam Formation. Thin crinoidal grainstones. Brachiopods, trilobites

iii) Verulam Formation. Thin crinoidal grainstones. Brachiopods, trilobites

iv) Verulam Formation. Thin crinoidal packstone

v) Verulam Formation. Skeletal wackestones (biomicrite)

78. **Trenton**

**Verulam Formation.**(Fig. A-10)
On the off ramp for highway 33 along Highway 401. North of Trenton. Approximately 4m of alternating thin to thick crinoidal packstones and thin calcareous mudstones with green shaley partings.

i) Verulam Formation. At top of section. Crinoidal packstones, with abundant corals, bivalves

ii) Verulam Formation. (30-35 cm from top). Crinoidal packstones, with abundant corals, bivalves.

iii) Verulam Formation. (50-55 cm). Crinoidal packstones, with abundant corals, bivalves

iv) Verulam Formation. (105 cm). Skeletal packstones.

v) Verulam Formation. (2.20 m). Skeletal packstone, with abundant corals, bivalves, gastropods and brachiopods. Minor silicification of brachiopods evident.

vi) Verulam Formation. (2.70 m). Crinoidal packstones, with abundant corals, bivalves

79. **Belleville**

**Verulam Formation.**
Abandoned quarry off Highway 401, close to the Moira River and Highway 62.

Figure A-9. Stratigraphic section of Verulam Formation at Lakefield Quarry near Peterborough. Numbering corresponds to sampling intervals listed in Appendix I. Modified from Brookfield and Brett (1988).
Figure A-10. Stratigraphic section of Verulam Formation outcropping along roadcuts at the intersection of Highways 33 and 401. Numbers refer to sampling intervals.
## Appendix II

Key to species identification

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LM = locality, see appendix ??.

Sample number superscripts refer to
- \(^1\text{pedicle valve}\)
- \(^2\text{brachial valve}\)
- \(^3\text{matrix from within brachiopod}\)
- \(^4\text{replicate}\)

I.R. = \%; Elemental contents are reported in ppm; BD = below detection limits
\(\delta^{18}\text{O}\) and \(\delta^{13}\text{C}\) are reported in \(^\circ\text{o}\) (PDB).
APPENDIX III. Elemental and isotopic data.

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Appendix IV

Statistical Tables
Table A-1. Factor analysis (varimax rotated factor matrix; Nie et al., 1975) of Devonian brachiopod elemental chemistries (n= 253). Interpretations are based on applied and theoretical geochemical considerations (cf. Brand and Veizer, 1980).

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<td>30.3</td>
<td>21.5</td>
<td>12.7</td>
<td></td>
</tr>
<tr>
<td>Eigenvalue</td>
<td>2.425</td>
<td>1.717</td>
<td>1.016</td>
<td></td>
</tr>
<tr>
<td>Interpretation</td>
<td>Diagenetic alteration?</td>
<td>Environmental control?</td>
<td>Silicification/ Minor leaching?</td>
<td></td>
</tr>
</tbody>
</table>

Table A-2. Factor analysis (varimax rotated factor matrix; Nie et al., 1975) of *Athyris spiriferoides* (Middle Devonian) elemental chemistries (n= 83). Interpretations are based on applied and theoretical geochemical considerations (cf. Brand and Veizer, 1980).

