**GEOCHEMISTRY AND SEDIMENTOLOGY OF UPPER
ORDOVICIAN MUDROCKS AND LIMESTONES, EASTERN
ONTARIO: A NEW SEDIMENTARY FRAMEWORK FOR THE
DISTAL TACONIC FORELAND**

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A thesis presented to the Faculty of Graduate Studies and Research

In partial fulfillment of the requirements for the degree of Doctor of Philosophy

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Abstract

In eastern Ontario, Upper Ordovician (Edenian–Richmondian) strata, now preserved in the Ottawa Embayment, represents the final stages of foreland basin fill related to Taconic orogenesis. The mostly mudrock succession buried a shallow–water carbonate ramp (Lindsay Formation). Passage from carbonates to mudrocks is recorded by the Eastview Member (eastern Ontario) and Collingwood Member (southern and central Ontario). In eastern Ontario and at Craigleith, central Ontario, inboard of the Michigan Basin to the west, this unit consists of an interbedded limestone and petroliferous claystone. The latter lithology indicates intermittent dysoxic conditions along the ramp. Geochemistry of the shale suggests that increased organic productivity may have caused dysoxic conditions that preserved elevated organic carbon (2–6%). Mineralogy and geochemical proxies indicate the first introduction of sediment derived from erosion of the Taconic island arc. Along the eastern margin of the Michigan Basin, the Collingwood Member consists of inter–laminated/ thinly bedded calciturbidites and organic–rich shale. This regional difference in carbonate stratigraphy may define formation of a distally–steepened ramp margin along the Michigan Basin, possibly arising from more rapid collapse of the carbonate platform. Subsequent shales of the lower Billings Formation (eastern Ontario) and the Blue Mountain Formation (southwestern Ontario) were deposited in dysoxic to anoxic deep–water basins, and record peak influx of mafic–rich, Taconic–derived, sediment.

In eastern Ontario, a K–bentonite (Russell Bed), dated (Ar–Ar) at 445 Ma, separates these deep–basin shales (lower Billings Formation) from subsequent influx of siliciclastic turbidites (upper Billings Formation), the latter deposited in an oxygenated

basin. Deep-water ventilation, coincidental graptolite extinction, volcanism, and appearance of turbidites, combined, identify major basin reorganization and paleoceanographic changes at this time linked to Taconic orogenesis. The K-bentonite contains rare, altered glass spherules. Compositionally, source magmatism was mildly alkaline and basic, with a continental crustal component, when compared to the older rhyolitic to rhyodacitic K-bentonites of eastern North America that predate carbonate platform collapse. This geochemical change may also signal evolution of the magmatic arc along eastern North America or a basin-restricted event marking local fracturing of the continental basement due to distal thrust loading.

Following volcanism, the Carlsbad (eastern Ontario) and Georgian Bay formations (southwestern Ontario) define a shallowing upward succession that records progressive basin fill by distal turbidites (flysch) sourced from the Taconic highlands. In both areas, the overlying Queenston Formation forms the topmost preserved Ordovician strata. It was deposited in peritidal environments. Its transition with the Carlsbad/Georgian Bay Formation contains geographically widespread ooid and bioclastic limestone beds finely interbedded with mudrock. Such intermittent, regional carbonate production was likely related to critical thresholds established by sea level fluctuation and shutdown/bypassing of siliciclastics. A few metres below the Ordovician-Silurian boundary, a thin (~1m) regional mudrock contains isolated ooids whose geochemistry records a positive $\delta^{13}\text{C}$ excursion. This may signal onset of a history of paleoceanographic change controlled by climate change, leading to Late Ordovician glaciation.

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I finally thank and appreciate the support and encouragement of my wife, Hema Sharma, during the entire period of the research. I also thank my parents and brother for their encouragement.

Statement of original contribution

During the course of the thesis research, two papers were published, and one manuscript has been submitted. These papers and manuscript form the middle three chapters of the thesis, bounded by Introduction and Discussion/Summary chapters. Research was conducted under the supervision of, and funded by, Dr. George R. Dix, Department of Earth Sciences, Carleton University, who also acted as editor and scientific advisor. There was required collaboration with three other researchers, two of whom are co-authors on separate papers, who provided different types of technical expertise: a) in the first paper (Chapter II), Dr. John F. V. Riva, Québec Geoscience Centre, Québec, provided identification of graptolite, trilobite and brachiopod specimens; b) in the submitted manuscript (Chapter III), Dr. Mike Villeneuve, Geological Survey of Canada, Ottawa, provided the results of Ar-Ar isotope analysis on phlogopites; and, c) in the final paper (Chapter IV), Dr. A.D. McCracken, Geological Survey of Canada, Calgary, provided identification of some conodont specimens. All papers were written and revised by myself, and submitted to my co-authors for revision. Journal reviewers' comments were addressed with the consultation of co-authors, manuscripts were resubmitted after approval from all co-authors.

Table of contents

Title page	i
Acceptance form	ii
Abstract.....	iii
Acknowledgements	v
Statement of original contribution.....	vi
Table of contents	vii

Chapter I **Introduction**

Regional Geological Framework.....	2
Previous Studies	7
Objectives and Framework of the thesis.....	8
Methods.....	11

Chapter II **Late Ordovician platform foundering, its paleoceanography and burial, as preserved in separate (eastern Michigan Basin, Ottawa Embayment) basins, southern Ontario**

Abstract	14
Introduction	16
Regional geological framework	21
Methods.....	23
Results	26
Lithostratigraphy.....	26

Russell core	26
Elizabeth core	30
Biostratigraphy.....	35
Russell core	35
Elizabeth core	36
Mineralogy	36
Russell core	36
Elizabeth core	37
Chemostratigraphy	37
Mafic/felsic content ratio	37
Cr, Ni, and Cr/Ni	40
Eu/Eu* and La _N /Sm _N	41
V/Rb, Mo/Rb, and Ua	44
Ba/Rb	48
TOC% and $\delta^{13}\text{C}_{\text{org}}$	49
Discussion	49
Timing and diachroneity of platform foundering	49
Basin development	50
Character of platform demise	52
Conclusions	54
Acknowledgements	55

Chapter III **Late Ordovician (440 Ma) volcanism in a deep-shale basin**

(Appalachian foreland), eastern Ontario: tectonic trigger for Taconic flysch, faunal extinctions, and paleoceanographic change

Abstract	57
Introduction	58
Stratigraphic framework	58
Methods	63
The Russell Bed	63
Occurrence and Distribution	63
Fabric, Texture, and Constituents	66
Geochemistry and Mineralogy	71
Ar-Ar isotope analysis.....	71
Discussion	71
Age of the Russell Bed	71
Magmatic source for Russell Bed volcanism	75
Tectonic Significance.....	75
Conclusions	82
Acknowledgements	82

Chapter IV **Magnesian calcite and chamositic ooids forming shoals**

peripheral to Late Ordovician (Ashgill) muddy siliciclastic shores: southern Ontario

Abstract.....	84
Introduction.....	86
Regional stratigraphic framework.....	91
Regional sedimentology and paleogeography.....	94
Methods.....	96
Results.....	99
Ooid Facies Associations.....	99
Type A Ooids.....	100
Stratigraphy.....	100
Microfacies, Petrographic Fabric, Mineralogy.....	103
Diagenetic characteristics.....	111
Type B Ooids.....	116
Stratigraphy.....	116
Petrographic fabric.....	119
Geochemistry of Type A and B Ooids.....	119
Discussions.....	127
Type A ooids:	
Carbonate Factory Start-Up in a Siliciclastic System.....	127

Type B Ooids:	
Late Ordovician tropical storms or transgressive unit?.....	130
Mineralogy of Ooids: a magnesian calcite precursor.....	131
Geological significance.....	132
Conclusions.....	133
Acknowledgements.....	135

Chapter V **Discussion and Summary**

Late Ordovician foreland basin in the Ottawa Embayment.....	136
Collapse of the foreland carbonate platform: eastern Ontario.....	141
Deep–water foreland basin: onset of siliciclastic basin fill.....	143
Russell K-bentonite:	144
An intra/inter basin correlation tool.....	144
Foreland basin dynamics and volcanism.....	145
Evolution of Appalachian volcanic arc vs. local tectonics.....	147
Upper Billings and Carlsbad Formations:	
Taconic flysch in eastern Ontario.....	148
Ooid limestones in foreland mollase:	
significance for basin development.....	149
Ooid beds, relative sea level change, and Hirnantian glaciation.....	149

References.....	151
------------------------	------------

List of Tables

Table 2-1. Geochemistry of Russell Bed and other selected units.....	45
Table 3-1. Geochemistry of the Russell bed, Ordovician K–bentonites and volcanic fragments.	64
Table 4-1. Well core and outcrop coordinates for the studied area.....	89

List of Figures

Figure 1-1. General distribution of Palaeozoic and Precambrian rocks and sedimentary basins in southern Ontario.....	3
Figure 1-2. General stratigraphy of eastern Ontario.....	5
Figure 2-1. Regional bedrock geology of southern Ontario.....	17
Figure 2-2. Stratigraphic nomenclature for the Upper Ordovician succession in the Quebec Basin, Ottawa Embayment, and northern Michigan Basin (Manitoulin Island)	19
Figure 2-3. Stratigraphic column showing the general lithology and Upper Ordovician graptolite ranges and zones in drill core, Russell GSC #2.....	24
Figure 2-4. Outcrop exposure on Aviation Parkway (Ottawa).....	27
Figure 2-5. Stratigraphic column, general lithology and Upper Ordovician graptolite zones and ranges for drill core GSC DDH2-Elizabeth from Manitoulin Island.	31
Figure 2-6. Downhole changes in various properties in the Russell GSC #2 section.....	33
Figure 2-7. Downhole changes in various properties in the GSC DDH2-Elizabeth section.....	38
Figure 2-8. Variation in Cr and Ni of claystone from various lithostratigraphic units from the Russell GSC #2 and GSC DDH2-Elizabeth (Manitoulin Island) cores.	42
Figure 3-1. Late Ordovician paleogeography of eastern North America.....	59
Figure 3-2. Lithology and graptolite biostratigraphy for Loc. A drill core.	61

Figure 3-3. Photomicrographs of volcanic ash.....	67
Figure 3-4. Volcanic glass spherules.	69
Figure 3-5. Argon isotopic spectra of gas release plots.	72
Figure 3-6. Geochemistry of the Russell Bed and older K-bentonites from the Russell GSC#2 core.....	76
Figure 3-7. Rare earth element compositions of apatites, Russell Bed, Deicke and Millbrig K-bentonites.....	80
Figure 4-1. Location of the study area.	87
Figure 4-2. Upper Ordovician stratigraphy, southern Ontario.....	92
Figure 4-3. Detailed outcrop and core lithostratigraphy.....	97
Figure 4-4. Ooid versus bioclast percentages in limestone beds in southern Ontario.....	101
Figure 4-5. Characteristic ooid microfacies in southern Ontario.	105
Figure 4-6. SEM photomicrographs of acid-etched ooids.....	107
Figure 4-7. Schematic model of a radially-concentric ooid.....	109
Figure 4-8. SEM photomicrographs of iron-oxide and chamosite distribution within ooids.....	112
Figure 4-9. SEM photomicrographs of ooid textures and cement.....	114
Figure 4-10. Textural attributes of Type B ooids.....	117
Figure 4-11. Fe, Mn, Sr (in ppm) and MgCO ₃ mol% in Type A and Type B ooids.....	121
Figure 4-12. Comparison of ooid geochemistry and Upper Ordovician inorganic and biogenic calcite.....	123
Figure 4-13. Stable isotope (C,O) variation for Type A and B ooids, and calcite cement, southern Ontario in comparison to reference Ordovician organic calcite.	125
Figure 5-1. General foreland basin model.	137
Figure 5-2. Locations of peripheral foreland basins	139

List of Appendices

Appendix 1. Sample numbers, corresponding depth and chemostratigraphic units for Russell GSC #2.....	173
Appendix 2. Clay mineralogy of Russell GSC #2.....	175
Appendix 3. X- ray diffractograms of clay minerals, Russell GSC #2.....	176
Appendix 4. Trace elements, Russell GSC #2.....	177
Appendix 5. Organic carbon % and isotope, Russell GSC#2.....	180
Appendix 6. Average of trace elements from upper Billings and Carlsbad formations.....	181
Appendix 7. Average of trace elements from lower Billings Formation.....	184
Appendix 8. Average of trace elements from Eastview Member, Russell GSC#2.....	185
Appendix 9. Average of trace elements from Eastview Member, Aviation Parkway....	186
Appendix 10. Average of trace elements from Quaternary Black Sea sediments.....	187
Appendix 11. Sample numbers, corresponding depth and chemostratigraphic units for GSC DDH2.....	190
Appendix 12. Clay mineralogy, GSC DDH2.....	191
Appendix 13. X-ray diffractograms of clay minerals, GSC DDH2.....	192
Appendix 14. Trace elements, GSC DDH2.....	193
Appendix 15. Major oxide compositions of Ordovician K-bentonites.....	196
Appendix 16. Major oxide composition of Ordovician K-bentonites, southern Ontario	202
Appendix 17. Methodology for Ar-Ar Analysis.....	203
Appendix 18. Ar-Ar data, phlogopites from Russell K-bentonite.....	205
Appendix 19. Chemical composition of phlogopites, Russell Bed.....	210

Appendix 20. LREE in apatites from Ordovician K-bentonites.....	211
Appendix 21. Geochemistry, Type A ooids, eastern Ontario.....	212
Appendix 22. Geochemistry, Type A ooids, southwestern Ontario.....	214
Appendix 23. Geochemistry, brachiopods, southern Ontario.....	215
Appendix 24. Geochemistry, Type B ooids southwestern Ontario.....	216
Appendix 25. Geochemistry, reference brachiopods.....	219
Appendix 26. Stable isotope (C,O) compositions of Type A ooids, southern Ontario....	220
Appendix 27. Stable isotope (C,O) compositions of Type B ooids, southern Ontario....	221
Appendix 28. Stable isotope (C,O) brachiopods and cement.....	222
Appendix 29. Stable isotope (C,O) compositions of brachiopods, eastern Ontario.....	223
Appendix 30. Stable isotope (C,O), reference Ordovician brachiopods.....	224

Chapter I

Introduction

Upper Ordovician strata in eastern Ontario record development of a foreland basin and carbonate platform overlain by basin fill comprising mudrock, sandstone, anomalous minor limestone, and at least one K-bentonite bed. Very little attention has been paid to the geology of this succession. First, there are few outcrops and cores that allow the development of a regional stratigraphic framework; and, second, extraction of sedimentological information from mudrock has always been a challenge due to paucity of sedimentary structures and the fine grained character of the host material (Potter et al., 1980). Thus, the history of the Late Ordovician basin fill for eastern Ontario, and timing of any tectonic events that might be registered sedimentologically, have been poorly known. However, mudrock is an important geological archive, and is a repository for higher concentrations of trace elements when compared to sandstones and limestones (Taylor and McLenan, 1985). Thus, whole rock geochemistry of mudrock becomes a quick and valuable tool for deciphering provenance and paleoceanography (Taylor and McLenan, 1985; Garver et al., 1996). In general, therefore, this study of the Upper Ordovician basin fill, its stratigraphy, general sedimentology, and whole rock geochemistry, is the first detailed study of the tectonostratigraphic framework for the Late Ordovician distal foreland basin, as preserved in eastern Ontario, adjacent to the Taconic orogen.

Regional Geological Framework

In southern Ontario, the Paleozoic sedimentary succession presently covers about 120,000 km², and ranges in age from Cambrian to Early Mississippian (Fig 1-1; Hutt et al., 1973; Legall et al., 1981). Four basins are represented (Fig 1-1): the Ottawa Embayment Basin and the Quebec Basin to the east of Frontenac Arch; and to the west of the arch the Allegheny Basin and the intracratonic Michigan Basin (Sanford; 1993). The Ottawa Embayment is a cratonic interior extension of the Quebec Basin, and is dissected in part by the Ottawa-Bonnechère Graben that runs orthogonal to the Appalachian Orogen (Fig. 1-1).

The principal area of study for my research is eastern Ontario. It is underlain by a Cambrian to Ordovician sedimentary succession, which defines an area of approximately 12,000 km², and attains a maximum thickness of 760 m (Hutt et al., 1973). This succession is divided into two broad stratigraphic components (Fig. 1-2): (1) the Sauk Super Sequence (Sloss, 1963) represented by a Cambrian to Middle Ordovician siliciclastic-to –carbonate succession of inner platform facies that accumulated along an epicontinental passive margin; and (2) the lower Tippecanoe Super Sequence (or the Tutelo phase) (Sloss, 1963), represented by a Middle to Upper Ordovician foreland basin succession. The foreland sequence is further divided into three parts: (a) a basal siliciclastic– to –carbonate transition (Rockcliff and Hog's Back formations); (b) a carbonate platform (Ottawa Group); and (c) basin–fill sediments consisting mostly of siliciclastics (Fig. 1-2; Dix et al., 1998). The basin fill represents an overall shallowing upward succession, from deep-water shale (lower Billings Formation) through flysch sediments (upper Billings and Carlsbad formations) to peritidal mudrock of the

Figure 1-1 General distribution of Palaeozoic and Precambrian rocks and sedimentary basins in southern Ontario. Isopachs of stratal thickness (in $\times 100$ metres) in the Late Ordovician (Edenian to Gamachian) (Sanford, 1993) show interpreted distribution for post-foreland platform basin-fill strata.

Figure 1-2. General stratigraphy of eastern Ontario (modified after Dix et al, 1998).
Approximate thickness of different stratigraphic intervals is based on Russell GSC#2
core (Williams, 1991).

Queenston Formation. Equivalent rock units in southwestern Ontario are represented by the Blue Mountain (basinal shale), Georgian Bay (flysch), and Queenston formations.

Previous studies

General description of the lithology, stratigraphy and the rich fossil assemblage of the Upper Ordovician basin-fill succession in eastern Ontario date back to the pioneers of geology for eastern North America (Logan, 1863; Foerste, 1916; Parks, 1925, 1928; Ruedemann, 1925; Wilson, 1946). Subsequently, Williams (1991) provided an overview of the general litho- and biostratigraphy of the siliciclastic basin fill. Barnes et al. (1981) and Sanford (1993) correlated the stratigraphy among the Ottawa Embayment, Québec, and Michigan basins. A few studies have dealt specifically with the carbonate-siliciclastic platform-basin transition and the overlying basin-fill, but focused on outcrops west of the Frontenac Arch (Russell and Telford, 1983; Kerr and Eyles, 1991; Lehmann et al., 1995; Brogly et al., 1998). Detailed studies of mineralogy and geochemistry of the basin fill succession are rare (e.g. Garver et al., 1996).

During this present study, a K-bentonite bed was discovered at the top of the lower Billings Formation in eastern Ontario. Elsewhere in Ontario, the occurrence of K-bentonite beds within the underlying carbonate platform rocks is well known. First reported by Maddox (1930) from the Collingwood area, central Ontario, Trevail (1990) and Kolata et al. (1996) have expanded the known occurrences of these beds in southern Ontario and southern Quebec. K-bentonite beds have not been reported from the basin-fill siliciclastics of southern Ontario, but Belt et al. (1979) reported such occurrences from equivalent siliciclastics of the Quebec Basin. Thus, the discovery of a

K-bentonite within the basal part of the Taconic foreland basin fill succession in eastern Ontario provides an important correlation tool, and, when coupled with detailed phenocryst and whole rock geochemistry, helps with understanding the evolution of the Appalachian island-arc system.

In eastern Ontario, Wilson (1946) identified a thin, predominantly limestone interval that acts as a stratigraphic transition separating the deeper water Carlsbad Formation (flysch sediments) from the overlying peritidal Queenston Formation (molassic) sediments. She referred to this transitional unit as the Russell Formation, but subsequent workers recommended that the unit be abandoned, and included it within the underlying Carlsbad Formation (Williams, 1991). No detailed lithology has ever been published. My study discovered that the unit is a series of ooid limestone beds, similar to those described by Brogly (1984, 1998), and Donaldson (1990) for the equivalent stratigraphy in southwestern Ontario.

Objectives and Framework of the thesis

The goal of my research is to develop a better tectonostratigraphic framework for Upper Ordovician basin fill sediments of eastern Ontario. Specific objectives are:

- 1) to document the geochemistry of the Upper Ordovician Taconic foreland basin fill in order to help discern changes in paleoceanography, during and following the carbonate platform foundering, and to define, if possible, the provenance of basin fill sediments;
- 2) to identify the origin of the previously unrecognized K-bentonite that caps the lower Billings Formation and identify its specific age and tectonic association with any changes in foreland basin sedimentation; and,

3) to define the character, stratigraphic significance, and paleoceanography of ooid limestone beds associated with the Queenston Formation, which record the final stages of the basin fill.

The thesis is arranged in five chapters, the middle three chapters (II, III, and IV) representing individual manuscripts addressing the above research objectives. Two of these (chapters II and IV) are in press while Chapter III has been recently submitted. While each chapter stands alone, they are interlinked, and contribute to an improved understanding of the distal Taconic foreland basin west of the Appalachian Orogen. The chapters (or topics) are presented in stratigraphic order. Chapter V presents a discussion and summary of general conclusions. Finally, references, cited in each chapter are presented at the end of the thesis. Data for each chapter are included in appendices at the end of the thesis as well.

A brief synopsis of the chapters II to IV follows.

Chapter II

Sharma, S., Dix, G.R. and Riva, J.F.V., 2003. Late Ordovician platform foundering, its paleoceanography and burial, as preserved in separate (eastern Michigan Basin, Ottawa Embayment) basins, southern Ontario. *Canadian Journal of Earth Sciences*, v. 40, p. 135-148.

The interbedded petroliferous shale and limestone succession of the Eastview Member (eastern Ontario) and Collingwood Member (southwestern Ontario) forms an important stratigraphic interval that separates the Middle to Late Ordovician carbonate platform deposits from the overlying foreland basin fill sediments. Russell and Telford (1983) published a review of the Collingwood Member in the context of its importance as a petroleum source rock. My research deals with the paleoceanographic and tectonic changes in eastern Ontario associated with this transition, and heralding the influx of

foreland siliciclastics, as inferred from a set of geochemical proxies. In addition, this paper defines a more detailed biostratigraphic framework (based on graptolite zones) for the foreland basin fill in eastern Ontario than was previously available. The paper compares the histories of platform foundering preserved in the Ottawa Embayment and eastern margin of the Michigan Basin.

Chapter III

Sharma, S., Dix, G.R., and Villeneuve, M., (submitted to *Geology*), Late Ordovician (445

Ma) volcanism in a deep-shale basin (Appalachian foreland), eastern Ontario: tectonic trigger for Taconic flysch, faunal extinctions, and palaeoceanographic change.

With the collapse of the carbonate platform, a deep-water shale basin developed, and subsequently was filled by a shallowing upward succession of Taconic flysch, then molassic sediments. A potassium (K)-bentonite bed separates the deep-water shale and basal flysch sediments. This paper examines the mineralogy, geochemistry (whole rock and phenocrysts) of this previously unknown volcanic unit. Ar-Ar isotopic age analysis, based on phlogopite phenocrysts, is compared to graptolite biostratigraphy, and illustrates a possible regional volcanic unit across other parts of eastern North America. Linkage between volcanic activity, sedimentation and biotic extinction is developed illustrating the role of volcanism and tectonism in basin development.

Chapter IV

Sharma, S., and Dix, G.R., (in press). Magnesian calcite and chamositic ooids forming shoals

peripheral to Late Ordovician (Ashgill) muddy siliciclastic shores: southern Ontario.

Palaeogeography, Palaeoclimatology, Palaeoecology.

In eastern Ontario, Late Ordovician foreland basin fill culminates with accumulation of peritidal mudrock of the Queenston Formation. This unit contains thin ooid limestone beds, interbedded with mudrock. Similar beds occur in equivalent stratigraphic intervals across southern Ontario. The regional geographical distribution coupled with allochem-cement geochemistry help to define the paleoceanographic changes that occurred during foreland basin fill sedimentation and allowed turning on and off of the carbonate factory.

Methods

The research is based on subsurface cores and well logs, and surface outcrops. Available cores were examined at research facilities of the Geological Survey of Canada, in Ottawa, the Ontario Oil, Gas and Salt Library, in London, and the Ontario Geological Survey, in Sudbury. Geophysical logs were provided by the Ontario Oil, Gas and Salt Library, and Mr. D. K. Armstrong of Ontario Geological Survey. Outcrops of the platform–basin transition and basin–fill succession are rare, but key exposures occur along the Aviation Parkway, Ottawa; Craigleith National Park, Collingwood, Ontario; and, along Bronte Creek, Toronto.

A sampling strategy was developed in keeping with the different types of required analysis. For graptolite biostratigraphy, each of the cores studied was split parallel to bedding every centimeter to few centimeters. For clay mineralogy and geochemical analysis, mudrock samples were carefully selected at a regular spacing of approximately one metre, where possible. Samples from specific stratigraphic intervals, such as the K-bentonite bed and ooid limestone beds, were collected at more frequent spacing.

Analytical techniques and sample preparation specific to individual research objectives are described in the relevant chapters. However, a common methodology related to mudrock desegregation for clay–mineral analysis and general petrology is discussed here. Mudrock samples were soaked overnight to soften the material, then gently pulled apart by hand in the presence of water. Use of pestel and mortar was restricted to some initial desegregation of big samples. This procedure avoided breakage of quartz, mica and other mineral grains, which would have otherwise contaminated the mud–size fraction.

Chapter II

Late Ordovician platform foundering, its paleoceanography and burial, as preserved in separate (eastern Michigan Basin, Ottawa Embayment) basins, southern Ontario

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Abstract

Comparison of litho-, bio- and chemostratigraphy in two cores from the northeastern margin of the Michigan Basin (Manitoulin Island) and from within the Ottawa Embayment (eastern Ontario) identifies interbasinal differences of Late Ordovician platform foundering linked to the Taconic orogenesis. Graptolite biostratigraphy defines an east-to-west younging (late Edenian to early Maysvillian) of platform burial. A regional unconformity likely caps the platform succession. In both basins, an increased supply of mafic material appears during the final stages of platform collapse, with the accumulation of organic-rich (< 8 %), petroliferous shales (Collingwood Member – Michigan Basin; Eastview Member – Ottawa Embayment). Both units preserve evidence for deposition coincident with increased dysoxic to possible anoxic bottom-water conditions, but the Collingwood Member accumulated under a relatively stable paleoceanographic environment. Rhythmic interbedding with platform limestone in eastern Ontario, combined with evidence for fluctuating paleoproductivity, suggests the depositional environment of the Eastview Member was more sensitive to higher-order controls affiliated with tectonic, oceanographic and/or sea level variations. Such interbasinal differences likely reflect a greater rate of subsidence in the Manitoulin region transforming platform sedimentation to a distal ramp facies. In eastern Ontario, a lesser rate of subsidence maintained a shallower-water, but open margin, setting. Burial of the Upper Ordovician platform, as preserved in eastern Ontario, occurred during peak dysoxic conditions, with deposition of a hemipelagic facies (Billings Formation) that marks the peak supply of clay-size mafic-derived sediment. Bottom-water ventilation

occurred only with appearance of abundant Taconic-derived distal turbidites. An equivalent hemipelagic facies appears to be absent from the Manitoulin region. However, equivalent resedimented deposits are represented by the Blue Mountain Formation.

