DOLOMITIZATION OF THE HATCH HILL ARENITES

AND

THE BURDEN IRON ORE

A thesis presented to the Faculty

of the State University of New York

at Albany

in partial fulfillment of the requirements

for the degree of

Master of Science

School of Science and Mathematics

Department of Geological Sciences

Peter Michael Hofmann

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ABSTRACT

The Taconic allochthon is a sequence of Cambrian or Precambrian to Ordovician rocks. It is composed of predominantly deep water argillaceous and subordinate arenaceous and calcareous rocks that were deposited on the continental rise and slope. During the Ordovician, the sediments which were earlier deposited in the slope-rise environment were incorporated into the accretionary prism of an island arc that approached from the east, and subsequently overthrust the carbonate platform.

The Hatch Hill Formation is part of the Taconic sequence. It consists of dominantly black-gray slates with minor amounts of sandstones and carbonates. Previous workers have recognized the presence of dolomite and a siderite ore (the Burden Iron Ore) in these sandstones. The stratigraphic position of the siderite ore was not clear prior to this study.

This study showed that the Burden Iron Ore is the basal part of the Hatch Hill Formation in the area studied, based on lithologic comparison with the northern Taconic stratigraphy. It conformably overlies the Bomoseen Formation. The contact between the Bomoseen Formation and the Hatch Hill Formation is marked by a disconformity that has not been noted elsewhere in the Taconics.

The origin of the iron ore is closely related to the origin of the dolomite of the Hatch Hill Formation. It can be demonstrated that both phases occur as cements that

formed after the deposition of the Hatch Hill arenites. The cements formed as a by-product of the decay and fermentation of organic matter that was probably deposited in the black-gray shales of the Hatch Hill Formation. Isotopic evidence and geochemical considerations show that the siderite cements formed after sulfate reduction was completed and that the development of dolomite cements most likely took place in the lower part of the zone of methanogenesis. Paleotemperatures determined from oxygen isotope analyses indicate that the dolomite cements probably formed at a temperature of approximately 75°C, if the pore fluid was not affected by meteoric or brine waters. This would imply a depth of formation of 2-3 km, if present day geothermal gradients for a passive continental margin sequence are assumed. The formation of dolomite therefore took place during or after the deposition of the Pawlet Formation (flysch sequence).

State University of New York at Albany

School of Science and Mathematics

Department of Geological Sciences

The thesis for the master's degree submitted by

Peter Michael Hofmann

under the title

DOLOMITIZATION OF THE HATCH HILL ARENITES

AND

THE BURDEN IRON ORE

has been read by the undersigned. It is hereby recommended for acceptance by the Faculty with credit to the amount of six semester hours.

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ACKNOWLEDGEMENTS

It is virtually impossible to adequately thank and acknowledge everybody who contributed to the completion of this thesis. I want to thank Bill Kidd for suggesting the topic of this thesis to me and his patience and help during its completion. Charlotte Schreiber and Rick Fairbanks were very helpful. Rich Faribanks analyzed the isotopic data presented in this thesis in his lab at Lamont-Doherty, and Charlotte Schreiber was always willing to discuss all kinds of problems associated with this thesis. I am grateful that Bill Kidd, John Delano and George Putman read my thesis and helped to improve it with many good comments. I especially want to thank John Delano who showed me how to think like a scientist and how to attack scientific problems. I am in debt to the facuties of SUNY Albany and the University of Wurzburg, who taught me most of the geology I know and supported me in many ways.

My friends, especially Thomas Will, Matthias Ohr, Christine Ebel, Mark and Linda Jessell, Greg Norrell, Mauricio Roma and Antonio Teixell had a great part in the completion of this thesis. They helped me in times of frustration with their support and example. They never failed to point out the bright side of life.

I want to express my thanks to Diane Paton for her help and friendship during the two and a half years I stayed at SUNY Albany.

My parents and my family have supported me all the way towards the completion of this thesis. There is no way to adequately express my deep appreciation.

Finally, I want to thank Kay Stone. This thesis could not have been completed without her. Besides her excellent typing, knowledge of geology, and patience in guiding me through the problems of the English language, she was always there to give me the support I needed. I want to thank her very much for her friendship, her caring and patience.

TABLE OF CONTENTS

		Page
Chapter 1.	Introduction to the Thesis	1
	Introduction	1
	Procedure	5
	Fieldwork	5
	Petrography	6
	Cathodoluminescence	7
	Oxygen and Carbon Isotopes	7
Chapter 2.	Dolomitization of the Hatch Hill Arenites	11
	Introduction	11
	Previous Work	14
	Regional Distribution	18
	Stratigraphy	20
	Section Descriptions	24
	Schodack Landing	24
	Browns Pond Formation	24
	Middle Granville Slate	24
	Hatch Hill Formation	26
	Judson Point	34
	Nutten Hook	39
	Stockport Station	39
	Poultney River	40
	Mettawee River	46
	Petrography and Mineralogy	47
	Introduction	47
	Arenites	47
	Breccias	49
	Limestones	52
	Shales	56
	Diagenesis	57
	Introduction	57
	Paragenesis	57
	Authigenic Phases	60
	Silica	60
	Pyrite	67
	Alkali Feldspar and Plagioclase	69
	Calcite	71
	Dolomite	74
	Oxygen and Carbon Isotopes	88
	Results	89
	Calcite	89
	Dolomite/Ankerite	91
	Discussion	91
	Summary and Conclusions	111
	Petrographic Record	111
	Isotopic Record	112
	Conclusions	114

		Page
Chapter 3.	The Burden Iron Ore	116
	Introduction	116
	Previous Work	120
	Stratigraphy	122
	Introduction	123
	Bomoseen Formation	124
	Browns Pond Formation	126
	Hatch Hill Formation	131
	Poultney Formation	137
	Mt. Merino Formation	139
	Discussion	141
	Stratigraphic Position	141
	Regional Distribution	144
	Petrography and Mineralogy	147
	Arenites	147
	Carbonates	151
	Breccias	151
	Origin of the Ore	153
	Previous Work	153
	Discussion	154
	Summary and Conclusions	161
Chapter 4.	Synthesis and Future Research	165
	Stratigraphy and Sedimentology	165
	Mineralogy	166
	Diagenesis	166
	Suggestions for Future Research	168
	Isotopic Studies	168
	Shales	170
References		171
Appendix		180

TABLES

Table		Page
I.	Summary of the Isotopic Composition of the Hatch Hill arenites and limestones.	10
II.	Diagenetic zones and characterizing chemical reactions during burial of organic rich matter (modified from Pisciotto and Mahoney, 1981).	97
III.	Paleotemperatures determined from cements of the Poultney River section.	102

PLATE

Plate: Geological Map of the Mt. Tom Area
(inside back cover)

LIST OF FIGURES

Figure Number		Page
1	Taconic thrust slices (after Zen, 1967).	2
2	Outcrops of the Hatch Hill Formation studied in this thesis.	19
3A	Key for Figures 3B, 11, 14, and 49.	21
3B	Stratigraphic Profile at Schodack Landing.	22
4	Browns Pond Formation at Schodack Landing.	25
5	Breccia within the Middle Granville Slate.	27
6	Contact between Middle Granville Slate and Hatch Hill.	28
7	Parallel laminated sandstones of the Hatch Hill Formation.	30
8	Preferential weathering of individual laminae.	31
9	"Pock Marks" (weathered out clasts in thick arenite bed).	32
10	Shale interlayered with fine grained sandstones in the upper part of the Hatch Hill Formation at Schodack Landing.	33
11	Profile of the Hatch Hill Formation at Judson Point.	35
12	Breccia with bedding parallel clast alignment (Judson Point).	35
13	Irregularly bedded, micritic carbonate beds.	38
14	Profile of the Hatch Hill Formation at Poultney River.	41
15	Parallel laminated sandstones in laminated shales. Typical of thinner bedded parts of the section at Poultney River.	42
16	Disk structures.	44
17	Thick sandstone bed at Poultney River.	45
18	Soft sediment deformation of clasts.	50
19	Photomicrograph of a dolomite clast breccia. Individual clasts are outlined by matrix with higher quartz content. (Field of View: 4 cm wide)	51

Figure Number		Page
20	Phosphatic clast (dark grain on the right) and dolomite matrix. (Field of View: 3.4 mm wide)	53
21	Insoluble residue outlines solution features in a sandy limestone from Judson Point. (Field of View: 2 mm wide)	55
22	Two cases of cross-cutting relationship occurring in the Hatch Hill arenites.	59
23	Dolomite rhombs replacing quartz (Judson Point). (stained) (Field of View: 0.85 mm wide)	61
24	Pyrite inclusions in dolomite cement (Mettawee River). (Field of View: 0.34 mm wide)	62
25	Quartz cement. Old grain boundaries are outlined by fine seams of fluid inclusions. (Field of View: 0.85 mm wide)	63
26	Poikilitic pyrite framboid (Mettawee River). (Field of View: 2 mm wide)	68
27	Euhedral alkali feldspars in micritic and blocky cement (stained) (Schodack Landing). (Field of View: 0.85 mm wide)	70
28	Coexisting micritic and blocky calcite cement (stained) (Schodack Landing). (Field of View: 0.85 mm wide)	72
29	Micritic dolomite grain replaced by zoned dolomite rhombs (stained) (Schodack Landing). (Field of View: 0.85 mm wide)	75
30	Cleavage parallel to the rhombohedral faces in dolomite (stained) (Schodack Landing). (Field of View: 0.85 mm wide)	77
31	Zoned dolomite rhomb (stained) (Judson Point). (Field of View: 0.35 mm)	79
32	Dolomite overgrowth with irregular concentric zones of birefringence (stained) (Judson Point). (Field of View: 0.2 mm wide)	80
33	Mosaic of W-type dolomite (stained) (Poultney River). (Field of View: 0.85 mm wide)	82
34	Summary plot for $\delta^{13}C$ versus $\delta^{18}O$ for samples from the Hatch Hill Formation.	90
35	Stratigraphic height versus $\delta^{13}C$ for the outcrop at Poultney River.	92

Figure Number		Page
36	Reactions and tracers of diagenetic processes (modified from Anderson and Arthur, 1983).	96
37	Diagenetic trends of $\delta^{13}C$ (from Pisciotto and Mahoney, 1981).	98
38	Paleotemperatures versus $\delta^{18}O$ of pore fluid.	105
39	Relatively fine grained dolomite mosaic. On the left is part of a clast (Sa 6008CL). The coarser grained dolomite on the right associated with the detrital quartz is cement (Sa 6008CE) (Mettawee River). (Field of View: 2 mm wide)	108
40	Sample 6008. 6008CE is taken from the cement of the matrix. 6008CL is taken from the clasts. (Mettawee River)	109
41	Location of field area.	117
42	Outcrop of the wackes of the Bomoseen Formation.	125
43	Carbonate clast breccia with dolomite matrix.	127
44	Dolomite breccia with sandy matrix.	129
45	Carbonate breccia from the Hatch Hill Formation.	133
46	Contact between Bomoseen and Hatch Hill. Top of field book marks contact (Long Cut).	135
47	Green slates of the Poultney Formation.	137
48	White weathering cherts of the Mt. Merino Formation.	140
49	Outcrops showing the contact between the Bomoseen and Hatch Hill Formations.	145
50	Profiles of the Bomoseen/Hatch Hill contact. The Hatch Hill Formation contains the ore body.	146
51	Coarse grained matrix of euhedral siderite and an original carbonate clast, replaced by micritic siderite (Long Cut). (Field of View: 0.85 mm wide)	149
52	Oolite replaced by siderite grains (Mt. Tom). (Field of View: 0.85 mm wide)	150
53	Breccia overprinted by the iron ore. Hatch Hill Formation (Mt. Tom)	152
54	Stability field of iron minerals (from Berner, 1971).	156

Figure Number		Page
55	Characteristics of diagenetic zones that develop during the burial of organic-rich sediment (from Curtis, 1978).	158

CHAPTER 1

INTRODUCTION TO THE THESIS

INTRODUCTION

The Taconic allochthon is a sequence of Cambrian or late Precambrian to Ordovician rocks extending from Lake Champlain, Vermont, in the north to Dutchess County, New York, in the south. It is an elongated belt approximately 200 km long with an average width of 20-30 km (Figure 1). The allochthon is composed of a sequence of predominantly deep water argillaceous and subordinate arenaceous and calcareous rocks that have undergone different degrees of metamorphism and deformation.

The major part of the Taconic allochthon resembles continental rise and slope facies (Bird and Dewey, 1970; Keith, 1974), which are time equivalent to carbonate rocks and sandstones of the shelf facies of the western edge of the early Paleozoic Appalachian Ocean. During Ordovician time, the sediments deposited earlier in the slope-rise environment were incorporated into the accretionary prism of an island arc that approached from the east, and subsequently overthrust the carbonate platform (Rowley and Kidd, 1981).

A stack of thrust slices has been recognized by Zen (1967). They are, from the structurally lowest (west) to highest (east), the Sunset Lake slice, the Giddings Brook slice, the Bird Mountain slice, the Chatham slice, the Rensselaer Plateau slice, the Dorsett Mountain-Everett slice

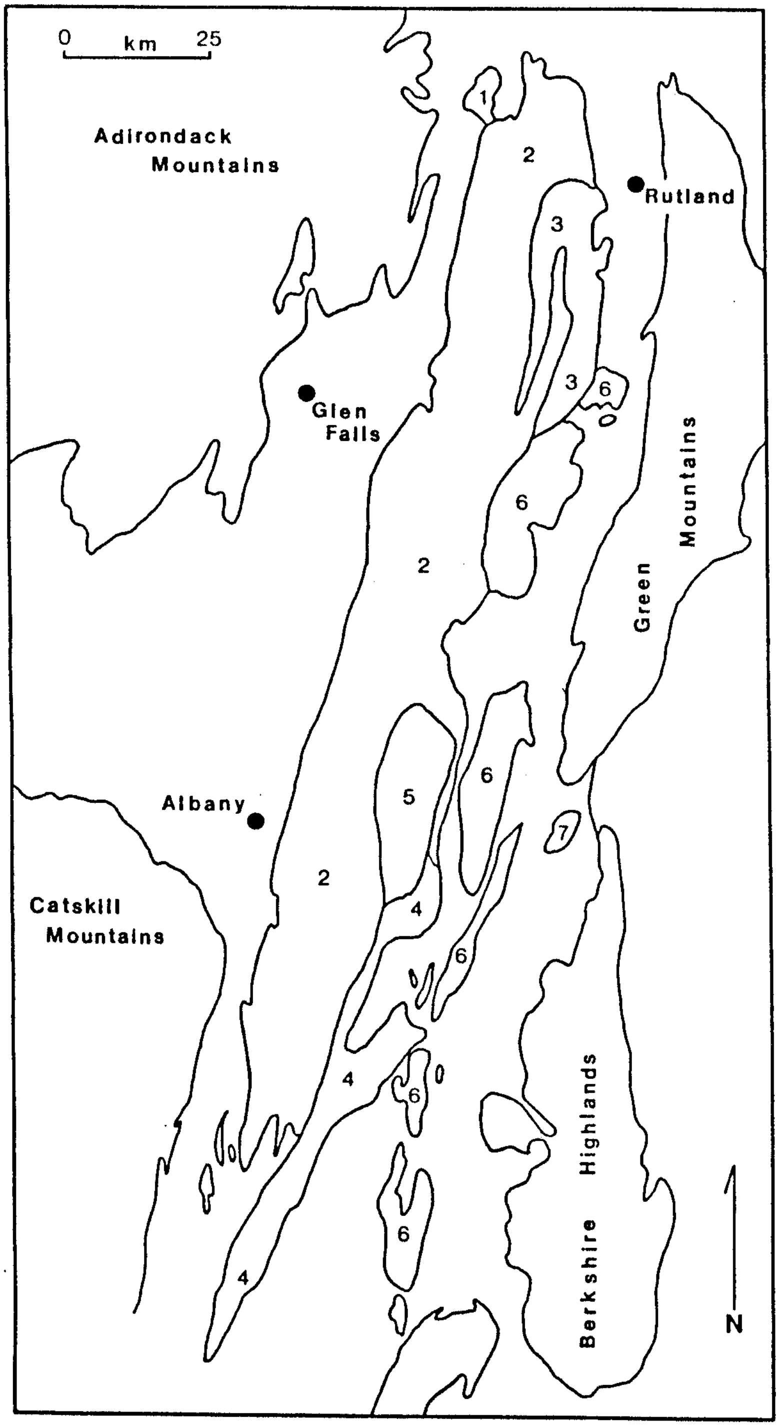

Figure 1. Taconic thrust slices (after Zen, 1967).

(1) Sunset Lake Slice
(2) Giddings Brook Slice
(3) Bird Mountain Slice
(4) Chatham Slice
(5) Rensselaer Slice
(6) Dorset Mountain Slice
(7) Greylock Slice

and the Greylock slice (Figure 1).

The Taconic sequence consists predominantly of multicolored slates or shales and only minor amounts of carbonates, cherts, wackes and sandstones. The majority of sandstones occur in only one stratigraphic milieu, which is known as the Hatch Hill Formation. Previous workers (e.g. Zen, 1964; Potter, 1972; Keith, 1974; Jacobi, 1977; Rowley et al., 1979; Metz, 1980) recognized the presence of dolomite in these sandstones and classified them accordingly as dolomitic quartz-arenites. The depositional environment of these sandstones is the continental rise or slope, and therefore in deep water (greater than 1000 m, Davis, 1983). Dolomite is only a minor constituent in modern deep sea environments (Lumsden, 1985). Recent dolomite formation has been observed in shelf and coastal settings (e.g. Zenger, 1972) that are more easily accessible.

Collecting detailed information on dolomitization and other processes affecting deep water sediments is more difficult and can only be done with expensive drilling equipment. The Hatch Hill Formation provides an excellent opportunity to study dolomite formation in deep water sediments in an ancient example with easy access.

Another rather unusual feature, a sideritic ore body (the Burden Iron Ore), has also been reported from the Taconic sequence (e.g. Ford, 1885; Eckel, 1905; Ruedemann, 1930; Ruedemann, 1942; Zen, 1967). It occurs in ferruginous sandstones that are shown here to be part of the Hatch Hill

Formation (this study). Siderite is usually associated with concretions in shales (Gautier and Claypool, 1984) or in terrestrial swamp environments. Its presence in marine deep water sandstones is rather suprising, since siderite formation requires rather restricted chemical conditions (Berner, 1971).