<table>
<thead>
<tr>
<th></th>
<th>Factor 1</th>
<th>Factor 2</th>
<th>Factor 3</th>
<th>Communality</th>
</tr>
</thead>
<tbody>
<tr>
<td>log Ca</td>
<td>.052</td>
<td>-.080</td>
<td>.714</td>
<td>.519</td>
</tr>
<tr>
<td>log Mg</td>
<td>.595</td>
<td>.404</td>
<td>-.283</td>
<td>.597</td>
</tr>
<tr>
<td>log Sr</td>
<td>-.057</td>
<td>.832</td>
<td>.366</td>
<td>.830</td>
</tr>
<tr>
<td>log Mn</td>
<td>.796</td>
<td>.050</td>
<td>.004</td>
<td>.637</td>
</tr>
<tr>
<td>log Na</td>
<td>-.081</td>
<td>.921</td>
<td>-.149</td>
<td>.876</td>
</tr>
<tr>
<td>log Fe</td>
<td>.820</td>
<td>-.225</td>
<td>.012</td>
<td>.724</td>
</tr>
<tr>
<td>log Al</td>
<td>.487</td>
<td>.097</td>
<td>.544</td>
<td>.542</td>
</tr>
<tr>
<td>log I.R.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% of variation explained</td>
<td>25.9</td>
<td>22.3</td>
<td>17.6</td>
<td></td>
</tr>
<tr>
<td>Eigenvalue</td>
<td>2.107</td>
<td>1.782</td>
<td>1.407</td>
<td></td>
</tr>
<tr>
<td>Interpretation</td>
<td>Diagenetic alteration?</td>
<td>Environmental control?</td>
<td>?</td>
<td></td>
</tr>
</tbody>
</table>
Table A-3. Factor analysis (varimax rotated factor matrix; Nie et al., 1975) of *Mucrospirifer mucronatus* (Middle Devonian) elemental chemistries (n = 74). Interpretations are based on applied and theoretical geochemical considerations (cf. Brand and Veizer, 1980).

<table>
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<th>Communality</th>
</tr>
</thead>
<tbody>
<tr>
<td>log Ca</td>
<td>-.351</td>
<td>.688</td>
<td>.596</td>
</tr>
<tr>
<td>log Mg</td>
<td>.777</td>
<td>.451</td>
<td>.712</td>
</tr>
<tr>
<td>log Sr</td>
<td>-.159</td>
<td>.921</td>
<td>.857</td>
</tr>
<tr>
<td>log Mn</td>
<td>.635</td>
<td>.008</td>
<td>.903</td>
</tr>
<tr>
<td>log Na</td>
<td>.064</td>
<td>.715</td>
<td>.605</td>
</tr>
<tr>
<td>log Fe</td>
<td>.831</td>
<td>-.314</td>
<td>.790</td>
</tr>
<tr>
<td>log Al</td>
<td>.745</td>
<td>-.157</td>
<td>.579</td>
</tr>
<tr>
<td>log I.R.</td>
<td>.415</td>
<td>.233</td>
<td>.221</td>
</tr>
<tr>
<td>% of variation explained</td>
<td>35.9</td>
<td>23.7</td>
<td>11.9</td>
</tr>
<tr>
<td>Eigenvalue</td>
<td>2.873</td>
<td>1.896</td>
<td></td>
</tr>
<tr>
<td>Interpretation</td>
<td>Diagenetic alteration?</td>
<td>Environmental control?</td>
<td></td>
</tr>
</tbody>
</table>

Table A-4. Factor analysis (varimax rotated factor matrix; Nie et al., 1975) of *Mediospirifer audaculus* elemental chemistries (n = 59). Interpretations are based on applied and theoretical geochemical considerations (cf. Brand and Veizer, 1980).