Introduction

In eastern Ontario, within the Ottawa-Bonnechère Graben (Fig. 2-1), and southwest and central Ontario, along the margin of the Michigan Basin (Fig. 2-1), there is a common history of platform foundering during the Late Ordovician that is linked to the Taconic orogenesis. As represented by a vertical lithostratigraphy varying from 5 to 11 metres in thickness (Johnson et al. 1992), the transition is defined by shelfal limestone, passing through petroliferous shale ($\pm$ interbedded limestone), and into deep-water basinal siliciclastics (Williams 1991; Sanford 1993; Melchin et al. 1994; Lehmann et al. 1995). The petroliferous shale (Collingwood Member or Eastview Member according to the area; Fig. 2-2) has attracted considerable attention due to its known petroleum source rock potential (Legall et al. 1981; Russell and Telford 1983; Snowdon 1984), with most previous work focused along the eastern and northeastern margins of the Michigan Basin (Melchin et al. 1994; Lehmann et al. 1995). For eastern Ontario, little detailed stratigraphic information is available, although there remain contradictory ages and interpreted contact boundaries (Barnes et al. 1981; Johnson et al. 1992; Sanford 1993).

To better understand the transformation of this regional Late Ordovician carbonate system into a deep-water foreland basin, this paper compares litho-, bio- and chemostratigraphy of shale from two drill cores from each basin that represent depositional sites once along the interior of their respective platforms. Mineralogy and geochemistry is used to extract provenance information (e.g., Björlykke 1974; Andersen 1995; Garver et al. 1996) and attributes of paleoceanography (Lewan and Maynard 1982; Brumsack 1986; Wignall and Myers 1988; Brumsack 1989; Wignall 1994). From this, inter-basinal differences in timing of platform demise and paleoceanographic character

Figure 2-1. Regional bedrock geology of southern Ontario showing general distribution of Lower Paleozoic and Precambrian rocks (modified from Sanford, 1993), and location of the two drill core sections: 1 - Russell GSC #2 (Russell county, eastern Ontario); 2 - GSC DDH-2 (Manitoulin Island, central Ontario). The dashed line west of Toronto defines the erosional limit of Silurian strata, demarcating to the north the northeastern edge of the Michigan Basin. Abbreviations: OBG - Ottawa Bonnechère Graben; AH - Adirondack Highlands; MB - Michigan Basin; FA - Frontenac Arch.

Figure 2-2. Existing and proposed (this study) formation distribution for the Upper Ordovician succession in the Quebec Basin, Ottawa Embayment, and northern Michigan Basin (Manitoulin Island) regions showing their position with respect to British Series, North American (N.A.) Series and Stages. The precise age of the Billings, Carlsbad and base of Billings is uncertain. Positions of the North American (N.A.) graptolite zones are from Goldman and Bergström (1997). Vertical line pattern in lower right of the figure shows hiatus. EM - Eastview Member; LM - Lower Member, Lindsay Formation; Ch., Champlainian; Sh., Shermanian.

System	British Series		N.A. Series		Sh.	ruede-spinif- manni- erus		pygmaeus	manitoulinensis		Georgian Bay	Manitoulin Island (Sanford and Mosher, 1978)	Ottawa Embayment				Quebec Basin (Sanford, 1993)	
	Ashgillian		Cincinnatian			Edenian			Maysvillian				Richmondian		(Barnes et al., 1981)	(Sanford, 1993)		This study
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmondian		Georgian Bay		Manitoulin Island (Sanford and Mosher, 1978)		Ottawa Embayment		Quebec Basin (Sanford, 1993)	
Ordovician	Caradocian		Ashgillian		Edenian		Maysvillian		Richmond									

of platform foundering appear to be linked to differences in the subsidence histories of the two basins.

Regional geological framework

The history of foundering and burial of the Late Ordovician carbonate platform in southern Ontario is related to increased subsidence linked to the Taconic continent-oceanic arc collision along proto-eastern North America (Hiscott 1984; Ettensohn 1991). From previous work in Quebec (Lavoie 1994), along the New York Promontory (Fisher 1977; Ettensohn 1991), and in western Newfoundland (Knight et al. 1991), an east-to-west diachronous collapse spans the Middle to Late Ordovician.

In eastern Ontario, the foreland basin platform is represented by the Ottawa Group. It is preserved within the Ottawa Embayment, which is surrounded today by Precambrian highlands and dissected by the Ottawa-Bonnechère Graben (Fig. 2-1). Platform stratigraphy defines a net upsection deepening from peritidal facies to open shelf or ramp facies (Sanford 1993; Salad Hersi and Dix 1999), the latter represented by the Verulam and Lindsay formations (Fig. 2-2). Within the uppermost Lindsay Formation, limestones become interbedded with brownish organic-rich claystone, and define the Eastview Member (EM in Fig. 2-2; Russell and Telford 1983; Williams 1991). Past work has provided contradictory interpretations concerning the age of this member: Barnes et al. (1981) assigned a Maysvillian age, and identified a hiatus beneath; Sanford (1993) refers to an Edenian age, and identified the upper contact to be unconformable. Russell and Telford (1983) and Williams (1991) recognized a gradational contact with the underlying limestone facies, and a sharp decrease in carbonate and organic carbon

content at the upper contact of the Eastview Member with the overlying basin-fill succession. This study confirms an Edenian age (see later in the text).

The Upper Ordovician platform of eastern Ontario extends to the west into southwest and central Ontario (Sanford 1993), where it underlies the eastern flank of the Michigan Basin as best exemplified by the erosional edge of the Lower Silurian (Fig. 2-1). The Simcoe Group defines an equivalent platform succession to that of eastern Ontario (Fig. 2-2). Similar petroliferous shale forms a discrete unit, the Collingwood Member (Russell and Telford 1983). In the Manitoulin region, the shale overlies platform limestone (Melchin et al. 1994), whereas east of the Silurian outcrop limit, along the southern shore of Georgian Bay near Craigeleith (Fig. 2-1), the petroliferous shale is interbedded with limestone (Lehmann et al. 1994, 1995), similar to that found in eastern Ontario. Regardless of the detailed stratigraphy, most workers accept that the petroliferous shale is part of the platform (Russell and Telford 1983; Melchin et al. 1994).

Across southern and central Ontario, basinal siliciclastics that overlie the Upper Ordovician platform define a depositional system clearly linked to basin fill of the Taconic foreland basin (Sanford 1993). Initial deep-water sediments (Billings and Blue Mountain formations; Figs. 2-2 and 2-3) are succeeded by shallower water deposits that culminated in accumulation of the prominent red-beds of the Queenston Formation (Fig. 2-2). Equivalent strata are mapped in central and southwestern Ontario, and the limit of Taconic derived sedimentation can be mapped through central Manitoulin Island (Sanford 1993).

Methods

Stratigraphy of the platform-to-basin succession is examined in two drill cores located in the Michigan and Ottawa basins: Russell-GSC #2, from Russell County, eastern Ontario, and GSC DDH2-Elizabeth, on Manitoulin Island (Fig. 2-1). Lithology of each section was mapped, and cores were examined along bedding plane fractures for graptolite fossils. Specimens collected by Kiernan (1999) from outcrop exposures of the Verulam Formation in the City of Ottawa are incorporated. For chemostratigraphic analysis, 52 shale samples were taken from the Russell core at approximately meter scale spacing through the platform-to-basin transition, and on either side of prominent lithological contacts within that interval (Fig. 2-3). For the Elizabeth core, 23 samples were taken.

Shale samples were rinsed with distilled water, dried, powdered and split. For clay mineral analysis, including illite crystallinity, the $< 2\mu\text{m}$ -size fraction was separated (see Moore and Reynolds 1997). X-ray diffractometry (Cu $K\alpha$ radiation) of oriented mounts used a Phillips PW1710 diffractometer (Carleton University) with operating conditions set at 40 kV and 25 Ma, and with a divergence-receiving-scatter slit arrangement of 1° -0.2 mm- 1° , respectively. A scan rate of $0.6^\circ/\text{min}$, and time constant (TC) of 2 follow the procedure of Kish (1990). With these same settings, chlorite (003)/illite (002) peak-ratios were calculated following the height-width method of Moore and Reynolds (1997), using the program Macdiff (Petschick © 1999, Geologisch-Paläontologisches Institut of the Universität Frankfurt, Germany). Selected samples were also treated with ethylene glycol and treated with HCl to help determine the presence of smectite and kaolinite clay groups (Moore and Reynolds 1997).

Figure 2-3. Stratigraphic column showing the general lithology and Upper Ordovician graptolite ranges and zones in drill core (Russell GSC #2) from Russell County, eastern Ontario. The Billings Formation is divided informally into lower (l) and upper (u) units. EM, Eastview Member; LM, lower member (Lindsay Formation). Core locality information: National Topographic System (NTS) map sheet no. 31 G/6; Universal Transverse Mercator (UTM) Zone 18, North American Datum (NAD) 1927 469400E, 5017600N.

Organic carbon percentages, as well as $\delta^{13}\text{C}_{\text{org.}}$, were determined at the University of Ottawa after treating the powdered samples with HCl for one hour, and then rinsing them with distilled water to remove inorganic carbon. Error for isotope values is approximately ± 0.01 ‰. Determination of trace element geochemistry was carried out at Geoscience Laboratories (Ontario Geological Survey, Sudbury, Ontario) using inductively coupled plasma–mass spectrometry (ICP-MS) and a total digestion method. For this study, analysis of Cr, Ni, $\text{La}_\text{N}/\text{Sm}_\text{N}$ and Eu, as well as the ratios V/Rb, U, Mo/Rb and Ba/Rb are reported. Clay mineral and geochemical data are presented in Appendix 1 to 14.

Results

Lithostratigraphy

Russell Core

The section (Fig. 2-3) begins in platformal limestones of the Verulam and Lindsay formations of the Ottawa Group (Fig. 2-2). The former contains interbedded micritic to coarse-grained fossiliferous limestone and calcareous dark gray shale. The latter possesses thin to thickly bedded (5-55 cm) nodular bioclastic packstone to wackestone. Upsection, this limestone becomes interbedded with thinly bedded (3 to 40 cm) petroliferous shale (Fig. 2-4), and defines the Eastview Member. In outcrop (Fig. 2-4) and core, the shale is a calcareous claystone, brownish gray in colour. Fossils include the trilobite *Pseudogygites latimarginatus* (Hall), indeterminate inarticulate brachiopods, orthocone fragments, and crinoidal ossicles. Minor phosphatic fossil fragments occur

Figure 2-4. Outcrop exposure on Aviation Parkway (Ottawa) showing rhythmic interbedding in lower Eastview Member (E) overlying (dashed line) platform limestone (L) of the lower Lindsay Formation. Outcrop locality information: NTS map sheet no. 31 G/5; UTM 449300E, 5032050N; UTM zone: 18, NAD 1983. Measuring stick (arrow) = 1.2 m long.

within the limestone interbeds. The total thickness of the Eastview Member is about 11 metres.

The lower unit of the overlying siliciclastic succession is the Billings Formation, a black to very dark gray claystone interlaminated with siltstone. In core, it is about 62 m thick. The Billings Formation contains two informal units. The lower 15 metres consist of black fissile claystone with very thin siltstone laminae that vary from a few grains thick to 1-2 mm. There are laminae that consist only of framboidal pyrite. Bioturbation is very rare, but graptolite fossils are common (see text section “Biostratigraphy”) and very well preserved. The overlying 47 metres of the Billings Formation consists of a dark gray claystone with abundant parallel- and cross- laminated siltstone and fine-grained sandstone beds that vary in thickness up to 3 cm (Fig. 2-3). Most of these beds are sharp based with gutter casts. The frequency of these beds increases gradually upsection, and the stratigraphic variation is recorded by the gamma ray record through the Russell core (see Fig. 2-6). Orthid brachiopods, the inarticulate brachiopod *Leptobolus insignis* Hall, and trilobites *Triarthrus eatoni* Hall and *Triarthrus spinosus* Billings, are present. So are cephalopod fragments, organic remains of noncalcareous algae, and graptolites (see below).

The overlying Carlsbad Formation is 187 m thick. It consists of dark- to light-gray, non-calcareous to calcareous shale interbedded with thin, greenish to greyish siltstone and minor fine-grained sandstone beds, 2 cm to 4 cm thick. Most of these beds are sharp based and display cross lamination and parallel lamination. The inarticulate brachiopod *Obolus* and articulate species *Dalmanella* sp. and *Platystrophia* sp. occur along with gastropod and pelecypod remains, fragments of branching bryozoans,

crinoidal ossicles, preserved fragments of noncalcareous algae, and graptolites. In the uppermost part of the formation, ooid and bioclastic grainstone beds bracket the boundary with the overlying Russell Formation (Fig. 2-3). This unit (Wilson, 1946) has been disputed by some, but appears to define a valuable transition unit separating the prominent red-bed Queenston Formation from the underlying Carlsbad Formation (Sharma and Dix, in press).

Elizabeth core

Within the platform-to-basin transition, the Collingwood Member is about 5 metres thick, bracketed by fossiliferous platform limestone of the Lindsay Formation and the dark gray shale facies of the basinal Blue Mountain Formation (Fig. 2-5). As noted for the Billings Formation of eastern Ontario, fine-grained sandstone and coarse siltstone facies become prominent higher up in the Blue Mountain Formation (about 10 m above the top of the section shown in Fig. 2-5).

In contrast to the Russell core, thin (3 cm) beds of phosphatic lithoclastic conglomerate occur at the base and top of the Collingwood Member (Fig. 2-5). In the lower bed, clasts are well rounded to subrounded, vary in size from 3 mm to 350 μm , and are siliceous phosphatized limestone that contains recognizable oncoids and peloids. Replacement of the calcite cement by chalcedony is relatively abundant in this bed. The conglomerate bed at the top of the formation consists of rounded to subrounded limestone clasts, 5 to 15 mm in size, of wackestone to packestone. The matrix consists of fine-grained quartz sand and fragments of phosphatized fossils (brachiopod, crinoid ossicles and bryozoans).

Figure 2-5. Stratigraphic column, general lithology and Upper Ordovician graptolite zones and ranges for drill core GSC DDH2-Elizabeth from Manitoulin Island. Abbreviations: CM - Collingwood Member of Lindsay Formation). Core locality information: NTS map sheet no. 41 H/13; UTM 423850 E, 5072200N; UTM zone: 17, NAD 1927.

Figure 2-6. Downhole changes in various properties in the Russell GSC #2 section.

Symbols are explained in Fig. 2-3. PDB, Peedee Belemnite; TOC, total organic carbon.

Biostratigraphy

Russell Core

Distribution of recovered graptolite species is shown in Fig. 2-3. *Amplexograptus praetypicalis* (Riva) and *Diplacanthograptus spiniferus* (Ruedemann) were reported by Kiernan (1999) from the upper 15 metres of the Verulam Formation in a downtown section from the City of Ottawa. To date, no graptolites have been recovered from within the Lindsay Formation. However, the following species appear abruptly at the base of the Billings Formation: *Geniculograptus typicalis posterus* (Ruedemann), *Geniculograptus pygmaeus* (Ruedemann), *Geniculograptus typicalis* (Hall), *Rectograptus amplexicaulis* (Hall) and *Orthograptus quadrimucronatus micracanthus* (Elles and Wood) (Fig. 2-3). Further upsection, there is a prominent disappearance of four species at the informal lower-upper member boundary within the Billings Formation (Fig. 2-3). This coincides with the first appearance of siltstone beds (Fig. 2-3).

With no graptolite fossils recovered from the Eastview Member (Fig. 2-3) its age is based on the age of the lower Billings Formation, which lies within the upper *pygmaeus* zone. Using zonations of Riva (1969), and distribution of zones with North American stages (Fig. 2-2), the lower Billings Formation appears to have a late Edenian to early Maysvillian age. Thus, the Eastview Member is likely Edenian in age. Present data cannot define whether or not the upper *spiniferus* and lower *pygmaeus* zones are missing (Fig. 2-3).

Elizabeth Core

The upper part of the Collingwood Member (Lindsay Formation) and lower Blue Mountain Formation have yielded the species *Orthograptus quadrimucronatus* (Hall), *Rectograptus amplexicaulis* (Hall), *Anticostia hudsoni* (Jackson) and “*Paraclimacograptus*” *manitoulinensis* (Caley) (Fig. 2-5). The Collingwood Member falls within the upper *pygmaeus* zone, and fits other studies that interpreted a Maysvillian age (Goldman and Bergström 1997). The number of fossil specimens is too low to illustrate assemblage variation with facies changes.

Mineralogy

Russell Core

Illite and chlorite are the principal clay minerals in the <2- μ m fraction of shale. There is a net increase in the ratio of chlorite (003) to illite (002) from 0.15 to 0.5 (Fig. 2-6). Values in the lowermost Billings Formation are similar to those near the top of the core section (Fig. 2-6). An increase in this ratio can be used to define increased mafic mineral content of sediment (Bjørlykke 1974; Andersen 1995). Data reveal a pronounced short-term increase across the platform-basin (Eastview-Billings) boundary, capping a slight increase through the Eastview Member (Fig. 2-6).

Elizabeth Core

Illite and chlorite are also the principal clay fractions in the < 2- μ m fraction. The chlorite (003)/illite (002) ratio increases up through the Collingwood Member from <0.1 to 0.6 (Fig. 2-7). A drop to about 0.4 occurs within the upper 1 metre, and values increase slightly through the lower Blue Mountain Formation (Fig. 2-7). There is no obvious lithologic change coincident with the drop in the ratio.

Chemostratigraphy

Several geochemical proxies help to define provenance and paleoceanographic variation across the platform-to-basin transition in both cores (Figs. 2-6, 2-7). On the basis of these proxies, several chemostratigraphic units are identified whose boundaries are defined by abrupt changes in prominent trends or intersample variation. For the Russell core, the inter-unit boundaries (R-1/2, R-2/3, respectively) coincide with the top of the Eastview Member and base of the upper unit of the Billings Formation (Figs. 2-6); for the Elizabeth core (E-1/2), the boundary occurs near the top of the Collingwood Member (Fig. 2-7).

Mafic/felsic content ratio

Changing abundance of mafic content in sediments can be calculated using the formula: $\sqrt[3]{(\text{Cr} \times \text{Ni} \times \text{Ti})/\text{Nb}}$ (Andersen 1995). This compares transition metals that commonly substitute for iron and magnesium in mafic igneous rocks to Nb that occurs in felsic sources (Krauskopf 1979; Garver et al. 1996).

Russell core: A prominent increase in this ratio (~ 14 to 18) occurs through R-1, within the platform succession. Its “peak” abundance (at ~20) occurs over the interval from 262 to 255 m within lower R-3, or the lowermost part of the upper unit of the Billings Formation. The ratio decreases upsection back to values similar to those of the lower Lindsay Formation (Fig. 2-6). This stratigraphic variation defines an initial increase in mafic content with the appearance of claystone in the Eastview Member, and

Figure 2-7. Downhole changes in various properties in the GSC DDH2-Elizabeth section.

Symbols are as in Fig. 2-5.

a peak abundance of mafic material with the appearance of siltstone laminae within the upper part of the Billings Formation (Fig. 2-6).

Elizabeth core: The mafic/felsic ratio shows elevated values (24-32) restricted to the Collingwood Member. Compared to the Russell Core, values through the rest of the core are of similar magnitude. There is little variation within the lower Blue Mountain Formation. (Fig. 2-7).

Cr, Ni, and Cr/Ni

These three proxies have been used to define ultramafic provenance for shale, wherein elevated Cr and Ni concentrations and Cr/Ni ratio (~1.6) suggest an ultramafic source for sediments (Garver et al. 1996).

Russell core: From the base of R-2 through lowermost R-3, Cr and Ni concentrations are similar (~80-90) and the profiles appear merged (Fig. 2-6). Cr concentrations gradually increase upsection above R-1 whereas nickel's profile mimics that of the mafic/felsic abundance (Fig. 2-6). The Cr/Ni ratio decreases markedly through the Lindsay Formation to the top of R-1, and is relatively invariant over the interval of merged Cr and Ni profiles. It then shows a slight increase over the rest of the section.

A crossplot of Ni and Cr concentrations (Fig. 2-8) shows that the claystone of the lower Billings Formation possesses greater variation in Ni over Cr when compared to shales of the platform succession (Eastview Member, Ottawa Group and older strata; Fig. 2-8).

Elizabeth core: Cr and Ni profile variation shows a general co-variance through the Blue Mountain Formation in contrast to a poor covariance within the Collingwood Member (Fig. 2-7). As noted for the Billings Formation in the Russell core, Cr

concentrations become higher than Ni values within the equivalent Blue Mountain Formation (Figs. 2-7). The Collingwood Member also shows greater variation in Ni versus Cr concentrations as found for the Billings Formation (Fig. 2-8).

Eu/Eu and La_N/Sm_N*

With progressive crustal differentiation, a pronounced negative Eu anomaly is preserved within sediments (Taylor and McLennan 1985). This anomaly is expressed by $Eu/Eu^* = Eu_N / \{(Sm_N \times Gd_N)^{0.5}\}$, where Eu* is the expected Eu value for a smooth chondrite-normalized rare-earth element (REE) pattern without any Eu anomaly, calculated as $\{(Sm_N \times Gd_N)^{0.5}\}$. There is also light REE (LREE) enrichment as defined by the normalized ratio La_N/Sm_N, where a subscript 'N' denotes chondrite normalized values (Taylor and McLennan 1985; McLennan 1989; Garver and Scott 1995). From these proxies, two sediment sources form geochemical end members: (1) those derived from weathering of the North American craton will provide a negative Eu anomaly and LREE enrichment; (2) those from an oceanic arc will display a much diminished Eu anomaly and lesser LREE enrichment (McLennan et al. 1990; Garver and Scott 1995).

Russell core: The La_N/Sm_N ratio decreases to the base of R-2 and remains relatively invariant throughout R-2. Within R-3, greater intersample variation is present, but no net directional change occurs. Thus, a decrease in LREE enrichment occurs with the appearance of the Eastview claystone. There is an overall lessening of the negative Eu anomaly upsection, and there is a prominent peak within the upper part of R-1, within the Eastview Member, with a value (0.76) similar to sediment found in the uppermost Billings Formation (Fig. 2-6). Together these data suggest a net increase in arc-derived sediment, with short-term influx preserved within the uppermost Eastview Member.

Figure 2-8. Variation in Cr and Ni of claystone from various lithostratigraphic units from the Russell GSC #2 and GSC DDH2-Elizabeth (Manitoulin Island) cores. Vertical and horizontal lines correspond to the average values of Ni (60 ppm) and Cr (105 ppm) defined for the North America Shale Composite (after Gromet et al. 1984).

- Blue Mountain Formation (BM)
- Collingwood Member (CM)
- + Queenston/Carlsbad Formation
- ◇ upper unit Billings Formation
- lower unit Billings Formation (IB)
- × drill core, Eastview Member (EV)
- outcrop, Eastview Member (EV)
- △ shale within Ottawa and Beekmantown groups (OG)

Elizabeth core: The La_N/Sm_N ratio decreases within the Collingwood Member (or E-1; Fig. 2-7), and remains relatively constant (~ 3.5) over the rest of the core section (Fig. 2-7). Absolute values are similar in magnitude compared with those found in the Russell core.

V/Rb, Mo/Rb, and Ua:

Organic rich shales can form either as a result of high biological productivity or from deposition in an anoxic basin (Brumsack 1986). Sediments underlying areas of high biological productivity do not tend to show enrichment of trace metals (Brumsack 1986). In contrast, sediments deposited within ancient and modern anoxic basins are often found to be enriched in several metals, including V and Mo (see Table 2-1; Brumsack 1986; Brumsack 1991). Elemental enrichment is largely linked to uptake within or adsorption onto biological material, with preservation of this material from oxidation (Lewan and Maynard 1982; Brumsack 1989; Breit and Wanty 1991).

Enrichment of authigenic uranium (Ua) also occurs within shales deposited under anoxic conditions (Wignall 1994), and can be calculated by the formula $\text{Ua} = \text{U} - \text{Th}/3$. This author has defined paleoredox conditions using Ua concentrations: < 2 = oxic conditions; $2-10$ = dysoxic conditions; $10-15$ = anoxic conditions. Values higher than this upper limit define euxinic conditions.

Russell core: The ratios V/Rb, Ua and Mo/Rb, with Rb used to normalize values, increase upsection to the top of R-2. There is also a good ($R^2=0.79$; R =regression coefficient) correlation between TOC % and Ua that suggests that a major source of diagenetic uranium is associated with organic matter. A Ua value of 6 in the upper metres

Table 2-1. Average concentrations of selected elements in R-1 through R-3, Russell GSC #2 core, and outcrop of the Eastview Member (EM) (this study) compared to: Upper Ordovician black shale (Lotbinière and Neuville formations), Quebec (Garver et al. 1996); Toarcian black shale (TBS), northwest Germany, and Recent diatomaceous sediments, Gulf of California (GC) (Brumsack 1986); and Quaternary Black Sea (BS) sediment (Brumsack 1989). NA – no data.

of R-2 suggests that there was an overall decrease in bottom-water oxygen content that created dysoxic conditions during the platform-to-basin transition and throughout deposition of the lower unit of the Billings Formation. Above the R-2/3 boundary, U_a rapidly decreases to $\ll 1$ by 235 m. This suggests that ventilation of the bottom-water environment occurred, and this coincides with the appearance of siltstone beds at the R-2/3 boundary.

Elizabeth core: The ratios V/Rb , U_a and Mo/Rb also increase upsection into the upper part (~3 m) of the Collingwood Member. Again, this suggests progressive decrease of bottom-water oxygen content. With a value of U_a being 8+, anoxic conditions were possibly present during accumulation of sediment now preserved between 196 and 201 m (Fig.2-7). Above 196 m, however, U_a decreases rapidly into the lower part of the Blue Mountain Formation suggesting ventilation of the bottom-water environment. There is no significant change in these proxies further upsection.

Ba/Rb

The ratio of barium (Ba) to rubidium (Rb) has been used to indicate high surface-water productivity (Bellanca et al. 1999). Ba occurs mainly as barite in sediments, and shows strong enrichment below equatorial zones of high productivity (Bishop 1988). As noted by Schmitz (1987), Ba-enriched sediments in the deep sea closely coincide with regions of upwelling and enhanced biological productivity, although no consensus exists as to a causal connection. Under these conditions, barite forms in microenvironments containing decaying organic matter and remains of siliceous plankton (Bishop 1988).

Russell core: Above R-1, there is an overall upsection reduction in the ratio Ba/Rb (Fig. 2-6). Within R-2, there is little sympathetic variation of Ba/Rb with V/Rb, Ua, Mo/Rb and TOC% (Fig. 2-6). This may indicate a change in factors that influenced organic matter production and/or preservation. Large fluctuations in this ratio (< 6) and values of TOC % and Ua occur within the Eastview Member. Compared to the other formations, the Eastview Member is chemostratigraphically anomalous, and illustrates likely strong variation in paleoproductivity, oxygen content of bottom waters, and organic matter preservation.

Elizabeth core: There is a dramatic increase upsection through the lower Collingwood Member (E-1), then no overall directional change further upsection. Once shale deposition was established, the geochemical proxy suggests that there was a relatively stable oceanographic framework. The magnitude of ratio values is no different from that found in the Russell core.

TOC% and $\delta^{13}C_{org}$.

Total organic carbon (TOC) content and $\delta^{13}C_{org}$ are available for the Russell core. A prominent peak in TOC% (6 %) occurs in the uppermost Eastview Member. Upsection, there is a net decrease to values of < 1 %. $\delta^{13}C_{org}$ values become more positive through the platform facies, then show no directional change further upsection, varying about -30 ‰ (Fig. 2-6). Such values fall within a broad range that encompasses terrestrial sources and marine sources that have suffered diagenetic alteration (Anderson and Arthur 1983). Snowdon (1984) reports TOC% for the Collingwood Member from Manitoulin Island of about 2 to 8 %, which is comparable to that of Eastview Member.