Therefore, the emphasis of this study is to elucidate the nature of both the dolomite and the siderite of the Hatch Hill Formation, and determine whether both features are related to one another. The approach to these problems is two-fold and this is reflected in the subdivision of this thesis into two major parts. In the first part (Chapter 2), the arenites that contain the dolomites of the Hatch Hill Formation are described. It is shown that the dolomitization of the arenites is primarily a product of diagenesis, and took place after the deposition of the arenites.

The second part (Chapter 3) of this thesis is focused on the Burden Iron Ore. Results of studies on its stratigraphic position, its regional distribution and its petrology are used to constrain the conditions under which the ore body formed.

PROCEDURE

The procedures concentrated on three major methods: field work, petrography, and oxygen- and carbon-isotope analyses. Cathodoluminescence was attempted as a supplement to the petrographic study of carbonates, but proved to be unsuccessful for the types of carbonate minerals present.

FIELD WORK:

The field work was subdivided into two parts, as was the entire approach to the Hatch Hill Formation and the Burden Iron Ore: (1) sampling and detailed description of selected Hatch Hill outcrops and (2) mapping of an area where the iron ore outcrops to obtain stratigraphic control for it, and to determine its geographical distribution pattern.

Six sections of the Hatch Hill Formation were selected with the help of W.S.F. Kidd. The criteria for selection were completeness and extensiveness of the section, lack of structural disturbance, coverage of the northern and southern parts of the Taconic allochthon, and unquestionable identification as part of the Hatch Hill Formation. The major emphasis was directed towards outcrops along the Poultney River, at Schodack Landing and at Judson Point. These sections are the most extensive available and are affected by only minor structural disturbances on an outcrop scale. Each of these sections was measured in detail, and then described and sampled bed-by-bed. Additional samples were collected from a section along the Mettawee River, and from outcrops at Nutten Hook and at Stockport Station.

The Burden Iron Ore outcrops at several locations along a North-trending morphological ridge east of the town of Linlithgo (Hudson South quadrangle, New York). To determine the stratigraphic position and possible structural disturbance, the ridge was mapped. The emphasis was on the stratigraphic position of the ore body and whether it is part of an intact sequence of Taconic lithologies. Structural information was only considered in order to exclude a possible disturbance of the sedimentary sequence. No attempt was made to collect sufficient data to unravel all the details of the structural history of the field area.

PETROGRAPHY:

Thin sections for detailed petrographic study were cut from the Hatch Hill arenites and sandstones containing the Burden Iron Ore. The criteria for thin section selection were to cover each stratigraphic level and to sample all major lithologies.

In the case of the dolomitic Hatch Hill arenites, special attention was directed toward carbonate beds and breccias. Breccias were studied intensively, since several different lithologic types of clasts within one bed underwent the same postdepositional history.

Thin sections that contained dolomite and/or calcite were etched with dilute hydrochloric acid and stained with combined alizarin red S and potassium ferricyanide (Katz and

Friedman, 1965) to identify calcite, ferrous calcite, ankerite and dolomite within the thin section.

For the stained photomicrographs, calcite is red, iron-rich dolomite is blue and iron-poor dolomite is unstained.

CATHODOLUMINESCENCE:

An attempt was made to apply cathodoluminescence on polished, uncovered, stained and unstained thin sections, to try to distinguish between dolomites of different chemistries. The procedure was unsuccessful, as even dolomites that appeared to have low Fe^{2+}/Mg^{2} ratios, as evaluated by staining, did not luminesce. This might be the effect of unidentified luminescence quenchers within the dolomite lattice.

OXYGEN AND CARBON ISOTOPES:

Eight samples were selected for oxygen and carbon isotope analysis. The samples were chosen to meet the following criteria: (1) dolomitic quartz arenites of different stratigraphic levels of the most extensive outcrop (Poultney River) were analyzed to be able to detect isotopic variations within one section; (2) two samples of micritic limestone that contained no dolomite were analyzed for the isotopic signature of calcite, to avoid contamination of a dolomitic phase; and (3) one sample with completely dolomitized clasts and a dolomitized matrix was analyzed for the isotopic signal of the clast dolomite and the cement dolomite, to detect possible differences.

Each sample was first studied in thin section to determine that only one carbonate phase, either dolomite/ankerite (ankerite present dominantly as overgrowths) or calcite, was present. Then 1-4 mm thick slabs of the original thin section chip were cut and drilled with a dentist's drill. For each sample, approximately 4 micrograms of fine powder were drilled and analyzed. Multiple analyses were performed for four dolomite samples (5049, 5080, 6008CE and 6008CL) and for the two calcite samples (2054, 997). The carbon isotope values for dolomite determined from multiple probing of one sample varied between 0.21‰ and 0.047‰; the oxygen values varied between 0.78‰ and 0.047‰. For calcite, the variation of carbon isotopes was 0.172 - 0.54‰ and the variation of oxygen isotopes was 0.491 - 0.059‰. The standard deviation for each individual analysis ranges from ±0.039‰ to ±0.005‰ for the carbon isotopes and from ±0.054‰ to ±0.020‰ for the oxygen isotopes. The isotopic values recorded in Table I are mean values for samples 5049, 5080, 6008CL, 6008CE, 2054 and 997. For samples 5020, 5073 and 5076, only one analysis was performed.

The analyses were performed by the courtesy of R. Fairbanks at the Isotope Laboratory at Lamont-Doherty on a Finnigan λ-MAT-251 mass spectrometer. The samples were dissolved in 100% phosphoric acid at 90°C and were processed on-line using an automated carbonate preparation device. Isotope values were calibrated to the PDB standard via the

NBS-20 standard.

Table I. Summary of the isotopic composition of the Hatch Hill arenites and limestones.

Sample No.	Location	Mineral Phase	$\delta^{18}O$ PDB	$\delta^{13}C$ PDB
5020	PR	cement: dolomite/ankerite	-7.14	-2.73
5049	PR	cement: dolomite/ankerite	-6.97	-1.37
5073	PR	cement: dolomite/ankerite	-7.39	-0.58
5076	PR	cement: dolomite/ankerite	-7.49	-0.15
5080	PR	cement dolomite/ankerite	-7.60	+0.20
6008CL	MR	clast: dolomite/ankerite	-7.29	-2.05
6008CE	MR	cement: dolomite/ankerite	-6.66	-1.60
2054	JP	micrite: calcite	-12.45	-0.35
997	SL	micrite: calcite	-11.97	-0.47

PR: Poultney River
MR: Mettawee River
JP: Judson Point
SL: Schodack Landing

Analyses by the courtesy of R. Fairbanks at the Isotope Labratory at Lamont-Doherty Geological Observatory, Palisades, New York

CHAPTER 2

DOLOMITIZATION OF THE HATCH HILL ARENITES

INTRODUCTION

This part of the thesis focuses on the dolomitic arenites of the Hatch Hill Formation. Dolomitization has been, and still is a very controversial topic. Many contributions toward solving the problem of dolomitization have been derived from the study of modern marine environments, such as the Bahamas Banks, Bonaire, the Florida Keys and the lagoons of Australia, to mention only a few. All of these models concentrate on shelf carbonates that were later dolomitized by a variety of processes. They clearly demonstrate that dolomitization is not a mechanism that works in the same way everywhere, but can be triggered by a variety of different factors.

Dolomites in deep sea sediments are not very abundant (Lumsden, 1985) and relatively difficult to sample. For this reason, dolomites of deep water sediments have not been studied in great detail. The dolomites within the arenites of the Hatch Hill Formation present an ideal situation to study dolomitization within deep water sediments, since the depositional environment and post depositional emplacement are well known (Bird and Dewey, 1970; Keith, 1974; Keith and Friedman, 1977; Rowley and Kidd, 1981; Rowley, 1983; Stanley and Ratcliffe, 1985).

At the beginning of this study, there were two competing hypotheses for the formation of dolomite within the Hatch Hill arenites: (1) the dolomite of the Hatch Hill arenites formed on the carbonate shelf adjacent to the depositional environment of the Hatch Hill Formation and was then transported as detrital material to its final depositional environment, and hence is strictly a product of the shelf environment; and (2) the dolomite formed after the deposition of the detrital phase and is an authigenic assemblage that might have been influenced by the diagenetic conditions during later burial of the Hatch Hill arenites.

The first step in evaluating which of these hypotheses appears to be more likely, or whether both hypotheses might be unsuitable to explain the occurrence of dolomite in the Hatch Hill Formation, was to sample selected outcrops of the Hatch Hill Formation in great detail and determine their stratigraphic succession. This procedure was followed by detailed petrographic studies, with an emphasis on determining which of the above working hypotheses would fit the petrologic data. The evidence that accumulated from the petrological study pointed towards a diagenetic origin for the dolomite. To develop further insight into the diagenetic processes that affected the development of the dolomite, isotopic analyses for $^{18}O/^{16}O$ and $^{13}C/^{12}C$ were performed. The composition of the oxygen isotopes allows the temperatures of formation to be calculated if the composition of the fluid is known, or can be reasonably assumed. The carbon isotope composition can reveal information about the influence of organic matter involved in the formation of diagenetic dolomite.

The combination of petrological and the isotopic evidence enable me to answer the following questions:

(1) Where was the dolomite formed?

(2) What was the environment of formation?

(3) Was dolomitization selective?

(4) Which process led to the dolomitization?

The following chapters are organized to show the chronological development used to solve the problem of dolomitization during the course of this study.

PREVIOUS WORK

The Hatch Hill formation has been the object of a strong controversy in the research history of the Taconic allochthon. Various different names were connected with the lithostratigraphic unit that was termed the Hatch Hill Formation by Theokritoff (1964). The type locality is placed on Hatch Hill in the Thorn Hill quadrangle. Originally it was described as "sooty black pyritic rusty-weathering shales interbedded with rotten-weathering bluish dolomitic sandstones locally cross-bedded, and characteristically traversed by numerous quartz veins" (Theokritoff, 1964). According to Zen (1964), names like ferruginous quartzite and sandstone (Dale, 1899), Zion Hill Quartzite (Larrabee, 1939; Fowler, 1950; Billings et al., 1952; Fisher, 1956), Unit 4 of the Poultney River Group (Zen, 1959), Unit 5 of the Mount Hamilton Group (Zen, 1961) and Hatch Hill Shale (Berry, 1962) are synonyms or partially describe the formational name used by Theokritoff for at least the northern part of the Taconic allochthon. In the southern part of the Taconics, some members of the Schodack shales and limestones (in the use of Ruedemann, in Cushing and Ruedemann, 1914), and of the Germantown Formation (Fisher, 1961) are indubitably Hatch Hill equivalents. Zen (1964) also assigns the Eagle Bridge quartzite of Prindle and Knopf (1932) as being of Hatch Hill age and equivalence. The upper, sandstone-dominated part of Ruedemann's type locality for the Schodack shales and limestones, two miles south of Schodack Landing, as well as a large part of the

Judson Point outcrop, have been identified as the lower part of the Hatch Hill formation by Jacobi (1977) and Rowley *et al.* (1979).

It was also Kidd *et al.* (1985) who extended Theokritoff`s original description of the Hatch Hill formation by placing the lower contact with the newly created Middle Granville Slate (formerly included either in the Mettawee slate formation or as part of West Castleton formation) at the point "where green or purple or pale-medium gray slates pass up into sooty fissile black shales." The upper contact separating the Hatch Hill formation from the Poultney formation, as described by Rowley (1983), is marked by the transition of black shales into variegated medium to dark gray, green and lesser black and maroon slates and silty argillites. The change is commonly sharp and occurs over less than 1-3 m.

Where the Hatch Hill Formation is well-exposed, which is dominantly in the northern Taconics, three subunits can be distinguished. The lowermost unit consists of black shales and gray calcareous micrites, lesser quartz arenites, buff- to yellowish-weathering dolostones and, rarely, pebbly limestone conglomerates. That member was formerly treated as part of the West Castleton Formation in the useage of Zen (1967). The unit in the middle is characterized by, in addition to black slate, hard, light blue-gray, fine- to coarse-grained, deep rusty brown weathering dolomitic sandstones, which are typically cross-cut by quartz and calcite veins. This member most closely resembles the Hatch Hill Formation described by Theokritoff (1959). The uppermost subunit consists of dark gray to black slates containing ribbon limestone and dolostone, thinly bedded quartzites and flat pebble limestone conglomerates (Rowley, 1983). This unit was originally named by Potter (1972) as the White Creek member, and placed at the bottom of the Poultney Formation because of its fossil content. Rowley (1983) included it in the Hatch Hill Formation by using the concept of color changes in slates to define formational boundaries. The use of color changes combined with lithology changes to mark formational boundaries appears to be quite successful for the Taconic sequence, even though it creates some problems. This method has been applied to define the contacts of the Truthville/Browns Pond (green/black), the Middle Granville Slate/Hatch Hill (green-purple/black), the Hatch Hill/Poultney (black/gray-green), the Poultney/Indian River (gray-green/red-green) and the Indian River/Mt. Merino (green, purple/black) formations. The advantage of this concept is the ease with which it can be applied by the field geologist. The color changes usually occur within shale- or slate-dominated sequences, which otherwise are very difficult to separate. The connection of only lithologic changes with formational boundaries must be less successful, since the depositional environment of the Taconic sequence (continental rise, Bird and Dewey (1970)) is characterized by many local events. Therefore, facies changes within individual units can be observed along the strike of the 200 km long Taconic Allochthon. The importance of determining formational boundaries within slates and shales is further stressed by average argillite accumulation rates of 4 m/m.y., as calculated by Baldwin (1983) for the West Castleton, Hatch hill and Poultney Formations in the northern Taconics along the Poultney River. Baldwin's (1983) argillite accumulation rate is probably too low, since he did not consider tectonic thinning during slaty cleavage development. Woods (1973, 1974) estimated 75% shortening perpendicular to slaty cleavage (see also Chapter 3). An argillite accumulation rate corrected for tectonic thinning is 16 m/m.y. Therefore, the inclusion or exclusion of argillite sequences can induce severe time differences to formational boundaries.

The age of the Hatch Hill Formation covers a wide range. Theokritoff (1964) found dendroid graptolites, which were identified by Berry as probably Tremadocian (early Ordovician age), near the top of the formation, while Bird and Rasetti (1968) distinguished middle Cambrian ages for the *Centropleura* fauna collected at Judson Point.

REGIONAL DISTRIBUTION

For this report six outcrops within the Hatch Hill formation were selected for detailed studies. They are part of the Giddings Brook (Figure 2) slice that extends 200 km from the Sudbury quadrangle, Vermont, in the north to the Clermont quadrangle, New York, in the south.

The outcrops described here are located at the Poultney River along the New York-Vermont state border, about 3 km northeast of Fairhaven (Thorn Hill quadrangle), at the Mettawee River between North Granville and Truthville (Granville quadrangle), at Schodack Landing along the side track of the New York Central Railroad about 3 km south of the center of Schodack Landing (Ravena Quadrangle), at Nutten Hook, Judson Point and Stockport Station (all Hudson North quadrangle). (For detailed descriptions, see Appendix.)

The outcrops were, as mentioned before, selected to cover as much of the length of the allochthon as possible. Coverage of the middle portion was not attempted due to lack of a suitably well-exposed section.

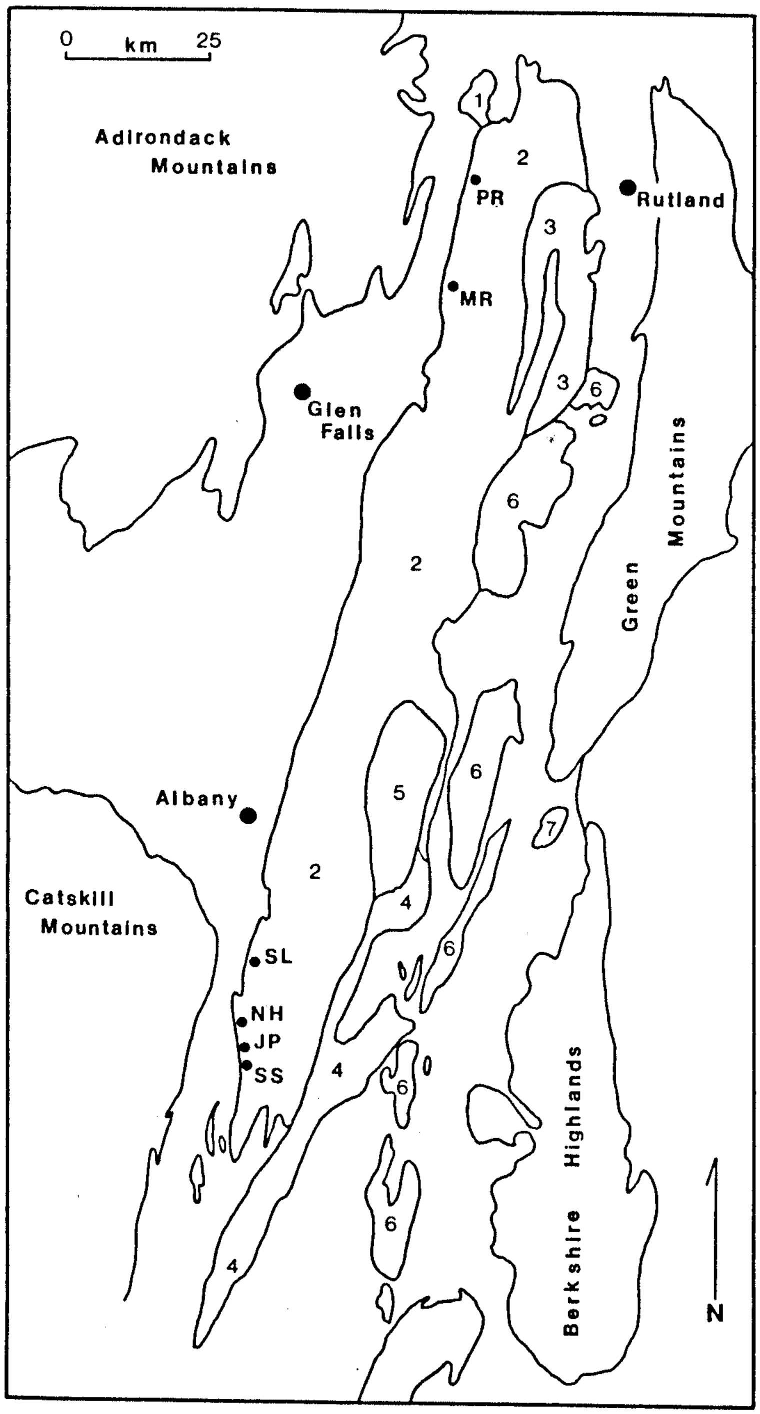

Figure 2. Outcrops of the Hatch Hill Formation studied in this thesis.