<table>
<thead>
<tr>
<th></th>
<th>Factor 1</th>
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<th>Communality</th>
</tr>
</thead>
<tbody>
<tr>
<td>log Ca</td>
<td>.229</td>
<td>.705</td>
<td>.549</td>
</tr>
<tr>
<td>log Mg</td>
<td>.865</td>
<td>-.023</td>
<td>.749</td>
</tr>
<tr>
<td>log Sr</td>
<td>.022</td>
<td>.851</td>
<td>.725</td>
</tr>
<tr>
<td>log Mn</td>
<td>.769</td>
<td>-.049</td>
<td>.593</td>
</tr>
<tr>
<td>log Na</td>
<td>-.137</td>
<td>.706</td>
<td>.518</td>
</tr>
<tr>
<td>log Fe</td>
<td>.884</td>
<td>-.124</td>
<td>.797</td>
</tr>
<tr>
<td>log Al</td>
<td>.681</td>
<td>.023</td>
<td>.464</td>
</tr>
<tr>
<td>log I.R.</td>
<td>.337</td>
<td>-.783</td>
<td>-.727</td>
</tr>
<tr>
<td>% of variation explained</td>
<td>36.9</td>
<td>27.1</td>
<td></td>
</tr>
<tr>
<td>Eigenvalue</td>
<td>2.955</td>
<td>2.169</td>
<td></td>
</tr>
<tr>
<td>Interpretation</td>
<td>Diagenetic alteration?</td>
<td>Environmental control?</td>
<td></td>
</tr>
</tbody>
</table>
Table A-5. Factor analysis (varimax rotated factor matrix; Nie et al., 1975) of *Tropidoleptus carinatus* elemental chemistries (n= 20). Interpretations are based on applied and theoretical geochemical considerations (cf. Brand and Veizer, 1980).

<table>
<thead>
<tr>
<th>Factor</th>
<th>Factor 1</th>
<th>Factor 2</th>
<th>Factor 3</th>
<th>Communality</th>
</tr>
</thead>
<tbody>
<tr>
<td>log Ca</td>
<td>.111</td>
<td>.312</td>
<td>.782</td>
<td>.721</td>
</tr>
<tr>
<td>log Mg</td>
<td>.866</td>
<td>-.186</td>
<td>.119</td>
<td>.799</td>
</tr>
<tr>
<td>log Sr</td>
<td>.179</td>
<td>-.217</td>
<td>.868</td>
<td>.833</td>
</tr>
<tr>
<td>log Mn</td>
<td>-.428</td>
<td>.733</td>
<td>-.349</td>
<td>.843</td>
</tr>
<tr>
<td>log Na</td>
<td>.754</td>
<td>-.085</td>
<td>.586</td>
<td>.919</td>
</tr>
<tr>
<td>log Fe</td>
<td>.223</td>
<td>.871</td>
<td>-.046</td>
<td>.810</td>
</tr>
<tr>
<td>log Al</td>
<td>.915</td>
<td>.121</td>
<td>.076</td>
<td>.858</td>
</tr>
<tr>
<td>log I.R.</td>
<td>.163</td>
<td>.803</td>
<td>-.274</td>
<td>.746</td>
</tr>
</tbody>
</table>

% of variation explained: 41.1 25.8 14.7

Eigenvalue: 3.286 2.064 1.179

Interpretation: Taxonomic control and alteration? storage in shell calcite?

Table A-6. Factor analysis (varimax rotated factor matrix; Nie et al., 1975) of *Rhipidomella vanuxemi* elemental chemistries (n= 17). Interpretations are based on applied and theoretical geochemical considerations (cf. Brand and Veizer, 1980).

<table>
<thead>
<tr>
<th>Factor</th>
<th>Factor 1</th>
<th>Factor 2</th>
<th>Factor 3</th>
<th>Communality</th>
</tr>
</thead>
<tbody>
<tr>
<td>log Ca</td>
<td>.905</td>
<td>.011</td>
<td>-.141</td>
<td>.839</td>
</tr>
<tr>
<td>log Mg</td>
<td>-.163</td>
<td>.184</td>
<td>.887</td>
<td>.847</td>
</tr>
<tr>
<td>log Sr</td>
<td>.887</td>
<td>.041</td>
<td>.456</td>
<td>.962</td>
</tr>
<tr>
<td>log Mn</td>
<td>.152</td>
<td>.935</td>
<td>-.171</td>
<td>.927</td>
</tr>
<tr>
<td>log Na</td>
<td>.277</td>
<td>.055</td>
<td>.921</td>
<td>.929</td>
</tr>
<tr>
<td>log Fe</td>
<td>-.095</td>
<td>.918</td>
<td>.242</td>
<td>.911</td>
</tr>
<tr>
<td>log Al</td>
<td>-.272</td>
<td>.497</td>
<td>-.620</td>
<td>.705</td>
</tr>
<tr>
<td>log I.R.</td>
<td>-.813</td>
<td>.041</td>
<td>-.094</td>
<td>.672</td>
</tr>
</tbody>
</table>

% of variation explained: 37.4 24.7 22.7

Eigenvalue: 2.995 1.979 1.817

Interpretation: Environmental control? Diagenesis alteration? Taxonomic control and storage in shell calcite?