Discussion

Timing and Diachroneity of Platform Foundering

Graptolite biostratigraphy is still somewhat inconclusive regarding the age of the platform-basin contact (Eastview-Billings) in eastern Ontario. It is possibly slightly older than the equivalent Collingwood-Blue Mountain contact along the eastern flank of the Michigan Basin. This slight westward younging (that is Edenian vs. Maysvillian) fits within, and extends, the known east-to-west (Newfoundland to the St. Lawrence Lowlands) diachroneity of platform foundering across eastern Canada (Knight et al. 1991; Lavoie 1994). However, it is possible that the two contacts are of similar age (Figs. 2-3 and 2-5).

As graptolites are yet to be recovered from the Lindsay Formation, including the Eastview Member, it remains indeterminate if a disconformity separates the Lindsay and Billings formations in eastern Ontario. A break is more obvious with the conglomerate at the top of the Collingwood Member in the Elizabeth core. As there are similar pronounced changes in the geochemical proxies across the Eastview-Billings contact (Fig. 2-6) as occur across the Collingwood-Blue Mountain contact (Figs. 2-6, 2-7), that a lacuna likely exists in eastern Ontario. The maximum amount of time that could be missing, on the basis of the Russell core stratigraphy, is represented by the absence of the upper *spiniferus* zone and most of the *pygmaeus* zone (Fig. 2-3).

Basin Development

Previous workers have stated that the petroliferous claystone of the Eastview Member of the Lindsay Formation in eastern Ontario is part of the platformal

architecture. It's interbedding with normal-marine limestones typical of the lower Lindsay Formation confirm this (Fig. 2-4).

However, there is a change in sedimentary provenance of clay during Eastview deposition that heralds events leading to subsequent basin fill. For the most part, the Ni and Cr trend within this interval is similar to that associated with shales interbedded within the underlying Ordovician platform succession (Fig. 2-8). But there is a net rise in the mafic/felsic ratio and decrease in LREE enrichment beginning within the Eastview Member (Fig. 2-6), that also reveals influx of a new source. Short-term variations in values of Eu/Eu^* , Cr/Ni , and $\text{La}_\text{N}/\text{Sm}_\text{N}$ might suggest that the upper part of this unit contains interfingering of beds containing different amounts of Taconic arc- and shield-derived sediment. Importantly, a similar rise in mafic/felsic ratio values and an upsection decrease in LREE enrichment are preserved within the section through the Collingwood Member (Fig. 2-7). Thus, while the petroliferous shale is viewed as being part of the platform, there was influx of Taconic-derived sediment.

In eastern Ontario, the Billings Formation signals the complete transformation of platform to deep-water basin. Its claystone lithology, a unique Ni-Cr field (Fig. 2-8) relative to younger and older shales, and elevated mafic/felsic ratios (Fig. 2-5) indicate a maximum supply of very-fine grained accretionary wedge (arc) derived mafic detritus. The merged concentration profiles of Ni and Cr (Fig. 2-6) likely arise from the equal potential of these cations to be adsorbed onto clay particles (Andersen 1995). The rise in value of U_a to the top of this unit defines deposition occurring under increasingly restricted dysoxic conditions (Wignall 1994), and the informal lower unit of the Billings Formation likely represents a hemipelagic facies that buried the Eastview Member. There

does not appear to be an equivalent facies in the Elizabeth core section or in the Manitoulin region in general (Melchin et al. 1994). Reduction in oxygen content was restricted to the bottom water mass because graptolite diversity during this period was relatively high compared to older and younger strata (Fig. 2-3). Elevated Mo, V, Co and Ni observed in this unit are comparable to values present in other ancient and modern dark and black shales that accumulated in dysoxic to anoxic basins (see Table 2-1; Brumsack 1986).

From the Elizabeth core, peak dysoxic or anoxic conditions occur within the uppermost Collingwood Member, not at the boundary with the Blue Mountain Formation. A short-term drop in Ua values also occurs within the upper few meters of the Eastview Member as well, but then increased Ua values in overlying sediment define this to be short-lived.

In eastern Ontario, the lithological uniformity of the lower Billings Formation was terminated by the appearance of siltstone beds that distinguish the upper unit of the formation (Fig. 2-6). These beds are likely distal turbidites (Kerr and Eyles 1991), and record a more diverse set of sediment types. There are two different sources of sediment within the upper Billings Formation: (1) a hemipelagic background clay-size sediment; and (2) quartzofeldspathic-bearing resedimented deposits. The chlorite/illite ratio, indicating an arc-derived source (Andersen 1995; Björlykke 1974), attains its maximum value in the lowermost upper Billings unit (Fig. 2-6). Above this interval, the mafic/felsic ratio decreases slightly upsection suggesting some felsic input. Indeed, the upsection divergence of Ni and Cr concentrations (Fig. 2-6) may reflect different source reservoirs for clay- and silt- to sand-size sediment. As the Cr/Ni ratio increases upsection (Fig. 2-6),

a greater proportion of arc-derived (Cr-bearing) sediment was confined to either the clay or coarser-size fractions. Influx of new sediment from varied sources may signify a re-organization of the basin geometry linked to tectonic factors.

Paleoceanographic conditions within the basin would also have been influenced by tectonic events. As shown by the very low U_a values in the upper Billings and Carlsbad formations, ventilation of bottom waters was maintained. However, the reduction in graptolite biodiversity coincident with the appearance of resedimented deposits (Fig. 2-3) suggests substantial oceanographic changes that affected the entire water column.

Character of platform demise

Paleoproductivity as represented in the Eastview Member, and notably the phosphatic beds at the base and top of the Collingwood Member, reveal attendant significant differences in the paleoceanographic framework during the waning stages of platform development. By itself, the Collingwood Member has disparate interpretations of depositional origin; from restricted shelf to deep-water platform facies (Churcher et al. 1991; Melchin et al. 1994). Differences in the Collingwood and Eastview stratigraphies reflect deposition along different parts of two subsiding ramps.

First, an open platform geometry would not restrict influx of extrabasinal sediment from a seaward source. This is borne out by sediment provenance indicators (Figs. 2-4, 2-6, 2-7) that record increasing admixture of a more mafic-bearing siliciclastic source during accumulation of the Eastview/Collingwood shales.

Second, the two cores preserve a contrast in the stability of the paleoceanographic framework during the transition between platform and deep foreland basin. Compare the

dramatic intersample variation of paleoproductivity proxies (Ba/Rb, TOC %) within the Eastview shales (Fig. 2-6) to the relatively sustained Ba/Rb values within the middle to upper parts of the Collingwood Member (Fig. 2-7). The latter core preserves a more seaward depositional site as indicated by the Collingwood Member representing a discrete lithologic unit on top of platform limestones. Moving east out of the Michigan Basin, and as also found in eastern Ontario, the interbedding of platform limestone with claystone in the Craigleith area (Fig. 2-1; Lehmann et al. 1995) records changing depositional conditions as might be affected by variation in water mass type, sea level, oceanographic processes, supply of siliciclastic sediment, and paleoproductivity. The geologic record in the Elizabeth core may indicate that greater subsidence rapidly shifted deposition to a deeper-water, distal ramp facies, where effect of the above processes were dampened. In contrast, for the Russell core (and for the Craigleith section by inference), a lesser increase in subsidence maintained a shallower-water ramp environment, but still sensitive to the above processes.

Conclusions

In eastern Ontario, the Russell GSC #2 core preserves a stratigraphic section that records foundering of the Late Ordovician foreland carbonate platform (Lindsay Formation) during the Edenian. Comparison with an equivalent core section from Manitoulin Island, along a similar craton-interior position, reveals platform demise to have been of Maysvillian age thereby defining an east-to-west diachroneity of platform foundering.

The appearance of a petroliferous claystone interbedded with limestone in the uppermost Lindsay Formation in eastern Ontario defines the Eastview Member, and denotes the incipient stages of sediment transport from a distal volcanic arc, episodic increases in paleoproductivity, and high-order lateral shifts in facies boundary along the seaward limit of carbonate deposition. Geochemical proxies (V/Rb, Mo/Rb, Ua, Cr and Ni) suggest that siliciclastic interbeds coincide with incursions of dysoxic water. In contrast, in the Manitoulin Island region, rhythmic interbedding with limestone is not present in the equivalent Collingwood Member, and geochemical proxies identify a more stable paleoceanographic framework. For both stratigraphic units, however, geochemical proxies reveal an increase from oxic to dysoxic conditions (to an anoxic condition for the Collingwood) through time.

In eastern Ontario, the initial deep-water basin sediments (lower Billings Formation) represent a very uniform hemipelagic (dark grey to black claystone) facies coincident with maximum dysoxic bottom waters. Graptolite diversity was moderate during this period reflecting well-oxygenated surface and near surface waters. Re-oxygenation of bottom waters, and loss of graptolite diversity occurred coincident with the appearance of distal resedimented deposits. This heralds a fundamental change in the paleoceanography of the entire water column, marking an overall increased supply of sediment from the Taconic highlands. An equivalent hemipelagic facies appears to be absent from the Manitoulin region, but the Blue Mountain Formation marks a similar appearance of resedimented deposits, as does the upper Billings Formation.

Stratigraphic details of the waning stages of the Late Ordovician platform suggest interbasinal differences. The Manitoulin site preserves a more rapid shift to distal ramp

facies; the eastern Ontario site preserves evidence of lesser subsidence, creating a more dynamic interaction of platform and oceanic water masses in a shallower- but open-margin position.

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Chapter III

Late Ordovician volcanism in a deep-shale basin (Appalachian foreland), eastern Ontario: tectonic trigger for Taconic flysch, faunal extinctions, and paleoceanographic change

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Abstract

A 6-cm thick K-bentonite in a Late Ordovician foreland deep-shale basin, eastern Ontario, defines an airfall or subsea volcanic eruptive from a Ba-rich, magmatic source dated (Ar-Ar) at about 445 Ma. Volcanic beds are well known from the Appalachian foreland basin, but this event separates anoxic deep-water conditions following foundering of the Trentonian carbonate platform from deep-sea ventilation triggered by Taconic flysch, and coincides with intrabasinal extinction of several graptolite species. Volcanic geochemistry identifies continental crustal incorporation, and a more alkaline magmatic source than older K-bentonites in the foreland platform. The volcanic event may reflect a change in subduction dynamics within an evolving Taconic arc, or is intrabasinal arising from crustal fracturing linked to thrust-load tectonism.

Introduction

Petrology and isotopically (Ar-Ar) determined ages of K-bentonite beds in the Middle to Upper Ordovician carbonate platform succession of eastern North America (Fig. 3-1) have proven to be invaluable for detailed basin analysis of the Taconic foreland basin, and for defining the sources of volcanism (e.g. Kolata et al., 1996; Min et al., 2001). Such detail is not available for ash beds in the deep-shale basins established following collapse of the carbonate platform, yet this archive exists (Baird and Brett, 2002). Detailed petrology and geochemistry of a thin (6-cm) K-bentonite (referred herein as the Russell Bed), is presented. The bed is newly discovered from a deep shale basin in eastern Ontario (Fig. 3-1), coincides with major sedimentary and paleoceanographic events, illustrating new aspects of the Taconic arc's development and basin history.

Stratigraphic framework

Foundering of the Middle to Late Ordovician foreland carbonate platform (e.g., Trenton Group) along the length of the Appalachian orogen to formation of deep-water shale basins (Fig. 3-1; Diecchio, 1991). In eastern Ontario, this history is recorded in the Lindsay to Billings Formation transition (Fig. 3-2; Sanford, 1993). The Billings Formation contains a lower clayshale, deposited in dysoxic conditions, succeeded by interbedded clayshale, siltstone, and fine-grained sandstone that represent the onset of Taconic flysch sedimentation (Fig. 3-2; Sharma et al., 2003). The K-bentonte, herein designated Russell Bed was found in core, the GSC Russell^{#2} well (Fig. 3-1), and occurs at the boundary of the above two units, about 12 metres above the highest carbonate unit, within the *Geniculograptus pygmaeus* graptolite biozone (Sharma et al., 2003).

Figure 3-1. Late Ordovician paleogeography of eastern North America (modified after Condie and Sloan, 1998). Dashed lines (wide and closely spaced) show the northern limit of the Taconic foreland basin (Hiscott et al., 1986), and southern margin of North American continent, respectively. UTM coordinates for Loc. A: 469400mE, 5017600mN, zone 18, NAD 1927. Sites in which possible stratigraphically equivalent deposits occur: B, Verchers well, Quebec, and C, House well, New York (both from Bergström and Mitchell, 1994); D, Illinois Power No. 2 Morell well, Illinois (Kolata et al., 1996). Alkaline intrusives (Cortlandt-Beemerville dikes; Ratcliff, 1981) of similar age as the Russell Bed occur at Loc. E.

Figure 3-2. Lithology and graptolite biostratigraphy for Loc. A drill core (A1) shown relative to general carbonate-shale division of the foreland succession. Gamma-ray logs for Loc. A2, B, C, D are shown. Well A2 (UTM: 468295 mE, 5012899 mN) is adjacent to Loc. A1. The well log is shown in API units. Scale for other localities are not available. Lithology patterns: white (interbedded shale and silt/sandstone), and rest as in Fig. 3-1. Abbreviations: Fm-formation; Mb- member.

Methods

Only half the core is preserved, and is 4 cm in width. Gamma-ray well logs offer tentative regional correlation (Fig. 3-2). Constituent abundance and type were estimated by point counting (n=300) thin sections from the base, middle and upper parts of the Russell Bed, and whole rock samples were gently disaggregated in water to release framework grains. These were examined by scanning electron microscopy (SEM). X-ray (CuK α) diffractometry (Carleton University) was used to analyze bulk composition (unoriented powder) and clay mineralogy (oriented mount with/without glycol solvation) following Moore and Reynolds (1997). A CAMEBAX microprobe (Carleton University), with operating conditions set at 17 kV, 10-20s counting time, 100 ppm detection limit, and 1-3% relative error, provided elemental spot analysis (Table 3-1). Elemental weight percentages were calculated using Cameca's PAP matrix programme. The MINPET program calculated biotite mineral formulae. Whole rock geochemistry (major and selected trace elements) was determined by x-ray fluorescence and inductively coupled plasma mass spectrometry at the Ontario Geological Survey laboratories (Sudbury). Laser Ar-Ar analysis of hand picked phlogopite crystals was carried out at the Geological Survey of Canada (Ottawa). Geochemical data, detailed methodology of Ar-Ar analysis and Ar-Ar data are given in Appendices 15 and 20.

The Russell Bed

Occurrence and Distribution

Very little of the foreland shale succession is exposed or preserved in eastern Ontario. In core, the Russell Bed is dark grey, and differs little macroscopically from surrounding

Table 3-1. Geochemistry of the Russell bed, Ordovician K-bentonites and volcanic fragments. Numbers in parenthesis indicate standard errors.

	Whole rock				Micas			Volcanic glass			Trace element (ppm)			
	A* (n=1)	B (n=4)	C (n=17)	D n=126	A† (n=13)	E (n=7)	F (n=8)	A (n=3)	G (n=20)	H (n=1)	A (n=1)			
SiO ₂	40.72 49.05	62.50 [0.73]	58.74 [0.67]	N.A. §	36.99 [0.07]	35.54 [0.26]	36.06 [0.32]	49.85 [0.42]	46.48 [0.04]	50.90	La	6.62	Nb	10.60
TiO ₂	0.90 1.00	0.78 [0.02]	0.40 [0.05]	0.40 [0.02]	5.47 [0.06]	4.30 [0.14]	4.75 [0.1]	0.06 [0.04]	4.51 [0.02]	0.29	Ce	14.22	Y	10.27
Al ₂ O ₃	27.56 29.76	16.38 [0.43]	22.52 [0.56]	N.A.	14.17 [0.1]	14.57 [0.44]	13.48 [0.1]	33.69 [0.45]	12.58 [0.03]	24.47	Pr	1.60	Zr	318.27
FeO	21.3# 8.40#	6.55# [0.22]	1.65# [0.15]	2.08# [0.11]	12.33 [0.2]	21.23 [0.7]	19.16 [0.72]	2.28 [0.78]	14.55 [0.04]	0.62	Nd	6.08	Pb	38.80
MnO	0.03 0.03	0.07 [0.00]	0.01 [0.00]	N.A.	0.18 [0.02]	0.14 [0.02]	0.18 [0.02]	0.01 [0.01]	0.20 [0.02]	0.02	Sm	1.11	U	10.00
MgO	2.84 2.84	2.82 [0.12]	4.12 [0.09]	N.A.	15.84 [0.12]	9.86 [0.60]	11.51 [0.42]	1.95 [0.3]	4.98 [0.07]	3.65	Eu	0.30	Th	9.05
CaO	0.28 0.28	2.20 [0.24]	2.90 [0.75]	N.A.	0.01 [0.00]	0.06 [0.01]	0.04 [0.01]	0.08 [0.05]	9.62 [0.19]	0.50	Gd	1.04		
Na ₂ O	0.55 0.55	1.13 [0.07]	0.65 [0.07]	0.05 [0.00]	0.61 [0.02]	0.49 [0.03]	0.37 [0.01]	0.16 [0.02]	3.03 [0.06]	1.07	Tb	0.17		
K ₂ O	6.13 6.65	3.89 [0.18]	7.67 [0.19]	9.39 [0.21]	8.26 [0.05]	8.89 [0.07]	8.87 [0.1]	7.68 [0.89]	0.74 [0.04]	7.26	Dy	1.38		
BaO	N.A. N.A.	N.A.	N.A.	N.A.	1.64 [0.06]	0.41 [0.09]	0.45 [0.07]	0.14 [0.13]	N.A.	N.A.	Ho	0.35		
P ₂ O ₅	0.15 0.21	0.19 [0.02]	0.08 [0.01]	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	Er	1.07		
Cl	N.A. N.A.	N.A.	N.A.	N.A.	0.03 [0.00]	0.11 [0.01]	0.14 [0.03]	0.19 [0.18]	N.A.	N.A.	Tm	0.19		
F	N.A. N.A.	N.A.	N.A.	N.A.	0.96 [0.02]	0.76 [0.07]	0.59 [0.06]	0.32 [0.21]	N.A.	N.A.	Yb	1.26		
Total	100.4	96.52	100.91	N.A.	96.50	96.38	95.61	96.41	96.70	99.56	Lu	0.20		

* A=Russell Bed (two separate samples for whole rock); B= Billings shale respectively (this study); C, D=Ordovician K-bentonites Trevail (1990) and Kolata et al. (1986); E, F=Millbrig and Deicke, respectively (Min et al. 2001); G=Basaltic Vedde ash shards, Late Quaternary (Davies et al., 2001); H=I/S altered from Ordovician volcanic glass (Huff and Türkmenoglu, 1981).

† A=Phlogopite; E, F=Biotite.

§ N.A.= not available; # Fe₂O₃

shale except for conspicuous large (<500 micrometers) euhedral phlogopite crystals. Clark and Stevenson (1960) reported similar micas from shale immediately above the highest carbonate unit near Montreal, < 200 km to the east of the Russell well. Well logs from sites within ~5 km of the well illustrate that the bed can have a relatively strong gamma ray deflection (Fig. 3-2). Similar deflections at possibly equivalent stratigraphic positions occur in cores at sites in Quebec, New York and Illinois (Fig. 3-2).

Fabric, Texture, and Constituents

The Russell Bed appears massive in core. In thin section, there is a fining-upward succession of phenocrysts in the lower few millimeters of the bed; there are infolded laminae that may identify soft-sediment deformation; and, there is an increased abundance of siliciclastic detritus in the uppermost 5 mm of the bed that defines a gradational boundary with shale that also contains reworked constituents of the bed.

About 45% of the Russell Bed is a clay matrix. Remaining grains comprise of phenocrysts (90 %), clay spherules (7 %), and rounded mudrock lithic fragments (3 %) (Fig. 3-3A). Of the phenocrysts, euhedral phlogopite and fluoroapatite represent <62 and <11 %, respectively, ranging in size from 100-500 micrometres (Figs. 3-3B). Fluorapatite occurs as inclusions in some phlogopite crystals, and some phlogopite crystals display a thin (2 to 4 micrometres) rim of clay similar in texture to, but disconformably demarcated from, the clay matrix (Fig. 3-3A). Accessory crystals include untwinned albite (<8 %), magnetite (<4%) and zircon (trace), along with replacement pyrite (<12%) and chalcopyrite (trace). Clay spherules (50-150 micrometres in size) are spherical, teardrop, and elongate in shape. They possess smooth to pitted surfaces (Figs. 3-3A, C; 3-4), and are pale yellow, orange and brown in colour (plain light).

Figure 3-3. Photomicrographs of volcanic ash. (A) Pseudo-hexagonal phlogopite (Ph), clay spherules (Sp), mudrock clast (Lf), albite (Ab) replaced by pyrite (Py), and clay rim (Cr) encasing phlogopite phenocryst. Thin section (plain light) photomicrograph. (B) Phlogopite (Ph), apatite (Ap) phenocrysts in matrix of I/S. Thin section (plain light) photomicrograph. (C) Teardrop-shaped spherule interpreted as devitrified *Pelee's tear*. Secondary electron image.

Figure 3-4. Volcanic glass spherules in different shapes, now altered to clay. Secondary electron image.

Geochemistry and Mineralogy

Whole rock geochemistry of the Russell Bed versus enveloping shale reveals elevated K_2O , Al_2O_3 , and FeO %, and lower SiO_2 , CaO , and Na_2O % (Table 3-1). Elevated FeO and lower SiO_2 values in one sample are likely due to replacement sulphides. Phlogopite contains an average BaO content of 1.64 % (Table 3-1). The bed's clay matrix is composed of mixed illite and smectite (I/S), the latter with an R3 (ISII) ordering, with > 90% illite. Spherules have similar clay and K_2O % compositions (Table 3-1).

Ar-Ar isotope analysis

Phlogopite crystals were separated from samples near the bottom (RB) and top (RT) of the unit. They were deep orange (plane light) with dark rims and discolouration bands that SEM imaging confirmed was interlayer chlorite alteration. For sample RB, steeply rising apparent ages with increasing laser power (Fig. 3-5A) suggests a thermal overprint. The irregularity of maximum ages clustered between 420 and 440 Ma (aliquots A through E) suggests a likely minimum age. For sample RT, a consistent near-plateau in the 440-445 Ma range (Fig. 3-5B) offers a better reproducible age.

Discussion

Age of the Russell Bed

The texture, mineralogy and K_2O content of the Russell Bed reflect accumulation of a fine-grained (ash) pyroclastic deposit – now a K-bentonite within a deep-water basin. The top of the Russell Bed was reworked by currents. With burial, diagenetic alteration is denoted by the presence of illite and smectite, chlorite-altered phlogopite, and diagenetic

Figure 3-5. Argon isotopic spectra of gas release plots from separate (A-E) aliquots of phlogopite crystals represented by sample RB (A) and RT (B).

sulphides. This alteration is the result of burial and multistage, post-Ordovician, regional to local hydrothermal activity in the basin (Dix and Robinson, 2003).

Fluorapatite and phlogopite phenocrysts identify coeval growth in a volcanic system prior to eruption. Clay-rimmed phlogopite crystals represent either ejecta enveloped by a thin layer of magma or rapid *in situ* reworking of the ash deposit (e.g., downslope movement) as suggested by possible soft-sediment deformation. The rare lithic fragments represent either xenoliths or reworked mudrock.

Clay spherules and matrix are likely to be altered devitrified glass. The spherules are of similar shape to, but smaller than, *Pelee's tears* (e.g. Hieken, 1972), or other glass droplets associated with volcanic eruptions, notably *fire fountains* (Figs. 3-3; 3-4). These form from rapidly cooled droplets of magma that take on dynamic shape during transport. Such spherules have not been documented previously from Ordovician K-bentonites in eastern North America, but altered glass shards occur in the Millbrig (448 Ma) deposit (Haynes, 1992). Altered volcanic glass in an Ordovician K-bentonite along the Cincinnati Arch (Huff and Türkmenoglu, 1981) and clay spherules in the Russell Bed have similar K₂O (~7 %) and SiO₂ (~50 %) values (Table 3-1). As shown by the contrast in K₂O% of the Russell Bed and enveloping shales, or interpreted glass in Ordovician K-bentonites versus Quaternary basaltic glass (Table 3-1), elevated K₂O% is likely due to fixation of potassium in newly formed clay during conversion of smectite (the initial devitrification product of glass) to illite, eventually producing I/S (Hower et al., 1976). The presence of R3 I/S with <10 % smectite suggests a final stage of smectite to illite diagenesis involving dissolution of I/S and crystallization of illite (Kolata et al, 1996). This is in keeping with regional burial maturation indices (Dix and Robinson, 2003).

Whole rock geochemical differences among the Russell Bed and the well known Deicke (450 Ma) and Millbrig (448 Ma) K-bentonites (Table 3-1) of the platform succession in eastern USA reflect differences in phenocryst mineralogy. In the Deicke deposit, plagioclase (<15%) is the dominant phenocryst, whereas the Millbrig contains plagioclase (<15%), quartz (<45%) and biotite (<50%) (Haynes, 1994). With the predominance of phlogopite in the Russell Bed, there is a net increase in sheet silicate framework grains with a younger age.

Magmatic source for Russell Bed volcanism

The BaO and TiO₂ contents of phlogopite are elevated when compared to most igneous rocks (Speer, 1984), apart from various mantle-or deep-crustal derived potassium-rich sources (Bachinski and Simpson, 1984). Using the discrimination diagrams of White (1989), Kolata et al. (1996), and Winchester and Floyd (1977), that use combinations of whole rock Pb, Ce, Nb, U, Th, and La (Table 3-1), and the ratios Nb/Y and Zr/TiO₂, the Russell Bed plots within the andesitic to trachyandesitic fields, with a noted incorporation of continental crust and/or oceanic sediment (Fig. 3-6). The presence of paleo-glass spherules supports eruption of a low-viscosity, fluid-rich magma (Heiken, 1972). Thus, the Russell Bed represents an ash derived from a silica-poor, mildly alkalic source (Winchester and Floyd, 1977; Nusbaum et al., 1988).

Tectonic Significance

The illustrated regional gamma-ray correlation (Fig. 3-2) identifies a subaerial, plinian-scale eruption. On the basis of phenocryst size, a minimum transport distance is 250 to 750 km (Fisher and Schimmincke, 1984), and, as with older Ordovician K-

Figure 3-6. Geochemistry of the Russell Bed and older K-bentonites from the Russell GSC#2 core. (A) Trace element ratios for the Russell Bed and older K-bentonites from the Russell GSC#2 core. (B) Trace element and major oxide ratios for the Russell Bed and older K-bentonites from the Russell GSC#2. Both diagrams are after Winchester and Floyd (1977).

● K-bentonites within carbonate platform (upper Verulam Formation)

■ Russell Bed at the boundary between deep-shale basin and Taconic derived flysch

➔ oldest to youngest

A andesite

A,B andesite, basalt

A-B alkali-basalt

S-A-B sub alkaline basalt

B,N basanite, nephelinite

P pantellerite

Ph phonolite

R,D rhyodacite, dacite

Rh rhyolite

T trachyte

Ta trachyandesite

bentonites, an Appalachian source is plausible (Kolata et al. 1996). However, stratospheric circulation could incorporate sources further afield (Delano et al., 1990).

The Russell Bed might provide an important age control for the latest Ordovician given that it lies near the Edenian-Maysvillian stage boundary. The age of the *G. pygmaeus* graptolite zone, within which the Russell bed occurs, has been defined to be from 451 to 452 Ma (Webby et al., 2004). Thus, the maximum possible age of Russell Bed deposition (~452 Ma) obtained from the phlogopite Ar-Ar isotopic data overlaps with the time. The error associated with the age estimate likely arises from subsequent thermal overprinting by hydrothermal fluids (Dix and Robinson, 2003).