PR: Poultney River
MR: Mettawee River
SL: Schodack Landing
NH: Nutten Hook
JP: Judson Point
SS: Stockport Station

STRATIGRAPHY

The stratigraphic positions of the outcrops selected were determined by previous workers. The Poultney River (PR) section was mapped by Rowley (1983). It is part of the east limb of the Mt. Hamilton syncline. Baldwin (1983) described the profile as part of a study on sedimentation rates of the Taconic sequence. The outcrop along the Mettawee River (MR) is mentioned by Jacobi (= Delano, 1977) and Rowley *et al*. (1979, Stop 5) as part of a continuous overturned stratigraphic section, starting with the Bomoseen formation and ending with a fault-bounded part of the Hatch Hill formation. The outcrops in the southern part of the Taconics were described by Ford as early as 1885, in the case of Schodack Landing (SL). This section has been described by, among others, Dale (1904), Ruedemann (in Cushing and Ruedemann, 1914), Theokritoff (1964), Bird and Rasetti (1968), Bird and Dewey (1975), Keith and Friedman (1977), and Friedman (1979). Fossils collected from the micritic limestones (Figure 3) below the Hatch Hill Formation revealed Lower Cambrian ages as determined by Dale (1904), Ruedemann (1930, 1942), Goldring (1943), Craddock (1957), Fisher (1961) and most recently Bird and Rasetti (1968). Stratigraphic names correlating the section with others of the northern Taconic were assigned by Jacobi (1977) and Rowley *et al*. (1979). They showed that the beds the fossils were taken from are Browns Pond equivalents, while the upper part of the section is lithologically equivalent to the Hatch Hill formation. Fossil ages of the

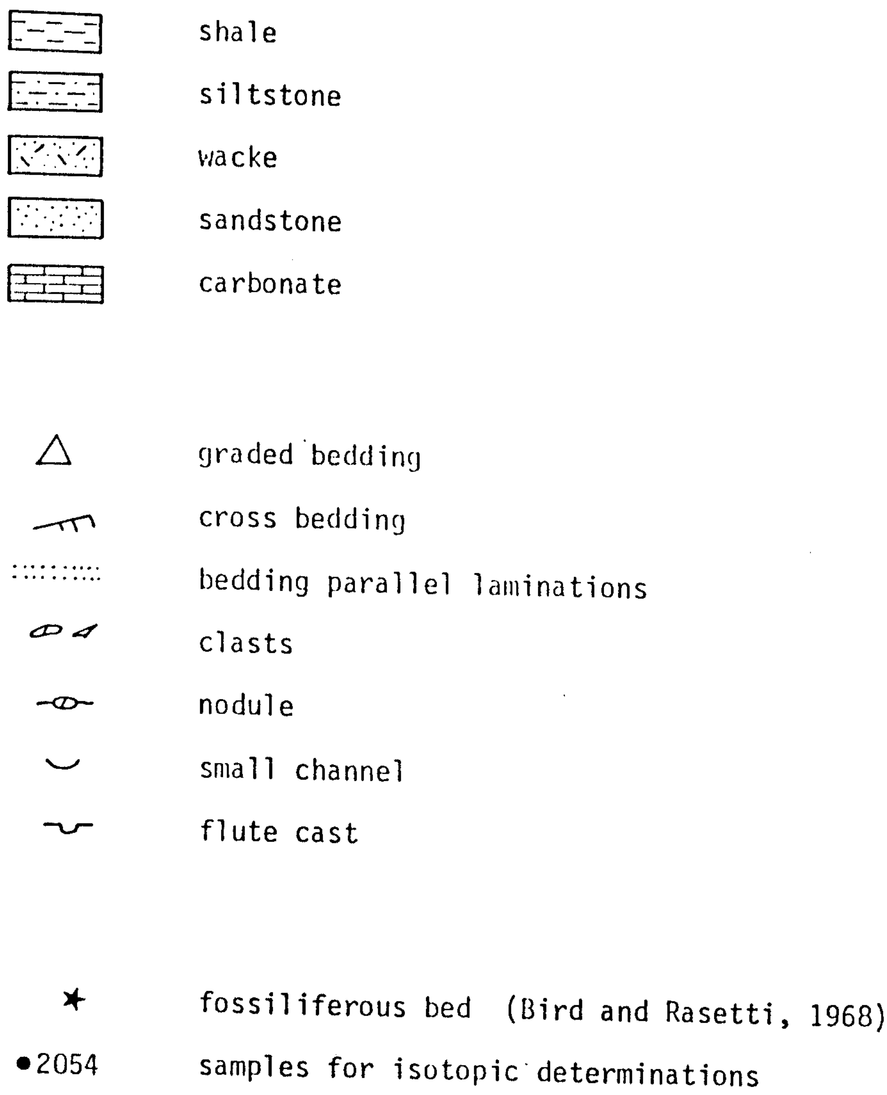

Figure 3A. Key for Figures 3B, 11, 14 and 49.

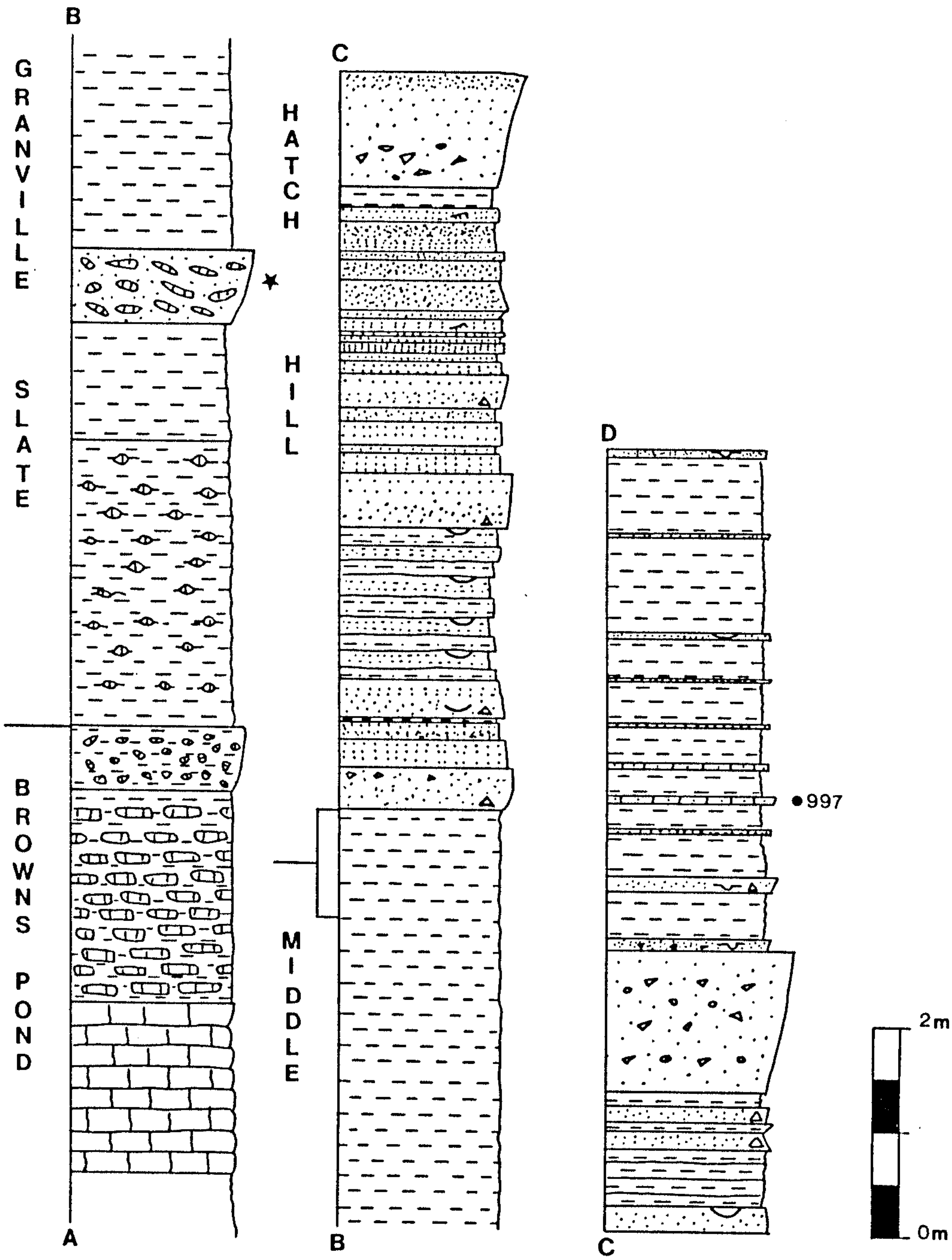

Figure 3B. Stratigraphic Profile at Schodack Landing profiles at Judson Point (lower-middle Cambrian), Nutten Hook (middle Cambrian) and Stockport Station (middle Cambrian), as determined by Bird and Rasetti (1968), as well as the lithologic composition of the sections exposed, justifies treating them as part of the Hatch Hill formation, even though Nutten Hook and Stockport Station are isolated outcrops lacking stratigraphic continuity with more extensive exposures.

SECTION DESCRIPTION

SCHODACK LANDING:

The locality Schodack Landing is the stratigraphically most extensive section described here. The profile shown in Figure 3 was taken from the base of the Browns Pond formation up to the highest level of the Hatch Hill formation exposed in this outcrop. Older members of the Taconic sequence are present, but were not profiled.

Browns Pond Formation

The Browns Pond formation can be described in three distinct units. The basal part is represented by a gray, light-gray weathering, thin (up to ca. 7 cm) bedded micritic limestone. The individual beds are irregularly bedded and often separated by thin layers of black, brown weathering layers of shale. The unit in the middle consists of nearly rectangular, at the edges rounded, micritic limestone blocks that are swimming in a black shale matrix. The individual blocks appear to define bedding planes. The blocks are enveloped by the shale matrix that bends around the edges. The uppermost unit is defined by a breccia. Micritic carbonate clasts (2-4 cm) are sitting within a shaly matrix. Both the carbonates of the middle and upper unit appear to consist of the same micritic limestone as the basal unit (Figure 4).

Middle Granville Slate

The base of the Middle Granville slate is placed at the first appearance of green slate above the Browns Pond

Figure 4. Browns Pond Formation at Schodack Landing

formation. It is dominated by well-cleaved green slate. The lower portion is characterized by tan weathering, disconnected layers of micritic limestone. In the middle part a polymict breccia is a distinct lithology. The breccia consists of clasts of micritic limestone, quartzitic sandstone, coarse to fine grained sandstones and scattered shale fragments (Figure 5). Individual clasts can range up to 35 cm in their longest dimension. The matrix is medium to coarse grained quartz sand. The breccia horizon extends approximately 6 m laterally in the eastern side of the railroad cut and pinches out. The green slate that dominates this formation becomes increasingly silty and less well-cleaved towards the transition zone with the Hatch Hill formation.

Hatch Hill Formation

The lower contact of the Hatch Hill formation is difficult to define. Unlike other sections (see Rowley *et al.*, 1979), there is no sharp color change from green to black in crossing the formation boundary. It occurs gradually over several meters. The contact is therefore placed at the position where well-cleaved, dark green slates grade into gray-black siltstones. The first obvious lithological change can be observed with the deposition of a sandstone bed (Figure 6), indicating the input of coarser grained clastic material. The lower part of the Hatch Hill section outcrop is characterized by coarse to medium grained sandstones (20-40 cm thick), often showing graded bedding,

Figure 5. Breccia within the Middle Granville Slate

Figure 6. Contact between Middle Granville Slate and Hatch Hill.

rarely with rip-up clasts, overlain by beds of fine grained, finely laminated sandstones (10-20 cm thick). The parallel laminations seem to be caused by layers of slightly coarser and finer grained material. The coarser clastic intervals are separated by beds of laminated, grayish black siltstones, and in a few cases by fissile black shales. Characteristic for this part of the profile are small (1-3 cm thick) chaotically sorted, coarse to medium grained channel-like beds at the top or the base of the coarser sandstones, which usually pinch out within 2-3 m laterally.

The overlying interval shows dominantly fine grained laminated sandstones (2-20 cm thick) (Figure 7). Siltstone or shale layers are usually not present, but sporadic cross-bedding can be observed. The laminations typical for this section become even more obvious in intensively weathered parts of the profile (Figure 8).

The following unit above is dominated by two massive coarse grained sandstone beds (100-110 cm thick) These beds show no grading, or delayed grading into finer material only towards the top (~10 cm) of the bed. Typical are angular to subrounded rip-up clasts (2-7 cm). Carbonate clasts dominate, but sandstone clasts are present. Due to differences in resistance to weathering, the surface appears to be scattered with pock-marks (Figure 9).

The top part of the exposed section is dominated by black shales. The shale sequence is interrupted only by irregular isolated beds of fine grained laminated sandstones (<5 cm thick) (Figure 10) and sporadic, often disrupted

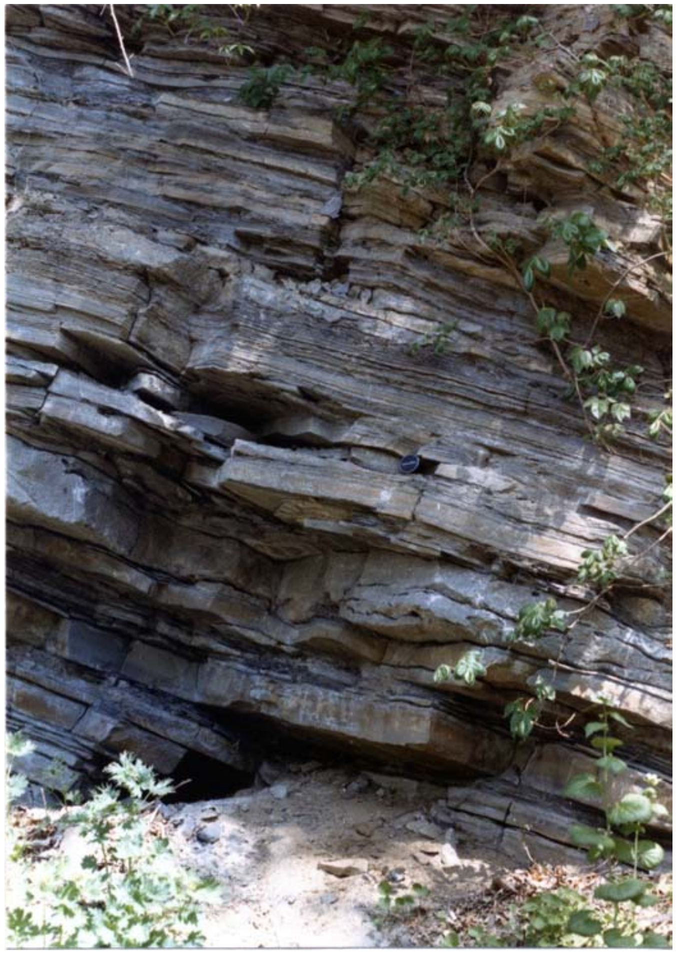

Figure 7. Parallel laminated sandstones of the Hatch Hill Formation.

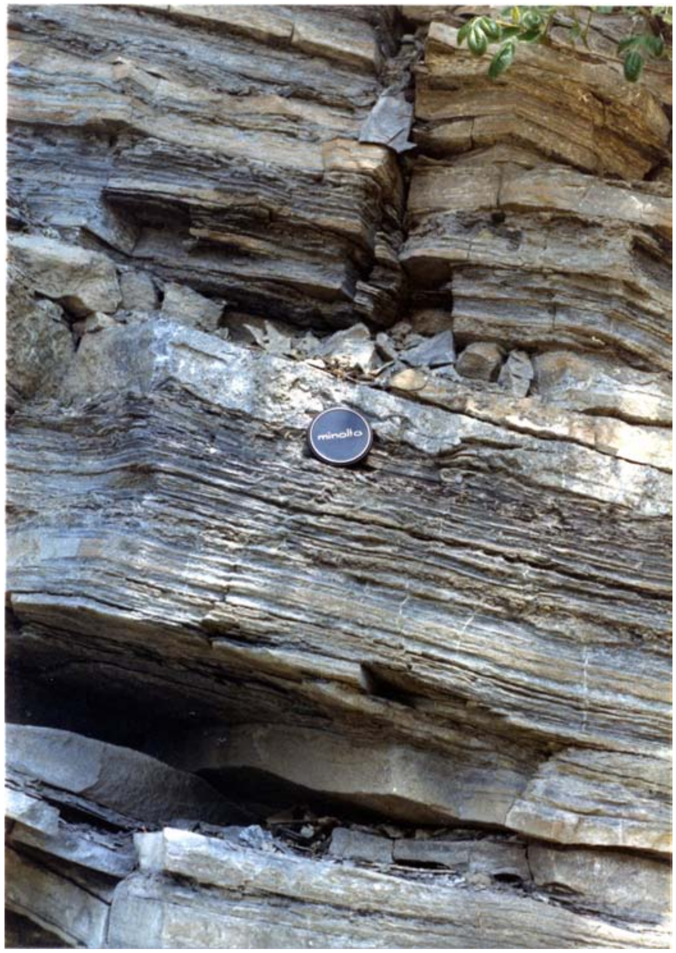

Figure 8. Preferential weathering of individual laminae.

Figure 9. "Pock Marks" (weathered out clasts in thick arenite bed).