251
Table A-7. Factor analysis (varimax rotated factor matrix; Nie et al., 1975) of Middle Devonian brachiopod elemental chemistries (N = 19). Interpretations are based on applied and theoretical geochemical considerations (cf. Brand and Veizer, 1980).

<table>
<thead>
<tr>
<th>Factor</th>
<th>Factor 1</th>
<th>Factor 2</th>
<th>Factor 3</th>
<th>Communality</th>
</tr>
</thead>
<tbody>
<tr>
<td>log Ca</td>
<td>0.388</td>
<td>-0.152</td>
<td>-0.765</td>
<td>0.759</td>
</tr>
<tr>
<td>log Mg</td>
<td>0.123</td>
<td>-0.738</td>
<td>0.159</td>
<td>0.576</td>
</tr>
<tr>
<td>log Sr</td>
<td>0.731</td>
<td>0.124</td>
<td>-0.201</td>
<td>0.589</td>
</tr>
<tr>
<td>log Mn</td>
<td>0.244</td>
<td>-0.740</td>
<td>0.381</td>
<td>0.753</td>
</tr>
<tr>
<td>log Na</td>
<td>0.863</td>
<td>-0.146</td>
<td>0.000</td>
<td>0.766</td>
</tr>
<tr>
<td>log Fe</td>
<td>0.339</td>
<td>-0.213</td>
<td>0.837</td>
<td>0.861</td>
</tr>
<tr>
<td>log Al</td>
<td>0.727</td>
<td>0.150</td>
<td>0.240</td>
<td>0.609</td>
</tr>
<tr>
<td>log I.R.</td>
<td>0.258</td>
<td>0.804</td>
<td>0.255</td>
<td>0.777</td>
</tr>
<tr>
<td>δ¹⁸O</td>
<td>0.311</td>
<td>-0.792</td>
<td>0.087</td>
<td>0.732</td>
</tr>
<tr>
<td>δ¹³C</td>
<td>0.645</td>
<td>0.663</td>
<td>0.043</td>
<td>0.858</td>
</tr>
</tbody>
</table>

% of variation explained | 33.9 | 23.8 | 15.2
Eigenvalue | 3.389 | 2.376 | 1.515
Interpretation

Table A-8. Factor analysis (varimax rotated factor matrix; Nie et al., 1975) of Silurian brachiopod elemental chemistries (n= 205). Interpretations are based on applied and theoretical geochemical considerations (cf. Brand and Veizer, 1980).

<table>
<thead>
<tr>
<th>Factor</th>
<th>Factor 1</th>
<th>Factor 2</th>
<th>Factor 3</th>
<th>Communality</th>
</tr>
</thead>
<tbody>
<tr>
<td>log Ca</td>
<td>-0.110</td>
<td>0.055</td>
<td>0.779</td>
<td>0.623</td>
</tr>
<tr>
<td>log Mg</td>
<td>0.844</td>
<td>0.105</td>
<td>0.123</td>
<td>0.738</td>
</tr>
<tr>
<td>log Sr</td>
<td>-0.390</td>
<td>0.733</td>
<td>0.078</td>
<td>0.695</td>
</tr>
<tr>
<td>log Mn</td>
<td>0.853</td>
<td>-0.018</td>
<td>-0.085</td>
<td>0.735</td>
</tr>
<tr>
<td>log Na</td>
<td>-0.073</td>
<td>0.848</td>
<td>-0.017</td>
<td>0.724</td>
</tr>
<tr>
<td>log Fe</td>
<td>0.868</td>
<td>0.222</td>
<td>0.163</td>
<td>0.830</td>
</tr>
<tr>
<td>log Al</td>
<td>0.249</td>
<td>0.042</td>
<td>0.692</td>
<td>0.542</td>
</tr>
<tr>
<td>log I.R.</td>
<td>0.210</td>
<td>0.634</td>
<td>0.082</td>
<td>0.452</td>
</tr>
</tbody>
</table>