It is interesting to note that the oldest bed of a series of metabentonites within the latest Ordovician to Silurian at Dob's Linn, southern Scotland possesses an age of 445.7 +/- 2.4 (Batchelor and Weir, 1988, Merriman and Roberts, 1990; Compston and Williams, 1992). Three of these metabentonites reveal trachyandesitic composition, with abundant apatite and phlogopites. The youngest one of Llandovery age contains sideromelane chips like the Russell Bed. A comparison of MgO vs. FeO and TiO₂ vs. MgO values of biotites separates the Ordovician from Silurian metabentonites in this area and Scandinavia (Batchelor, 2003). The Russell Bed phlogopites have compositions similar to the Silurian metabentonites. This suggests that the Russell Bed and the Scottish/Scandinavian deposits record temporally offset eruptions, but likely from similar magmatic sources.

But if the shale-hosted gamma ray deflections define deposits separate in space and time, the Russell Bed becomes intrabasinal, and an origin related to subsea eruption cannot be excluded. Such eruptions occur at bathyal depths along an arc (Carey, 2000),

the same water depth for the Billings Formation deposition (Sharma et al., 2003). No attributes of the Russell Bed, including glass spherules, seem unique to subaerial eruptions.

Russell Bed volcanism was likely linked to a tectonic “trigger” for two major events in the basin. First, it coincides with the initial influx of distal turbidites related to regional Taconic basin fill (Hiscott et al., 1986). The anoxic setting following platform subsidence became ventilated abruptly (Sharma et al., 2003), possibly, due to downwelling of dense oxygenated surface water. Second, four graptolite species became extinct within the basin (Sharma et al., 2003); productivity may have been affected by either ash falling through the water or geochemical changes in the water.

The Russell Bed offers a geologic “window” into the potential evolution of magmatism along the Taconic arc. The apparent shift from silicic (rhyolitic to rhyodacitic) magma sources for the Deicke and Millbrig deposits (Kolata et al., 1996) to a more basic source for the Russell Bed (this study) coincides with a reduction in LREE enrichment; Deicke ($La_N/Yb_N = 11.2$), Millbrig ($La_N/Yb_N = 9.1$), Russell ($La_N/Yb_N = 3.1$) (Kolata et al., 1996; this study). This appears to define a less fractionated magma for Russell Bed volcanism as supported by a calculated Eu/Eu* ratio, ~0.85 (from Table 3-1). A few samples of K-bentonites within the carbonate succession recovered from the Russell GSC#2 core also suggest a similar trend (Fig. 3-6).

Rare earth element compositions of apatite from Ordovician K-bentonites within carbonate platform have been successfully used to geochemically fingerprint them. A comparison of the apatite rare-earth element geochemistry between the Russell Bed, Deicke and Millbrig K-bentonites identifies a) the Russell Bed is a separate deposit; and,

Figure 3-7. Rare earth element compositions of apatites from the Russell Bed, Deicke and Millbrig K-bentonites.

b) an evolutionary trend with increase in Sm/Ce ratio with increasing ages (Fig. 3-7).

Elevated BaO values and evidence for continental crustal material associated with the Russell Bed magmatic source (see above) may define formation of a Taconic continental arc following platform foundering. But if the Russell Bed is basin-restricted, its geochemistry may only identify eruption along fractures and/or faults through continental crust. The Cortlandt-Beemerville dikes of New Jersey (Fig. 3-1; Ratcliffe, 1981) are of similar age, and define local intrusion of deep-crustal or mantle derived material along the orogen's structural fabric. For the Russell Bed, change in Taconic thrust loading leading to flysch input may have triggered fracturing aided by an already weakened continental crust: eastern Ontario contains part of the Ottawa-Bonnechère Graben, a deeply rooted fault system with a 400 million year history (Kumarapeli, 1985).

Conclusions

The Russell Bed is likely a ~445 Ma K-bentonite within a deep-water Taconic shale basin. Volcanism was derived from a mildly alkaline magmatic source, with incorporation of continental-derived sediment or crust, and heralded local Taconic flysch deposition and extinction of several graptolite species. The magmatic source contrasts with earlier silicic volcanic sources recorded from the Taconic foreland, and defines either evolution of continental arc or a fracture-controlled intrabasinal eruption in response to Taconic thrust-loading.

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Chapter IV

Magnesian calcite and chamositic ooids forming shoals peripheral to Late Ordovician (Ashgill) muddy siliciclastic shores: southern Ontario

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In press, Palaeogeography, Palaeoclimatology, Palaeocology.

Abstract

In southern Ontario, ooids are associated with two distinct facies suites in the Queenston Formation, the final stage of Late Ordovician (Ashgill) Taconic basin fill. One facies consists of thin ooid and bioclastic grainstones interbedded with mudrock, and lies near the base of the formation, and, in southwestern Ontario, also forms a local NW-thickening wedge near the middle of the formation. Ooids have radial-fibrous and radial-concentric fabrics (Type A), with chamosite, illite, and Fe-oxide laths at intercrystalline sites. Vertical lithologic and ooid abundance patterns indicate that thresholds for carbonate production were sensitive to changes in terrigenous sediment supply, sea level, circulation, accommodation space, and tectonism. Ooids in the second facies association are admixed with abraded fragments of open-marine biota, or occur as burrow fills, within a < 30-cm thick interval of mudrock near the top of the preserved Queenston succession, a few metres below the Ordovician-Silurian unconformity. Ooids have radial concentric and crosscutting patchy microcrystalline fabrics (Type B). This unit may represent a transgressive or stillstand deposit modified by bioturbation.

The extent of preserved fabric suggests that both ooid types were originally magnesian calcite, but Type A ooids underwent greater burial alteration. This is shown by a) crystalline mosaics that cross-cut relict primary fabrics; b) $\delta^{13}\text{C}$ values (-1.82 to +0.67 ‰) and $\delta^{18}\text{O}$ values (-4.46 to -10.57 ‰) more negative than marine calcite of similar age; c) Mn and Fe concentrations more elevated above expected marine values; and d) a luminescence similar to that of intergranular cements. Burial meteoric diagenesis was likely promoted by excellent permeability of the host sand. Authigenic chamosite and Fe-oxide reflects diagenesis of iron-bearing and clay detritus trapped during ooid growth.

Type B ooids suffered less alteration: $\delta^{13}\text{C}$ (+ 1.1 to + 6.64 ‰) and $\delta^{18}\text{O}$ (-3.04 to -4.81 ‰) values overlap the expected marine range, including ^{13}C enrichment that occurs within the Hirnantian (latest Ordovician) excursion. Although Mn and Fe values are still higher than those of modern calcitic ooids, negligible luminescence suggests that recrystallization occurred in the presence of marine-derived pore fluids. Further burial alteration was inhibited due to low permeability of the host mud.

Type A ooid facies in the Queenston Formation forms an ancient analogue for lesser known Quaternary ooid shoals peripheral to tropical deltaic systems. The facies of Type B ooids, while more enigmatic, may preserve a geochemical herald of latest Ordovician climate change. The presence of minor chamosite in Type A ooids defines a possible distal facies of the well-known oolitic ironstones of similar age in the mid-continental USA.

Introduction

Ooids are most commonly associated with tropical carbonate platforms, and are important indicators of shallow water, high-energy, facies (Milliman, 1974). However, ooid shoals are also found along the ocean-fronts of mud- and sand-rich deltaic environments of large tropical river systems, particularly those developed during the sea-level lowstand of the last glacial maximum (Milliman and Barretto, 1975; Wiedicke et al., 1999; Milliman, 2000). Furthermore, the mineralogy of these ooids is typically high magnesium calcite, not the aragonite usually found on Holocene carbonate platforms (Milliman, 1974).

In eastern and southwestern Ontario, ooid-bearing limestones of Late Ordovician age occur within and immediately beneath a geographically broad paralic mudrock succession, the Queenston Formation. This widely distributed unit (Fig. 4-1A and 1B) is well known as the final stage of basin fill linked to erosion of the Taconic highlands (Sanford, 1993; Lehmann et al., 1995; Brogly et al., 1998). Two ooid facies associations are recognized: (1) relatively pure, thin beds of ooid and bioclastic limestones are interbedded with peritidal mudrock near the base and middle of the formation, and contain micrometre-size authigenic chamosite and iron-oxide at intercrystalline sites; and (2) within metres of the Ordovician-Silurian unconformity in southwestern Ontario, ooids are scattered within a thin bed (<30 cm) of mudrock. For this study, host rock sedimentology, stratigraphy, and ooid petrofabric and geochemistry are used to interpret the origins of these two distinct Late Ordovician ooid facies in the context of sediment supply, tectonism and sea level change that influenced a predominantly siliciclastic system. Of particular interest is the minor (< 6%) presence of chamosite in ooids of

Figure 4-1. (A) Location of study area (box) relative to Late Ordovician paleogeography and lithofacies in central North America (modified from Condie and Sloan, 1998). Distribution of oolitic ironstones (filled circles; Houten, 1990), and chamositic ooids (present study; open circle) is shown. Dashed line (bold) indicates the extent of the alluvial plain (Prothero and Dott, 2002). (B) Geology of the study area in southern Ontario (modified from Sanford, 1993) with core and outcrop localities (numbered open circles) (see Table 4-1 for detail of locations). Abbreviation: AH, Adirondack High; MB, Michigan Basin; OBG, Ottawa Bonnechere Graben.

Table 4-1. Location of the study area.

Well cores/outcrop*	Location	Coordinates
OGS-82-2, core (Loc. 1)	Chatham	NTS map sheet no. 40J/8UTM 411225 mE, 4693200 mN; UTM zone: 17; NAD 1927
OGS-82-1, core (Loc. 2)	Lambton	NTS map sheet no. 40 J/16; UTM 380250 mE, 4739425 mN; UTM zone: 17; NAD 1927
OGS-89-10, core (Loc. 3A)	Streetsville	NTS map sheet no. 30 M/12; UTM 602349 mE, 4826531N; UTM zone: 17, NAD 1927
Canada Brick Ltd quarry, (Loc. 3B)	Streetsville	NTS map sheet no. 30 M/12; UTM 602409 mE, 4826995 mN; UTM zone: 17, NAD 1927
Bronte Creek outcrop (Loc. 3C)	Oakville	NTS map sheet no. 30 M/5 UTM: 602010 E, 4806050 N; UTM zone: 17; NAD 1927
OGS-00-C1, core (Loc. 4)	Meaford	NTS map sheet no. 41 A/10; UTM 532847 mE, 4932652 mN; UTM zone 17; NAD 1927
OGS-82-4, core (Loc. 5)	Warton	NTS sheet 41 A/14; UTM481750 mE and 4959880 mN; UTM zone 17; NAD 1983
GSC Russell #2, core (Loc. 6)	Russell County	NTS map sheet no. 31 G/6; UTM 469400mE, 5017600mN; UTM zone: 18, NAD 1927

* OGS- Ontario Geological Survey (Sudbury, Ontario); GSC- Geological Survey of Canada (Ottawa, Ontario).

southern Ontario, which may define a distal northern extension of the prominent paleogeographic belt of iron oolite production in the mid-continent USA (Fig. 4-1A; Van Houten, 1990).

Regional stratigraphic framework

Across southwestern and eastern Ontario (Fig. 4-1B), the Queenston Formation forms the final stage of a thick (2–3 km) shallowing-upward, siliciclastic, basin-fill succession following foundering (by Edenian time) of a broad foreland basin carbonate platform (Fig. 4-2; Johnson et al., 1992; Sanford, 1993). In both areas, the age of the Queenston Formation is late Ashgill (Fig. 4-2). The underlying Georgian Bay Formation in southwestern Ontario is equivalent depositionally (Kerr and Eyles, 1991; Lehmann et al., 1994) and biostratigraphically (graptolite zone: *Amplexograptus manitoulinensis*) to the Carlsbad Formation of eastern Ontario (Fig. 4-2; Sanford, 1993; Lehmann et al., 1994).

In both regions, the transition from interbedded sandstone and grey shales of the Georgian Bay and Carlsbad Formations (Fig. 4-2) up into interbedded grey and red shales of the Queenston Formation contains an interval of thinly interbedded limestone and mudrock. In eastern Ontario, the lower part of this interval with interbedded grey shale and limestone was originally defined as the Russell Formation by Wilson (1946). Some debate of its status has ensued (e.g. Barnes et al, 1981; Williams, 1991; Sanford, 1993).

The basin-fill succession is best preserved in southwestern Ontario where it is overlain disconformably by Llandovery shallow-water carbonates. Regionally, the

Figure 4-2. Proposed distribution of Upper Ordovician stratigraphy, southern Ontario. Stratigraphic succession of Shermanian (Sh.) to Richmondian formations of eastern and southwestern Ontario (after Johnson et al., 1992; Sanford, 1993). Graptolite zone distribution is from Goldman and Bergström (1997). Abbreviation: EM, Eastview Member; LM, Lower Member (Lindsay Formation); CM, Collingwood Member; Ch., Champlainian. Sea-level curves: dashes from Ross and Ross (1992); solid line, Zhang and Barnes (2002) from Anticosti Island, Québec. Vertical lines indicate hiatus. Arrows and open circles indicate stratigraphic locations of the ooids.

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Queenston Formation varies in thickness from 45 to 335 m, and can be traced by core along the eastern margin of the Michigan Basin to cover an area of about 12,500 km² (Fig. 4-1B). East of the Frontenac Arch (Fig. 4-1B), most of what was likely a similar thick succession (Sanford, 1993) was eroded. Here, lower Queenston Formation is an erosional remnant preferentially preserved within a narrow fault block, part of the Ottawa-Bonnechère Graben.

Regional sedimentology and paleogeography

Vertical change in biofacies and lithofacies from the base of the Blue Mountain and Billings formations, which overlie the foundered carbonate platform, up to the Queenston Formation characterizes an overall shallowing upward succession. The Billings Formation in eastern Ontario, for example, records an initial deep-water basin with anoxic bottom waters that was disrupted by appearance of distal turbidites heralding influx of Taconic-derived, coarser-grained sediment (Sharma et al., 2003). An overall drop in sea-level at this time has been determined by sequence stratigraphic and biofacies studies (Fig. 4-2; Ross and Ross, 1992; Zhang and Barnes, 2002). During the time that Georgian Bay and equivalent Carlsbad Formation sediments were accumulating, their depositional environment was between the fair-weather and storm wave bases as illustrated by trace fossils (*Planolites*, *Teichichnus*, *Phycodes*, and *Chondrites*) in mudrock, and interbedded sandstone tempestite deposits (Kerr and Eyles, 1991).

Net shallowing continued across the base of the Queenston Formation as suggested by an increase in frequency of sandstone beds (Kerr and Eyles, 1991; Lehmann et al. 1994), and an increased presence of desiccation cracks, halite hopper impressions

and gypsum nodules within red and grey shales (Brogly et al., 1998). There is also an up-section faunal change from a deeper water conodont fauna (dominated by the genus *Phragmodus*) at the base of Georgian Bay Formation to shallow-water species (dominated by the genera *Rhipidognathus*, *Aptielognathus*, and *Oulodus*) at the top of this same formation (Davison, 1985). A typical shallow-water conodont species *Rhipidognathus symmetricus* is common in ooid limestones sampled near the base and middle of the Queenston Formation (Loc. 3B, 3C and 5; Fig. 4-1B) in southwestern Ontario (McCracken, 2002), as well as from the limestones at the upper part of the Georgian Bay Formation (Tarrant, 1977).

On the basis of the above bio- and lithofacies information, ooid and bioclastic limestones of the uppermost Georgian Bay and Carlsbad formations, and overlying Queenston Formation, are shallow-water deposits. Estimates of sea-level illustrate a high frequency fluctuation throughout the record of basin fill (Fig. 4-2; Ross and Ross, 1992; Zhang and Barnes, 2002). Brogly et al. (1998) and Middleton (1987) described shale rip-up clasts within the thin limestones, which likely illustrates a storm-influenced shallow shelf to peritidal setting well seaward of the regional limit of the Queenston's alluvial facies (Fig. 4-1A). In summary, the marine Queenston succession defines westward progradation throughout western New York and Ontario (Fig. 4-1B; Dennison, 1976; Brogly et al., 1998). Although often referred to as the Queenston "delta", there was likely a complex of deltas, sandy coasts, estuaries, sandy braided streams, and muddy shores (Dennison, 1976; Lehmann et al., 1994; Brogly et al., 1998). Sanford (1993) defines a possible NE-SW oriented limit to the Queenston depositional facies at about 100 km northwest of Loc. 5 (Fig. 4-1B).

Methods

This study is based on cores and two outcrop sections (Appendix, and Fig. 1B and 3). The latter were also described by Brogly (1984). Loc. 3 represents a composite section of these outcrop sections and a core from one of these locations (Fig. 3).

Sections were measured, and polished and unpolished thin sections were made for petrographic and microprobe analyses. Allochem and cement percentages were determined by point counting ($n=300$). Cathodoluminescence microscopy was carried out with working conditions of 50 mA, 12 kV, and ~40 millitorr. Skeletal and ooid grains were handpicked from limestone for carbon and oxygen isotope analysis after gently disaggregating 100-micrometre-thick rock sections. Ooids scattered within mudrock were extracted by gently disaggregating samples in water. X-ray diffraction ($\text{CuK}\alpha$) patterns of ooids, bulk limestones, and oriented clay samples were produced using a Phillips PW1710 diffractometer (Carleton University). Microprobe (Wavelength Dispersive X-ray) analyses were carried out using a Camebax MBX electron probe (Carleton University). For carbonate minerals, Ca, Mg, Fe, Mn and Sr concentrations were determined; for clay minerals, Al, Si and Ti were also determined. Operating conditions were 17 kV, with 10-20 s counting times offering a detection limit of 100 ppm and relative error of 1-3%. Beam diameters of 5 and 1 micrometres were used for carbonate and clay analysis, respectively. Raw data were converted to elemental weight percent by Cameca's PAP matrix correction program.

Figure 4-3. Detailed outcrop and core lithostratigraphy. Localities 3, 4, and 5 define a SE-to-NW transect (see Fig. 4-1B). Outcrop stratigraphy from Brogly (1984) is incorporated into a composite section 3(A–C). Well spacing distance is not to scale. Abbreviation: RF, Russell Formation. Star indicates mudrock with ooids.

The ultrastructure of ooid grains was examined using secondary (SEI) and backscatter (BSE) electron microscopy following Lasemi and Sandberg's (1984) technique for acid-etching of the carbonate. A JEOL (JSM-6400) scanning microscope (Carleton University) was used with operating conditions of 15 kV and a working distance set at 15 mm. $\delta^{13}\text{C}$ (PDB) and $\delta^{18}\text{O}$ (PDB) values for ooids, skeletal components, and cements were determined by analyzing CO_2 generated by the reaction with 100 % phosphoric acid (McCrea, 1950) on a triple collector VG SIRA 12 mass spectrometer (University of Ottawa) following standard procedure, with an analytical error of $\pm 0.1\text{‰}$ for $\delta^{13}\text{C}$ and $\pm 0.2\text{‰}$ for $\delta^{18}\text{O}$. Data are reported in Appendices 21 through 30.

Results

Ooid Facies Associations

In southern Ontario, ooid and/or bioclastic limestones occur interbedded with mudrock in the Georgian Bay/Carlsbad immediately beneath the Queenston Formation or across this boundary (Fig. 4-3). The thickest section (~15 m) occurs at Loc. 6 in eastern Ontario (Fig. 4-3). In southwestern Ontario, a similar limestone-mudrock association forms a NW-thickening wedge within the middle of the Queenston succession, Loc. 3 to 5 (Fig. 4-3). A second distinct ooid facies association, found at all sites in southwestern Ontario, is a thin interval of weakly lithified ooid-bearing mudrock positioned about 0.3 to 6.0 metres below the Ordovician–Silurian unconformity (Fig. 4-3). There is no data to demonstrate whether this mudrock interval is chronostratigraphic or time-transgressive. Erosion in eastern Ontario has removed equivalent upper Queenston strata. The above

two ooid facies associations are further distinguished by their distinct ooid petrographic fabrics, and here are identified as Type A and B ooids, respectively.

Type A Ooids

Stratigraphy

The host limestones are typically hard, well cemented, and relatively pure (> 95 %) grainstones to packstones. In both outcrop (Loc. 3B and 3C; Fig. 4-3), and in cores, beds are thin (1-5 cm). Outcrops indicate these thin beds are lenticular to continuous over metres. As also noted by Brogly et al. (1998), some beds have claystone rip-up clasts and bioclastic gravel-size sediment at their base, and grade upward into finer-grained wave-rippled sediment.

The characteristic mudrock and limestone interbedding defines a rhythmic pattern of reciprocal (siliciclastic-carbonate) sedimentation (Fig. 4-4). The top and bottom boundaries of a given limestone bed are typically abrupt, with minor evidence of erosion along the base as indicated locally by shale rip-up clasts. However, at Loc. 6 in eastern Ontario, the uppermost limestone unit is capped by a prominent disconformity defined by truncation of well-cemented ooids. Calculation of ooid and bioclast abundances in the limestone intervals, that bracket the base of the Queenston Formation at Locs. 6 and 3A illustrates a high-frequency variation (Fig. 4-4).

Figure 4-4. Ooid versus bioclast percentages in limestone beds in eastern (Loc. 6) and southwestern (Loc. 3A) Ontario near the base of Queenston Formation (see Fig. 4-3). The vertical scale for the two locations is not equal. MF 1–4 refers to ooid microfacies.

Microfacies, Petrographic Fabric, Mineralogy

Within the succession of ooid-bearing limestones, four ooid microfacies (MF-1 to -4) are recognized from eastern and southwestern Ontario (Fig. 4-4). Study of sections at Locs. 6 and 3 demonstrates a net change upsection from MF-1 to MF-4 (Fig. 4-4).

MF-1 facies consists of cross-planar (minimum angle of 12°) and parallel-laminated, fossiliferous, ooid grainstone with less than 5 % of fine-grained sand and silt-sized quartz (Fig. 4-5A). Associated bioclastic fragments include brachiopods, bivalves and bryozoans. Grains make up 80 to 90 % of the rock, the rest being intergranular cement. Ooids form 77 to 100% of the grains, are relatively coarse-grained (250 to 500 micrometres), well-sorted, and define a moderately packed fabric. Most of the ooids have a radial fibrous fabric, and are low-magnesium calcite. Radially arranged elongate crystals are truncated by concentric rims (Fig. 4-6A). Ooid nuclei are bioclast fragments, and grains of quartz or glauconite. Other ooids display a finely crystalline mosaic of low-magnesium calcite within which relict radial fabric is preserved. Most of these have no nucleus.

X-ray diffraction (XRD) confirms the presence of ankerite, dolomite and rare chamosite in the host limestone. SEM and petrography shows that ankerite and dolomite replace intergranular calcite cement whereas chamosite occupies intercrystalline sites within ooids (see below). Cathodoluminescence (CL) of calcite crystals associated with both ooid fabrics is a dull orange, and highlights the crystalline fabric.

MF-2 facies is represented by poorly sorted (200 to 900 micrometres) ooids and bioclasts, the latter being fragments of brachiopods, bivalves, and bryozoans (Fig. 4-5B). Grains represent up to 60% of the rock, and ooids represent between 50 to 100% of the

grains. Ooids are low-magnesium calcite in composition, and have a radial fibrous fabric in their inner cortex, and a pronounced dark (as viewed by plain light petrography), or white (as viewed under SEM), concentrically laminated fabric in their outer cortex (Fig. 4-6B and 6C). Nuclei of MF-2 ooids are mostly fossil fragments. Silt-sized siliciclastic grains occur scattered within the cortex. Plain light petrography and SEM examination of acid-etched samples reveal two orders of concentric layering: (1) dark laminae (1st order) range up to 10 micrometres in thickness; and (2) a finer scale layering that appears to consist of concentrically accreted grains of calcite about 1 micrometre in diameter (Figs. 4-6D-F, and 4-7).

The dark concentric laminae of MF-2 ooids arises from the presence of randomly oriented crystalline fibres and laths, 2 to 5 micrometres in length and less than 0.5 micrometre in width (Fig. 4-6C). The crystals occupy intercrystalline sites as well as irregular masses within the center of some ooids (Fig. 4-8A). From XRD and SEM examination, laths are iron-oxide (hematite) whereas the fibrous texture is associated with chamosite (Fig. 4-8B and 8C) with a delicate ultrastructure (Fig. 4-8D). CL emission is a dull orange for these ooids, and highlights the host crystalline fabric.

MF-3 facies represents a well-sorted grainstone. Grains consists up to 60 % of the rock; ooids forming about 10 to 60% of the grains. Ooids are well-sorted, vary between 200 and 300 micrometres in diameter, and show a subtle concentrically laminated, radial fibrous fabric. Nuclei of these ooids are mostly fossil fragments and siliciclastic grains. Strong preferred orientation of elongate (bivalve and brachiopod) skeletal material, oriented parallel to bedding, is typical of this microfacies and absent in the other facies

Figure 4-5. Characteristic ooid microfacies in southern Ontario. Transmitted light photomicrographs illustrate four characteristic ooid microfacies in eastern and southwestern Ontario: (A) MF-1, well-sorted grainstone, ooids have a radial fibrous fabric (R). Ooids showing no nucleus (S) likely represent section that does not pass through the core. B represents bladed cement. (B) MF-2, poorly sorted fossiliferous grainstone, with ooids showing concentric and radial-concentric fabric. (C) MF-3, poorly sorted fossiliferous ooid grainstone with elongated bioclasts showing a preferred orientation. (D) MF-4, well-sorted fine-grained ooid grainstone associated with cryptomicrobial mat (CM).

Figure 4-6. SEM photomicrographs of acid-etched ooids. (A) Radial fibrous fabric truncated by concentric laminae. (B) Inner and outer cortex (IC and OC) defined by radial fibrous and concentric laminae respectively. (C) Inset in (B) with iron-bearing minerals (white) clustered along 1st order concentric laminae. (D) Radial concentric fabric in ooid. (E) Inset in (D) shows 2nd order concentric laminae (F) Inset in (E) shows laminae consisting of single layers of concentrically accreted calcite grains.

Figure 4-7. Schematic model of a radially-concentric ooid. At a diameter greater than 400 to 500 micrometres, there is a change to accretion of micrometre-sized calcite grains.

(Fig. 4-5C). CL emission for ooids is dull orange, and again, highlights the crystalline petrofabric.

MF 4 facies is a well-sorted grainstone. Grains make up about 80 to 90% of the rock, and cements represent rest of the rock. Ooids comprise 85 to 95 % of the grains. This facies contains interlaminated dark brown to black cryptomicrobial laminae (Fig. 4-5D), that are, in part, also stylolitic seams. Ooids range from 200 to 250 micrometres in diameter, are low-magnesian calcite in composition, and have a fabric of radially arranged crystals. Nuclei are fossil fragments and siliciclastic grains. CL emission of MF-4 ooids is orange.

Diagenetic characteristics

Intergranular low-magnesium calcite cements comprise upto 20 % of MF 1 microfacies. The first generation is bladed, represents about 10 % of the microfacies, and forms discontinuous isopachous rims around ooids (Fig. 4-9A). Each crystal reveals an inner non-luminescent core (~40%) surrounded by a bright orange luminescent rim. Equant (blocky) cement (Fig. 4-9A) fills the remaining intergranular space and has a bright orange CL emission.

In MF-2 facies, intergranular cement makes up about 40 % of the rock. The core-rim luminescence pattern is similar to that in MF-1, and reveals about 14 % early bladed cement. Late blocky (~26 %) calcitic cement has a bright orange CL colour. Ankerite and dolomite locally replace these intergranular calcite cements. MF-2 ooids show local spalling and geopetal structure (Fig. 4-9B and 9C), the latter structure similar to features described by Mazzullo (1977).