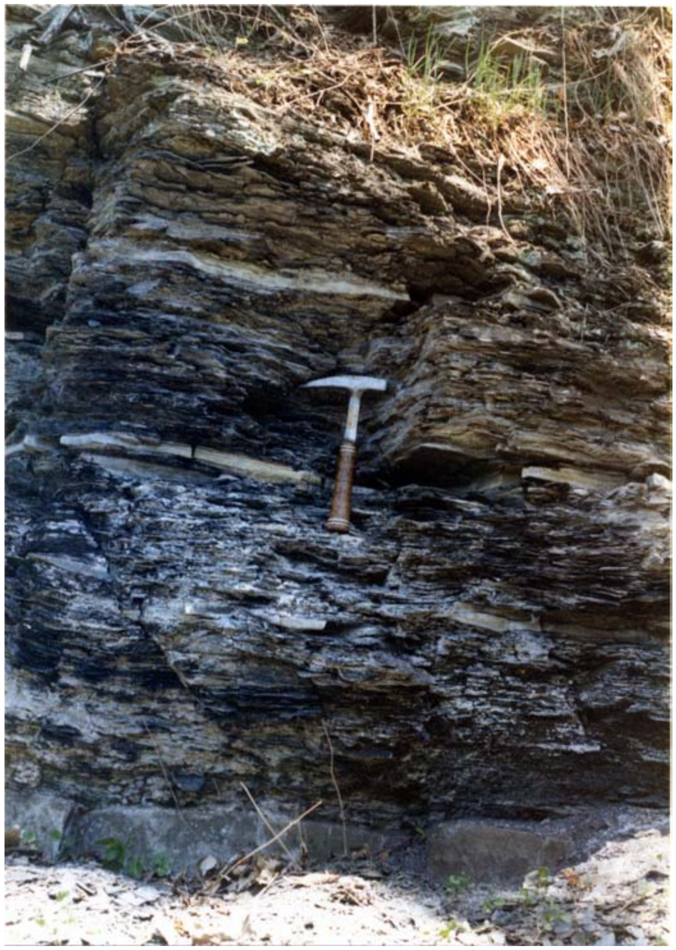

Figure 10. Shale interlayered with fine grained sandstones in the upper part of the Hatch Hill Formation at Schodack Landing.

micritic limestones. The top of the section appears to be fault-bounded. Load marks have been observed in various parts of the section and in all lithologies present.

JUDSON POINT:

The profile at Judson Point includes fewer stratigraphic formations than at Schodack Landing. I did not observe the contact of the Hatch Hill formation with the Middle Granville slate, but Bird and Rasetti (1968) describe a progressive change from olive-green calcareous shales to dark gray shales and siltstones. Fossils of lower Cambrian age have been recovered from calcareous shale lenses approximately 10 m below the first coarse grained sandstone bed. The exact position of the contact cannot be determined, as it lies in a poorly exposed interval between the fossil-bearing shales and the first sandstone bed. The measured profile (Figure 11) is taken from the first massive sandstone bed.

The lower part of the section is dominantly made up of coarse to medium grained, rusty weathering sandstone beds. Only a few beds show identifiable laminations, and these are usually faint. There are two prominent beds of coarse grained sandstone (~150 cm thick). They show uniform grain sizes and lack or have only delayed, grading within the uppermost 10 cm. Rip-up clasts are absent. Several of the beds are separated by thin layers of black shales or siltstones, with thicknesses less than 1 cm. Three beds

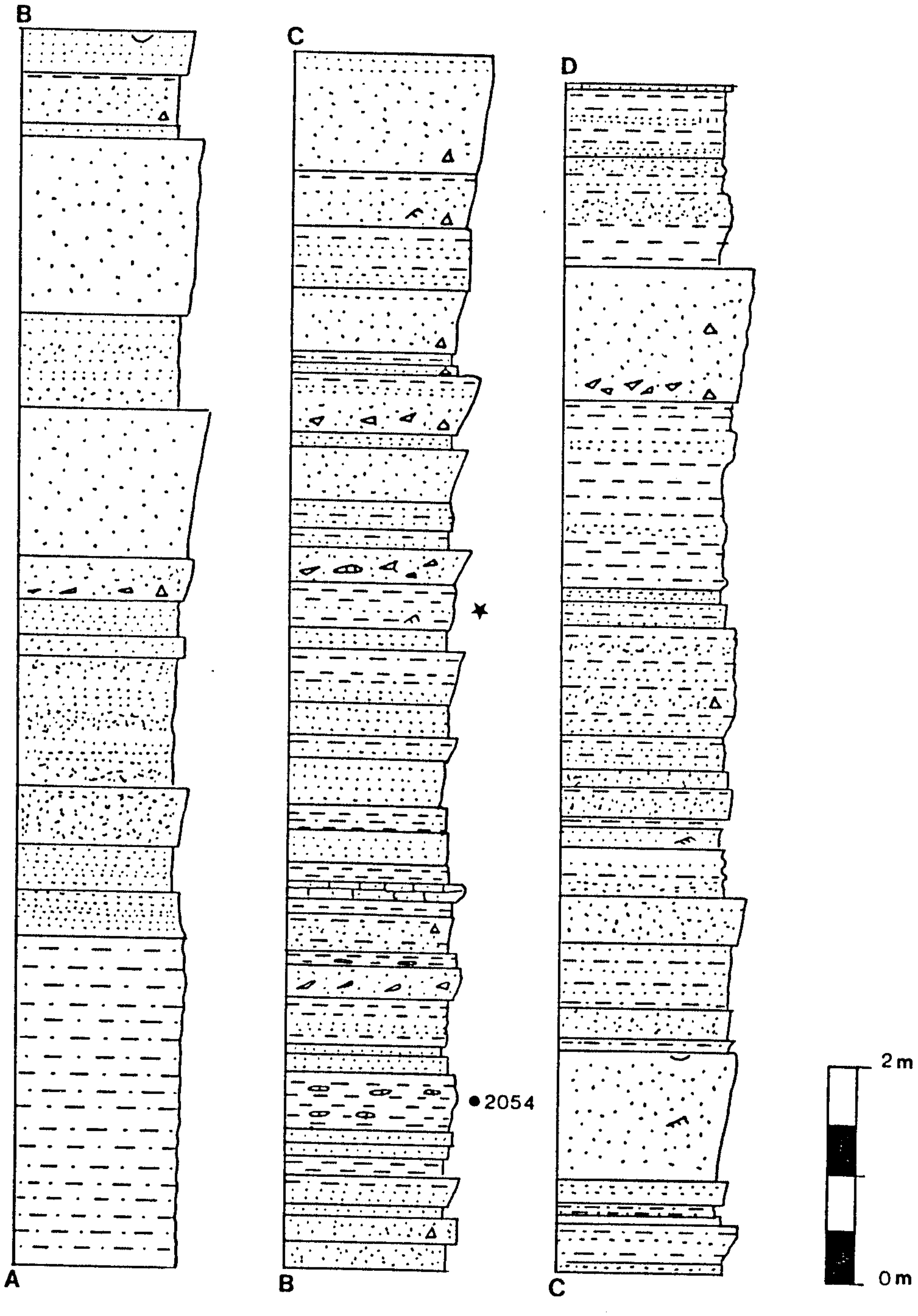

Figure 11. Profile of the Hatch Hill Formation at Judson Point.

clearly show graded bedding, one of which has carbonate and sandstone rip-up clasts at the base.

The middle and upper parts of the profile are characterized by the presence of fine grained units. Shale and siltstones are more common. Typical for the middle part are fine grained laminated sandstones and thin (up to 10 cm) graded beds that are topped by thin layers of shales or siltstones. Coarse grained beds are still present but occur only at widely spaced intervals. Two breccia horizons merit special interest. They are unsorted and consist of angular fragments of micritic limestones, fine to medium grained sandstones and black shales. The clasts show orientations in all directions, but an overall bedding-parallel alignment of their longest axes seems to be present (Figure 12). The matrix is in both cases sandy, rusty weathering and coarse grained. The first occurrence of carbonates should also be noted. Carbonates are present in the form of micritic limestones. They appear in either irregular beds or disconnected nodules within shale beds (Figure 13).

The upper part of the profile reveals dominantly thin, medium grained, laminated sandstone beds. A few graded beds are present and there are isolated thick beds of coarse grained sandstones with rip-up clasts at the base. Thin shale layers (<3 cm) are typically separating coarser-grained beds from each other.

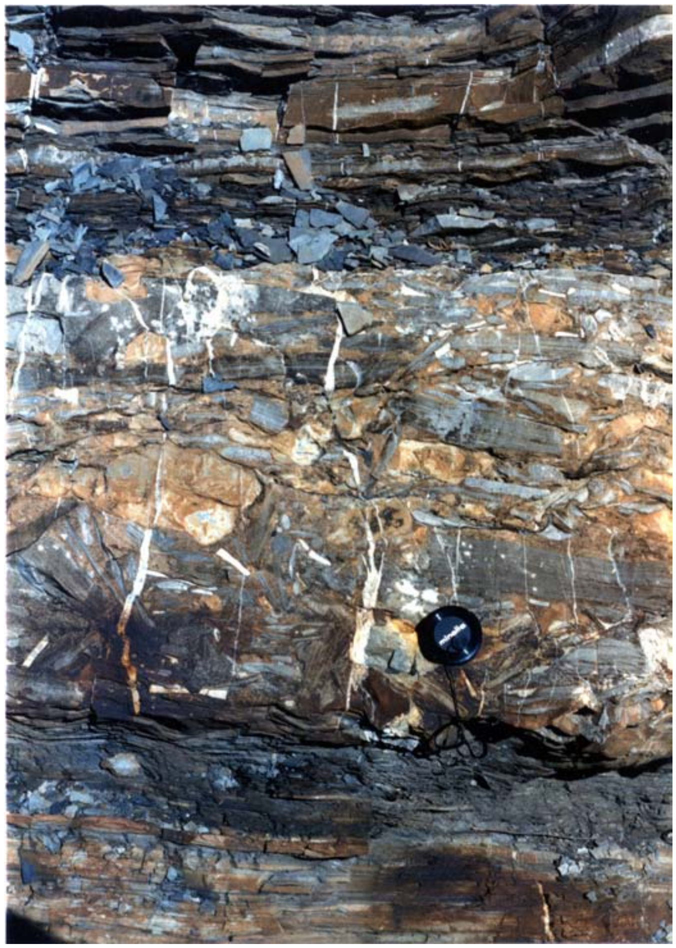

Figure 12. Breccia with bedding parallel clast alignment (Judson Point)

Figure 13. Irregularly bedded, micritic carbonate beds.

NUTTEN HOOK:

The section at Nutten Hook is incomplete and the stratigraphic correlation is based only on similarities of the lithologies and fossil ages determined by Bird and Rasetti (1968). No profile was made as the section is cut by several faults and partly covered. Correlation between single fault blocks was not possible. Therefore, only major lithologies are described based on my own observations and descriptions by Bird and Rasetti (1968) and Keith and Friedman (1977).

The section shows the major lithologies described above. The lower part of the section is dominated by black shales. The strata contain a few thin, medium grained laminated sandstones and there are two beds of sandstone clast conglomerates. Massive sandstones are rare. The upper part consists of thinly interbedded micrite and laminated limestones. In a few places, carbonate conglomerates and a few sandstones can be found. Compared to Judson Point and Schodack Landing, coarse grained sandstones are missing while the amount of calcareous material is larger.

STOCKPORT STATION:

The outcrop at Stockport Station is very small. Nevertheless, it is important, because it supplied the most complete middle Cambrian fauna (see Bird and Rasetti, 1968) known for the southern Taconics.

The lithologies exposed here are dominantly sandy limestones and a few beds of medium grained sandstones. Individual beds are separated by dark gray to black shales.

POULTNEY RIVER:

The outcrop at Poultney River is not continuously connected by exposed rock with lower formations of the Taconic sequence. Its stratigraphic position is nevertheless clear, as determined by mapping by Rowley (1983). The outcrop is part of the eastern limb of the Mt. Hamilton syncline and is located in close proximity to the northeast-southwest trending syncline axis. The profile is approximately 70 m thick and therefore is the thickest continuous sequence measured in this study (Figure 14).

The dominant lithology of this profile is medium-fine grained parallel laminated quartz arenite (Figure 15). The thickness of the arenites varies considerably within the profile (2-20 cm). Individual beds are usually separated by thin layers of black to grayish-black, partially laminated shales (1-2 mm thick). Intervals with no shale partings are also present.

The lowermost two-thirds of this section consists dominantly of the lithologies described above. Coarser material is only present in a few isolated beds. These beds often show graded bedding and some reveal finer-grained sandstone rip-up clasts in the lower part. The coarse clastic beds are in almost all cases overlain by fine (up to 2 cm) layers of laminated shales.

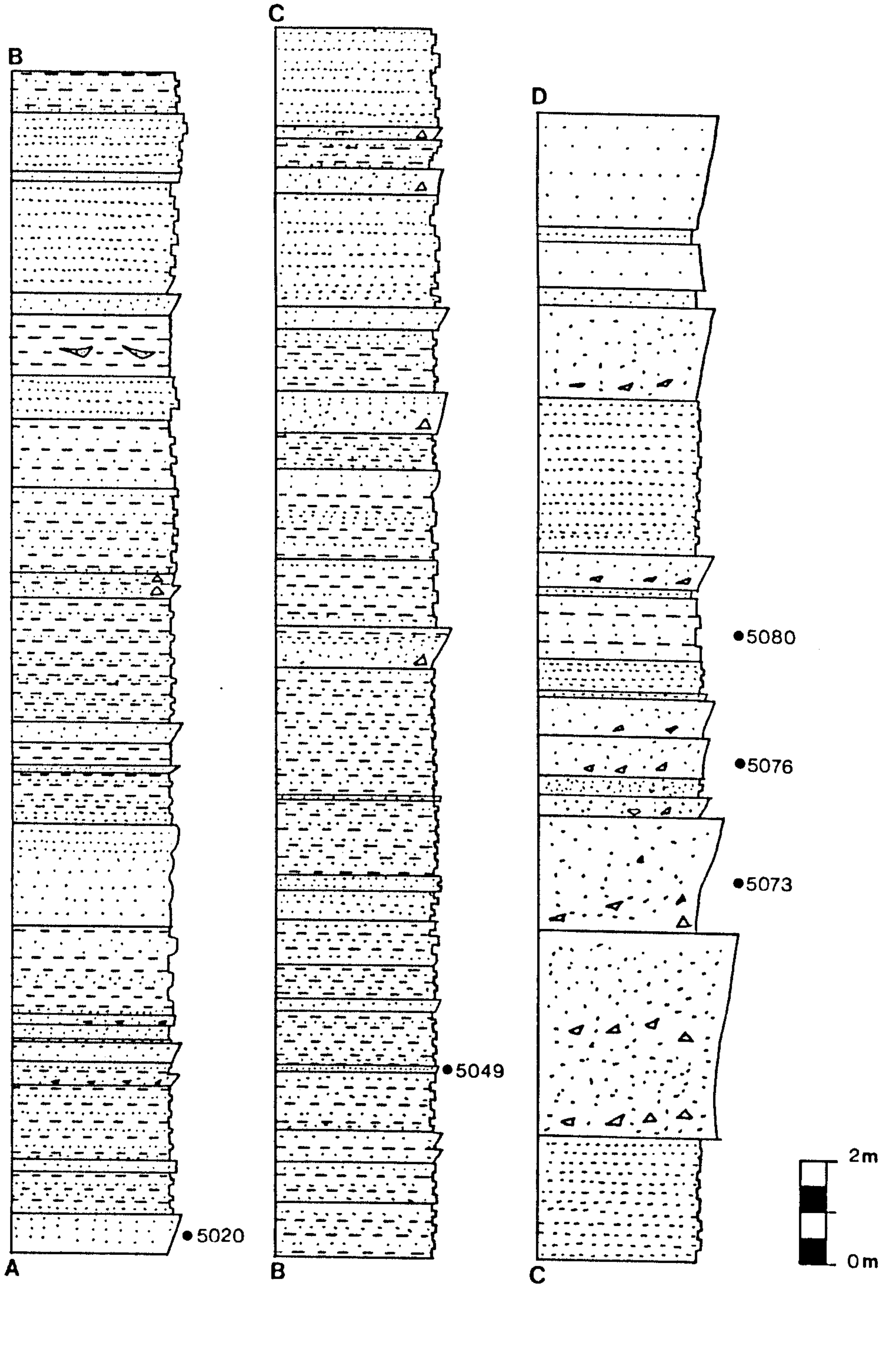

Figure 14. Profile of the Hatch Hill Formation at Poultney River.

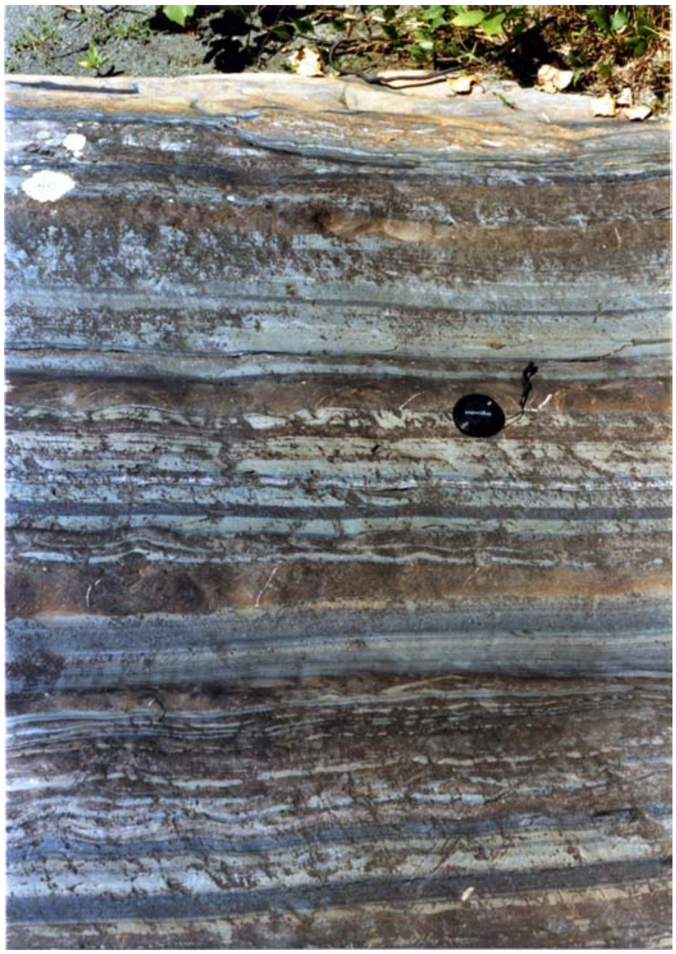

Figure 15. Parallel laminated sandstones in laminated shales. Typical of thinner bedded parts of the section at Poultney River.

The upper third of the section is characterized by the influx of coarser material. Massive beds with clasts in the bottom part decreasing upwards in number are typical. The clasts are fine to medium grained sandstones and dolostones and, less frequently, shales. Clasts consisting of more than one lithology have not been observed. The thickness of individual beds increases and ranges from 70-400 cm. The matrix of these beds consists of coarse quartz grains. Graded beds are present in only a few layers. The grading is in most cases not defined by the matrix, but by the frequency and distribution of clasts. Delayed grading within the upper 10 cm of a bed is the only form of grading observed within the matrix. Disk structures have been observed in one bed (Figure 16). A very prominent bed is a 392 cm thick, coarse grained, rusty weathering sandstone (Figure 17). It can be split up into four smaller sub-units. The lowermost unit in this prominent bed is characterized by a high frequency of clasts. The clasts are dominantly dolostones, with fewer sandstones. They can reach up to 35 cm in their longest dimension. The bigger clasts are oriented roughly bedding parallel with respect to their longest extension. The frequency diminishes upwards and proceeds to unstructured coarse grained sandstone. The upper part repeats the lower.