% of variation explained | 32.7 | 21.1 | 13.0
Eigenvalue | 2.617 | 1.686 | 1.038
Interpretation Diagenetic alteration? Environmental control? ?
Table A-9. Factor analysis (varimax rotated factor matrix; Nie et al., 1975) of *Eospirifer radians* elemental chemistries (n= 31). Interpretations are based on applied and theoretical geochemical considerations (cf. Brand and Veizer, 1980).

<table>
<thead>
<tr>
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<th>Factor 1</th>
<th>Factor 2</th>
<th>Factor 3</th>
<th>Communality</th>
</tr>
</thead>
<tbody>
<tr>
<td>log Ca</td>
<td>.057</td>
<td>.171</td>
<td>.780</td>
<td>.641</td>
</tr>
<tr>
<td>log Mg</td>
<td>.908</td>
<td>.065</td>
<td>.166</td>
<td>.856</td>
</tr>
<tr>
<td>log Sr</td>
<td>.036</td>
<td>.699</td>
<td>.081</td>
<td>.496</td>
</tr>
<tr>
<td>log Mn</td>
<td>.933</td>
<td>.059</td>
<td>.115</td>
<td>.888</td>
</tr>
<tr>
<td>log Na</td>
<td>.040</td>
<td>.245</td>
<td>-.476</td>
<td>.289</td>
</tr>
<tr>
<td>log Fe</td>
<td>.962</td>
<td>-.095</td>
<td>.115</td>
<td>.947</td>
</tr>
<tr>
<td>log Al</td>
<td>.257</td>
<td>-.053</td>
<td>.719</td>
<td>.586</td>
</tr>
<tr>
<td>log I.R.</td>
<td>.001</td>
<td>.782</td>
<td>-.172</td>
<td>.641</td>
</tr>
</tbody>
</table>

% of variation explained:
- Factor 1: 36.9
- Factor 2: 16.2
- Factor 3: 13.8

Eigenvalue:
- Factor 1: 2.948
- Factor 2: 1.299
- Factor 3: 1.101

Interpretation: Diagenetic alteration?

Table A-10. Factor analysis (varimax rotated factor matrix; Nie et al., 1975) of *Whitfieldella nitida* elemental chemistries (N= 48). Interpretations are based on applied and theoretical geochemical considerations (cf. Brand and Veizer, 1980).

<table>
<thead>
<tr>
<th></th>
<th>Factor 1</th>
<th>Factor 2</th>
<th>Factor 3</th>
<th>Factor 4</th>
<th>Communality</th>
</tr>
</thead>
<tbody>
<tr>
<td>log Ca</td>
<td>.047</td>
<td>-.215</td>
<td>.002</td>
<td>.085</td>
<td>.869</td>
</tr>
<tr>
<td>log Mg</td>
<td>.891</td>
<td>.240</td>
<td>-.028</td>
<td>.168</td>
<td>.880</td>
</tr>
<tr>
<td>log Sr</td>
<td>-.404</td>
<td>.438</td>
<td>.617</td>
<td>-.219</td>
<td>.784</td>
</tr>
<tr>
<td>log Mn</td>
<td>.850</td>
<td>-.253</td>
<td>.048</td>
<td>-.011</td>
<td>.789</td>
</tr>
<tr>
<td>log Na</td>
<td>.001</td>
<td>.402</td>
<td>-.053</td>
<td>.734</td>
<td>.704</td>
</tr>
<tr>
<td>log Fe</td>
<td>.867</td>
<td>.219</td>
<td>-.099</td>
<td>.052</td>
<td>.813</td>
</tr>
<tr>
<td>log Al</td>
<td>.186</td>
<td>.893</td>
<td>.110</td>
<td>.012</td>
<td>.844</td>
</tr>
<tr>
<td>log I.R.</td>
<td>.134</td>
<td>.239</td>
<td>-.038</td>
<td>.815</td>
<td>.741</td>
</tr>
</tbody>
</table>