Figure 4-8. SEM photomicrographs of iron-oxide and chamosite distribution within ooids. (A) Iron-rich minerals (white) in the core and along concentric laminae of an ooid with radially concentric ooid fabric. (B) Backscatter SEM photomicrograph of iron-oxide laths (hematite) clustered along concentric laminae. (C) Backscatter SEM photomicrograph of inset in Fig. 4-8A, showing fibrous chamosite at the core of the ooid. (D) Fibrous chamosite along concentric laminae of an ooid.

Figure 4-9. SEM photomicrographs of ooid textures and cement. (A) SEM photomicrograph of bladed (B) and blocky (BL) cement in ooid microfacies MF-1. (B) Transmitted light photograph of intergranular point contacts (PC) between ooids, and spalling (SP) in MF 2 facies. (C) Transmitted light photography showing dissolved cortex of a collapsed ooid filled with late stage calcite. (D) Backscatter SEM photomicrograph of ooids in Fig. 4-5D showing interpreted erosional contact between ooid and dolomite (arrow).

MF-3 facies consists of up to 40 % of intergranular cement; bladed calcite cement (< 5%) forms discontinuous isopachous rims, with remaining space occupied by blocky calcite cement. Dolomite and ankerite patchily replace these cements as well. CL zonation and colour for intergranular cements is similar to that in the MF-1 and MF-2 facies.

MF-4 facies consists of up to 20 % of intergranular cement, and is characterized by the absence of early bladed cement that occurs in the other 3 facies. Late calcite blocky cement shows a bright orange luminescence. There is usually a layer of dolomite encircling the ooids. From SEM and CL analyses, the dolomite rims are isopachous, non-luminescent, and reveal no internal crystalline fabric (Fig. 4-9D). There is, however, an irregular contact with the underlying ooid body. These observations suggest dolomite precipitation after the ooid, or dolomite replacement of the outer margins of the ooid.

Type B Ooids

Stratigraphy

Ooids occur scattered within a narrow (<30 cm) interval of weakly lithified mudrock within metres of the Ordovician-Silurian boundary in southwestern Ontario (Fig. 4-3). Equivalent strata were eroded in eastern Ontario. Ooids represent up to 20-30% of the host rock, and are either dispersed (Fig. 4-10A) or occur as burrow fill sediment (Fig. 4-10B). In both cases, rounded fragments of bryozoans, echinoderms (also pitted), calcareous algal rhodoliths, peloids, and microcrystalline lithoclasts of similar size as the ooids are intermixed.

Figure 4-10. Textural attributes of Type B ooids. (A) Transmitted light photograph showing Type B ooids, with subtle radial fabrics, are dispersed within mudrock showing. (B) Reflected light photograph of ooids and other allochems as burrow fill (arrows) within mudrock. Horizontal line across the photograph is an artifact of thin section preparation. (C) SEM photomicrograph of microcrystalline calcite (arrow). (D) Backscatter SEM photomicrograph of ooid shown in Figure 4-10A (inset), following acid etching, reveals distribution of microcrystalline calcite and radially-oriented coarse calcite crystals.

Petrographic fabric

Ooids are large, and range in size from 400 to 600 micrometres (Fig. 4-10A). Nuclei of Type B ooids are usually not observed, although some do have bioclast fragments in their centers. The edges of some rounded lithoclasts indicate truncation of an apparent radial fabric suggesting that they too may be derived from large ooids. The majority of Type B ooids have a microcrystalline mosaic fabric of low-magnesian calcite, with crystal sizes of 1 to 3 micrometres (Fig. 4-10C). However, some preserve a radial fabric of coarse, bladed crystals (Fig. 4-10A and 10D) crosscut by a microcrystalline fabric (Fig. 4-10C). CL emission for Type B ooids is either absent or a dull orange, and lesser in intensity than noted for Type A ooids.

Geochemistry of Type A and B Ooids

While there is geochemical variation that distinguishes the two types of ooids, there is also a regional commonality among Type A ooids in southern Ontario. With some overlap, Type A ooids tend to have higher Mn (~5000 to 12,000 ppm; average 5440 ppm) concentrations and MgCO₃ mol % values (> 2 %) when compared to Type B ooids (Fig. 4-11A, 11B, and 11C). There is lesser distinction according to variation in Fe concentrations (Fig. 4-11A and 11C). The majority of Type A and Type B ooids have similar Sr values. A comparison of Mn, Sr, and Fe concentrations between Type A ooids and intergranular cements at Loc. 6 (eastern Ontario) indicate little difference (Fig. 4-12A and 12B).

These elemental data are compared with those associated with brachiopod calcite from the Queenston Formation and a reference dataset for open-marine brachiopod calcite for the Ashgill (Popp et al., 1986). First, Mn and Fe concentrations of Type A

ooids are higher than the marine reference, and brachiopod calcite of the Queenston Formation (Fig. 4-12A). Second, with the exception of one data point, Sr concentrations in Type A ooids are less than in the marine reference (Fig. 4-11B). However, about six data points overlap the field of Sr concentration for Queenston brachiopod calcite (Fig. 4-11B). Of particular importance is that the Queenston brachiopod calcite is non-luminescent, suggesting that samples with elevated Fe and Mn do not necessarily reflect diagenetic alteration.

There are regional isotopic differences between Type A and B ooids. First, Type A ooids from eastern (Loc. 3A) and southwestern (Loc. 6) Ontario define separate, but parallel $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ trends, with the former group shifted to more negative $\delta^{18}\text{O}$ values (Fig. 4-13A). Both groups define a negative $\delta^{18}\text{O}$ displacement from the Late Ordovician marine calcite field (Fig. 4-13A; Wadleigh and Veizer, 1992), but the trend for southwestern Ontario does intersect the marine field. In comparison, most $\delta^{13}\text{C}$ values for Type A ooids in both regions fall within the reference marine field (Fig. 4-13A). Brachiopod calcite from Queenston Formation falls within the marine field defined by Popp et al. (1986) and Wadleigh and Veizer (1992), whereas intergranular cements from Loc. 3, 5 and 6 have a more negative $\delta^{18}\text{O}$ isotopic composition (Fig. 4-13B) similar to the Type A ooids.

In contrast to the above, $\delta^{18}\text{O}$ values for Type B ooids appear to fall within the range for Late Ordovician marine calcite as defined by both Wadleigh and Veizer (1992) and Popp et al. (1986) (Fig. 4-13A). All but one of samples has $\delta^{13}\text{C}$ values ($<+6.64$

Figure 4-11. Fe, Mn, Sr (in ppm) and MgCO₃ mol% in Type A and Type B ooids. (A) and (B) Fe, Mn, and Sr concentrations in Type A ooids and Type B ooids (this study) compared to brachiopod calcite of Ashgill (Popp et al., 1986) and Hirnantian (Marshall et al., 1997) ages. (C) and (D) MgCO₃ mol% versus Fe and Mn concentrations in Type A and B ooids.

Figure 4-12. Comparison of ooid geochemistry and Upper Ordovician inorganic and biogenic calcite. (A) Fe and Mn concentrations of bladed and blocky cement in Type A ooid facies and Queenston brachiopod calcite (this study) in comparison to Ashgill brachiopod calcite (from Popp et al., 1986). (B) Sr concentrations in bladed and blocky calcite cement and Queenston brachiopod calcite (this study) in comparison to the reference brachiopod calcite for the Ashgill (Popp et al., 1986).

Fig. 13. Stable isotope (C,O) variation for Type A and B ooids, and calcite cement, southern Ontario in comparison to reference Ordovician organic calcite. (A) Stable isotope variation for Type A ooids in eastern and southwestern Ontario reveal parallel but offset trends ($\sim 5\text{‰}$) moving away from the field for marine calcite. Type B ooids have $\delta^{18}\text{O}$ values similar to the marine reference field but exhibit $\delta^{13}\text{C}$ enrichment of 5‰ . (B) Carbon and oxygen isotope values for bladed and blocky cements from ooid facies from southern Ontario.

Ooids (Type A)

- Carlsbad Formation, Loc. 6
- Queenston Formation, Loc. 6
- ⊠ Queenston Formation, Loc. 3A

Ooids (Type B)

- Loc. 1
- Loc. 2
- + Loc. 4
- ⊠ Loc. 5

Brachiopod calcite

- ◆ Queenston Formation, this study
- ▨ Ashgill, (Popp et al., 1986)
- Ordovician, (Wadleigh and Veizer, 1992)
- Hirnantian, (Marshall et al., 1997)
- ⊠ Hirnantian (avg.) (Middleton et al., 1991)

Intergranular cement

- ⊠ Bladed and blocky calcite, Loc. 6
- ⊠ Blocky calcite, Loc. 3A
- ⊠ Blocky calcite, Loc. 5

‰) greater than the upper limit of the marine calcite field, and such elevated values are similar to those that define a terminal Ordovician (latest Ashgill or Hirnantian) global isotopic enrichment linked to glaciation (Fig. 4-13A; Middleton et al., 1991; Marshall et al., 1997).

Discussion

Ooids are classic indicators of agitated, shallow-water tropical sedimentation (Milliman, 1974). Their fabric and geochemistry are well known proxies used to define changes in Phanerozoic seawater chemistry, depositional environments, and paleoclimatic conditions (Wilson, 1975; Sandberg, 1983; Wilkinson et al., 1985). For the waning stage of Taconic basin-fill in southern Ontario, the stratigraphic patterns of the limestone-mudrock facies association and petrogenetic differentiation of Type A and B ooids offer improved resolution of changing depositional and paleoclimatic records during the Late Ordovician.

Type A ooids: Carbonate Factory Start-Up in a Siliciclastic System

There are several different aspects of ooid and bioclastic carbonate stratigraphy within the Queenston and the uppermost part of underlying formations that provide new information about the dynamics of sedimentation within what was predominantly a muddy siliciclastic depositional system.

(1) In context of the Taconic basin fill, the first appearance of ooid limestone near the base of the Queenston Formation, along with sedimentary structures of the interbedded mudrock, provides evidence that there was sufficient reduction of accommodation space, compared to deeper-water conditions overall in the lower parts of

the basin fill succession (Kerr and Eyles, 1991; Sharma et al., 2003) to allow start-up of shallow-water carbonate production.

(2) The apparent northward thickening of limestone-mudrock interbeds within the middle Queenston Formation of southwestern Ontario (Loc. 3 to 5; Fig. 4-3) may indicate temporal establishment of a regional north-facing embayment of carbonate deposition. Its occurrence illustrates possible differences in relative sea level change across the northwestern prograding leading edge of the Queenston succession as governed by the interplay of subsidence, sediment supply and eustasy.

(3) Type A ooid-bearing strata, interbedded with mudrock, define short intervals of carbonate production in an otherwise muddy siliciclastic depositional system. This signals the repeated crossing of a threshold linked to the start-up of biological and abiotic (ooid) production. Such a threshold defines interplay of subtle changes in accommodation space, salinity, turbidity and siliciclastic input, and possibly temperature; all factors that influence the carbonate factory (James, 1984). Although there is a general regional appearance of bioclastic and ooid limestones along the base or immediately below the Queenston, (Fig. 4-3), lenticularity of limestone bedding over metres suggests "patchwork" arrangement of small, thin, bioclastic and ooid shoals separated by shallow muddy intershoal regions.

(4) The repetitive variation in ooid and bioclast abundances that characterizes the limestone succession near the base of the Queenston Formation at Loc. 3A and 6 (Fig. 4-4) is interpreted to reflect subtle differences in circulation during each stage of flooding and reduced input of siliciclastics. Kindler and Hearty (1996) proposed that a change from bioclastic- to ooid dominated grainstones in the Quaternary of the Bahama

platforms signaled an increase in circulation and area of submergence of the shelf. For Queenston deposition, only a minor change in relative sea level would be needed to translate a muddy, low-energy coastal region (Broglie et al., 1998) into a site of higher energy, peritidal carbonate production. Such reciprocal sedimentation requires effective backstepping, redirecting, or bypassing of siliciclastic sediment in order to allow for relatively pure carbonate sediment accumulation (Milliman and Barretto, 1975; Wiedicke et al., 1999; Dalrymple, 2002).

(5) The succession of microfacies, from MF-1 to -4, moving upsection within the lower Queenston Formation (Fig. 4-4) likely identifies an overall change in the energy regime. Characteristics of the oldest microfacies, MF-1, including the radial fibrous fabric of ooids, may identify a weakly agitated, shallow marine setting (Reijers and ten Have, 1983). MF-2 and MF-3 indicate progressively shallower, higher energy facies. The preferred orientation of elongated bioclasts in the MF-3 facies (Fig. 4-5C) supports increased energy. The transition from an inner radial fibrous cortex to an outer concentric cortex in MF-2 ooids might also record transition from a suspension to bedload mode of transportation (Heller et al., 1980). MF-2 ooids indicate a unique microstratigraphy that is likely linked to changes in the depositional environment. When ooid diameters exceed 400 to 500 micrometres, the concentric laminae consist of apparent stacking of micrometer-scale calcite grains (Fig. 4-7). This change may indicate a growth threshold, linked to a change from suspension to bedload transport. The micrometre-sized calcite grains (Fig. 4-6F) may identify growth limited by abrasion. The threshold diameter is similar to the diameter (600 micrometres) defined by Heller et al. (1980), based on quartz hydroequivalency measures.

The growth of apparent cryptomicrobial laminae separating thin beds of ooid grainstone within the MF-4 facies indicates a higher order variation in carbonate production and shutdown; the latter defined by stabilization of the ooid shoals. In contrast, the capping disconformity of the MF-4 facies indicates early cementation, but absence of obvious marine cement suggests one of shallow burial prior to subsequent exhumation and erosion.

Type B Ooids: Late Ordovician tropical storms or a transgressive unit?

The origin of Type B ooids is enigmatic. It is unclear if the unit of ooid-bearing mudrock at each of the localities from southwestern Ontario (Fig. 4-3) defines a single regional unit; and if it does, is it chronostratigraphic or time-transgressive? The widespread occurrence of a thin interval of ooid-bearing mudrock located near the Ordovician-Silurian boundary suggests that there was a regional control to its formation. Furthermore, as illustrated by ancient and modern ooids (e.g. Milliman, 1974; Tucker and Wright, 1990), it is unlikely that Type B ooids formed in an environment in which abundant terrigenous material was admixed in the water column. This unit may reflect extensive bioturbation of a thin carbonate layer that mixed carbonate grains and siliciclastic mud. Burrows filled with carbonate sediment during storms (cf. Wanless et al., 1988) or during regional transgression of a thin ooid-bioclastic barrier system across southwestern Ontario.

Such a regional distribution of Type B ooids beneath the Ordovician-Silurian unconformity, with $\delta^{13}\text{C}$ values in keeping with the known terminal Ordovician isotopic excursion (Middleton et al., 1991; Qing and Veizer, 1994), may herald incipient changes

in paleoclimatic and/or tectonic conditions that terminated supply of Taconic-derived sediment to southern Ontario.

Mineralogy of Ooids: a magnesian calcite precursor

The extent of preservation of microfabric of Type A and B ooids is interpreted to identify magnesian calcite as a precursor mineralogy. The radial fibrous fabric indicates either an original low-Mg calcite or high-Mg calcite mineralogy that has suffered minor disruptive structural alteration (Wilkinson et al., 1985). Diagenetic alteration is reflected by finely crystalline mosaics of anhedral crystals that locally cross cut the relict fabric; an orange cathodoluminescence similar to intergranular burial cement; and, by Mn and Fe concentrations elevated compared to modern magnesian calcite ooids (Milliman, 1974). Given that the CL emission of ooids is of similar colour as the bulk of intergranular calcite, it is likely that their alteration defines a burial process. The carbon and oxygen isotopic grouping of Type A ooids (Fig. 4-13) defines an expected meteoric diagenetic trend away from the Ordovician marine calcite field (Lohmann, 1985).

For Type B ooids, the observed patchy distribution of microcrystalline and bladed calcite fabrics (Fig. 4-10C and 10D) suggests that diagenetic alteration has also occurred. However, the carbon and oxygen isotope data appears to preserve signatures similar to early Ashgill to late Ashgill (or Hirnantian) marine calcite (Fig. 4-13A; Brenchley et al., 1994; Marshall et al., 1997; Wang et al., 1997; Wadleigh and Veizer, 1992; Popp et al., 1986). The Mn concentrations are lower compared to those in Type A ooids, suggesting less substitution of Mn^{2+} for Ca^{2+} (Heydari and Moore, 1994). Finally, there is no sympathetic C, O-isotope association as noted for Type A ooids (Fig. 4-13A), and CL

emission is negligible compared to Type A ooids. Thus, the microcrystalline calcite fabric may form from micritization, either on the seafloor or in the subsurface in the presence of marine-derived pore fluids. A lower permeability of the host mud compared to the lime sand host to Type A ooids likely hindered extensive alteration, and certainly impeded intergranular cementation.

Geological significance

This study presents new information about global stratigraphy of ooids, ooid development in siliciclastic systems, and offers a new link to formation of ooid ironstones of Late Ordovician age in the mid-continent USA. Also, a gap has existed for the Ashgill in the published compilation of Phanerozoic ooid mineralogy by Wilkinson et al. (1985). These new data reinforce the dominance of calcite mineralogy for ooids in Upper Ordovician strata.

Type A ooid-bearing shoals of the Queenston and underlying uppermost Georgian Bay and Carlsbad formations, represent valuable ancient analogues for lesser known Quaternary shoals peripheral to tropical deltaic complexes, and, unlike their tropical carbonate counterparts, are typically associated with glacial lowstands. Along the continental margin of Brazil and Guianas, for example, Amazon River sediment is currently trapped along the inner shelf under present highstand conditions. However, during the last glacial lowstand it was bypassing the outer shelf. This allowed start-up of carbonate production, and the sediment contains, locally, up to 75% calcium carbonate with Fe- rich, high magnesium calcite ooids that have a radial-fibrous to partially recrystallized radial fabric (Milliman and Barretto, 1975). Likewise, ooid shoals are also known from along the outer Bengal shelf, formed during the last glacial lowstand, where

sediment from the enormous Ganges-Brahmaputra deltaic complex bypassed the shelf edge (Wiedicke et al., 1999). Relict ooid rich deposits, associated with last glacial maximum have also been reported from the outer shelf of Papua New Guinea, and off many large rivers like Godavari, Indus and Fly (Milliman, 2000). Like the Queenston depositional system, an important factor for the areal distribution of carbonate is removal, or considerable reduction, of siliciclastic input.

Finally, the occurrence of minor chamosite and Fe-oxide mineralization of Type A ooids may identify a distal northeastern limit to the trend of well known Late Ordovician oolitic ironstones found in the mid-continent USA (Fig. 4-1A; Van Houten, 1990). The delicate ultrastructure of chamosite and Fe-oxide laths revealed by SEM (Fig. 4-8C and 8D) indicates a diagenetic origin. These phases could not have been contemporaneous with ooid formation because the two require different oxidative states (Odin et al., 1988). Following Gygi (1981), detrital (possibly iron hydroxide) detritus carried by seawater in this siliciclastic-dominated system became trapped during ooid growth. With subsequent burial and reducing conditions, chamosite and Fe-oxides were formed that partially replaced the ooids.

Conclusions

In southern Ontario, shallow-shelf to peritidal facies characterize the depositional environments of the Late Ordovician (Ashgill) Queenston Formation. This unit defines the culmination of basin fill within Taconic foreland basin. Ooid and bioclastic limestones occur at discrete stratigraphic intervals within this unit, and also in the uppermost part of the underlying Georgian Bay Formation (southwestern Ontario) and

Carlsbad Formation (eastern Ontario). Near the base and middle part of the Queenston Formation, ooids (Type A) preserve a concentrically laminated radial fibrous fabric that was originally magnesian calcite. Element and stable isotope (C, O) geochemistry, along with CL emissions indicate burial alteration in likely meteoric derived fluids. Regionally, thin ooid shoals formed a patchwork distribution of widely distributed shoals separated by muddy intershoal regions. Onset of regional limestone production, local reciprocal (limestone, mudrock) sedimentation, and changing dominance of ooid versus bioclastic limestones, reflects a net reduction in accommodation space linked to basin-fill superimposed by an intimate interplay of relative sea level fluctuation, circulation, and terrigenous sediment supply. Type A ooids contain chamosite and Fe-oxide laths at intercrystalline sites, that were likely alteration products of Fe-bearing detritus trapped during ooid growth.

Within metres of the Ordovician–Silurian unconformity, in southern Ontario, ooids reappear in a thin (15–30 cm) mudrock unit. It remains unclear if this unit is time-transgressive or chronostratigraphic. Ooids and open marine skeletal debris are admixed with siliciclastic sediments, and locally fill burrows. These ooids display a microcrystalline fabric, and locally a relict precursor bladed calcite fabric. Geochemistry suggests that the ooids were also magnesian calcite in composition, and that recrystallization occurred in the presence of marine or marine-derived fluids. Type B ooids preserve elevated $\delta^{13}\text{C}$ compositions similar to the global positive excursion associated with the latest Ordovician.

Type A and B ooids reinforce the dominance of a magnesian calcite mineralogy for ooids of Late Ordovician age. Whereas Type A ooids could define a northern, distal

edge of the prominent ooid ironstones found in the mid-continent USA at this time, distribution and isotope geochemistry of Type B ooids may herald incipient paleoclimatic or tectonic events that terminated of Taconic-derived sediment to southern Ontario.

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Chapter V

Discussion and Summary

Late Ordovician foreland basin in the Ottawa Embayment

A foreland basin develops as a result of the load of the thickened crust resulting from continental collision (Dickinson, 1974). The basin sediment fill reflects an interplay of the growth of the thrust wedge, isostatic adjustments of the cratonic lithosphere to thrust loading, eustasy, and surface processes that redistribute material from the developing mountain belt to the basin (Sinclair, 1997). The commonality of these processes in many orogenic belts in space and time has allowed development of a model to explain division of the sedimentary fill of a foreland basin into distinct and predictable stratigraphic packages (Fig. 5-1). The four division consists of: a) carbonate deposition on the cratonic margin of the basin (lower unit); b) hemipelagic mud sedimentation (middle unit); and c) deep-water turbiditic siliciclastic sedimentation (upper unit) (Fig. 5-1; Sinclair, 1997). These three sedimentary units are eventually overlain by d) molassic sediments (Fig. 5-1). Many basins on which this model is based (Fig. 5-2) also display unique aspects according to their development histories.

In eastern North America, the Middle to Late Ordovician Taconic orogeny created a broad foreland within the cratonic Appalachian basin. Eventual collapse of the Middle to Upper Ordovician carbonate platform (e.g., Trenton or Ottawa groups; Fig. 5-1), equivalent to the lower unit of Sinclair (1997), was followed by westward inundation by deep-water hemipelagic siliciclastics (e.g., Utica shale or lower Billings Formation;

Figure 5-1. General model of a peripheral foreland basin. Stratigraphic packages in response to the tectonic evolution of a basin is shown (after Sinclair, 1997).

Figure 5-2. Locations of peripheral foreland basins (after Sinclair, 1997).

Fig. 5-1), the middle unit of Sinclair (1997). Continued basin fill is locally represented by the upper Billings and Carlsbad formations (Fig. 5-1), which represent the upper unit of Sinclair (1997). These sediments are derived from more intense erosion of the uplifted Taconic margin of the basin. The final unit of basin fill corresponds to mollase deposition, regionally and locally defined by the Queenston Formation (Fig. 5-1).

The objectives of this thesis (see Chap I) were to examine timing, character of the foreland platform collapse, and aspects of the history of the basin fill as preserved in the Ottawa Embayment. Detailed conclusions drawn from this work have been elaborated on in the relevant chapters, and are briefly drawn together here as a summary.

Collapse of the foreland carbonate platform: eastern Ontario

As shown in Chapter II, the Eastview Member of the Lindsay Formation is an important stratigraphic unit within the Upper Ordovician stratigraphy of the Ottawa Embayment because it records the transition from the foreland carbonate platform to the overlying deep-shale foreland basin siliciclastics, i.e. from the lower unit to the middle unit of Sinclair (1997). The interbedded petroliferous claystone and limestone of this unit defines the incipient stages of influx of arc-derived sediments with higher mafic components. Intraformational stratigraphy also records fluctuating paleoceanographic conditions; namely, petroliferous shales record incursions of dysoxic water onto the platform margin, whereas the interbedded limestone beds define apparent normal marine conditions, typical of the underlying carbonate platform. Geochemical parameters useful as paleoceanographical proxies define paleoproductivity fluctuations directly linked to

the occurrence of the interbedded petroliferous claystone. Subsea organic oxidation, therefore, may have created an oxygen minimum layer that intersected the seafloor, defining the episodic dysoxic conditions. Lateral shifts in this low oxygen layer along the foreland platform may have influenced facies boundaries today revealed by the interbedded petroliferous claystone and normal marine limestone. This interpretation defines a dynamic depositional environment along a distal ramp setting.

How is this transitional unit manifested in other parts of southern Ontario where collapse of the foreland carbonate platform, and subsequent development of foreland siliciclastic basins, are well documented? In the Craigleith area (southwestern Ontario), along the northern margin of the Allegheny Basin, a similar interbedding of limestone and petroliferous shale within the equivalent Collingwood Member identifies similar stratigraphic patterns of fluctuating oceanographic conditions along a distal ramp setting. By contrast, along the eastern margin of the Michigan Basin, the equivalent Collingwood Member is a discrete package of dark gray calcareous shale with two phosphatic limestone beds at the top and bottom. In outcrop on the Manitoulin Island, the Collingwood Member contains higher order (centimeter-scale) interlamination/interbedding of claystone and mudstone. This is interpreted to represent a relatively stable paleoceanographic framework but one positioned more seaward or along a steeper platform margin than shown by the geology of the Craigleith and eastern Ontario regions.

This interlaminated stratigraphy defines transport by carbonate turbidity flows into an environment of petroliferous shale. There is a sustained high paleoproductivity (e.g. Ba/Rb) compared to the fluctuating paleoproductivity during deposition of the Eastview/Collingwood members in eastern Ontario and Craigleith regions. Geochemical

proxies indicate, however, that all areas define a net transition from an oxic to dysoxic/anoxic environment.

Thus, the Manitoulin record likely reflects a more basinward position compared to Eastview and Collingwood Members in eastern Ontario and Craigeleith areas. The stratigraphic differences may reflect a more rapid subsidence in the Manitoulin area (along the margin of the Michigan Basin) creating a distally steepened ramp where allochthonous sediments (turbidites) were concentrated.

Diachroneity of the collapse of the foreland carbonate platform along the Canadian Laurentian margin has been well established in the Upper Ordovician geology of eastern North America (Knight et al., 1991; Lavoie, 1994). However, there has been considerable debate regarding the age of this transition in eastern Ontario (Barnes et al., 1983; Sanford, 1993). As shown in Chapter II, the Newfoundland to Quebec diachroneity can now be extended through to the eastern margin of Michigan Basin, occurring in Maysvillian time.

Deep–water foreland basin: onset of siliciclastic basin fill

The foreland basin model (Fig. 5-1) illustrates that the carbonate platform will be succeeded by deep–water siliciclastics (Sinclair, 1997). Deposition of the lower Billings Formation (Ottawa Embayment, eastern Ontario) and Blue Mountain Formation (southern Ontario and eastern margin of Michigan Basin) represents these deposits in southern Ontario, and are equivalent to the Utica Shale within the Quebec Appalachians.