Only a single bed of micritic dolostone has been observed.

Figure 16. Disk structures.

Figure 17. Thick sandstone bed at Poultney River.

METTAWEE RIVER:

The stratigraphic position of this section was determined by Jacobi (1977). No detailed profile was established, and only a few prominent quartz arenites have been sampled. The description here is based on field observations and a stratigraphic profile measured by W.S.F. Kidd.

The lower contact with the Middle Granville Slate is placed at the top of a micritic limestone bed where green slates disappear and black slates start to appear.

The typical thickness of individual sandstone beds is approximately 10 cm. The upper part (about 20 m) of the section consists of quartz arenites with only minor amounts of shale. The arenites are dominantly coarse to medium grained, with thicknesses ranging from 5-40 cm. Dolostone clasts are present in several beds. Laminations are usually restricted to thin beds. The top of the section is fault-bounded and marked by a small waterfall. The overall exposure of this section of the Hatch Hill depends on the water level of the Mettawee River; very little can be seen if the water is high.

PETROGRAPHY AND MINERALOGY

INTRODUCTION:

The Hatch Hill Formation involves only four sedimentologically discrete rock types: arenites, breccias, limestones or dolostones, and shales or slates (depending on the degree of deformation). From the outcrops observed, no systematic vertical distribution pattern for any rock type could be observed. The distribution is triggered by the stability of the depositional environment (rise) and by the source material (presumably rocks deposited on the shelf or in higher portions of the rise or slope). Each rock type has been observed in the major sections described (Schodack Landing, Judson Point, Mettawee River and Poultney River).

ARENITES:

Arenites are the dominant rock type observed. They range from mature quartz-cemented arenites to carbonate-cemented subarkoses (classification from Pettijohn et al., 1973). The mineralogy of the arenites is monotonous. The dominant mineral observed is quartz. It ranges from granule to silt size (3 mm - 0.01 mm). Bimodal distributions are usually observed. The bimodal character of the grains is not restricted to certain grain size ranges, but almost always two distinct fractions can be observed. Individual grain shapes vary considerably. Well rounded to subangular grains are present. The degree of roundness is positively correlated with increasing grain size. Most quartz grains show undulose extinction, but clear grains and a few grains showing recrystallization mosaics are also present. Fluid inclusions and impurities often outline grain boundaries and form a parallel or subparallel alignment within the grains. Cathodoluminescence reveals different luminescence colors for several quartz grains ranging from dull red to blue to non-luminescent, indicating the varying chemistry of different grains. This is not suprising, since the source of the clastic quartz grains was probably the Grenville basement, which in itself consists of various types of quartz (e.g. vein quartz, pegmatite quartz, metamorphic quartz, and igneous quartz). Accessory minerals are alkali feldspar, plagioclase, clastic micritic grains of dolomite and calcite, tourmaline and zircon. The feldspars occur as clastic and authigenic material in various grain shapes. The carbonate grains and zircon are always rounded to subrounded. The clastic grains are cemented dominantly by carbonates and to a minor degree by quartz overgrowths. (For a more detailed description, see Chapter 2 on diagenesis.) The only opaque mineral observed is pyrite. It occurs as irregularly distributed anhedral grains. In a few cases, accumulation of pyrite grains along individual laminae of the fine grained laminated arenites has been observed.

Further subdivision of arenites is only possible when such criteria as sedimentological features (lamination, grading) and grain sizes are used (see profiles, Figures 3, 11, and 14).

BRECCIAS:

Monomict carbonate and polymict breccias occur in the sections described. A monomict carbonate breccia was observed only at Schodack Landing and is not part of the Hatch Hill Formation, but part of the upper Browns Pond Formation. The breccias of the Hatch Hill are all polymict. The clast composition resembles rock types present within the formation: shales, carbonates and sandstones. The matrix is always sandy. Typical clast sizes range from 3 - 10 cm (cobble to boulder size), but individual clasts can be as large as 35 cm in their longest dimension. Carbonate and sandstone clasts are more frequent than shale clasts. The clasts are all usually angular to subangular and are tabular-shaped. An overall orientation parallel or subparallel to bedding with respect to the longest axis is typical, even though other orientations are also present. Some clasts show soft sediment deformation features indicating they were not completely lithified before they were re-deposited (Figure 18). The carbonate clasts consist of either structureless micritic calcite, or a close network of euhedral to subhedral dolomite rhombs surrounded by isolated quartz grains (Figure 19). Both features indicate neomorphism and complete recrystallization of the original clasts.

Sandstone clasts are fine to coarse grained, but in most cases finer grained than the surrounding breccia

Figure 18. Soft sediment deformation of clasts.

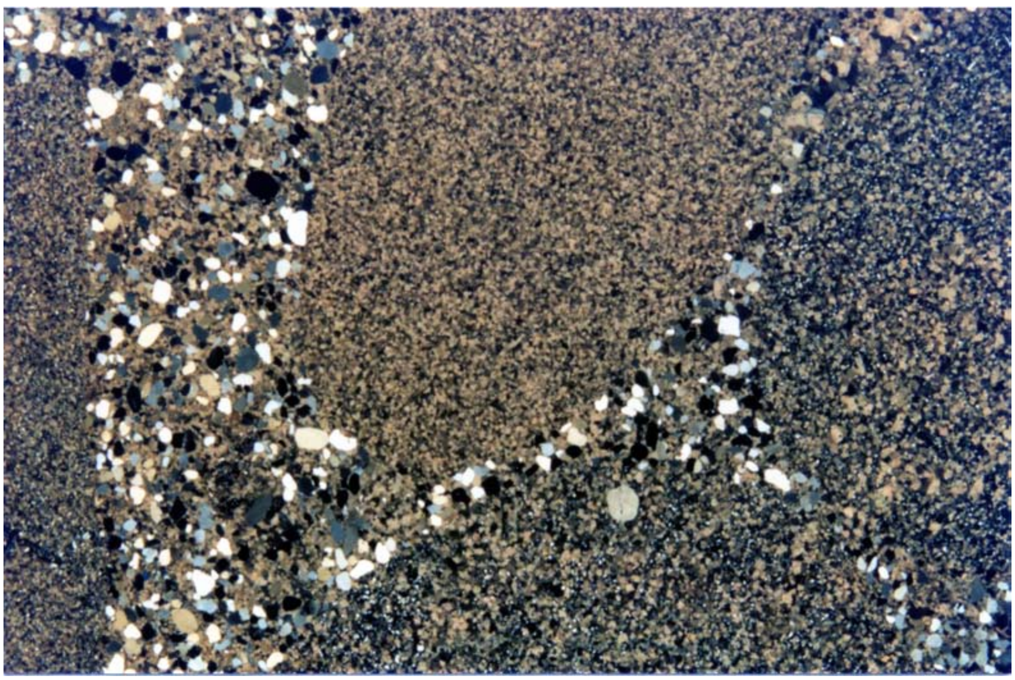

Figure 19. Photomicrograph of a dolomite clast breccia. Individual clasts are outlined by matrix with higher quartz content. (Field of View: 4 cm wide)

matrix. They show the same mineralogy as the arenites described above.

The matrix consists of coarse to very coarse, rounded to subrounded quartz grains cemented by euhedral to subhedral dolomite. The dolomite cement accounts for up to 60% of the matrix. Contacts of quartz grains with each other are an exception. Clast-matrix contacts of dolomite clasts and the matrix dolomite are difficult to distinguish in thin section, especially when similar grain sizes are present. Accessory minerals are feldspars, pyrite and zircon.

Phosphate pebble breccias and conglomerates have also been observed in the Hatch Hill formation (e.g. Zen, 1967; Bird and Dewey, 1970; Rowley, 1983). A sample collected by W.S.F. Kidd was studied, from a roadcut about 450 m east of the New York-Vermont border on the north side of Route 4, about 2.5 km SSE of the Poultney River section. It showed tabular, rounded to subrounded, 1-3.5 cm phosphatic clasts cemented by a sparry dolomitic matrix. The clasts appear to be pure phosphate in the specimen studied and do not show any inclusions or reactions with the surrounding matrix (Figure 20).

LIMESTONES:

Limestone beds are not very common in the sections of the Hatch Hill Formation studied. They usually occur in thin (up to 3 cm thick), gray weathering, micritic beds

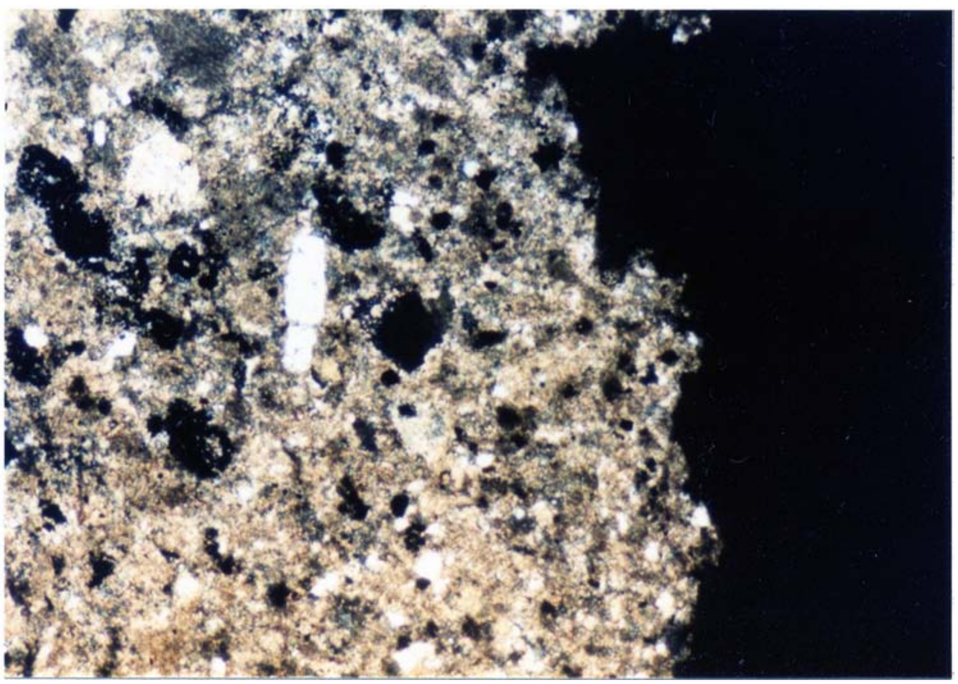

Figure 20. Phosphatic clast (dark grain on the right) and dolomite matrix. (Field of View: 3.4 mm wide)

enveloped by layers of shale. Disrupted beds and nodules within shale sequences are also present. The limestones can be classified as structureless micrites, pelmicrite and biomicrites (classification after Folk, 1962). All of these carbonate rock types are endmembers which are not present as such in the Hatch Hill formation, since clastic grains are always present in a micritic matrix. The clastic fragments are angular to subangular, silt-sized quartz and feldspar grains, and rounded to subrounded micrite grains. Ooides and calcitic fossils occur in fragments.

Stylolites, outlined by insoluble organic material and clay minerals (Wanless, 1979) indicate that parts of the original beds have been dissolved. The stylolite frequency increases towards both the upper and lower bedding planes, forming closely spaced ribbons (Figure 21).

Pyrite is the only opaque mineral observed. The distribution is irregular and probably controlled by the original distribution of sulfur-bearing organic material.

The matrix consists of sugary-textured micrite (< 5 um) showing uniform grain size. It probably crystallized from lime mud.

The presence of grain and fossil fragments and grains of various degrees of roundness indicates that the lime mud, now present in the form of micritic matrix, was originally deposited elsewhere (upper slope or shelf) and has been transported and redeposited in its present stratigraphic position.

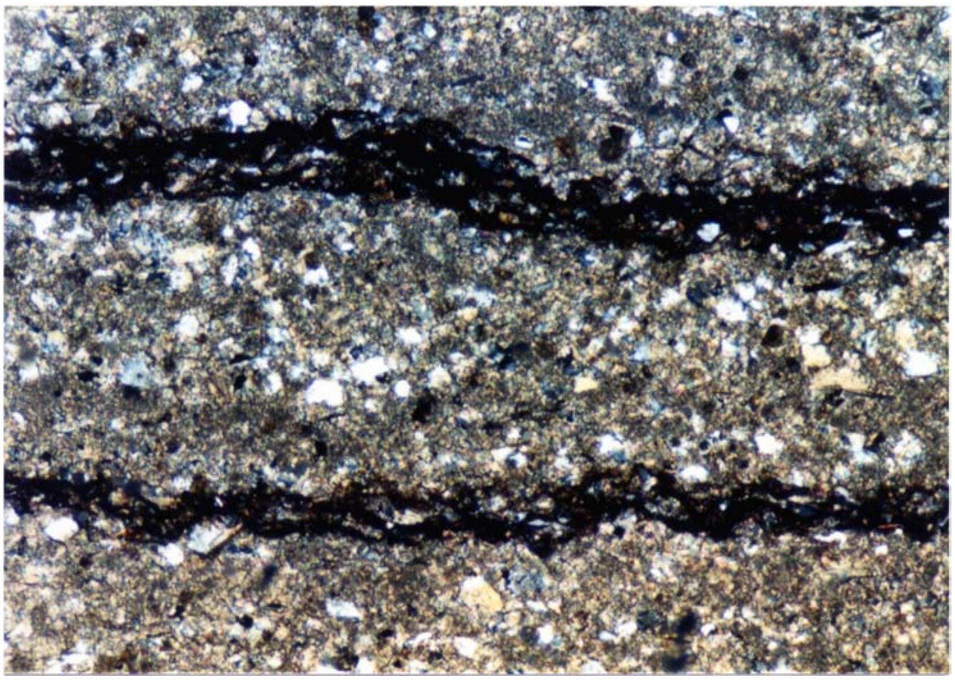

Figure 21. Insoluble residue outlines solution features in a sandy limestone from Judson Point. (Field of View: 2 mm wide)

SHALES:

The shales of the Hatch Hill are black to gray and consist of a dense clay matrix with various amounts of silt-sized quartz grains. The quartz grains are angular to subangular. The matrix consists of platy clay minerals that are usually parallel to bedding. When laminations are present, they are due to zones of higher clay/quartz ratio and lower clay/quartz ratio relative to the rest of the rock.

Calcite is only present as a very minor constituent, together with zircon and pyrite.

DIAGENESIS

INTRODUCTION:

The main interest of the study of the Hatch Hill Formation was to determine the nature of the dolomite. Two hypotheses could be envisioned for the origin of the dolomite: (1) dolomite formed on the shelf, for example, in a sabhka-type environment (e.g. Patterson and Kinsman, 1982) and was then redeposited within the Hatch Hill arenites, or (2) the dolomitization took place after the final deposition of the Hatch Hill arenites. Most, if not all, of the dolomite, as is demonstrated below, is clearly a product of the diagenesis and is present as authigenic cements. The focus has therefore to be shifted to processes that lead to the precipitation of the dolomite, and the diagenetic environment in which it formed. The accompanying authigenic phases, silica, calcite, alkali feldspar and plagioclase, might provide further information about the diagenetic environment, and the diagenetic history of the Hatch Hill arenites. The first part of this chapter describes the paragenetic relationships of each individual phase. This is followed by a description of the phases involved in the cementation of the Hatch Hill Formation and a discussion of their possible origin.

PARAGENESIS:

The paragenetic sequence of the authigenic mineral phase is based on two criteria: (1) the inclusion of older mineral phases in younger ones, and (2) the cross cutting relations of individual phases with each other. The second criterion is especially difficult to apply and is often ambiguous. Figure 22 shows two examples of cross cutting relationships observed in the Hatch Hill Formation. Figure 22A can be interpreted in two ways: (1) formation of the dolomite rhombs and later development of a blocky calcite cement, which filled the open pore space, or (2) development of a blocky calcite cement that was later replaced by larger dolomite crystals. Both interpretations are valid and can be observed in diagenetic sequences reported. I would tend to use interpretation (2) in this type of situation, as the calcite probably is the predecessor of the dolomite phase.

Figure 22B is somewhat easier to interpret, but it is more the exception than the rule in the Hatch Hill arenites. The cross cutting relationships here clearly indicate that the rhombohedral dolomite grain postdates the formation of quartz overgrowths and micritic cement.

These two simple examples show that each paragenetic sequence has to be handled with care, and is always affected by the interpretations of the observer.

I interpret the record of authigenic minerals of the Hatch Hill sequence as follows (in order of formation)

(1) Pyrite formation

(2) Development of quartz overgrowths

(3) Precipitation of calcite cements

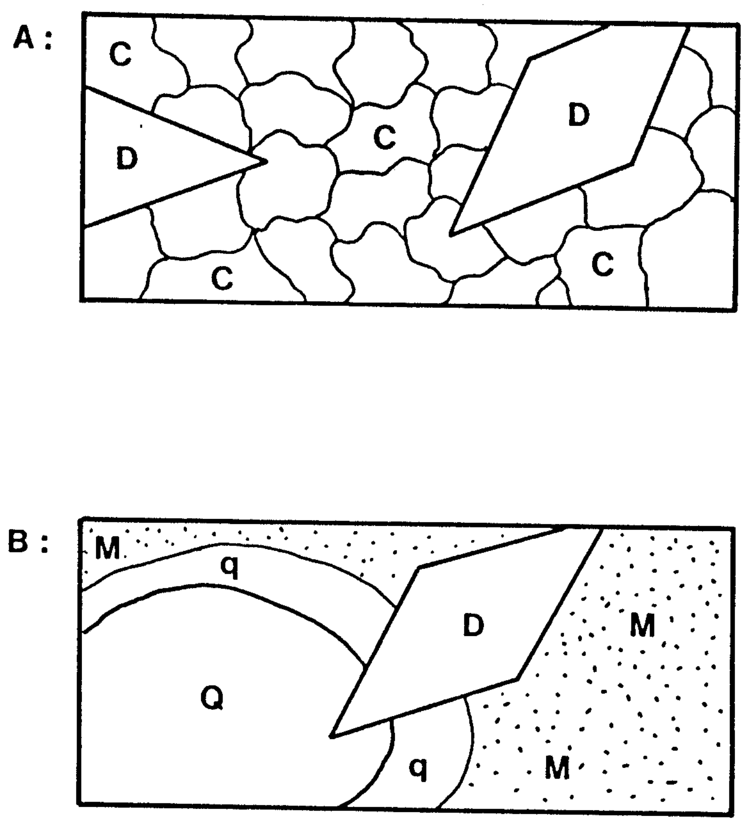

Figure 22: Two cases of cross-cutting relationship occurring in the Hatch Hill arenites.
C = calcite (blocky)
M = micrite
D = dolomite
Q = quartz
q = quartz overgrowth

(4) Precipitation of dolomite cements

(5) Growth of authigenic alkali feldspar and plagioclase.