% of variation explained:
- Factor 1: 33.6
- Factor 2: 19.1
- Factor 3: 14.3
- Factor 4: 13.2

Eigenvalue:
- Factor 1: 2.690
- Factor 2: 1.527
- Factor 3: 1.147
- Factor 4: 1.059

Interpretation: Diagenetic alteration? Environmental control?
Table A-11. Factor analysis (varimax rotated factor matrix; Nie et al., 1975) of *Atrypa reticularis* elemental chemistries (n= 50). Interpretations are based on applied and theoretical geochemical considerations (cf. Brand and Veizer, 1980).

<table>
<thead>
<tr>
<th></th>
<th>Factor 1</th>
<th>Factor 2</th>
<th>Factor 3</th>
<th>Communality</th>
</tr>
</thead>
<tbody>
<tr>
<td>log Ca</td>
<td>.215</td>
<td>.766</td>
<td>.014</td>
<td>.632</td>
</tr>
<tr>
<td>log Mg</td>
<td>-.233</td>
<td>.556</td>
<td>.639</td>
<td>.772</td>
</tr>
<tr>
<td>log Sr</td>
<td>.861</td>
<td>.060</td>
<td>.001</td>
<td>.745</td>
</tr>
<tr>
<td>log Mn</td>
<td>-.677</td>
<td>-.031</td>
<td>.535</td>
<td>.745</td>
</tr>
<tr>
<td>log Na</td>
<td>.867</td>
<td>.179</td>
<td>.114</td>
<td>.797</td>
</tr>
<tr>
<td>log Fe</td>
<td>-.487</td>
<td>.510</td>
<td>.397</td>
<td>.654</td>
</tr>
<tr>
<td>log Al</td>
<td>.094</td>
<td>.793</td>
<td>-.011</td>
<td>.638</td>
</tr>
<tr>
<td>log I.R.</td>
<td>.129</td>
<td>-.051</td>
<td>.869</td>
<td>.774</td>
</tr>
</tbody>
</table>

% of variation explained: 32.6 26.3 13.0

Eigenvalue: 2.612 2.103 1.044

Interpretation: ? ? ?

---

Table A-12. Factor analysis (varimax rotated factor matrix; Nie et al., 1975) of Ordovician brachiopod elemental chemistries (n= 133). Interpretations are based on applied and theoretical geochemical considerations (cf. Brand and Veizer, 1980).

<table>
<thead>
<tr>
<th></th>
<th>Factor 1</th>
<th>Factor 2</th>
<th>Factor 3</th>
<th>Communality</th>
</tr>
</thead>
<tbody>
<tr>
<td>log Ca</td>
<td>.039</td>
<td>.411</td>
<td>.430</td>
<td>.362</td>
</tr>
<tr>
<td>log Mg</td>
<td>.686</td>
<td>.144</td>
<td>.001</td>
<td>.506</td>
</tr>
<tr>
<td>log Sr</td>
<td>-.088</td>
<td>.890</td>
<td>.201</td>
<td>.841</td>
</tr>
<tr>
<td>log Mn</td>
<td>.778</td>
<td>-.079</td>
<td>-.004</td>
<td>.612</td>
</tr>
<tr>
<td>log Na</td>
<td>.037</td>
<td>.838</td>
<td>.052</td>
<td>.810</td>
</tr>
<tr>
<td>log Fe</td>
<td>.847</td>
<td>-.099</td>
<td>.129</td>
<td>.743</td>
</tr>
<tr>
<td>log Al</td>
<td>-.163</td>
<td>-.185</td>
<td>.804</td>
<td>.708</td>
</tr>
<tr>
<td>log I.R.</td>
<td>.230</td>
<td>.029</td>
<td>.670</td>
<td>.503</td>
</tr>
</tbody>
</table>