In eastern Ontario, the lower Billings Formation represents a hemipelagic facies. Peak dysoxic bottom water conditions were attained during its deposition, although well-

oxygenated surface or near surface water sustained moderate graptolite diversity. Lack of oxygen in the bottom waters and the sediments ensured excellent preservation of the planktonic and benthic fauna. This facies was succeeded by the basin-fill sediments deposited by turbidity currents (upper Billings Formation). Transition from the hemipelagic sediments to the overlying distal turbidites coincided with reoxygenation of bottom water. One explanation (see Chapter II) is that turbidity currents transported relatively coarser sediments and oxygen-bearing water to the basin. Sediments rich in mafic components were sourced from erosion of the Taconic highlands. This source is further revealed with the deposition of flysch sediments in eastern Ontario by the upsection trend in geochemical proxies as well as parameters deduced from the clay mineralogy (see Chapter II). Another explanation for the basin ventilation arises from volcanic activity (see below).

Russell K-bentonite

An intra/inter basin correlation tool

The transition from hemipelagic to flysch sedimentation within the middle of the Billings Formation appears to have been abrupt and coincident with a K-bentonite (Russell Bed). Biostratigraphically (see Chapter II), the present study has narrowed the likely ages for the two subunits of the Billings Formation. The lower Billings Formation is now dated to be late Edenian to early Maysvillian in age following graptolite zonation scheme of Goldman and Bergström (1997), whereas the upper Billings Formation is Maysvillian in age. Thus, in eastern Ontario, the hemipelagic-to-turbidite transition lay at or near the stage boundary, similar to that in the type Maysvillian area of Kentucky.

K-bentonites are excellent stratigraphic markers. Being of volcanic ash derivation, their base represents an isochronous surface as a result of their short interval of deposition (days to weeks). Thus, using Ar-Ar isotope age dating, they offer a stratigraphic resolution unattainable by any other means, and have been widely used for intra- and inter-basin correlation in sedimentary basins (Obradovich, 1993; Kolata et al., 1996).

There appear to be no previous isotopic age data from K-bentonites associated with the Taconic foreland basin fill siliciclastics in eastern North America. Thus, the Russell Bed provides an opportunity to date the deep-water foreland basin shale, and to integrate Ar-Ar isotopic data, graptolite biostratigraphy and geophysical data to facilitate a possible regional correlation.

From biostratigraphy, and incorporating geochronological time scale of Harland et al. (1989) and Webby et al. (2004), the maximum age range for the lower Billings Formation is approximately 440 to 451 Ma. Phlogopite crystals extracted from the Russell Bed are dated as approximately 445 Ma, giving a minimum age of 445 Ma for the lower Billings Formation or Late Edenian. Whether the possible gamma-ray correlation shown in Chapter III is correct- that is the spikes represent one bed, traceable in wells in Russell County (eastern Ontario), New York, Quebec and the Illinois Basin –must await discovery and geochemical fingerprinting of K-bentonites within the latter three areas.

Foreland basin dynamics and volcanism

Numerous studies on foreland basins of different ages suggest that explosive volcanism, thrust loading, initiation of synorogenic sedimentation, subsidence events, and

intrusive activities are all closely linked in basin development. However, the response of change in relative sea level following a volcanic event can be opposite. A comparison between the Mesozoic history of the Western Canada Sedimentary Basin (WCSB) (Kauffman and Caldwell, 1993) and foreland basin-fill of the Ottawa Embayment provides an interesting example.

In both basins foreland thrust belts and volcanic highlands are the source of basin-fill sediments. In the WCSB, sediment fill occurs after an initial rapid subsidence linked to thrust loading. Subsequent appearance of relatively coarser sediments is indicative of erosion following this thrust event, leading to a period of basin fill. A similar history may be reflected by the foreland siliciclastic succession in eastern Ontario. Thrusting events are often related to an increased rate of subduction, linked globally to higher rates of oceanfloor spreading. Volcanic activity is typically associated. In the western Canada foreland basin, the initial shales reflecting rapid subsidence often contain bentonites. Thus volcanic events here are associated with a net rise in sea level (linked to thrust load subsidence) (Kauffman and Caldwell, 1993). For the Ottawa Embayment, however, the volcanism appears to signal the onset of relative sea level fall through basin fill by turbidites.

Volcanic ash fall deposits can trigger changes in oceanographic conditions in a basin, irrespective of whether the eruption is of regional or local magnitude/dimension. It has been documented (Botting, 2002) that mixing of ash with well oxygenated surface water results in a water mass of greater density causing downwelling of oxygenated waters. Thus, in addition to turbidity flows carrying oxygenated water to the deep shale

basin, this phenomenon could have been responsible for the change in oceanographic conditions in the basin coincident with deposition of the Russell Bed (see Chapter III).

Evolution of Appalachian volcanic arc vs. local tectonics

Textural attributes, mineralogy, whole rock and phenocryst geochemistry are key parameters to characterize any volcanic deposit including a K-bentonite. Comparison of the geochemistry and mineralogy between the Russell Bed and older well-known K-bentonites (Millbrig, Deicke) from the carbonate platform identifies differences in the mineral assemblage, trace and rare-earth elements, and phenocryst geochemistry (Chapter III). Importantly the Russell Beds geochemistry identifies a magma source of trachyandesitic origin, a shift away from the rhyolitic-rhyodacitic compositions for the older Ordovician K-bentonites. The Russell Bed represents a mildly alkaline magmatic source, which incorporated some component of oceanic sediment and/or continental crust.

Precise regional correlation of the Russell Bed is speculative at this point (see above). If it is of regional distribution, it may identify a major trend in the Appalachian island arc volcanism during an important period (~10 my) of foreland basin development; namely, in comparison with the platform-hosted Millbrig and Deicke K-bentonites, bracketing the collapse of the foreland carbonate platform. The change in geochemistry from platform to basinal K-bentonites may be associated with a change in convergent plate subduction dynamics. For example, greater incorporation of oceanic sediments or continental crust may reflect an increased rate of subduction, or transition from island arc to continental arc. If, on the other hand, the Russell Bed is intrabasinal in magnitude, it

would indicate changes in local tectonics. Alkaline magmatism is often associated with extensional tectonism and hence presence of a source for the Russell Bed within the vicinity of eastern Ontario is unusual because Late Ordovician tectonism in eastern North America is primarily that of the convergence. Possible basement reactivation and crustal fracturing due to change in thrust loading subsidence (see Chapter III) requires further study.

Upper Billings and Carlsbad Formations: Taconic flysch in eastern Ontario

With onset of flysch sedimentation initiated, the stratigraphic record of basin–fill sediments as preserved in the Russell core is one of net shallowing, reflecting a decrease in accommodation space. The Carlsbad Formation reveals an upsection increase in thickness and frequency of the coarser sediments. Bottom water of the basin remained well oxygenated during its deposition. Initially, the Carlsbad Formation was deposited by distal turbidites mostly below storm wave base, but appears to have been influenced occasionally by likely bigger storms (Kerr and Eyles, 1991). Geochemical proxies identify a peak in derivation of sediment from the volcanic arc. A reduction of accommodation space continued such that water depth eventually allowed the formation of ooid and bioclastic limestone beds. However, this also records episodic shutdown of the siliciclastic input, and signifies a major change in sedimentation patterns within the basin. This present study has built on previous work that identified local occurrences of similar siliciclastic-to-carbonate transition (top of the Georgian Bay Formation) in southern Ontario. It now appears that this transition is of regional extent, and marks a

fundamental change in basin fill history adjacent to the Appalachian orogen (see Chapter IV).

Ooid limestones in foreland molasse: significance for basin development

The regional distribution of limestone beds first appearing in the upper Carlsbad/Georgian Bay formations, through the Russell Formation and into the lower Queenston provides an opportunity to better understand the paleoceanographic conditions of the evolving basin.

When limestone is produced regionally within a siliciclastic succession, it indicates a greatly reduced input of siliciclastics allowing startup of the carbonate factory. However, production of ooids requires even more restrictive conditions: agitated, shallow-water tropical sedimentation (Milliman, 1974). Thus, onset of regional development of bioclastic and ooid limestones in an otherwise siliciclastic succession can be linked to relative sea level fluctuation that controls input of terrigenous sediments. Once a carbonate factory is established, higher order oceanic circulation or sea level fluctuations appear to dictate change in the dominance of ooid versus bioclastic percentages, as exemplified by the Quaternary limestones of the Bahamas (Kindler and Hearty, 1996). Within the Russell Formation, the interbedding of ooid and bioclastic limestones with siliciclastic mudrock indicate repeated crossing of a threshold for the startup of abiotic as well as biotic carbonate production. This allowed a patchwork of ooid shoals to form in a shallow marine environment fronting muddy siliciclastic shores across southern Ontario, the shores corresponding to incoming molassic sediments from the Taconic highland (see Chapter IV).

The best analogy found to date for the Late Ordovician ooid beds in the Carlsbad, Russell, and Queenston formations is Late Quaternary ooid shoals along the mouths of large rivers delivering siliciclastics; for example, shoals peripheral to the tropical deltas found along the continental margin of Brazil and Guiana, or in front of large river outlets like the Amazon, Ganges–Brahmaputra, and Indus, associated with the last glacial lowstand. Siliciclastic sediments from these large rivers bypassed the outer shelf resulting in the startup of carbonate production. What is most characteristic of these shoals in comparison to Quaternary shoals on carbonate platforms is the high magnesian (8-14 mol% MgCO_3) mineralogy of the ooids. Further studies may prove such ancient or recent ooids could be more common in the geological record, and will merit a new model, an antithesis of the classical Bahamian model of ooid formation.

However, a second occurrence of ooid-bearing sediment, found at the top of the Queenston Formation, differs even from these slightly older ooid beds. The appearance of a regionally widespread mudrock interval with scattered ooids found only a few metres below the Ordovician–Silurian unconformity are of considerable geological significance. These ooids preserve a marine diagenetic signature comparable to unaltered Late Ashgill brachiopods, and record a positive shift in $\delta^{13}\text{C}$ (compared to the older Queenston ooids) similar to the global excursion associated with the latest Ordovician. A pronounced sea level drop linked to glaciation has been interpreted to explain the Ordovician-Silurian unconformity. Thus, these enigmatic, upper Queenston ooids may herald paleoclimatic and paleoceanographic changes attendant to the Late Ordovician (Hirnantian) glaciation.

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Appendix 1. Sample numbers, corresponding depth and chemostratigraphic units for Russell GSC #2

Sample No.	Depth (metres)	Chemostratigraphic unit
60	16.16	
59	19.89	
58	20.20	
57	24.31	
56	58.48	
55	118.90	
54	134.22	
53	136.59	
52	137.85	
51	138.72	
50	139.76	
49	153.20	
48	176.17	
47	206.50	
46	211.38	
45	213.90	
44	215.45	
43	220.05	
42	225.43	
41	227.64	
40	235.72	
62	236.53	R3
39	240.68	
38	243.95	
37	246.37	
36	249.70	
35	251.93	
34	253.55	
33	255.13	
32	256.66	
30	258.00	
29	259.17	

Appendix 1. (cont.)

Sample No.	Depth (metres)	Chemostratigraphic unit
28	259.91	R2
27	260.37	
25	262.63	
24	264.79	
31	266.51	
22	269.08	
21	270.58	
20	271.80	
19	274.77	
18	275.81	R1
17	275.89	
16	276.83	
15	277.84	
14	279.27	
13	280.11	
12	280.97	
11	283.54	
10	285.70	

Appendix 2. Clay mineralogy of Russell GSC # 2

Sample No.	Half width area of clay minerals (square unit)		
	Chlorite (003) peak	Illite (002) peak	Chlorite (003)/Illite (002)
47	9964	26248	0.38
46	9869	24483	0.40
45	8303	20264	0.41
44	10672	24658	0.43
43	7835	17389	0.45
42	8371	26612	0.31
41	8899	23190	0.38
40	5258	16128	0.33
62	5690	17995	0.32
39	6565	23738	0.28
38	5432	14242	0.38
37	9750	35650	0.27
36	6145	21419	0.29
35	7089	23114	0.31
34	8340	35948	0.23
33	6148	22308	0.28
32	6134	21395	0.29
30	6032	25978	0.23
29	9160	34776	0.26
28	7440	27782	0.28
27	7985	30304	0.26
25	6120	23841	0.26
24	5860	21528	0.27
31	4896	18046	0.27
22	5172	21443	0.24
21	4328	17796	0.24
20	4962	11604	0.43
19	5286	16792	0.31
18	3427	14534	0.24
17	5033	21362	0.24
16	4628	20744	0.22
15	5951	25888	0.23
14	4140	18649	0.22
13	4187	19639	0.21
12	2768	16961	0.16
11	2528	15178	0.17
10	2404	17739	0.14

Appendix 4. Trace elements, Russell GSC #2

Sample No.	Cr [1.00] [†] (ppm)	Ni [5.00] (ppm)	Ti [10.00] (ppm)	Nb [0.08] (ppm)
47	94	57	4206	17.53
46	102	57	4554	17.97
45	78	37	4032	16.51
44	81	44	3333	12.59
43	85	50	3474	13.20
42	97	54	4027	15.46
41	115	52	4214	16.02
40	85	52	3792	14.59
62	83	70	3788	14.52
39	86	53	3966	15.38
38	72	68	3154	11.56
37	95	39	4199	16.45
36	91	84	3787	14.15
35	99	73	4022	14.50
34	96	85	3819	13.64
33	84	72	3868	14.76
32	93	93	3898	14.21
30	88	105	3703	15.78
29	80	86	3668	14.62
28	80	92	3912	15.83
27	85	99	3772	14.56
25	92	77	4278	16.96
24	77	90	4220	16.30
31	80	85	3804	14.23
22	81	67	3912	14.87
21	82	70	3908	14.57
20	77	90	3988	15.47
19	71	66	3376	12.46
18	30	29	1620	6.44
17	50	34	2576	9.87
16	11	19	635	2.45
15	72	35	3710	16.40
14	62	44	2811	10.94
13	53	44	2369	10.50
12	45	34	2145	10.20
11	89	45	3687	17.61
10	59	24	2098	10.30
† = numbers within parenthesis indicate detection limit				

Appendix 4. (cont.)

Sample No.	Eu [0.004] [†] (ppm)	Sm [0.03] (ppm)	La [0.20] (ppm)	Gd [0.03] (ppm)
47	1.21	6.18	42.08	4.58
46	1.34	6.73	44.69	4.95
45	1.88	8.68	35.62	7.40
44	1.65	7.17	28.28	6.30
43	1.48	6.54	29.82	5.69
42	1.25	6.31	41.42	4.65
41	1.11	5.31	37.72	4.07
40	1.40	6.66	38.92	5.42
62	1.56	7.32	36.13	6.15
39	1.32	6.49	38.50	5.10
38	1.29	6.04	31.02	5.27
37	1.07	5.44	45.13	3.85
36	1.43	6.67	35.63	5.48
35	1.24	5.76	39.63	4.62
34	1.40	6.42	31.34	5.37
33	1.45	7.04	36.62	5.70
32	1.33	6.36	31.92	5.19
30	1.27	6.37	42.86	5.21
29	1.36	6.40	37.76	5.19
28	1.41	6.83	37.87	5.71
27	1.25	6.41	41.12	5.08
25	1.29	6.56	42.94	5.44
24	1.32	6.75	41.27	5.50
31	1.47	7.07	39.55	5.65
22	1.56	7.48	42.93	6.48
21	1.46	7.07	39.25	5.77
20	1.42	6.80	39.22	5.80
19	1.05	5.57	34.71	4.71
18	0.99	4.98	21.06	4.36
17	0.87	3.81	27.79	3.24
16	0.43	2.06	9.93	1.70
15	0.74	3.87	39.05	3.05
14	0.85	4.08	30.60	3.59
13	0.82	4.51	30.06	3.56
12	0.68	3.61	26.25	2.92
11	0.61	3.26	34.24	2.59
10	0.50	2.48	22.35	1.97

† = numbers within parenthesis indicate detection limit

Appendix 4. (cont.)

Sample No.	V [1.00] [†] (ppm)	U [0.01] (ppm)	Th [0.05] (ppm)	Mo [1.00] (ppm)	Ba [5.00] (ppm)	Rb [0.20] (ppm)
47	149	4.17	12.02	3	229	145.58
46	163	4.26	12.43	2	227	146.10
45	118	3.40	10.67	N.D. [§]	512	140.42
44	97	2.87	9.13	1	382	118.24
43	111	3.65	9.15	3	313	129.16
42	143	4.07	11.26	2	297	164.03
41	149	3.60	10.97	2	234	172.98
40	132	3.70	10.54	3	365	142.05
62	127	5.24	10.73	7	268	141.91
39	132	4.29	10.83	4	333	150.60
38	109	5.10	8.41	6	326	120.84
37	159	4.36	11.69	1	203	126.24
36	132	6.75	10.13	9	214	144.37
35	143	5.68	10.90	8	388	166.75
34	133	6.10	9.82	18	268	148.40
33	128	6.25	10.08	9	254	144.66
32	131	6.31	10.41	12	250	144.83
30	165	9.81	10.59	16	397	140.98
29	181	8.61	10.19	15	340	150.37
28	169	10.21	10.58	19	194	129.21
27	199	10.56	10.15	20	196	135.94
25	198	6.48	11.46	8	319	163.35
24	194	9.07	11.32	10	259	160.79
31	178	7.92	9.90	10	267	143.68
22	166	6.89	10.62	8	333	151.56
21	163	6.60	10.48	6	296	139.59
20	149	6.14	10.51	8	306	147.01
19	91	6.06	9.28	3	238	95.43
18	48	3.98	4.17	N.D.	164	52.64
17	70	3.71	7.44	N.D.	249	80.56
16	22	1.58	1.92	N.D.	49	21.57
15	102	5.08	14.00	N.D.	849	144.73
14	77	5.46	8.62	1	189	89.75
13	63	5.44	8.41	1	188	89.16
12	63	4.09	8.12	1	277	83.29
11	108	5.50	13.06	1	616	149.37
10	62	1.91	7.60	1	159	93.65

[†] = numbers in parenthesis are detection limit; [§] N.D.= not detected

Appendix 5. Organic carbon % and carbon isotope values, Russell GSC#2

Sample No.	Organic Carbon	$\delta^{13}\text{C}_{\text{org. PDB}}$
	[0.10] [†] (%)	(‰)
47	0.54	-30.00
46	0.37	-29.93
45	0.25	-29.71
44	0.26	-29.43
43	0.46	-29.85
42	0.42	-29.82
41	0.27	-29.74
40	0.73	-29.87
62	1.17	-29.99
39	0.74	-29.98
38	2.29	N.A. [§]
37	0.37	-29.91
36	1.87	-30.03
35	1.64	-29.94
34	2.12	-29.92
33	1.64	-29.91
32	2.24	-29.89
30	3.02	-29.88
29	2.88	-29.79
27	3.29	-29.73
25	2.64	-30.40
24	2.81	-29.75
31	3.57	-29.89
22	2.95	-30.06
21	3.09	-29.81
20	2.37	-29.62
19	3.14	-29.84
18	1.12	-30.21
17	5.98	N.A.
15	0.86	-30.14
11	1.49	N.A.
10	3.89	-30.43

[†] = numbers in parenthesis indicate detection limit

[§] N.A.= not available

Appendix 6. Average of trace elements from upper Billings and Carlsbad formations (Unit R3)

Elements	D.L. [†]	Sample No.													
		60	59	58	57	56	55	54	53	52	51	50	49	48	
Ba	ppm	312	295	435	391	273	337	315	148	245	271	248	335	405	
Co	ppm	15	14	17	13	18	19	26	12	14	12	17	15	20	
Cr	ppm	60	56	81	53	77	78	88	33	78	63	71	91	84	
Cu	ppm	12	17	11	16	28	38	152	15	31	26	38	36	33	
Mn	ppm	954	794	512	651	522	598	535	2374	510	543	505	499	680	
Mo	ppm	1	2	3	2	N.D. [§]	N.D.	2	N.D.	N.D.	N.D.	N.D.	N.D.	1	
Ni	ppm	36	34	41	31	44	42	54	30	41	30	36	42	49	
Pb	ppm	9	7	11	6	8	7	19	11	10	9	25	33	30	
Sb	ppm	1	1	1	1	N.D.	1	1	N.D.	N.D.	N.D.	1	N.D.	1	
Sr	ppm	129	121	130	159	147	165	171	>450	158	149	164	163	185	
V	ppm	106	89	128	91	123	119	132	49	118	92	97	121	132	
Zn	ppm	64	61	75	54	79	71	175	98	63	67	100	64	99	
S	%	0.0	0.0	0.0	0.0	0.2	0.2	1.2	N.A. [#]	N.A.	N.D.	N.D.	1.1	1.1	
TOC	%	0.0	0.0	0.0	0.0	0.2	0.1	0.2	N.A.	N.A.	N.D.	N.D.	0.3	0.3	

† D.L.= detection limit
§ N.D.= not detected
N.A.= not available

Appendix 6. (cont.)

Elements	D.L. [†]	Sample No.													
		47	46	45	44	43	42	41	40	62	39				
Ba	ppm	5.00	229	227	512	382	313	297	234	365	268	333			
Co	ppm	1.00	22	24	12	16	15	19	16	21	22	18			
Cr	ppm	1.00	94	102	78	81	85	97	115	85	83	86			
Cu	ppm	2.00	45	47	49	56	38	37	29	54	57	54			
Mn	ppm	0.10	510	604	929	1294	1029	547	525	686	529	549			
Mo	ppm	1.00	3	2	N.D. [§]	1	3	2	2	3	7	4			
Ni	ppm	5.00	57	57	37	44	50	54	52	52	70	53			
Pb	ppm	0.10	37	32	6	21	28	29	23	22	50	26			
Sb	ppm	0.50	1	1	N.D.	N.D.	1	1	N.D.	1	1	1			
Sr	ppm	2.00	184	181	174	223	207	188	192	209	168	175			
V	ppm	1.00	149	163	118	97	111	143	149	132	127	132			
Zn	ppm	5.00	84	77	118	112	65	83	72	114	60	102			
S	%	0.10	1.4	1.4	0.2	1.1	1.4	1.3	1.0	1.7	2.0	1.5			
TOC	%	0.10	0.5	0.4	0.3	0.3	0.5	0.4	0.3	0.7	1.2	0.7			

† D.L.= detection limit

§ N.D.= not detected

Appendix 6. (cont.)

Elements	D.L. [†]	Sample No.										AV.	SD.	SE.
		38	37	36	35	34	33	32	30	29				
Ba	ppm	5.00	326	203	214	388	268	254	250	397	340	306	77.1	13.6
Co	ppm	1.00	16	14	22	18	18	19	19	19	20	18	3.5	0.6
Cr	ppm	1.00	72	95	91	99	96	84	93	88	80	82	16.0	2.8
Cu	ppm	2.00	49	38	59	60	68	63	61	65	60	45	25.7	4.6
Mn	ppm	0.10	1767	436	544	459	527	494	455	445	612	707	412.7	73.0
Mo	ppm	1.00	6	1	9	8	18	9	12	16	15	6	5.1	0.9
Ni	ppm	5.00	68	39	84	73	85	72	93	105	86	54	19.9	3.5
Pb	ppm	0.10	33	10	32	32	32	32	38	47	27	23	12.5	2.2
Sb	ppm	0.50	1	N.D. [§]	1	1	1	1	1	1	1	1	0.2	0.0
Sr	ppm	2.00	243	148	198	178	183	177	169	170	203	174	26.7	4.7
V	ppm	1.00	109	159	132	143	133	128	131	165	181	125	26.3	4.6
Zn	ppm	5.00	58	86	79	71	149	108	54	69	113	86	27.9	4.9
S	%	0.10	1.5	0.9	1.6	1.8	1.7	1.7	2.0	1.6	1.5	1.1	0.7	0.1
TOC	%	0.10	2.3	0.4	1.9	1.6	2.1	1.6	2.2	3.0	2.9	0.8	0.9	0.2

† D.L.= detection limit
§ N.D.= not detected
N.A.= not available;
Note: AV.= average; SD.= standard deviation; S.E.= standard error

† D.L.= detection limit

§ N.D.= not detected

N.A.= not available;

Note: AV.= average; SD.= standard deviation; S.E.= standard error

Appendix 7. Average of trace elements from lower Billings Formation (Unit R2), Russell GSC#2

Elements	D.L. [†]	Sample No.									AV.	SD.	SE.	
		28	27	25	24	31	22	21	20	19				
Ba	ppm	5.00	194	196	319	259	267	333	296	306	238	268	51.0	17.0
Co	ppm	1.00	21	20	19	20	19	16	17	19	11	18	3.0	1.0
Cr	ppm	1.00	80	85	92	77	80	81	82	77	71	81	5.9	2.0
Cu	ppm	2.00	67	71	59	61	59	53	53	46	50	58	8.3	2.8
Mn	ppm	0.10	387	373	431	396	434	474	401	400	380	408	32.1	10.7
Mo	ppm	1.00	19	20	8	10	10	8	6	8	3	10	5.8	1.9
Ni	ppm	5.00	92	99	77	90	85	67	70	90	66	82	12.0	4.0
Pb	ppm	0.10	30	23	22	22	19	17	18	26	10	21	5.7	1.9
Sb	ppm	0.50	1	1	1	1	1	1	1	1	N.D. [§]	1	0.3	0.1
Sr	ppm	2.00	160	174	240	204	289	355	256	247	332	251	66.5	22.2
V	ppm	1.00	169	199	198	194	178	166	163	149	91	168	33.5	11.2
Zn	ppm	5.00	98	185	109	119	107	92	78	73	80	105	33.9	11.3
S	%	0.10	N.D.	1.5	1.5	1.6	1.5	0.6	1.4	1.8	1.1	1.4	0.3	0.1
TOC	%	0.10	N.D.	3.3	2.6	2.8	3.6	3.0	3.1	2.4	3.1	3.0	0.4	0.1

† D.L.= detection limit
§ N.D.= not detected
Note: AV.= average; SD.= standard deviation; S.E.= standard error

Appendix 8. Average of trace elements from Eastview Member (Unit R1), Russell GSC#2

Elements	D.L. [†]	Sample No.										AV.	SD.	SE.
		18	17	16	15	14	13	12	11	10				
Ba	ppm	164	249	49	849	189	188	277	616	159	305	257.4	85.8	
Co	ppm	6	7	3	8	7	6	7	8	6	6	1.5	0.5	
Cr	ppm	30	50	11	72	62	53	45	89	59	52	22.8	7.6	
Cu	ppm	12	16	4	17	19	18	13	17	6	13	5.2	1.7	
Mn	ppm	335	347	198	241	247	213	173	172	192	235	65.2	21.8	
Mo	ppm	N.D. [§]	N.D.	N.D.	N.D.	1	1	1	1	1	1	0.2	0.1	
Ni	ppm	29	34	19	35	44	44	34	45	24	34	9.2	3.1	
Pb	ppm	5	6	3	5	5	6	5	6	5	5	0.9	0.3	
Sb	ppm	N.D	N.D.	N.D.	N.D	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	
Sr	ppm	>450	>450	>450	393	>450	>450	>450	>450	>450	393	N.A.	N.A.	
V	ppm	48	70	22	102	77	63	63	108	62	68	25.9	8.7	
Zn	ppm	61	92	44	81	74	45	94	56	32	64	22.1	7.4	
S	%	0.4	0.2	N.A. [#]	0.3	N.A.	N.A.	N.A.	0.4	0.4	0.4	0.1	0.0	
TOC	%	1.1	6.0	N.A.	0.9	N.A.	N.A.	N.A.	1.5	3.9	2.7	2.2	0.7	

† D.L.= detection limit

§ N.D.= not detected

N.A.= not available

Note: AV.= average; SD.= standard deviation; S.E.= standard error

Appendix 9. Average of trace elements from Eastview Member, Aviation Parkway

Elements	D.L. [†]	Sample No.										AV.	SD.	SE.
		23	5	61	4	3	2	1						
Ba	ppm	5.00	192	173	304	127	151	143	66	165	73.2	27.7		
Co	ppm	1.00	7	5	4	5	3	3	3	4	1.6	0.6		
Cr	ppm	1.00	75	47	40	50	58	50	54	53	11.2	4.2		
Cu	ppm	2.00	18	16	13	18	10	8	9	13	4.4	1.7		
Mn	ppm	0.10	160	173	169	186	182	206	221	185	21.5	8.1		
Mo	ppm	1.00	N.D. [§]	1	N.D.	N.D.	N.D.	N.D.	N.D.	1	N.A. [#]	N.A.		
Ni	ppm	5.00	55	40	33	38	30	38	29	38	9.0	3.4		
Pb	ppm	0.10	6	4	4	4	4	3	3	4	0.9	0.3		
Sb	ppm	0.50	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.A.	N.A.		
Sr	ppm	2.00	421	>450	>450	>450	>450	>450	>450	421	N.A.	N.A.		
V	ppm	1.00	91	44	42	51	50	40	37	51	18.2	6.9		
Zn	ppm	5.00	50	135	38	46	38	35	23	52	37.6	14.2		

[†] D.L. = detection limit
[§] N.D. = not detected
[#] N.A. = not available
 Note: AV.= average; SD.= standard deviation; S.E.= standard error

Appendix 10. Average of trace elements from Quaternary Black Sea sediments
(Brumsack, 1986)

Elements		Sample No.								
		1	2	3	4	5	6	7	8	9
Ba	ppm	355	360	790	845	1240	995	535	1090	370
Co	ppm	47.5	51.1	35.8	22.1	19.2	25.2	17	25.9	10.5
Cr	ppm	62	83	60	49	83	75	35	100	60
Cu	ppm	110	114	175	59	82	112	45	75	48
Mn	ppm	420	530	230	415	390	590	395	400	245
Mo	ppm	50	140	185	50	100	130	50	100	75
Ni	ppm	115	115	125	70	100	125	50	103	80
Pb	ppm	18	22	16.5	14.5	22.5	19.5	12	23	13.5
Sb	ppm	N.D. [†]	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Sr	ppm	520	315	175	970	275	255	1140	225	1625
V	ppm	210	250	415	100	150	145	73	150	130
Zn	ppm	94	105	88	63	100	93	46	108	64
S	%	1.76	1.94	1.82	0.78	0.87	1.48	0.71	0.80	0.72
TOC	%	8.44	6.52	14.74	3.62	5.86	11.36	3.24	4.60	5.98

Note: detection limit for the data set is not reported

[†] N.D.= not detected

Appendix 10. (cont.)