The only well-established part of this sequence is that dolomite formation postdates quartz overgrowth and pyrite formation. This is documented (Figures 23 and 24) by pyrite inclusions in dolomite and the replacement of detrital quartz and authigenic quartz overgrowth by dolomite rhombs.

AUTHIGENIC PHASES:

Silica

Silica, when present, is one of the phases involved in the cementation of the Hatch Hill quartz arenites. It occurs as quartz overgrowths and as a silica cement. Chert is sparse and biogenic silica (e.g. Radiolaria) has not been observed. Both phases are always restricted to individual detrital quartz grains or quartz grain clusters. The distinction between quartz cement and overgrowths is somewhat artificial in this rock. In the discussion below, cement refers to material between grains that are in contact with each other (Figure 25), while quartz overgrowth refers to material that is not in contact with detrital grains, but with other cements. Both the quartz overgrowths and the quartz cement usually show fluid inclusions and impurities that are also present in the detrital phase. They are always syntaxial overgrowths of the host grain (in the case of overgrowths), or one of the quartz grains cemented, if grain clusters occur. Undulose extinction has not been

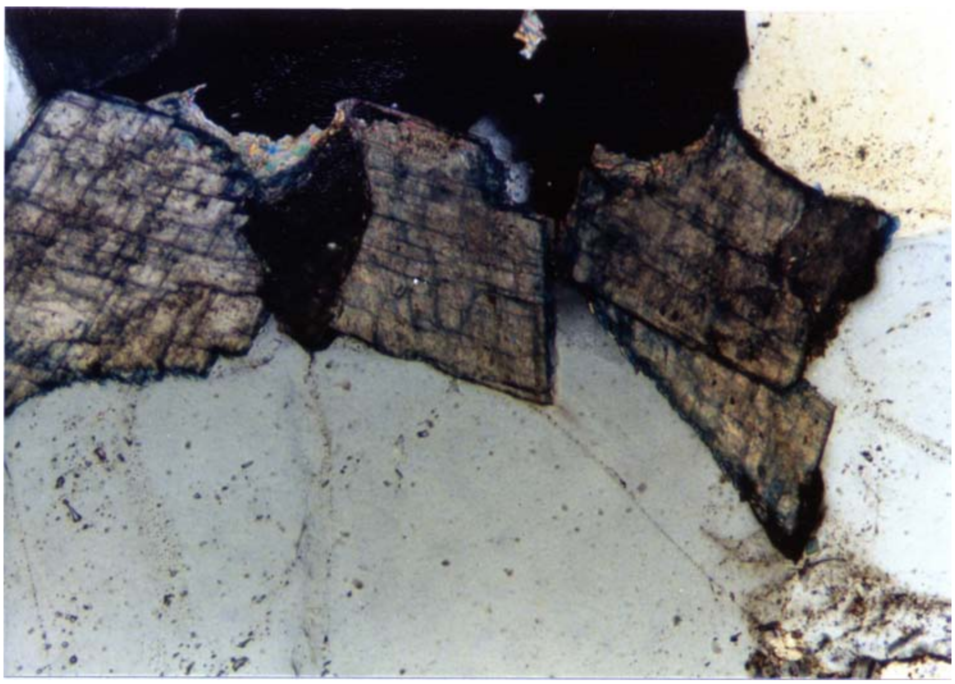

Figure 23. Dolomite rhombs replacing quartz (Judson Point). (stained) (Field of View: 0.85 mm wide)

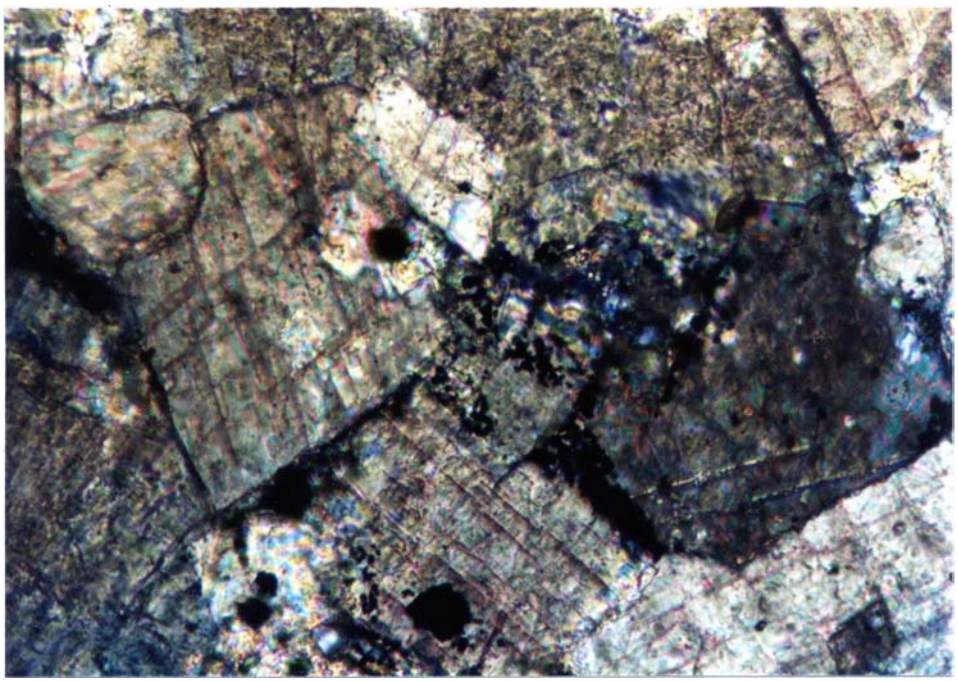

Figure 24. Pyrite inclusions in dolomite cement (Mettawee River). (Field of View: 0.34 mm wide)

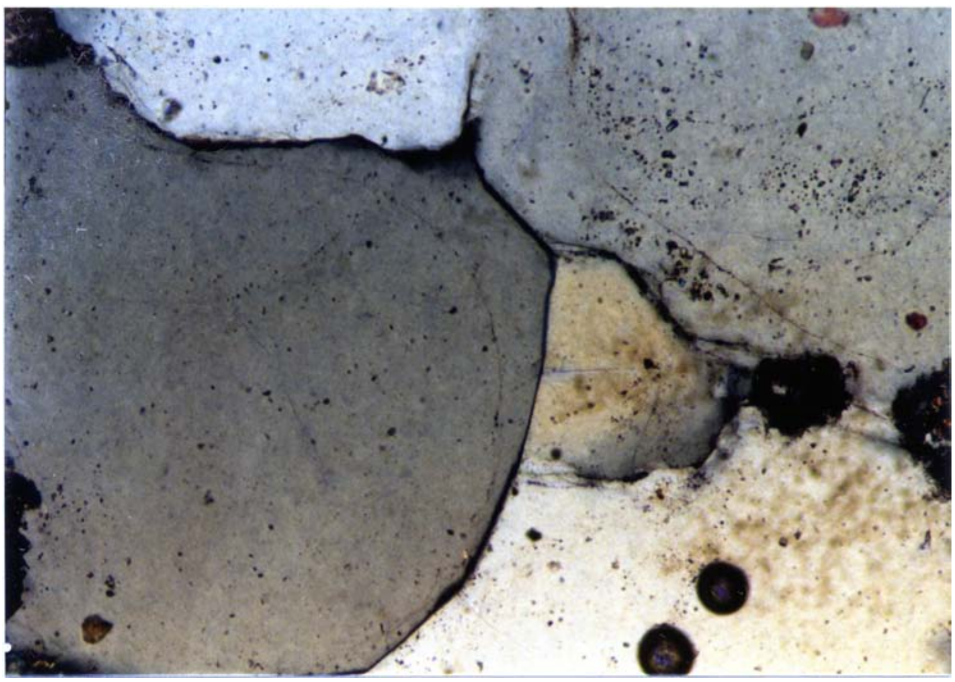

Figure 25. Quartz cement. Old grain boundaries are outlined by fine seams of fluid inclusions. (Field of View: 0.85 mm wide)

observed in any of the authigenic silica phases. Quartz overgrowths are usually associated with the rhombohedral face that grows faster than the prism faces in quartz (Blatt, 1979). If quartz grain clusters are present, the quartz cement is in optical continuity with the detrital quartz nucleus with the least internal stress, as indicated by even extinction of the grain. The cements therefore appear to nucleate preferentially along the grain boundaries of stress-free grains. Both silica phases together can account for up to 3% of the total cement volume of individual samples.

The amount of silica is positively correlated with grain size. Coarse grained sandstones that are supported by the detrital phase are most likely to show silica cementation. Grain-grain contacts (quartz) are always associated with the presence of any authigenic silica phase. Even though silica cements and overgrowths are almost always present in the samples studied, they do not account for more than 3% of the total cement volume.

No obvious source for silica can be deduced from the thin sections. Pressure solution is one process that has been stressed by many workers (Sprunt and Nur, 1977; DeBoer et al., 1977; Robin, 1978). Pressure solution is usually referred to as a process during which pressure along grain-grain contacts causes quartz to enter solution. This quartz may later reprecipitate on surfaces of quartz grains within the same rock that are adjacent to fluid spaces with lower pressure. Only a small amount of evidence for this type of silica liberation is preserved in the Hatch Hill Formation. Grain-grain contacts are typical for finer-grained sandstones. Sutures or stylolites along these grain-grain contacts, which are often observed in rocks that have undergone pressure solution (Hutcheon, 1983), are common, but silica cementation or overgrowth is rather sparse. On the other hand, coarse grained sandstones with a lower grain contact frequency often display silica cementation. The precipitation of silica is probably dependent on the availability of dissolved material and open pore space around detrital quartz grains, rather than on the liberation of silica alone. Pressure solution requires a fair amount of compaction that was not reached when the early diagenetic phase was precipitated. Therefore, if pressure solution was active during the precipitation of the silica phase, it most likely contributed only a little to the amount of cement present today. Other sources of silica may include unstable rock fragments and biogenic silica. Rock fragments are chemically and mechanically less stable than quartz (Hayes, 1979) and will be more likely to dissolve. The same is true for biogenic silica (silica oozes and radiolaria), which consists of opal-A (Williams and Crerar, 1985a), an amorphous silica phase that dissolves easily and yields a solution of relatively high silica content which may precipitate quartz after several steps of diagenetic maturation (Williams and Crerar, 1985b). Since no biogenic silica has been detected in the Hatch Hill quartz arenites, two possible explanations might occur: (1) There was no biogenic material to start with, and (2) all biogenic material is dissolved and possibly reprecipitated in the form of more stable quartz phases. Since biogenic silica predominates in marine sediments (Mizutani, 1977; Calvert, 1983), the second explanation seems to be more likely. The contribution of originally biogenic silica towards the total amount of silica cements depends on the mass of biogenic silica present, and its degree of reprecipitation in the Hatch Hill Formation. Unfortunately, both are unknown.

All sources discussed are internal sources that act within one given sandstone bed or sandstone packet. An external source for silica is dissolution of siliceous shales (Pittman, 1979) or the liberation of silica during shale diagenesis, e.g. transformation of smectite to illite (Burst, 1969). Both mechanisms cannot be ruled out, since all Hatch Hill sandstone beds are interlayered with black shales that could function as silica donors. If these processes were active during silica cementation, they must have taken place in a rather early diagenetic stage, when high permeability permitted the transport of dissolved material.

The record preserved in the Hatch Hill sandstones gives only direct evidence that pressure solution has acted as a silica-producing mechanism, but none of the processes discussed above can be ruled out as possible contributors to the silica cementation observed.

Pyrite

Pyrite is common as a minor constituent (less than 2%) in every sample studied. It occurs as irregularly distributed patches or as fine, irregularly shaped grains that are often aligned parallel to the lamination of the host rock. If burrows are present in the rock, they are typically filled and outlined by rounded pyrite. Poikilitic pyrite is sparse and contains inclusions of quartz (Figure 26). The conditions for pyrite formation are well known. Pyrite production is triggered by the reduction of sulfate from organic matter and the presence of dissolved iron under anoxic conditions (Berner, 1971). These conditions are only fulfilled below the sediment-water interface in normally oxygenated waters (Berner, 1983). Hence, pyrite can only form as a diagenetic mineral under normal marine conditions. Berner (1983) states that pyrite forms during shallow burial via the reaction of detrital iron minerals with H_2S. Two components in naturally occurring systems can account for H_2S production: decay of organic matter and the presence of $CaSO_4$. The ions produced by $CaSO_4$ dissolution are Ca^{2+} and SO_4^{2-}. The sulfate ions are then reduced to H_2S. However, it is much more likely that the pyrite present is connected to the reduction of organic matter. This is supported by the distribution of individual pyrite grains in burrows and along laminations of fine grained sandstones, which are areas where organic matter is usually enriched. The source of iron is assumed to be limonitic goethite, hematite and clay-sized chlorite (Berner, 1971), since organic material

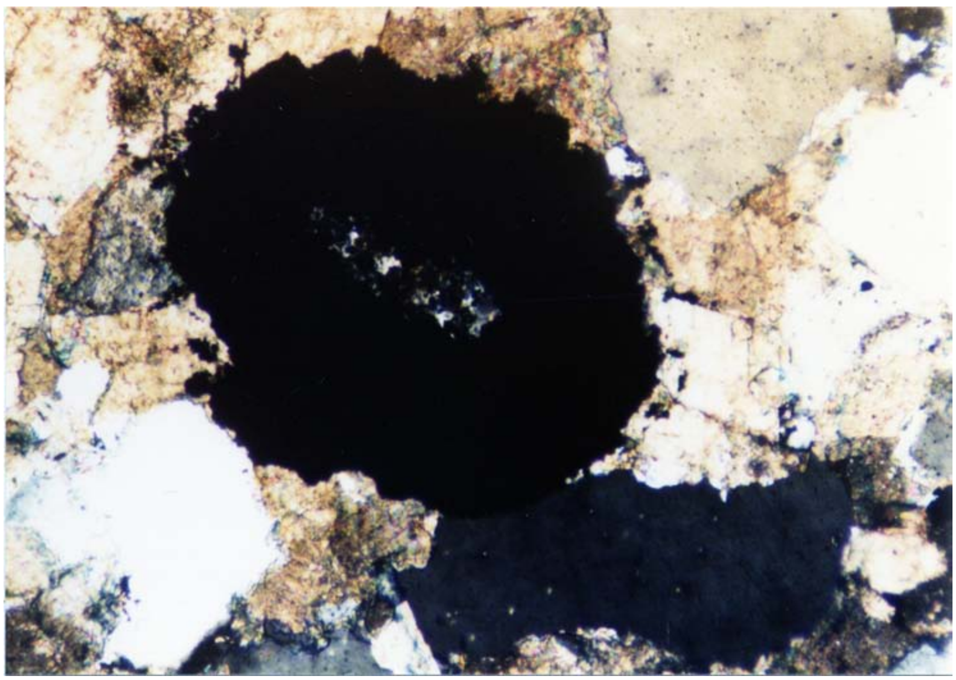

Figure 26. Poikilitic pyrite framboid (Mettawee River). (Field of View: 2 mm wide)

itself only contains very small amounts of iron. However, terrigenous marine sediments deposited under normal oxygenated conditions apparently contain sufficient iron material to allow pyrite formation (Berner, 1983).

Alkali Feldspar and Plagioclase

Alkali feldspar and plagioclase are both present as detrital and authigenic phases. Authigenic alkali feldspar occurs almost always in euhedral crystals in micritic carbonate cements (Figure 27). It can be distinguished from detrital alkali feldspar by its euhedral shape and by the fact that almost all detrital grains have microcline textures and are rounded to subrounded.

The determination of authigenic plagioclase is very difficult. The authigenic grains do not occur as euhedral or subhedral grains, but are usually anhedral. Twinning is typical and most grains are elongated parallel to the twin lamellae. Conclusive evidence for the authigenic nature of a plagioclase grain can only be found when cross-cutting relationships beween a grain and other authigenic or detrital phases can be demonstrated.

Both minerals are sparse and account for less than 1% of the total authigenic phases. The occurrence of authigenic alkali feldspar in Cambro-Ordovician shelf carbonates of the Appalachian basin has been observed before (e.g. Bryce and Friedman, 1975) and has been interpreted as evidence for the migration of hypersaline brines. More recent $^{39}Ar/^{40}Ar$ dating of these alkali feldspars showed

Figure 27. Euhedral alkali feldspars in micritic and blocky cement (stained) (Schodack Landing). (Field of View: 0.85 mm wide)

that they are much younger than their host rocks and might be related to brine migration associated with later deformational events, such as the Alleghenian Orogeny (Hearn and Sutter, 1985). The Hatch Hill arenites show no evidence for brine migration, hence the question of the origin of the alkali feldspar still remains unanswered.

Calcite

Calcite is the only diagenetic phase that is geographically restricted, being only present in the outcrops of the southern part of the Taconics: Schodack Landing, Judson Point, Nutten Hook and Stockport Station. It occurs in two different varieties that reflect three periods of diagenetic development as determined by cross-cutting relations of the individual phases. The first phase is micritic calcite, which shows the same sugary texture as that described above for detrital calcite grains. Its presence is dependent on the degree of recrystallization of the matrix minerals. In highly recrystallized rocks, micritic calcite is restricted to filling pores between grains, where the dominant calcite variety present is blocky calcite, the successor of the original micritic material. In rocks with a lower degree of recrystallization, micritic calcite coexists with blocky calcite (Figure 28) and can be found in direct contact with this calcite phase. The blocky calcite is preferentially present around detrital grains of quartz and forms a corona around those grains. The detrital grains probably functioned as nuclei for the development of this type of cement. The grain size varies from 50-100 um.