% of variation explained: 24.7 22.8 16.0

Eigenvalue: 1.974 1.826 1.284

Interpretation: Diagenetic alteration? Environmental control/ Laboratory leaching/
Table A-13. Factor analysis (varimax rotated factor matrix; Nie et al., 1975) of *Dalmanella rogata* elemental chemistries (n= 40). Interpretations are based on applied and theoretical geochemical considerations (cf. Brand and Veizer, 1980).

<table>
<thead>
<tr>
<th>Factor</th>
<th>Factor 2</th>
<th>Factor 3</th>
<th>Communality</th>
</tr>
</thead>
<tbody>
<tr>
<td>log Ca</td>
<td>-.138</td>
<td>.176</td>
<td>.880</td>
</tr>
<tr>
<td>log Mg</td>
<td>.522</td>
<td>-.093</td>
<td>.688</td>
</tr>
<tr>
<td>log Sr</td>
<td>-.525</td>
<td>.598</td>
<td>-.042</td>
</tr>
<tr>
<td>log Mn</td>
<td>.914</td>
<td>-.218</td>
<td>.069</td>
</tr>
<tr>
<td>log Na</td>
<td>-.227</td>
<td>.896</td>
<td>.001</td>
</tr>
<tr>
<td>log Fe</td>
<td>.933</td>
<td>.273</td>
<td>-.019</td>
</tr>
<tr>
<td>log Al</td>
<td>.376</td>
<td>.631</td>
<td>-.031</td>
</tr>
<tr>
<td>log I.R.</td>
<td>-.104</td>
<td>.660</td>
<td>.184</td>
</tr>
</tbody>
</table>

% of variation explained: 34.7 25.7 14.6

Eigenvalue: 2.775 2.011 1.167

Interpretation: Diagenesis alteration (meteoric) Environmental control/lab leaching?

---

Table A-14. Factor analysis (varimax rotated factor matrix; Nie et al., 1975) of *Rafinesquina deltoidea* elemental chemistries (n= 64). Interpretations are based on applied and theoretical geochemical considerations (cf. Brand and Veizer, 1980).

<table>
<thead>
<tr>
<th>Factor</th>
<th>Factor 2</th>
<th>Factor 3</th>
<th>Communality</th>
</tr>
</thead>
<tbody>
<tr>
<td>log Ca</td>
<td>.332</td>
<td>.024</td>
<td>.612</td>
</tr>
<tr>
<td>log Mg</td>
<td>.421</td>
<td>.406</td>
<td>-.367</td>
</tr>
<tr>
<td>log Sr</td>
<td>.935</td>
<td>.024</td>
<td>-.184</td>
</tr>
<tr>
<td>log Mn</td>
<td>.153</td>
<td>.792</td>
<td>.070</td>
</tr>
<tr>
<td>log Na</td>
<td>.924</td>
<td>.098</td>
<td>.059</td>
</tr>
<tr>
<td>log Fe</td>
<td>.014</td>
<td>.830</td>
<td>-.052</td>
</tr>
<tr>
<td>log Al</td>
<td>-.322</td>
<td>.077</td>
<td>.717</td>
</tr>
<tr>
<td>log I.R.</td>
<td>-.270</td>
<td>.437</td>
<td>.494</td>
</tr>
</tbody>
</table>

% of variation explained: 31.0 20.3 13.7

Eigenvalue: 2.477 1.626 1.095

Interpretation: Environmental control? Diagenetic alteration? Laboratory leaching?
Table A-15. Factor analysis (varimax rotated factor matrix; Nie et al., 1975) of *Sowerybella* sp. elemental chemistries (n= 21). Interpretations are based on applied and theoretical geochemical considerations (cf. Brand and Veizer, 1980).