Elements		Sample No.				AV.	SD.	SE.
		19	20	21	22			
Ba	ppm	290	290	315	330	478	301.2	64.2
Co	ppm	24.2	24.7	26.4	26.4	27	9.0	1.9
Cr	ppm	185	175	170	169	117	55.9	11.9
Cu	ppm	45	40	38	50	71	38.4	8.2
Mn	ppm	1390	1470	1350	990	889	589.3	125.6
Mo	ppm	2.5	1.8	1.3	1.2	45	54.5	11.6
Ni	ppm	140	130	135	150	118	34.6	7.4
Pb	ppm	12.5	11.5	12.5	14	16	3.8	0.8
Sb	ppm	N.D. [†]	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Sr	ppm	330	300	305	255	449	391.6	83.5
V	ppm	135	120	155		160	74.1	15.8
Zn	ppm	74	70	73	83	82	17.9	3.8
S	%	0.90	0.27	0.70	0.23	1.1	0.6	0.1
TOC	%	0.89	0.53	0.53	0.60	3.9	4.0	0.9

[†] N.D.= not detected

Note: detection limit for the data set is not reported ;

AV.= average; SD.= standard deviation; SE.= standard error

Appendix 11. Sample numbers, corresponding depth and
chemostratigraphic units for GSC DDH2

Sample No.	Depth (metres)	Chemostratigraphic unit
MMT-23	170.02	E2
MMT-22	170.43	
MMT-21	173.17	
MMT-20	174.09	
MMT-19	176.22	
MMT-18	176.83	
MMT-17	185.06	
MMT-16	185.37	
MMT-15	186.59	
MMT-14	187.40	
MMT-13	187.80	
MMT-12	189.63	
MMT-11	190.85	
MMT-10	191.16	
MMT-9	193.29	E1
MMT-8	193.60	
MMT-7	194.21	
MMT-6	195.63	
MMT-5	196.44	
MMT-4	196.85	
MMT-3	199.39	
MMT-2	199.70	
MMT-1	200.91	

Appendix 12. Clay mineralogy, GSC DDH2

Sample No.	Half width area of clay minerals (square units)		
	Chlorite (003) peak	Illite (002) peak	Chlorite (003)/Illite(002)
MMT-22	2794	7018	0.40
MMT-21	3538	8176	0.43
MMT-19	3390	6929	0.49
MMT-18	3156	6839	0.46
MMT-17	3367	8416	0.40
MMT-16	2500	6350	0.39
MMT-15	2776	7641	0.36
MMT-14	3888	9638	0.40
MMT-13	2843	6886	0.41
MMT-12	2714	6605	0.41
MMT-11	2072	5506	0.38
MMT-10	2257	5493	0.41
MMT-9	2049	5693	0.36
MMT-7	2360	6321	0.37
MMT-6	933	2478	0.38
MMT-5	200	498	0.40
MMT-4	275	443	0.62
MMT-3	39	273	0.14
MMT-2	58	244	0.24
MMT-1	318	7459	0.04

Appendix 13. Representative X-ray diffractograms from bottom and top of GSC DDH2

Appendix 14. Trace elements, GSC DDH2

Sample No.	Cr [1.00] [†]	Ni [5.00]	Ti [10.00]	Nb [0.08]
	(ppm)	(ppm)	(ppm)	(ppm)
MMT-23	114	59	5417	20.40
MMT-22	114	58	5313	19.94
MMT-21	107	53	4944	18.61
MMT-20	122	61	5543	19.21
MMT-19	120	57	5414	18.51
MMT-18	100	52	5215	18.44
MMT-17	113	58	5175	18.36
MMT-16	122	63	5262	18.47
MMT-15	112	57	5013	18.08
MMT-14	105	55	4955	18.01
MMT-13	120	66	5092	17.86
MMT-12	117	67	5110	17.41
MMT-11	106	50	4896	17.25
MMT-10	107	51	4945	17.33
MMT-9	101	57	4768	16.90
MMT-8	104	63	4844	17.45
MMT-7	103	66	4602	17.46
MMT-6	83	71	3288	13.02
MMT-5	96	116	2944	12.27
MMT-4	76	132	2590	10.76
MMT-3	45	44	922	4.05
MMT-2	74	83	1805	7.39
MMT-1	122	25	3132	11.28
† numbers in parenthesis indicate detection limits				

Appendix 14. (cont.)

Sample No.	Eu [0.004] [†] (ppm)	Sm [0.03] (ppm)	La [0.20] (ppm)	Gd [0.03] (ppm)
MMT-23	1.59	7.28	41.38	6.11
MMT-22	1.47	6.67	37.16	5.46
MMT-21	1.57	6.96	32.35	5.94
MMT-20	1.68	7.65	35.21	6.33
MMT-19	1.52	6.71	39.78	5.56
MMT-18	1.82	8.07	38.12	7.07
MMT-17	1.39	6.38	33.46	5.29
MMT-16	1.52	6.75	31.56	5.74
MMT-15	1.43	6.38	35.55	5.41
MMT-14	1.44	6.42	37.47	5.30
MMT-13	1.49	6.67	35.43	5.74
MMT-12	1.57	7.06	33.85	5.93
MMT-11	1.87	8.32	37.86	7.22
MMT-10	1.64	7.20	35.60	6.27
MMT-9	1.30	5.78	36.37	5.08
MMT-8	1.45	6.39	32.88	5.58
MMT-7	1.66	7.33	34.43	6.40
MMT-6	2.47	10.56	45.98	10.44
MMT-5	1.93	8.02	41.83	8.52
MMT-4	1.16	5.12	31.37	4.96
MMT-3	0.61	2.55	20.02	2.65
MMT-2	0.71	3.21	22.97	2.93
MMT-1	0.46	2.01	27.41	1.40
† numbers in parenthesis indicate detection limits				

Appendix 14. (cont.)

Sample No.	V [1.00] [†] (ppm)	U [0.01] (ppm)	Th [0.05] (ppm)	Mo [1.00] (ppm)	Ba [5.00] (ppm)	Rb [0.20] (ppm)
MMT-23	158	4.13	13.60	N.D. [§]	352	174.01
MMT-22	154	4.14	13.60	N.D.	303	157.15
MMT-21	147	4.08	12.66	1	267	137.19
MMT-20	168	4.16	12.56	N.D.	299	139.25
MMT-19	167	4.50	13.28	2	337	162.55
MMT-18	135	4.24	12.10	1	298	110.56
MMT-17	163	4.49	12.86	3	266	149.38
MMT-16	173	4.89	12.60	3	233	126.38
MMT-15	168	4.73	12.94	3	278	150.59
MMT-14	154	4.49	13.05	2	303	154.96
MMT-13	166	4.86	13.34	3	285	143.36
MMT-12	164	4.66	12.31	3	284	141.58
MMT-11	134	4.27	11.86	2	311	110.62
MMT-10	143	4.19	12.02	2	315	123.72
MMT-9	139	4.36	11.12	3	305	112.75
MMT-8	142	4.48	12.62	2	248	118.61
MMT-7	144	5.52	12.24	4	246	111.06
MMT-6	105	5.92	10.28	3	258	125.19
MMT-5	117	7.66	8.48	5	221	92.67
MMT-4	142	13.85	7.72	19	203	89.62
MMT-3	45	2.60	3.01	3	74	33.69
MMT-2	81	5.46	5.44	6	147	63.38
MMT-1	83	2.14	10.51	N.D.	220	170.09

[†] numbers in parenthesis indicate detection limits

[§] N.D. = not detected

Appendix 15. Major oxide composition of Ordovician
K-bentonites in foreland platform carbonates,
eastern North America (Kolata et al., 1986).

Sample No.	Na ₂ O (wt%)	K ₂ O (wt%)	TiO ₂ (wt%)	Fe ₂ O ₃ (wt%)
DRK-192	0.07	6.50	0.53	1.13
MKB-9	0.03	11.87	0.38	0.94
DRK-291	0.02	11.96	0.52	0.91
MKB-23	0.02	11.73	0.38	0.83
MKB-19	0.02	11.13	0.41	1.07
MKB-4	0.04	10.62	0.45	0.80
DRK-187	0.02	7.70	0.47	1.27
MKB-3	0.02	9.55	0.42	1.07
MKB-8	0.02	10.47	0.57	1.14
DRK-228	0.02	8.99	0.72	1.20
DRK-225	0.02	11.65	0.58	0.89
DRK-227	0.02	10.38	0.42	3.94
DRK-229	0.02	6.32	0.88	7.13
MKB-35	0.02	12.23	0.40	1.35
MV11-1	0.08	8.49	0.37	1.31
MV12-1	0.02	6.20	0.81	1.55
DRK-202	0.03	13.74	0.32	2.21
MV10-1	0.02	8.50	0.64	1.23
MV9-1	0.03	13.83	0.39	1.86
MV7-1	0.04	14.12	0.41	2.70

Appendix 15. (cont.)

Sample No.	Na ₂ O (wt%)	K ₂ O (wt%)	TiO ₂ (wt%)	Fe ₂ O ₃ (wt%)
MV13-1	0.03	10.15	0.49	3.14
MV-1-1A	0.03	13.98	0.39	4.36
MV14-1	0.03	15.50	0.28	2.32
MV6-1	0.03	13.99	0.52	1.48
MV6-2	0.03	14.61	0.27	1.69
DRK-290	0.03	15.52	0.32	1.47
DRK-278	0.03	9.26	0.44	2.63
DRK-289	0.03	8.49	0.38	2.46
DRK-189	0.03	11.23	0.23	1.40
MV2-1	0.03	7.97	0.44	3.06
DRK-193	0.03	11.56	0.25	1.59
DRK-196	0.04	8.11	0.51	2.20
DRK-283	0.03	8.56	0.41	2.82
DRK-191	0.05	7.95	0.45	2.44
DRK-277	0.08	8.19	0.42	1.90
DRK-275	0.16	9.93	0.67	2.59
DRK-273	0.13	10.30	0.68	2.62
MO-4	0.03	9.13	0.74	0.38
DRK-260	0.03	10.05	0.52	0.53
DRK-255	0.03	9.38	0.47	0.73
DRK-236	0.02	7.09	0.46	1.14

Appendix 15. (cont.)

Sample No.	Na ₂ O (wt%)	K ₂ O (wt%)	TiO ₂ (wt%)	Fe ₂ O ₃ (wt%)
DRK-205	0.02	7.19	0.45	1.19
DRK-206	0.02	8.42	0.51	3.20
DRK-239	0.02	6.84	0.45	2.69
MO-3	0.02	7.11	0.59	2.87
DRK-269	0.02	6.69	0.43	1.05
DRK-213	0.02	5.14	0.41	2.98
DRK-211	0.04	8.93	0.44	3.48
MKB-30	0.06	8.37	0.42	1.64
MKB-25	0.06	7.09	0.30	1.84
MKB-10	0.04	6.94	0.26	1.62
MKB-11	0.04	7.22	0.26	1.71
DRK-226	0.05	6.91	0.27	2.39
DRK-230	0.04	7.42	0.23	1.92
MKB-34	0.03	7.39	0.26	1.30
MV11-2	0.04	10.83	0.28	1.98
MV12-2	0.03	9.29	0.20	1.18
MV8-2	0.04	7.78	0.27	1.22
MV7-2	0.05	8.31	0.24	1.51
MV13-2	0.04	13.18	0.16	0.78
DRK-287	0.04	9.91	0.18	0.77
DRK-280	0.05	12.33	0.20	1.25

Appendix 15. (cont.)

Sample No.	Na ₂ O (wt%)	K ₂ O (wt%)	TiO ₂ (wt%)	Fe ₂ O ₃ (wt%)
DRK-250	0.04	12.22	0.18	1.14
MV15-1	0.06	11.14	0.18	1.29
MV16-1	0.05	9.74	0.17	1.14
DRK-279	0.04	10.17	0.12	1.28
DRK-286	0.04	9.28	0.20	0.98
DRK-197	0.05	10.93	0.24	1.10
DRK-288	0.04	7.12	0.21	1.09
MV2-2	0.05	7.42	0.20	1.54
MV3-1	0.05	13.22	0.18	1.50
MV4-1	0.04	7.55	0.21	1.80
DRK-249	0.04	8.38	0.21	1.35
DRK-190	0.04	7.56	0.20	1.22
DRK-248	0.04	9.07	0.31	1.93
MV1-1	0.04	8.27	0.24	1.03
DRK-284	0.05	9.06	0.26	1.74
MKB-36	0.04	10.03	0.27	1.65
DRK-188	0.04	6.98	0.22	1.32
DRK-276	0.13	11.55	0.19	1.32
DRK-274	0.16	11.54	0.22	1.49
DRK-272	0.16	10.07	0.21	1.40
MO-2	0.05	10.26	0.24	1.11
DRK-242	0.03	8.86	0.22	2.27
DRK-261	0.04	9.15	0.27	1.61
DRK-232	0.04	9.79	0.25	2.23
DRK-237	0.04	11.28	0.25	2.66

Appendix 15. (cont.)

Sample No.	Na ₂ O (wt%)	K ₂ O (wt%)	TiO ₂ (wt%)	Fe ₂ O ₃ (wt%)
DRK-204	0.04	8.89	0.33	0.89
DRK-207	0.03	8.57	0.28	0.50
DRK-233	0.03	7.89	0.25	1.01
DRK-234	0.03	7.65	0.31	2.32
DRK-259	0.03	7.41	0.24	2.27
MO-1	0.04	7.29	0.25	0.47
DRK-268	0.03	5.21	0.27	0.61
DRK-241	0.02	4.36	0.28	2.44
DRK-281	0.06	9.44	0.46	3.29
DRK-253	0.08	9.62	0.55	3.61
DRK-251	0.19	8.65	0.62	5.02
MV15-2	0.14	9.40	0.52	3.54
MV1-2	0.06	10.07	0.53	4.04
DRK-285	0.07	10.75	0.45	3.19
DRK-252	0.06	9.61	0.51	3.06
DRK-282	0.06	8.13	0.46	3.90
DRK-198	0.03	7.37	0.32	2.45
MV1-3	0.04	7.17	0.42	1.29
DRK-194	0.04	7.99	0.27	3.85
DRK-195	0.04	6.88	0.66	1.56
DRK-199	0.03	7.02	0.46	1.43
DRK-247	0.08	6.98	0.52	2.84

Appendix 15. (cont.)

Sample No.	Na ₂ O (wt%)	K ₂ O (wt%)	TiO ₂ (wt%)	Fe ₂ O ₃ (wt%)
DRK-217	0.07	15.48	0.15	1.00
DRK-223	0.057	12.61	0.98	1.23
DRK-224	0.054	12.91	0.69	4.17
DRK-222	0.055	10.13	0.45	3.06
DRK-243	0.081	12.43	0.53	2.63
DRK-235	0.061	10.11	0.71	1.14
DRK-238	0.047	7.95	0.68	3.07
DRK-208	0.055	12.06	0.58	4.19
DRK-245	0.056	10.98	0.7	4.53
DRK-271	0.061	9.42	0.72	4.27
DRK-266	0.049	7.46	0.73	6.45
DRK-267	0.054	9.35	0.9	4.77
DRK-210	0.044	7.84	0.76	3.91
DRK-218	0.054	7.28	0.25	3.56
DRK-240	0.055	6.62	0.23	2.28
DRK-265	0.027	6.86	0.23	1.5
DRK-270	0.05	7.02	0.19	3.27

Appendix 16. Major oxide composition of Ordovician K-bentonites, southern Ontario,
after Trevaill (1990)

S.N.*	SiO ₂ [†]	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO	Total	LOI [§]
RT84-1	56.77	21.84	1.84	4.46	3.09	0.34	7.67	0.82	0.15	0.01	96.98	10.7
RT84-2	58.72	24.28	1.11	4.26	0.39	0.39	7.97	0.29	0.14	0.01	97.56	9.4
RT84-3	59.09	24.39	1.06	4.48	0.43	0.41	7.78	0.51	0.18	0.00	98.34	9.8
RT86-1	59.43	25.52	1.33	4.77	0.51	0.28	7.32	0.59	0.15	0.00	99.90	8.3
RT87-17	54.42	19.52	1.69	4.54	10.44	0.01	6.45	0.15	0.05	0.02	97.28	12.9
RT87-21	58.89	21.59	3.01	4.35	2.07	0.72	8.43	0.45	0.10	0.02	99.63	8.3
RT87-22	56.65	18.00	2.92	3.90	9.14	0.57	6.98	0.68	0.09	0.02	98.97	12.8
RT87-23	59.52	22.08	2.36	4.30	1.02	1.08	8.55	0.90	0.11	0.01	99.92	7.6
RT87-24	54.93	19.95	1.66	4.36	10.28	0.79	6.88	0.08	0.00	0.01	98.94	12.8
RT87-25	60.24	24.27	2.03	3.07	0.79	0.48	7.87	0.27	0.00	0.01	99.01	7.7
RT87-26	60.18	19.47	2.30	3.72	4.35	0.80	6.69	0.31	0.04	0.01	97.86	10.1
RT87-27	59.01	22.54	1.96	3.80	2.92	0.85	7.24	0.33	0.07	0.01	98.72	9.5
RT87-28	60.30	24.73	0.88	4.02	0.46	0.76	7.87	0.21	0.04	0.01	99.28	7.8
RT87-29	60.11	22.26	0.99	3.47	1.35	1.01	9.30	0.16	0.03	0.01	98.70	7.0
RT87-30	59.74	23.63	1.09	4.41	1.23	0.94	7.87	0.26	0.05	0.01	99.23	8.6
RT88-2	60.52	24.51	0.89	3.77	0.41	0.84	7.85	0.20	0.07	0.01	99.07	7.8
RT88-8	60.00	24.24	0.98	4.40	0.46	0.83	7.62	0.54	0.11	0.01	99.18	8.0

* S.N. = sample number

† oxide percentage shown in a LOI free basis

§ LOI = loss on ignition

Appendix 17. Methodology for Ar-Ar Analysis

Methods for Ar-Ar analysis is described here, with references listed at the end.

Selected samples were processed for $^{40}\text{Ar}/^{39}\text{Ar}$ analysis of phlogopite phenocrysts by standard mineral separation techniques, including hand-picking apparently unaltered crystals in the size range 0.5 to 1 mm. Individual mineral separates were loaded into aluminum foil packets along with a single grain of Fish Canyon Tuff Sanidine (FCT-SAN) to act as flux monitor (apparent age = 28.02 ± 0.28 Ma; Renne et al., 1998). The sample packets were arranged radially inside an aluminum can. The samples were then irradiated for 12 hours at the research reactor of McMaster University in a fast neutron flux of approximately 3×10^{16} neutrons/cm².

Upon return from the reactor, samples were split into several aliquots and loaded into individual 1.5 mm-diameter holes in a copper planchet. The planchet was then placed in the extraction line and the system evacuated. Heating of individual sample aliquots in steps of increasing temperature was achieved using a Merchantek MIR10 10W CO₂ laser equipped with a 2 mm x 2 mm flat-field lens. The released Ar gas was cleaned over getters for ten minutes, and then analyzed isotopically using the secondary electron multiplier system of a VG3600 gas source mass spectrometer; details of data collection protocols can be found in Villeneuve and MacIntyre (1997) and Villeneuve et al. (2000). Neutron flux gradients throughout the sample canister were evaluated by analyzing the FCT-san flux monitors included with each sample packet and interpolating a linear fit against calculated J-factor and sample position. The error on individual J-factor values is conservatively estimated at $\pm 0.6\%$ (2 σ). Because the error associated with the J-factor is systematic and not related to individual analyses, correction for this uncertainty is not

applied until calculation of dates from isotopic correlation diagrams (Roddick, 1988). Excess ^{40}Ar was not observed in any of the samples and, therefore, all regressions are assumed to pass through the $^{40}\text{Ar}/^{36}\text{Ar}$ value for atmospheric air (295.5). All errors are quoted at the 2σ level of uncertainty.

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Appendix 18. Ar-Ar data, phlogopites from Russell K-bentonite

Power	* Volume $^{39}\text{Ar} \times 10^{-11}$ (cc)	$^{36}\text{Ar}/^{39}\text{Ar}$	$^{37}\text{Ar}/^{39}\text{Ar}$	$^{38}\text{Ar}/^{39}\text{Ar}$	$^{40}\text{Ar}/^{39}\text{Ar}$	% ^{40}Ar	* $^{40}\text{Ar}/^{39}\text{Ar}$	$f_{39}^{\dagger}$ (%)	Apparent Age Ma §
<u>RB Phlogopite; J=0.00289650Billings Formation* (Z7700; 45.3132°N 75.3904°E)</u>									
<u>Aliquot: A</u>									
2.4	0.2208	0.3660±0.0182	0.098±0.016	0.083±0.015	174.886±7.246	67.3	57.196±4.447	0.8	276.55±19.94
3.0	1.0956	0.0023±0.0028	0.014±0.003	0.049±0.011	80.354±0.958	0.9	79.609±1.012	4.2	374.33±4.30
3.9	1.7877	0.0010±0.0018	0.013±0.002	0.062±0.011	94.378±0.816	0.3	94.054±0.849	6.8	434.65±3.49
4.6	1.5808	0.0014±0.0019	0.027±0.002	0.066±0.011	95.930±0.780	0.5	95.478±0.815	6.0	440.49±3.34
5.5	1.2927	0.0006±0.0024	0.015±0.003	0.066±0.011	96.348±0.917	0.3	96.104±0.968	4.9	443.05±3.96
12.0	1.165	0.0010±0.0027	0.017±0.002	0.067±0.011	97.653±0.986	0.4	97.288±1.044	4.4	447.88±4.26
<u>Aliquot: B</u>									
3.0	1.5779	0.0078±0.0020	0.029±0.003	0.032±0.011	52.559±0.461	4.5	50.188±0.515	6.0	244.86±2.35
4.6	3.1811	0.0019±0.0010	0.008±0.001	0.030±0.011	65.579±0.347	0.9	64.982±0.370	12.1	311.12±1.63
5.5	1.5611	0.0007±0.0020	0.015±0.002	0.049±0.011	76.495±0.869	0.3	76.246±0.901	6.0	359.99±3.86
12.0	0.6389	0.0016±0.0048	0.030±0.004	0.057±0.012	79.305±1.174	0.7	78.714±1.341	2.4	370.53±5.71

* As measured by laser in % of full nominal power (10W)

† Fraction ^{39}Ar as percent of total run

§ Errors are analytical only and do not reflect error in irradiation parameter J

Nominal J, referenced to FCT-SAN=28.02 Ma (Renne et al., 1998)

Note: All uncertainties quoted at 2σ level

Appendix 18. (cont.)

Power [*]	Volume ³⁹ Ar x10 ⁻¹¹	³⁶ Ar/ ³⁹ Ar	³⁷ Ar/ ³⁹ Ar	³⁸ Ar/ ³⁹ Ar	⁴⁰ Ar/ ³⁹ Ar	% ⁴⁰ Ar ATM	⁴⁰ Ar/ ³⁹ Ar	f ₃₉ [†] (%)	Apparent Age Ma [§]
(cc)									
<u>RB Phlogopite; J=.00289650Billings Formation[#] (Z7700; 45.3132°N 75.3904°E)</u>									
<u>Aliquot: C</u>									
3.0	0.6813	0.0390±0.0050	0.035±0.002	0.065±0.011	71.482±1.064	16.7	59.546±1.288	2.6	287.06±5.74
4.6	2.5896	0.0072±0.0013	0.012±0.001	0.031±0.011	64.727±0.392	3.4	62.551±0.425	9.9	300.40±1.88
5.5	1.1137	0.0018±0.0027	0.042±0.002	0.052±0.011	84.239±0.877	0.7	83.641±0.940	4.2	391.37±3.96
12.0	2.2754	0.0007±0.0014	0.056±0.002	0.063±0.011	91.250±0.605	0.3	91.020±0.641	8.7	422.15±2.65
<u>Aliquot: D</u>									
3.0	0.5135	0.1747±0.0084	0.068±0.044	0.068±0.012	107.620±2.356	49.9	53.970±2.174	2.0	262.03±9.83
4.6	1.1912	0.0102±0.0026	0.066±0.020	0.030±0.011	65.046±0.660	4.8	61.933±0.715	4.5	297.67±3.17
5.5	0.6994	0.0053±0.0046	0.101±0.032	0.037±0.012	84.059±1.421	2.0	82.367±1.568	2.7	386.00±6.62
12.0	1.654	0.0018±0.0019	0.035±0.019	0.059±0.011	88.549±0.820	0.7	87.970±0.864	6.3	409.49±3.60

* As measured by laser in % of full nominal power (10W)

† Fraction ³⁹Ar as percent of total run

§ Errors are analytical only and do not reflect error in irradiation parameter J

Nominal J, referenced to FCT-SAN=28.02 Ma (Renne et al., 1998)

Note: All uncertainties quoted at 2σ level

Appendix 18. (cont.)