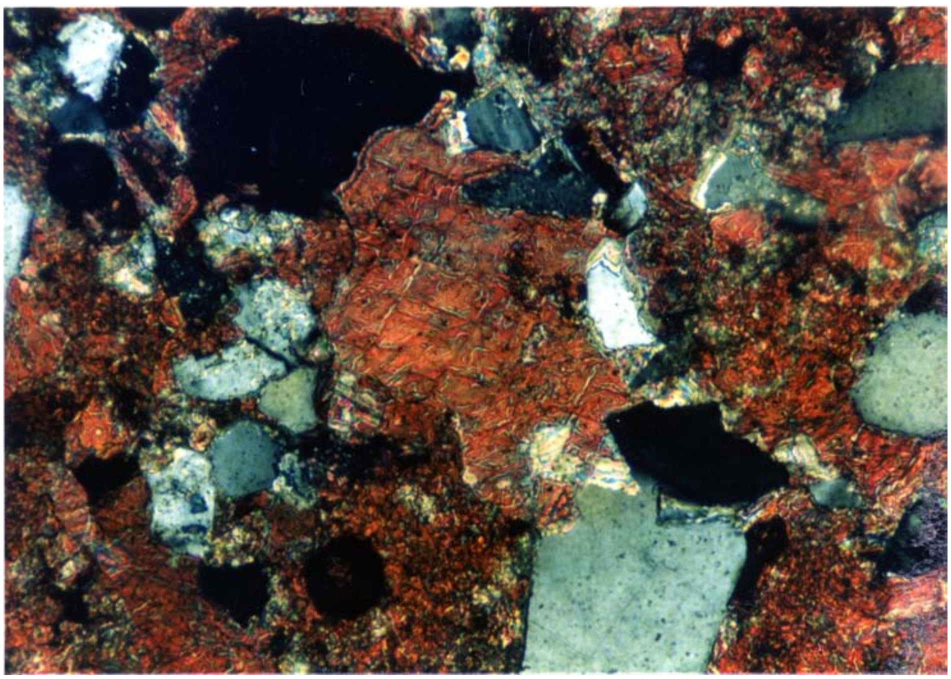

Figure 28. Coexisting micritic and blocky calcite cement (stained) (Schodack Landing).
(Field of View: 0.85 mm wide)

Larger grains are often twinned, with two sets of twin lamellae parallel to the rhombohedral planes, producing a mosaic of perfect rhombs within the grains. Both types of cement seem to have formed in a very early stage of diagenesis. Compaction could not have proceeded very far, since the cements occupy up to 50 percent of the total rock volume. The cement/detrital grain ratio increases with increasing grain size. The reason for this trend lies in the fact that fine grained areas in the rock were already closer packed when deposited than coarser grained ones. Coarse grained sections are completely supported by the cement, leaving detrital grains floating in the cement matrix. This suggests that they must have replaced a preexisting phase that covered these portions of the rock shortly after deposition. Two possibilities might account for this type of distribution: (1) the arenites consisted originally of quartz and carbonate grains, and the carbonate grains have later been replaced by the cement, or (2) the space now filled by carbonates was occupied by carbonate oozes that were later replaced by cement. Possibility (2) seems to be more reasonable, since rounded detrital grains of micritic calcite can still be observed and show little evidence for replacement by the later calcite cements.

The cements probably crystallized directly from the dissolution of the original carbonate oozes. The composition of this carbonate mud is not preserved in the rock. Modern analogues of shelf-deposited carbonate oozes contain aragonite, calcite, Mg-calcite, and minor amounts of proto-dolomite (Taft, 1967). These phases were most likely the reservoir for subsequent cement formation. The growth of carbonate cements nucleated at detrital grains and subsequently reduced the pore volume of the rock considerably. The development of blocky calcite is probably contemporaneous with the micritization of the original substrate, but its growth was favored, as can be concluded by the replacement of micritic calcite by blocky calcite. Pre-existing pore space and nucleation loci, preferentially at detrital grain boundaries and vugs, triggered the distribution of the sparry cement. At this stage, the concentration of dissolved Fe^{2+} must have been very low, since no iron-bearing calcite phases are recorded. The fluids from which both cements precipitated was probably seawater that was saturated or supersaturated with respect to Ca^{2+} and $CO_3{}^{2+}$ obtained from the dissolution of carbonate oozes.

Dolomite

Dolomite is present as detrital micritic grains and as a diagenetic phase. The origin of the detrital dolomite is not quite clear. The detrital grains might have originally been slightly consolidated carbonate grains that were later dolomitized or they may have already been dolomitized prior to their deposition within the arenites. The relation of the detrital dolomites to the calcite cements is difficult to interpret. Figure 29 shows a dolomite grain that has partially been replaced by diagenetic dolomite, now

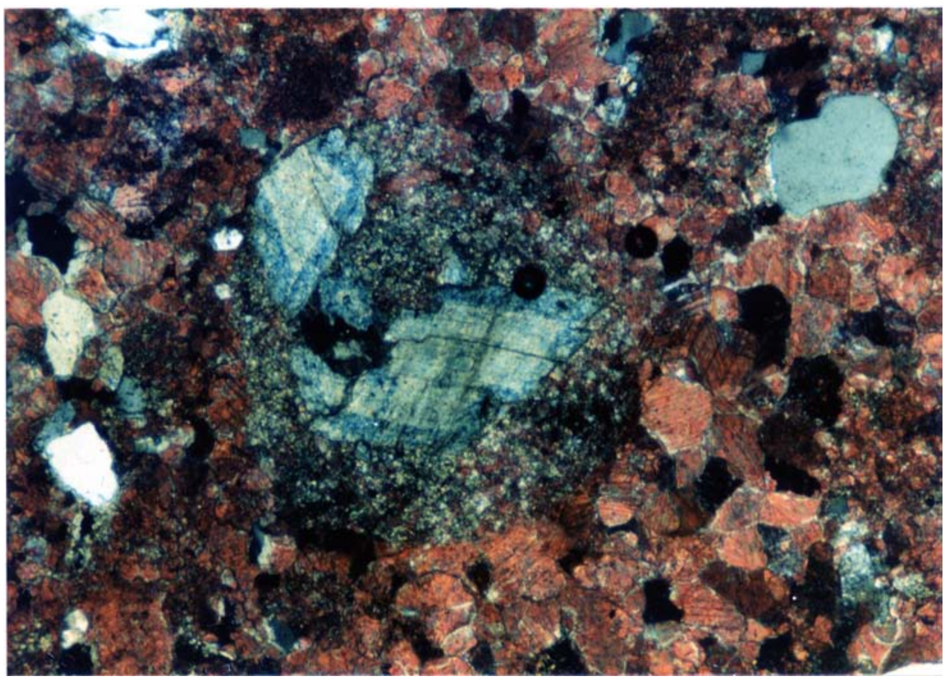

Figure 29. Micritic dolomite grain replaced by zoned dolomite rhombs (stained) (Schodack Landing). (Field of View: 0.85 mm wide)

preserved as zoned dolomite rhombs. The micritic detrital grain consists dominantly of slightly ferruginous dolomite and micritic calcite patches. It can be assumed that an originally micritic calcite grain was partially dolomitized and subsequently replaced by diagenetic dolomite rhombs. However, the possibility of a detrital dolomite grain partially de-dolomitized during calcite cement development that then functioned as a loci for the nucleation of the diagenetic dolomite rhombs also has to be considered. Hence, it is debatable whether micritic dolomite was part of the original detrital assemblage or is strictly a product of diagenesis. However, even if clastic dolomite is present it only accounts for less than 5% of the total amount of dolomite.

This problem is not associated with the dolomite cements observed. They are undoubtedly products of diagenesis and reveal no hints of transport and mechanical reworking. The diagenetic dolomites occur in euhedral to subhedral rhombs that have usually at least one well-developed rhombohedral face. A wavy, undulose extinction is typical for these grains. In plane polarized light each grain shows a cloudy texture and a pronounced pleochroism. Most grains show cleavage planes with up to two sets of cleavage parallel to the rhombohedral faces (Figure 30). A maximum of three different generations of dolomite could be found within one grain. Each generation reflects a growth period of the grain and can be identified by its iron

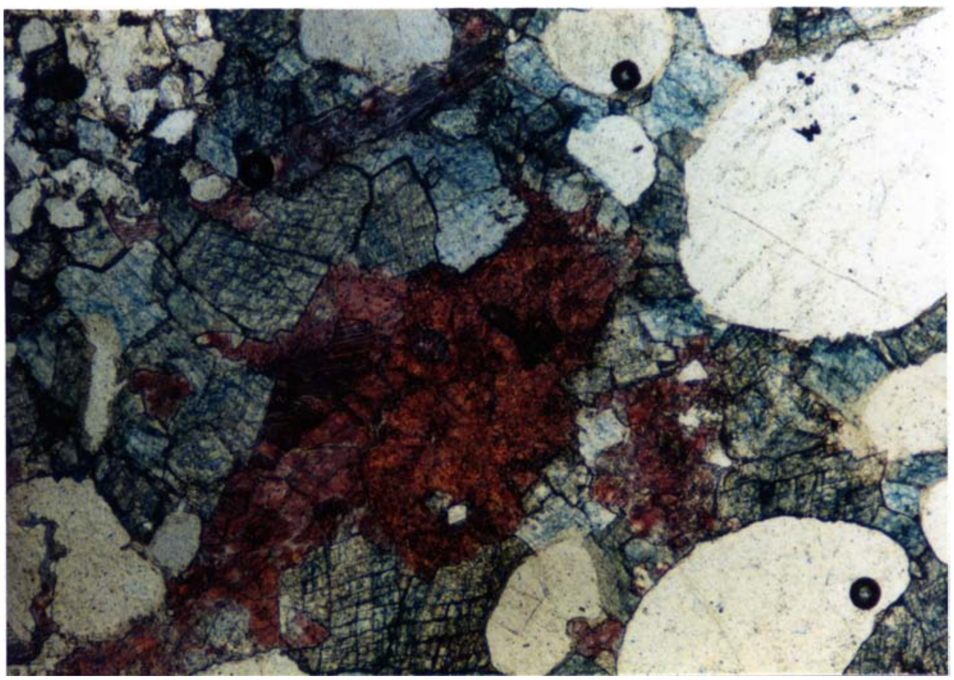

Figure 30. Cleavage parallel to the rhombohedral faces in dolomite (stained) (Schodack Landing). (Field of View: 0.85 mm wide)

content as revealed by staining with potassium ferricyanide. The oldest generation is iron-free cores, which are subsequently overgrown by an iron-rich (Figure 31) phase of more ankeritic composition. The contact between both phases is sharp and often follows the outline of the whole grain. The iron-rich overgrowth is restricted to the outer edge of the grain and makes up less than 10% of the total grain volume.

The third, and youngest, generation of dolomite is an iron-free overgrowth structure. This overgrowth is not restricted to dolomite grains, but also occurs on calcite grains when either phase is in contact with a silica phase. Unlike the grain cores, this dolomite phase is clear in plane polarized light and reveals irregular concentric zones of birefringence under crossed polarizers (Figure 32). Cleavage or twin related features of the host grain do not extend into zones occupied by this type of dolomite. Iron free overgrowth dolomite is the least abundant of the observed varieties. It only accounts for less than 2% of the total dolomite cement.

Dolomite is overall the most abundant cement. It accounts for up to 99% of the total cement volume and 45% of the total rock.

The grain sizes of individual dolomite grains range from 50-500 µm. They are generally dependent on the grain size (and hence packing) of detrital grains in each arenite bed in which they occur, i.e., larger grains occur in coarser rocks.

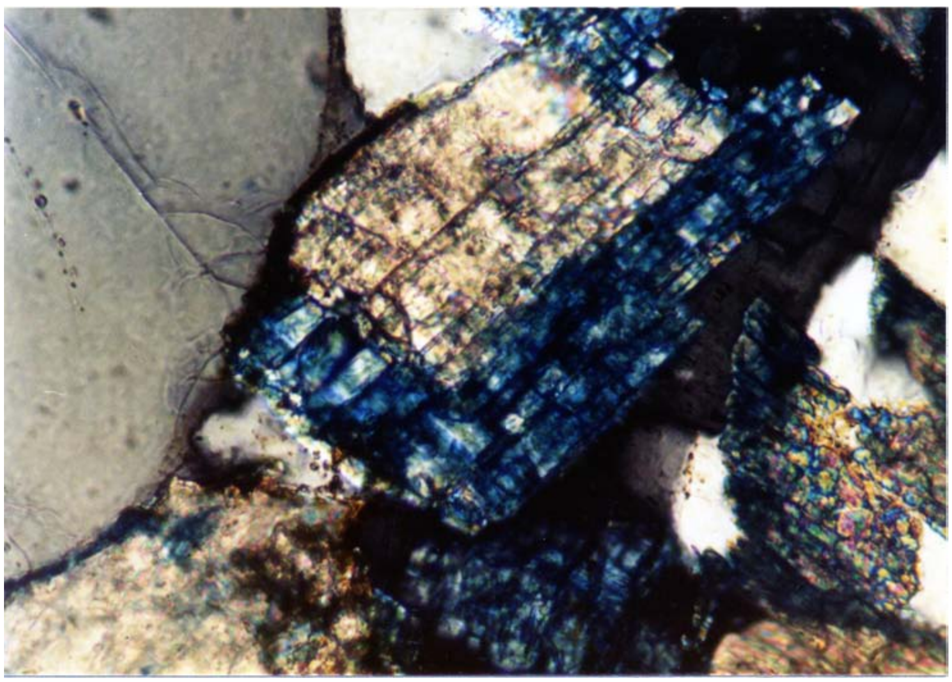

Figure 31. Zoned dolomite rhomb (stained) (Judson Point). (Field of View: 0.35 mm)

Figure 32. Dolomite overgrowth with irregular concentric zones of birefringence (stained) (Judson Point). (Field of View: 0.2 mm wide)

In the sections of the northern part of the Taconics, another variety of dolomite can be distinguished. It is very similar to the iron-free cores described above, but has a less pronounced pleochroism and only a weakly developed cleavage. In contrast to the previously described grains, straight extinction is characteristic for this type of dolomite. Iron-rich and iron-free overgrowth structures are not as common and can be completely absent. In the discussion below, I refer to this type of dolomite as type S (for straight extinction) and the previously described, zoned dolomite as type W (for wavy extinction) (Figure 33).

Inclusions of pyrite in the type W dolomites are present in some samples (Figure 24). The time of formation of both types of dolomites are difficult to determine, since they do not occur together in one sample. Thus the only known constraint is that both are older than the formation of ankerite overgrowth, which occurs on both types of dolomite.

The distribution of dolomite is obviously not regulated by the grain size of individual beds, but is more dependent on the geographic location of the outcrops. The Poultney River and Mettawee River sections are the only outcrops studied that do not display any calcite cement. At Nutten Hook, Stockport Station, Judson Point and Schodack Landing, calcite cements and dolomite cements coexist in individual samples. However, the grain size of single dolomite crystals seems to be positively correlated with the degree of packing of the detrital grains or the pore volume that was available

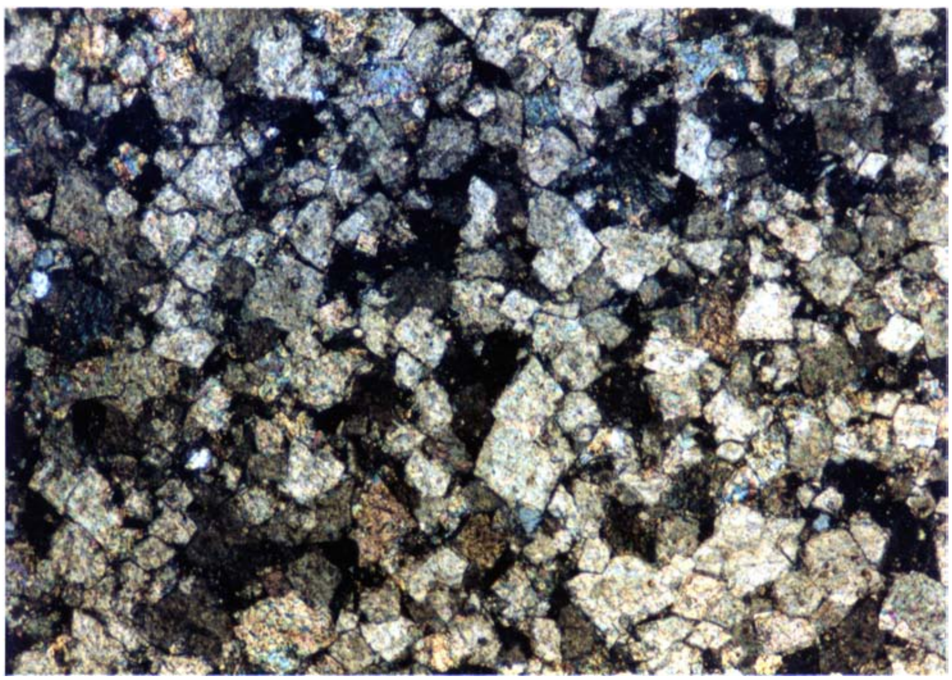

Figure 33. Mosaic of W-type dolomite (stained) (Poultney River). (Field of View: 0.85 mm wide)

for dolomite growth.

It is necessary to discuss possible sources and mechanisms of dolomitization to explain the presence of dolomite within the Hatch Hill Formation. Dolomitization is defined as the replacement of calcium carbonate by dolomite, and is believed to be a multi-step process that involves dissolution of calcite and later precipitation of dolomite out of solution (e.g. Land, 1985; Katz and Matthews, 1977). The principal factors that influence the formation of dolomite are (1) the Ca^{2+}/Mg^{2+} ratio, (2) the Ca^{2+}/CO_3^{2-} ratio, and (3) temperature (Machel and Mountjoy, 1986). Many other parameters also limit or favor the precipitation of dolomite but are less understood. These include, but are not limited to, the presence of SO_4^{2-} (Baker and Kastner, 1981), complex reactions of Mg^{2+} ions (Zemolich, 1983), the activity of HCO_3^- (Busenberg and Plummer, 1982) and the activity of Mg^{2+}/Ca^{2+} on crystal surface reaction zones (Mucci and Morse, 1983). Many of these factors are derived from experimental work and complex theoretical considerations and can only be applied with difficulty to naturally occurring systems. The following discussion is therefore focused on possible sources for ions involved in dolomitization (Mg^{2+}, Ca^2, Fe^{2+}, CO_3^{2-}, or HCO_3^-) and the environment of dolomitization.