<table>
<thead>
<tr>
<th></th>
<th>Factor 1</th>
<th>Factor 2</th>
<th>Communality</th>
</tr>
</thead>
<tbody>
<tr>
<td>log Ca</td>
<td>0.655</td>
<td>-0.379</td>
<td>0.573</td>
</tr>
<tr>
<td>log Mg</td>
<td>0.722</td>
<td>0.492</td>
<td>0.764</td>
</tr>
<tr>
<td>log Sr</td>
<td>0.845</td>
<td>-0.230</td>
<td>0.798</td>
</tr>
<tr>
<td>log Mn</td>
<td>-0.053</td>
<td>0.929</td>
<td>0.866</td>
</tr>
<tr>
<td>log Na</td>
<td>0.993</td>
<td>-0.154</td>
<td>0.822</td>
</tr>
<tr>
<td>log Fe</td>
<td>-0.039</td>
<td>0.907</td>
<td>0.824</td>
</tr>
<tr>
<td>log Al</td>
<td>0.516</td>
<td>0.012</td>
<td>0.267</td>
</tr>
<tr>
<td>log I.R.</td>
<td>-0.262</td>
<td>0.789</td>
<td>0.690</td>
</tr>
<tr>
<td>% of variation</td>
<td>42.0</td>
<td>28.0</td>
<td></td>
</tr>
<tr>
<td>explained</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eigenvalue</td>
<td>3.363</td>
<td>2.241</td>
<td></td>
</tr>
<tr>
<td>Interpretation</td>
<td>Environmental control?</td>
<td>Diagenetic alteration?</td>
<td></td>
</tr>
</tbody>
</table>
Appendix V. Table of summarized taphonomic features for selected beds from the Hamilton Group (Middle Devonian) of New York and Ontario.

<table>
<thead>
<tr>
<th>Locality</th>
<th>Bed</th>
<th>Biofacies</th>
<th>Deform.</th>
<th>Taph.</th>
<th>Articulation Ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>A/D</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.</td>
</tr>
</tbody>
</table>

1A (i) Widder N/A N/A 47/52
1B (ii) Hungry Hollow N/A N/A 5/53
1B (iii) Arkona N/A N/A 35/16
1B (iv) Arkona N/A N/A 35/16
2 (i) 4A -10 10/- 9/-
2 (ii) 5A 26/7 6/55 12/-
2 (iii) Pleurodictyum 5B S>C>T B/E 14/4 5/7
3 (i) Ambucoeliid 3A T>S 5/- 4/-
3 (ii) Demissa 5A S>C>T -58 8/52 -46 6/-
3 (iii) 5A 9/3
6 (ii) Smoke Creek 4A C>S 12/7 -6
6 (iii) Bay View Bed 5B B/E/F -52 25/- -2 6/4 6/2
6 (v) Demissa 5A S>C>T -52 25/- -2 6/4 6/2
6 (vi) Concretion 4A S>T 17/- 5/-
7 (ii) Demissa 5A S>T 20/58 12/12 -5 10/- 12/10
7 (iii) Mucrosp. 4B 2/35
8 (ii) 5/15 3/10 7/29
8 (iii) Demissa 5A S>T 36/65 37/- 8/- 39/-
13 (ii) Demissa 5A S>T 13/35 59/115 -14
20 (iii) Demissa 4A S>T 8/3 5/3

n.b. 1. Brachiopods belong to biofacies association listed in Fig. 3.1
2. Dominance of type of shell deformation. S = splayed; C = carinate; T = telescoped (Alexander, 1986).
3. Presence of significant B = boring; E = encrustation; F = shell fragmentation
4. Articulation ratios i.e. articulated valves to disarticulated