Power [*]	Volume [*]	³⁹ Ar x10 ⁻¹¹	³⁶ Ar/ ³⁹ Ar	³⁷ Ar/ ³⁹ Ar	³⁸ Ar/ ³⁹ Ar	⁴⁰ Ar/ ³⁹ Ar	% ⁴⁰ Ar ATM	* ⁴⁰ Ar/ ³⁹ Ar	f ₃₉ [†] (%)	Apparent Age Ma [§]
(cc)										
RB Phlogopite; J=.00289650Billings Formation [#] (Z7700; 45.3132°N 75.3904°E)										
<u>Aliquot: E</u>										
3.0		0.3837	0.0288±0.0042	0.218±0.061	0.042±0.012	64.022±0.968	13.3	55.497±1.426	1.5	268.92±6.42
4.6		0.7013	0.0019±0.0022	0.076±0.058	0.056±0.011	89.110±0.833	0.6	88.536±1.010	2.7	411.84±4.20
5.5		0.2088	0.0046±0.0071	0.132±0.159	0.068±0.013	92.178±1.704	1.5	90.786±2.513	0.8	421.18±10.40
12.0		0.1325	0.0054±0.0125	0.315±0.181	0.086±0.018	92.649±3.562	1.8	91.024±4.872	0.5	422.16±20.15
<u>Aliquot: F</u>										
3.0		0.355	0.0801±0.0066	0.303±0.093	0.070±0.013	83.828±1.322	28.2	60.162±2.106	1.3	289.80±9.37
4.6		0.4605	0.0038±0.0030	0.140±0.060	0.027±0.012	77.715±1.303	1.5	76.585±1.500	1.7	361.44±6.42
5.5		0.1826	-0.0001±0.0000	0.352±0.120	0.052±0.014	92.808±1.938	-1.2	93.914±1.955	0.7	434.07±8.03
12.0		0.3979	0.0017±0.0029	0.235±0.051	0.047±0.011	73.949±0.908	0.7	73.430±1.154	1.4	347.90±4.97

* As measured by laser in % of full nominal power (10W)

† Fraction ³⁹Ar as percent of total run

§ Errors are analytical only and do not reflect error in irradiation parameter J

Nominal J, referenced to FCT-SAN=28.02 Ma (Renne et al., 1998)

Note: All uncertainties quoted at 2σ level

Appendix 18. (cont.)

Power *	Volume $^{39}\text{Ar} \times 10^{11}$	$^{36}\text{Ar}/^{39}\text{Ar}$	$^{37}\text{Ar}/^{39}\text{Ar}$	$^{38}\text{Ar}/^{39}\text{Ar}$	$^{40}\text{Ar}/^{39}\text{Ar}$	$\%^{40}\text{Ar}$	$^{40}\text{Ar}/^{39}\text{Ar}$	$\text{f}_{39}^{\dagger}$	Apparent Age
	(cc)					ATM		(%)	$\text{Ma}^{\S}$
RT Phlogopite: J=00290220Billings Formation [#] (Z7657; 45.3132°N 75.3904°E)									
<u>Aliquot: A</u>									
3.0	2.2027	0.0052±0.0012	0.011±0.001	0.050±0.011	73.495±0.587	2	72.036±0.616	4.4	342.50±2.67
3.9	3.1977	0.0008±0.0008	0.011±0.001	0.057±0.011	93.088±0.534	0.2	92.922±0.549	6.4	430.75±2.26
4.6	5.4968	0.0002±0.0004	0.006±0.001	0.060±0.011	95.854±0.595	0	95.817±0.601	11.0	442.65±2.46
5.0	2.7617	0.0007±0.0009	0.010±0.002	0.063±0.011	97.032±0.745	0.1	96.907±0.763	5.5	447.11±3.12
6.0	2.8177	0.0005±0.0010	0.004±0.002	0.066±0.011	96.819±0.649	0.1	96.743±0.686	5.6	446.43±2.81
12.0	2.4583	0.0006±0.0010	0.009±0.001	0.061±0.011	96.874±0.653	0.1	96.760±0.674	4.9	446.51±2.76
<u>Aliquot: B</u>									
3.0	1.8144	0.0109±0.0021	0.022±0.001	0.035±0.011	61.272±0.502	5.6	57.838±0.519	3.6	279.94±2.33
3.9	1.8721	0.0034±0.0021	0.017±0.002	0.053±0.011	79.105±0.636	1.5	77.924±0.672	3.7	367.81±2.87
4.2	0.8887	0.0019±0.0043	0.031±0.003	0.076±0.012	87.306±1.152	1.1	86.366±1.216	1.8	403.51±5.09
5.0	2.3407	0.0000±0.0019	0.040±0.002	0.072±0.011	90.079±0.826	0.2	89.940±0.853	4.7	418.41±3.54
6.0	2.2764	0.0003±0.0017	0.111±0.003	0.093±0.012	93.871±0.573	0.3	93.632±0.597	4.5	433.67±2.46
12.0	4.1385	0.0001±0.0008	0.046±0.003	0.087±0.011	96.819±0.495	0	96.776±0.509	8.3	446.57±2.08

* As measured by laser in % of full nominal power (10W)

† Fraction ^{39}Ar as percent of total run

§ Errors are analytical only and do not reflect error in irradiation parameter J

Nominal J, referenced to FCT-SAN=28.02 Ma (Renne et al., 1998)

Note: All uncertainties quoted at 2σ level

Appendix 18. (cont.)

Power*	Volume $^{39}\text{Ar} \times 10^{-11}$ (cc)	$^{36}\text{Ar}/^{39}\text{Ar}$	$^{37}\text{Ar}/^{39}\text{Ar}$	$^{38}\text{Ar}/^{39}\text{Ar}$	$^{40}\text{Ar}/^{39}\text{Ar}$	% ^{40}Ar ATM	* $^{40}\text{Ar}/^{39}\text{Ar}$	$f_{39}^{\dagger}$ (%)	Apparent Age Ma §
<u>RT Phlogopite; J=00290220Billings Formation# (Z7657; 45.3132°N 75.3904°E)</u>									
<u>Aliquot: C</u>									
3.0	0.5279	0.0133±0.0017	0.013±0.004	0.064±0.011	80.264±0.836	4.9	76.328±0.872	1.1	360.99±3.74
3.9	3.3323	0.0012±0.0005	0.004±0.001	0.063±0.011	93.290±0.386	0.4	92.943±0.407	6.7	430.83±1.68
4.2	1.5178	0.0012±0.0011	0.004±0.002	0.064±0.011	94.913±0.758	0.4	94.549±0.807	3.0	437.45±3.32
5.0	1.9994	0.0009±0.0006	0.012±0.002	0.069±0.011	95.375±0.347	0.3	95.095±0.379	4.0	439.69±1.56
6.0	1.9238	0.0006±0.0008	0.002±0.002	0.064±0.011	96.036±0.791	0.2	95.851±0.822	3.8	442.79±3.37
12.0	1.1054	0.0029±0.0009	0.005±0.004	0.072±0.011	96.249±0.518	0.9	95.380±0.546	2.2	440.85±2.24
<u>Aliquot: D</u>									
15.0	0.4974	0.0164±0.0030	0.528±0.131	0.074±0.011	80.242±0.899	6.1	75.377±1.168	1.0	356.90±5.02
3.0	0.9449	0.0449±0.0017	0.214±0.060	0.037±0.011	73.127±0.671	18.2	59.853±0.727	1.9	288.95±3.24
3.9	1.2662	0.0039±0.0007	0.069±0.020	0.048±0.060	84.438±4.152	1.4	83.280±4.097	2.5	390.54±17.29
4.2	0.9463	0.0053±0.0011	0.117±0.040	0.048±0.011	87.518±3.423	1.8	85.937±3.370	1.9	401.71±14.13
5.0	0.1081	0.0286±0.0135	0.704±0.384	0.039±0.017	81.498±2.748	10.4	73.005±4.389	0.2	346.69±18.96
6.0	0.9462	0.0052±0.0010	0.093±0.035	0.054±0.011	89.249±1.639	1.7	87.713±1.625	1.9	409.14±6.78
12.0	2.7315	0.0014±0.0004	0.027±0.021	0.058±0.011	94.815±1.158	0.4	94.399±1.155	5.5	436.83±4.75

* As measured by laser in % of full nominal power (10W)

† Fraction ^{39}Ar as percent of total run

§ Errors are analytical only and do not reflect error in irradiation parameter J

Nominal J, referenced to FCT-SAN=28.02 Ma (Renne et al., 1998)

Note: All uncertainties quoted at 2σ level

Appendix 19. Chemical composition of phlogopites, Russell Bed

Major Oxides	Sample													AV†	SD§	SE*
	B-2-1	B-2-2	B-2-3	B-2-4	A-1-1	B-2-1	B-1-1	A-2-1	A-3-1	DH- B-1	DH- B-2	G-1-3	DH- B-6			
SiO ₂	36.95	36.98	36.95	36.79	36.92	37.17	37.29	36.71	36.98	37.19	36.74	37.53	36.68	36.99	0.25	0.07
Al ₂ O ₃	14.11	14.33	14.19	13.86	13.99	14.68	14.12	13.67	14.00	14.02	14.08	15.06	14.14	14.17	0.36	0.10
TiO ₂	5.52	5.59	5.41	5.47	5.32	5.32	5.45	5.16	5.53	5.88	5.63	5.15	5.74	5.47	0.21	0.06
Cr ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FeO	11.84	12.07	12.05	12.36	12.51	13.97	13.41	11.17	12.46	11.77	12.09	12.48	12.15	12.33	0.71	0.20
MgO	15.99	15.99	16.07	15.97	15.76	14.60	15.31	15.93	15.79	16.29	16.02	16.09	16.12	15.84	0.44	0.12
MnO	0.12	0.11	0.15	0.18	0.20	0.27	0.33	0.19	0.18	0.12	0.14	0.18	0.19	0.18	0.06	0.02
NiO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K ₂ O	8.46	8.18	8.23	8.16	8.21	8.04	8.38	7.89	8.35	8.33	8.46	8.16	8.56	8.26	0.19	0.05
CaO	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.03	0.00	0.01	0.01	0.00
Na ₂ O	0.66	0.69	0.63	0.66	0.59	0.45	0.61	0.65	0.60	0.63	0.61	0.55	0.62	0.61	0.06	0.02
BaO	1.77	1.82	1.79	1.66	1.60	1.29	1.67	1.37	1.45	1.90	1.93	1.30	1.80	1.64	0.22	0.06
F	0.96	0.97	0.99	0.92	0.89	0.92	0.99	1.02	1.08	0.83	0.93	1.11	0.85	0.96	0.08	0.02
Cl	0.02	0.03	0.02	0.03	0.04	0.05	0.03	0.03	0.03	0.02	0.03	0.01	0.02	0.03	0.01	0.00
Total	96.40	96.76	96.48	96.09	96.03	96.76	97.59	93.79	96.45	96.98	96.70	97.65	96.87	96.50	0.95	0.26

† AV= average; § SD= standard deviation; * SE= standard error

† AV= average; § SD= standard deviation; * SE= standard error

Appendix 20. LREE in apatites from Ordovician
Kbentonites, eastern Ontario and
North America

K-bentonite	LREE			
	Ce	Sm	La	Nd
	(ppm)	(ppm)	(ppm)	(ppm)
Russell	1195	517	597	1243
	1494	992	640	1029
	1110	690	469	257
	1238	517	512	857
	1238	1038	341	600
Millbrig [†]	1950	432	602	1785
	2100	488	635	1820
Deicke [§]	3209	431	1343	2452
	2460	344	870	1770
	2675	382	905	1830
	2990	410	1030	1990
†, § after Samson (1988)				

Appendix 21. Geochemistry, Type A ooids, Russell GSC#2
(eastern Ontario)

Sample No.	Sr (ppm)	Mg (ppm)	Mn (ppm)	Fe (ppm)	MgCO ₃ (mol%)
RU31-1-1	0	10000	5000	8700	2.51
RU31-1-2	0	9700	4500	7300	2.39
RU31-1-3	700	9800	4100	3500	2.27
RU31-1-4	400	10500	4100	5900	2.63
RU31-2-1	300	9000	5000	4600	2.19
RU31-2-2	400	9300	4300	2900	2.22
RU31-2-3	500	9700	4800	3600	2.26
RU31-2-4	300	9400	4000	2200	2.34
RU31-2-5	200	9200	4400	3900	2.27
RU31-3-1	400	9600	4400	7400	2.39
RU31-3-2	200	8400	5000	6400	2.03
RU31-3-3	200	10500	5300	8800	2.52
RU31-3-4	200	9100	4000	4300	2.23
RU31-3-5	400	9200	4800	3000	2.17
RU31-5-1	300	10900	3900	6000	2.68
RU31-5-2	500	8800	5200	8700	2.13
RU31-5-5	400	9200	5700	10400	2.21
RU31-6-1	300	10200	5600	6100	2.44
RU31-6-2	300	9900	4800	4200	2.40
RU31-10-	500	10400	5900	5600	2.52
RU31-10-	200	9400	4400	8700	2.36
RU33-1-1	300	11100	8700	4300	2.79
RU33-1-3	500	10900	9600	3600	2.79
RU33-3-1	300	11200	14000	5100	2.57

Appendix 21. (cont.)

Sample No.	Sr (ppm)	Mg (ppm)	Mn (ppm)	Fe (ppm)	MgCO ₃ (mol%)
RU33-3-2	300	10500	8400	7300	2.57
332O1a	0	10000	9100	6000	2.50
332O1b	0	10400	9600	4400	2.54
828O1a	0	11000	7200	4900	2.69
828O1b	0	9100	5500	6300	2.28
828O1c	900	8700	4200	600	2.10
828O1d	200	10800	4700	4800	2.56
828O1e	0	11500	5200	11500	2.97
828O1f	200	10300	4000	5200	2.55
828O1g	500	4400	4900	1100	1.06
828O1i	300	12300	5200	0	2.87
RU33-3-5	200	21600	15100	23100	5.09
RU33-3-7	500	9600	10700	2800	2.26
RU33-3-8	500	11000	12000	2100	2.66
RU33-3-1	300	9500	15800	12400	2.27
RU31-10-	200	2500	3500	400	0.62
RU31-10-	300	2700	2900	1000	0.68
RU31-11-	800	10000	2800	2100	2.44
RU31-11-	1100	9200	3600	4300	2.22
RU31-11-	300	10700	4000	9500	2.57
31201a	0	9900	4500	6900	2.54
31201a	200	8800	4400	7700	2.17
31201b	0	13800	5000	19500	3.65
1004O1a	0	8900	5400	8200	2.24
1004O1b	0	8600	4100	6000	2.10
1004O1c	200	7400	4900	4800	1.80
1004O2a	0	7700	5100	6300	1.93
1004O2a	0	7600	5100	5900	1.81
1004O2c	100	7800	5200	5900	1.95

Appendix 22. Geochemistry, Type A ooids, from outcrop (O) and core (C), southwestern Ontario

Sample No.	Sr (ppm)	Mg (ppm)	Mn (ppm)	Fe (ppm)	MgCO ₃ (mol%)
<i><u>Streetsville (C)</u></i>					
ST549-1A	0	10000	4400	1100	2.31
ST549-1B	0	9200	3700	5200	2.30
ST549-1C	300	10400	4300	8000	2.55
ST549-2A	500	8200	3800	2100	1.95
ST549-2B	900	9400	2400	500	2.28
ST549-2C	700	9000	3700	1600	2.18
ST596-1A	0	8800	3200	5600	2.13
ST596-1B	0	8400	4000	5300	2.10
ST596-2A	0	8900	5000	6500	2.18
ST596-2B	0	6800	4000	3600	1.64
<i><u>Bronte Creek (O)</u></i>					
BRT1-1A	300	12000	9700	6800	3.10
BRT1-1B	100	10700	10500	5900	2.82
BRT1-1C	500	9400	28900	1500	2.23
BRT1-2A	0	12200	3800	12000	3.41
BRT1-2B	0	10500	6500	6200	2.71
<i><u>Warton (C)</u></i>					
W4857-1A	0	9300	700	3300	2.24
W4857-1B	0	9200	2000	3900	2.20
W4857-2A	0	9200	1900	3300	2.25
W4857-2B	300	10500	2200	1600	2.54
W4857-2a	300	10300	1400	4300	2.52
W4857-2b	0	10100	1400	5000	2.49
W4857-2c	0	10200	1500	10400	2.59

Appendix 23. Geochemistry, brachiopods from cores,
southern Ontario

Sample No.	Sr (ppm)	Mg (ppm)	Mn (ppm)	Fe (ppm)	MgCO ₃ (mol%)
<i><u>Russell GSC#2</u></i>					
332BR1a	1800	7200	700	300	1.80
332BR1b	1700	7100	500	0	1.83
332BR1c	1700	8000	1600	1800	1.95
332BR1d	0	10200	8200	4500	2.67
332BR1e	0	9600	9600	3700	2.51
332BR1f	0	10700	9100	3500	2.73
332BR1g	0	10100	8400	5100	2.60
3120BR1a	1300	16500	1700	1000	2.26
3120BR1a	200	11000	3300	1800	2.70
3120BR1b	500	8300	3600	2900	2.06
312BR2a	1000	6200	900	600	1.49
312BR2b	1200	6700	800	1400	1.62
336BV1a	100	11300	12200	200	2.74
336BV1b	0	9800	10600	3700	2.36
336BV1c	0	14000	11900	6100	3.46
<i><u>Streetsville</u></i>					
ST549BRA	1700	10600	0	500	3.13
ST549BRB	2100	11800	300	400	2.67
ST549BRC	1700	12600	900	300	2.92

Appendix 24. Geochemistry, Type B ooids from core,
southwestern Ontario

Sample No.	Sr (ppm)	Mg (ppm)	Mn (ppm)	Fe (ppm)	MgCO ₃ (mol%)
<i>Meaford</i>					
C-2-2a	1700	3400	400	3500	0.89
C-2-2b	2800	2500	600	3700	0.65
CW-1a	0	4900	700	900	1.25
CW-1b	0	5400	100	300	1.34
CW-1c	0	5300	200	600	1.33
CW-1d	0	5000	300	900	1.26
CW-2a	0	4900	500	100	1.25
CW-2b	0	5600	0	500	1.42
CW-2c	100	5700	100	300	1.46
CW-2d	0	5100	100	900	1.35
CB-1a	0	5200	100	1000	1.30
CB-1b	0	5800	300	3500	1.51
CB-1c	0	6300	600	5200	1.66
CB-1d	0	5700	300	1600	1.57
CB-2a	0	5000	600	600	1.28
CB-2b	0	6600	200	300	1.68
CB-2c	0	6600	500	300	1.69

Appendix 24. (cont.)

Sample No.	Sr (ppm)	Mg (ppm)	Mn (ppm)	Fe (ppm)	MgCO ₃ (mol%)
<u>Lambton</u>					
L3-1	300	5700	400	1600	1.44
L2-1a	200	6200	100	1200	1.52
L2-1b	300	8900	200	0	2.08
L2-1c	100	6800	900	1400	1.65
L2-1d	0	6900	400	900	1.74
L2-3a	500	5400	0	700	1.34
L2-3b	100	5200	300	500	1.27
L2-3c	0	6900	1300	3100	1.78
L2-3c	300	6100	300	500	1.47
L2-4a	0	2300	600	1800	0.57
L2-4b	0	3800	1400	6300	0.95
L2-4c	0	3200	200	2500	0.79
L2-4d	0	3200	600	3000	0.78
L1-3-1a	200	6400	300	600	1.56
L1-3-1b	200	7400	500	0	1.78
L1-3-1c	500	8700	0	700	2.04
L1-3-1d	300	7000	800	100	1.72
L1-2a	400	6400	400	1400	1.57
L1-2b	200	5900	700	1000	1.44
L1-2c	100	4800	0	1300	1.18
L1-2d	0	6100	400	7100	1.70

Appendix 24. (cont.)

Sample No.	Sr (ppm)	Mg (ppm)	Mn (ppm)	Fe (ppm)	MgCO ₃ (mol%)
<i><u>Lambton</u></i>					
L3-2	0	6400	0	3900	1.65
L3-1C	0	7500	400	1200	1.82
L2-2a	200	6900	200	600	1.68
L2-2b	100	6900	100	700	1.71
L2-2c	100	7100	400	1400	1.78
L2-2d	200	7600	0	500	1.88
L2-5-1a	600	9500	1000	300	2.28
L2-5-1b	300	8200	1000	500	2.05
L2-5-1c	200	7600	1500	900	1.89
L3-2-1a	0	9000	500	4700	2.34
L3-2-1b	0	7500	800	6800	1.98
L3-3-1a	0	4400	1000	6100	1.13
L3-3-1b	300	5000	500	2700	1.23
L1-1a	0	7400	3900	600	1.82
L1-1b	100	7000	3100	100	1.76
L1-1c	0	7500	2000	700	1.89
L1-1d	100	6800	2500	800	1.68

Appendix 25. Geochemistry, reference brachiopods

Sample No.	Sr (ppm)	Mg (ppm)	Mn (ppm)	Fe (ppm)
<i>Popp et al., 1986</i>				
Ord-1-1-SL-1	1933	2437	42	189
Ord-1-2-SL-1	1087	3342	136	163
Ord-2-NL-1	1303	2981	258	387
Ord-4-NL-1	1300	3700	167	267
Ord-5-1-NL-1	1405	1653	41	62
Ord-5-2-NL-1	1563	1760	33	165
Ord-5- 3- NL-1	1726	2842	50	114
Ord-5-4-NL-1	1775	2150	25	88
Ord-6-WB	2102	3056	369	278
<i>Marshall et al., 1986</i>				
ARGORD/10	1145	2504	536	815
ARGORD/11	1188	3455	613	1408
ARGORD/12	814	3619	2229	4959
ARGORD/13	1040	2759	735	1280
ARGORD/14	1181	2612	361	686
ARGORD/15	1160	2449	404	744
ARGORD/16	1171	2521	444	760
ARGORD/19	1180	2299	184	262
ARGORD/18	1150	3781	355	1090

Appendix 26. Stable isotope (C,O) compositions of Type A ooids from cores, southern Ontario

Sample No.	Mineral	$\delta^{18}\text{O}_{\text{VSMOW}}$ (‰)	$\delta^{18}\text{O}_{\text{VPDB}}$ (‰)	$\delta^{13}\text{C}_{\text{VPDB}}$ (‰)	Comments
<i>Warton</i>					
W-343-O-D	calcite	25.96	-4.81	+1.10	ooid, dark
W-485/8-O	calcite	26.31	-4.46	+0.59	ooid
<i>Russell GSC #2</i>					
R-79-O	calcite	21.76	-8.72	+0.41	ooid
R85/9-O-CRF	calcite	17.88	-12.64	-1.62	ooid, radial fibrous, cortex
R85/9-O-WRF	calcite	22.14	-8.51	+0.41	ooid, radial fibrous, whole
R-32-O	calcite	21.96	-8.68	+0.67	ooid
R-90/10	calcite	22.07	-8.58	+0.67	ooid
R91/9-O	calcite	20.01	-10.57	-0.10	ooid
R95-OD	calcite	21.45	-9.18	+0.53	ooid, dark
R95-OW	calcite	20.43	-10.16	-0.11	ooid, white
R103/8	calcite	21.50	-9.13	+0.24	ooid
<i>Streetsville</i>					
ST-56-O	calcite	24.68	-6.04	+0.39	ooid

Appendix 27. Stable isotope (C,O) compositions of Type B ooids from core, southern Ontario

Sample No.	Mineral	$\delta^{18}\text{O}_{\text{VSMOW}}$ (‰)	$\delta^{18}\text{O}_{\text{VPDB}}$ (‰)	$\delta^{13}\text{C}_{\text{VPDB}}$ (‰)	Comments
C1-D	calcite	27.56	-3.25	+3.31	ooid
C1-O-W	calcite	26.17	-4.60	+5.31	ooid, white
C1-D	calcite	27.56	-3.25	+3.31	ooid
L-O-B	calcite	27.78	-3.04	+3.96	black
L-O-W1	calcite	27.38	-3.42	+6.59	white
L-O-W2	calcite	26.68	-3.93	+6.64	white
L-O-dol	calcite	27.54	-3.27	+3.82	

Appendix 28. Stable isotope (C,O) brachiopods and cement from cores, southern Ontario

Sample No.	Mineral	$\delta^{18}\text{O}_{\text{VSMOW}}$ (‰)	$\delta^{18}\text{O}_{\text{VPDB}}$ (‰)	$\delta^{13}\text{C}_{\text{VPDB}}$ (‰)	Comments
<u>Russell GSC #2</u>					
RT-580-BR-WH	calcite	25.44	-5.31	-0.10	brachiopod
RT-580-BR	calcite	26.21	-4.56	-0.17	brachiopod
RT-612-BR	calcite	24.60	-6.12	-1.40	brachiopod
R91/9-BR	calcite	26.70	-4.08	+0.40	brachiopod
R79-C-BLKY	calcite	16.79	-13.69	-2.34	cement, equigranular, blocky
R88/2-C4	calcite	24.82	-5.91	+1.52	late calcite vug replacement
R79-C-MLKY	calcite	22.96	-7.71	-0.24	cement, milky white
R103-C-BLKY	calcite	24.42	-6.29	+0.02	cement, equigranular, blocky
R107/8-WHRK	calcite	22.03	-8.61	+0.26	limestone, minor dolomite
R88/2-WHRK	calcite	23.24	-7.44	+0.62	limestone, some clay
<u>Warton</u>					
W-485-C	calcite	25.10	-5.63	+0.02	cement, dark-matrix
W-485/8-BR	calcite	26.54	-4.24	+0.71	brachiopod
<u>Streetsville</u>					
ST-3-BLK	calcite	26.02	-4.74	-0.24	cement, blocky, within brachiopod

Appendix 29. Stable isotope (C,O) compositions of brachiopods and whole rock,
from Russell GSC#2, eastern Ontario

Sample No.	Mineral	$\delta^{18}\text{OVSMOW}$ (‰)	$\delta^{18}\text{OVPDB}$ (‰)	$\delta^{13}\text{CVPDB}$ (‰)	Comments
R79-BR-WH	calcite	(-38.45)	-7.32	-5.11	brachiopod
R79-BR-FIB	calcite	19.59	-10.98	-1.99	brachiopod, fibrous
R91/9-BR	calcite	26.70	-4.08	+0.40	brachiopod
R79-WHRK	calcite	23.34	-7.34	+0.34	limestone, some clay

Appendix 30. Stable isotope (C,O) composition of reference
Ordovician brachiopods

Sample No.	$\delta^{18}\text{O}_{\text{VPDB}}$ (‰)	$\delta^{13}\text{C}_{\text{VPDB}}$ (‰)
<u><i>Popp et al. 1986</i></u>		
Ord-1-1-SL-1	-4.16	1.38
Ord-1-2-SL-1	-4.81	0.89
Ord-1-3-NL-1	-3.83	1.16
Ord-2-NL-1	-3.97	1.42
Ord-4-NL-1	-4.99	0.23
Ord-5-1-NL-1	-4.24	0.79
Ord-5-2-NL-1	-4.36	0.63
Ord-5- 3- NL-1	-4.71	0.32
Ord-5-4-NL-1	-4.34	0.36
<u><i>Wadeligh and Veizer, 1992</i></u>		
Ord-3(a)	-4.47	-0.14
Ord-12(b)	-4.17	0.52
Ord-3(b)	-4.41	0.57
Ord-13(b)	-4.01	0.20
Ord-10(a)	-4.60	-0.34
Ord-11(d)	-4.33	-0.26
Ord-21-1	-4.60	-0.40
Ord-7	-4.46	1.24
Ord-19(b)	-4.75	-0.99
Ord-EB-14	-3.08	1.01
Ord-1(a)	-4.96	-0.18
Ord-20-2	-4.88	-0.66
Ord-6	-4.80	0.84
Ord-8(a)	-4.90	0.37
Ord-12(a)	-5.40	0.55
Ord-13(a)	-4.80	0.67
Ord-14(a)	-5.30	0.42
Ord-18(b)	-4.60	-0.01
Ord-19(a)	-4.80	0.69