The only source that is well-documented in the specimens studied is calcite. Therefore, if calcite was present as a predecessor to the dolomite phase, it must have dissolved and can account for Ca^{2+}, CO_3^{2-}, or HCO_3^- and even some of the Mg^{2+} if high magnesium calcite was stable and present in the original carbonate oozes or carbonate cements. Indications of calcite dissolution can be found in limestone beds of the sequences at Schodack Landing and Judson Point, where stylolites and clay seams are remnants of this process (see also Chapter 2, Petrography and Mineralogy, and Wanless, 1979). In samples where populations of both calcite and dolomite grains are present, cross-cutting relations support the replacement of calcite by dolomite. Nevertheless, the conversion of calcite to dolomite in a closed system should create porosity, since two moles of calcite are 13% larger than one mole of dolomite (Weyl, 1960). Since the Hatch Hill arenites have very little porosity, an external source for Ca^{2+} and CO_3^{2-} or HCO_3^- is required. The same is true for magnesium ions, since no originally Mg-bearing phase is recorded in the Hatch Hill sandstones, and high magnesium calcite (~10% $MgCO_3$) alone cannot account for the full amount of magnesium required for dolomitization, if a closed system is assumed. Therefore, an external source and an open system, at least with respect to Mg^{2+}, Fe^{2+}, and CO_3^{2-}, must be considered. Furthermore, the source area for these ions has to be near the beds, because prograding dolomite formation destroys the permeability of the rock considerably. The depositional environment of Hatch Hill arenites is the upper part of the continental rise, or the lower part of the slope. The arenites are interlayered with black shales. Therefore, two end-members of the possible environment of dolomitization can be envisioned: (1) a penecontemporaneous or early diagenetic dolomitization, during which the carbonate phase of the Hatch Hill arenites was still in free exchange with sea water, and (2) a late stage diagenetic environment that has been separated by burial processes from free exchange with seawater. The petrological evidence shows that the dolomite formation postdates the precipitation of calcite cements, the development of silica cementation and, at least in part, the formation of pyrite. This can be documented by inclusions of pyrite in dolomite rhombs and cross-cutting relations between dolomite and silica cements (Figures 23 and 24). The presence of silica cement, if precipitated from dissolved organic silica and other unstable silica phases, as well as pressure solution, requires some degree of burial. The same is true for ankerite cements, which are often associated with deep burial and elevated temperatures (Boles, 1978; Land and Dutton, 1978; Muffler and White, 1969). It therefore seems reasonable that the dolomite formation took place under conditions separated from active exchange with seawater. Seawater is saturated with respect to dolomite (e.g. Blatt _et al._, 1980) and hence so are pore fluids trapped in the sediment, but it is undersaturated with respect to ankerite. However, trapped pore fluids alone cannot account for dolomitization; active pumping of a large volume of seawater is required (Hsu and Siegenthaler, 1969; Land, 1983). One possible mechanism to provide an active flow of water could be the dewatering of shales during compaction (Magara, 1980). This process, in combination with late diagenetic silica reactions in clays, may provide both a source and mechanism for dolomitization. One well-known reaction is the transformation of smectite to illite, which liberates several moles of calcium, magnesium and iron, depending on the initial composition of the smectite (Boles, 1978). This reaction progrades with the depth of burial and leads to well-developed, well-ordered smectite-illite layers (Blatt et al., 1980). Perry and Howes (1970), for example, have shown that the reaction of smectite to illite occurs progressively from 50^{o} to 100^{o} in Gulf Coast Tertiary sediments. Magnesium is also liberated from structural Mg^{2+} lost during the montmorillonite to illite transformation (Mattes and Mountjoy, 1980).

Unfortunately, nothing is known about the composition of shales associated with the Hatch Hill arenites, or the clay mineralogy in detail. It requires further studies to elucidate the influence of the shale mineralogy on the cement composition. It also cannot be discounted that fluids with the potential to dolomitize had access to the Hatch Hill arenites at some point during diagenesis, but it is not possible to prove this, or even to speculate about their origin and migration through the arenites.

In general, regardless of the setting of dolomitization and the origin of the dolomitizing fluid, the fluid chemistry must have changed considerably during dolomitization. This is recorded in iron zoning of individual crystals. The iron rich rims, later coated by iron-free dolomite, clearly show that iron was only available for a relatively short time compared with the time required to build up iron free cores and overgrowths. Partial dissolution of already precipitated phases occurred during several periods of dolomite formation (Figure 32). In general, the formation of dolomite cannot be linked conclusively to one period during diagenesis when only petrographic criteria are applied.

OXYGEN AND CARBON ISOTOPES

Carbon and oxygen isotopes are tools used to collect information on the environment and conditions of dolomite formation. However, several problems complicate the rigorous use of isotope data to delineate the origin and diagenesis of dolomitized carbonates. The relationships between $\delta^{18}O_{water}$, $\delta^{18}O_{dolomite}$, $\delta^{18}O_{ankerite}$ and temperature are imperfectly known, and depend on the crystalline structure of a particular dolomite (Land, 1983). Further complications derive from the fact that the initial dolomitization of a sediment appears to require an open system to impart sufficient amounts of magnesium for dolomitization. Finally, many dolomitized sediments, in particular older ones, may have undergone several periods of recrystallization to more stable phases of different isotopic composition. In addition to chemical factors, sample preparation also influences the final isotopic signature of carbonate-bearing rocks. This is especially true if several carbonate cements coexist in one sample or even in one grain, as is the case in the Hatch Hill arenites. The isotopic signature will then record the whole grain composition instead of individual periods in the grain's history. Deciphering the evolution of one grain population is dependent upon sampling techniques. The values recorded in the following discussion always refer to the isotopic signature of several grains, which in themselves definitely display more than one generation of dolomite. To determine a more accurate grain evolution and hence the conditions of small scale dolomite formation within one grain, much finer sampling techniques would have to be applied. However, even bulk grain analysis should reveal some information about the overall conditions of dolomite formation.

RESULTS:

The oxygen and carbon isotopic data for the Hatch Hill arenites from nine analyses are presented in Table I and Figure 34. Carbon and oxygen values are presented relative to the Chicago PDB standard. All samples refer to the bulk cement analyses, since individual grains could not be separated. The samples described for dolomite/ankerite were chosen from outcrops in the northern part of the Taconics, since they appear to be rather homogeneous with respect to their dolomite composition, and contain dominantly Type S dolomite, even though minor amounts of Type W might be present. Two samples from micritic limestones were analyzed for calcite composition, since individual calcite cement grains could not be separated.

<u>Calcite</u>

The carbon isotopes for calcite occur within the common range of marine limestones between $-2\delta^{13}C$ and $+1\delta^{13}C$ (Mattes and Mountjoy, 1980). The very negative $\delta^{18}O$ values (-12 ± 0.5 ‰) indicate that at least the distribution of the $\delta^{18}O$ did not take place during exchange with "seawater" under "normal" marine conditions. The difference between calcite

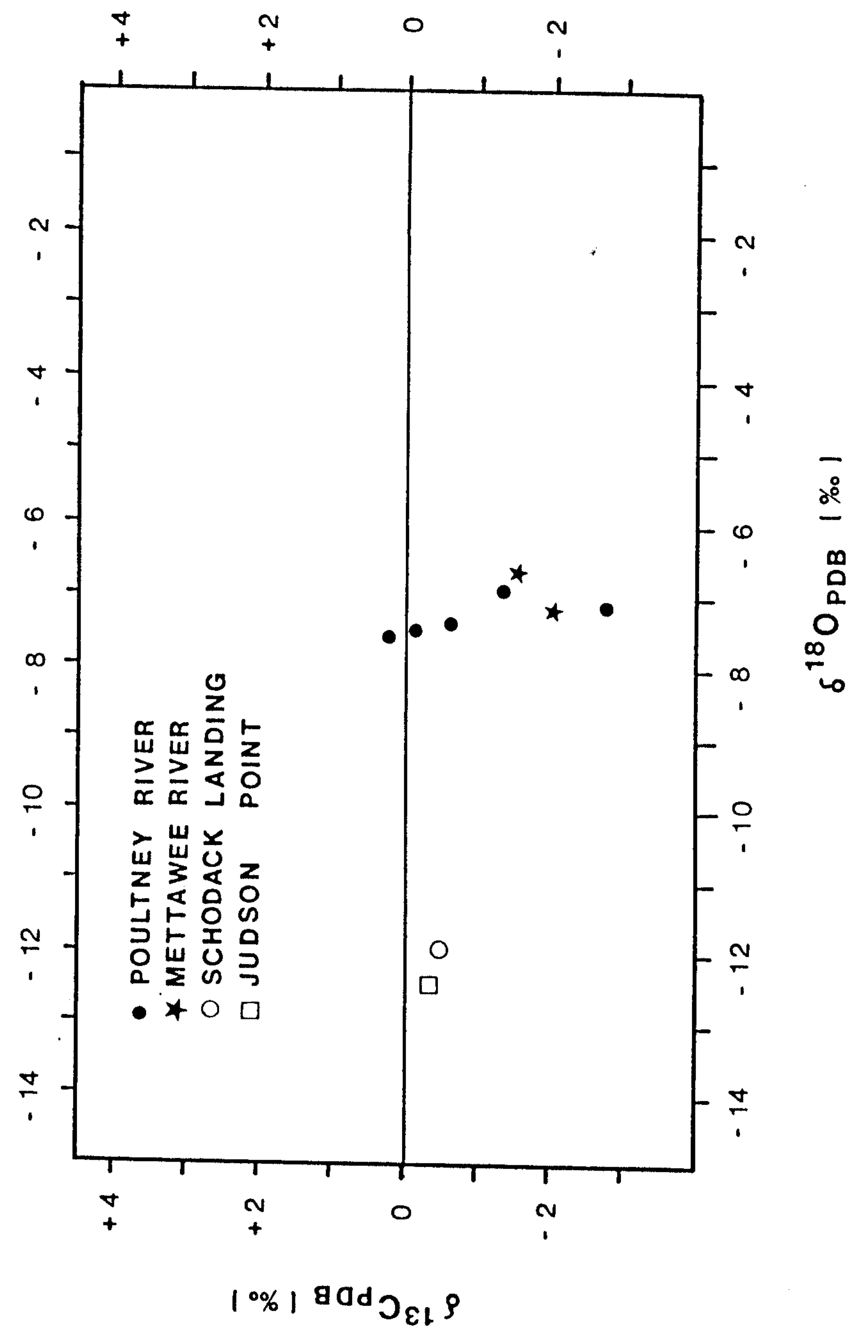

Figure 34. Summary plot for $\delta^{13}C$ versus $\delta^{18}O$ for samples from the Hatch Hill Formation.

and dolomite ($\Delta^{18}O_{dolomite-calcite}$) ranges from 4.4‰ to 5.8‰ and lies within the previously known ranges of coexisting calcite and dolomite (3‰ to 6‰, at 25°C) (Land, 1983).

Dolomite/Ankerite

The analyses for oxygen and carbon isotopes reveal a rather well-defined field for all samples. The dolomite/ankerite cements are characterized by a rather narrow range of $\delta^{18}O$ of about 1‰ and a range of $\delta^{13}C$ of about 2.93‰. The oxygen values do not show any systematic variation; however, if the carbon isotopes are plotted against their position in the stratigraphic column (Figure 35) a trend toward lighter $\delta^{13}C$ values in higher (younger) strata can be determined.

DISCUSSION:

Two general trends can be extracted from the isotopic data: (1) the variation of $\delta^{18}O$ is narrow and less than 1‰ for each carbonate phase, and (2) the $\delta^{13}C$ values define a trend toward more heavy carbon with decreasing depth. It is apparent that whatever caused the fractionation of the carbon isotopes has not affected the oxygen isotopes in the same manner. The signature of both isotope pairs $^{18}O/^{16}O$ and $^{13}C/^{12}C$ should record the last precipitation and recrystallization event, since exchange reactions with pore fluids or diffusional processes (Land, 1980; Veizer, 1983; Longstaffe, 1983) are of minor importance (Hudson, 1977). The oxygen data of both the calcite and the dolomite are

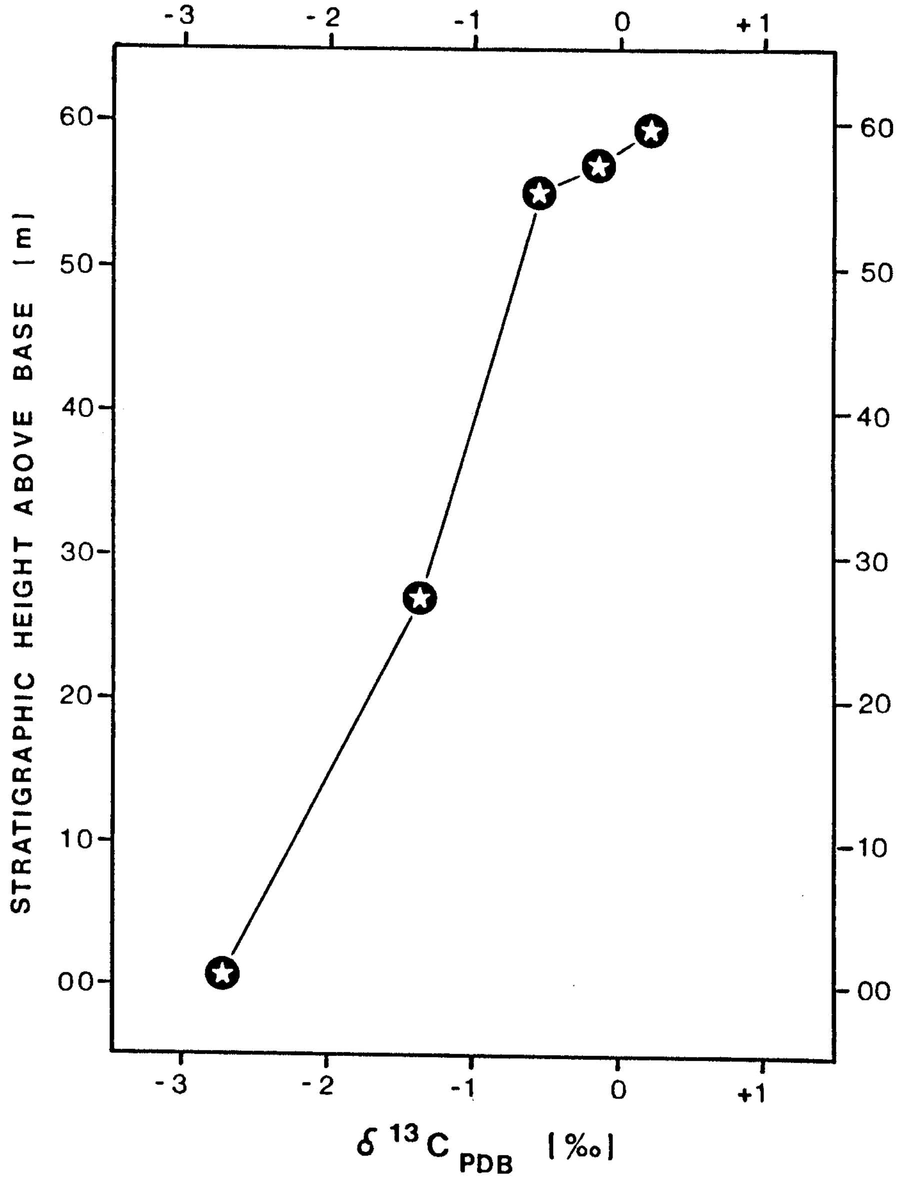

Figure 35. Stratigraphic height versus $\delta^{13}C$ for the outcrop at Poultney River.

considerably more negative than if they had crystallized from normal marine waters. Land (1983) states that dolomites with oxygen values smaller than -2‰ (PDB) must have either formed from or been affected by either water depleted in ^{18}O with respect to seawater, or by elevated temperatures. The formation of the Hatch Hill dolomite cements clearly took place after the deposition of the original sediments and hence in the general location of the upper continental rise or the lower continental slope (Bird and Dewey, 1970; Keith and Friedman, 1977). Therefore, formation from meteoric waters (depleted in ^{18}O with respect to seawater) alone can clearly be excluded. Dolomites have nevertheless been reported from schizohaline environments, where mixing of meteoric water with seawater takes place (e.g. Badiozamani, 1973; Folk and Land, 1975; Choquette and Steiner, 1980). This process, however, usually takes place on carbonate platforms, where exchange with continent-derived groundwaters and the shelf carbonates appears to be much more likely. Textural characteristics of this type of dolomite are typically smaller grain sizes (5-20 μm) than present in the Hatch Hill Formation (50-500 μm) (Zenger, 1981; Choquette and Steiner, 1980). Hence, the Hatch Hill dolomites most likely formed under the influence of elevated temperatures, even though the influence of light isotopic formational waters of unknown origin cannot be completely excluded, based on the present data set. Whatever the processes were that triggered the isotopic fractionation of

^{18}O and ^{16}O, they resulted in a narrow range of $\delta^{18}O$ compositions over a stratigraphic range of 60 m, and thus indicate rather constant conditions for oxygen fractionation. The stable conditions reflected by the oxygen isotope compositions are in contrast to the trend defined by the carbon isotopes. If this trend is real, and one has to keep in mind that it is based on only five analyses, it documents an evolution of the carbon isotopes towards a lighter composition with increasing depth of burial. A process that can explain this trend must satisfy two conditions: (1) it has to change the fractionation of carbon isotopes, and (2) it has to leave the fractionation of oxygen isotopes unaffected. Strong carbon isotope fractionation trends of authigenic carbonates with depth are reported from diagenetic environments that are characterized by the successive decay and fermentation of organic matter (e.g. Irwin et al., 1977; Curtis, 1978; Irwin, 1980; Wada et al., 1982; Pisciotto and Mahoney, 1981; Kelts and McKenzie, 1982; Claypool and Threlkeld, 1983; Anderson and Arthur, 1983; Gautier and Claypool, 1984).

The decay of organic matter is a process that is influenced by the chemical properties of four distinct diagenetic zones of the sub-seafloor environment. These zones are (1) the zone of aerobic oxidation, (2) the zone of anaerobic sulfate reduction, (3) the zone of anaerobic methanogenesis and carbonate precipitation, and (4) the zone of thermocatalytic decarboxylation (Berner, 1981; Pisciotto and Mahoney, 1981; Irwin et al., 1977; Anderson and Arthur, 1983). Each zone is characterized by a variety of chemical reactions, which are summarized in Figure 36 (from Anderson and Arthur, 1983). The general trends that influence the precipitation of authigenic carbonates are the progressive production of carbon dioxide that (1) dissolves in the pore fluids (in Zones 1 and 2 and again in Zone 4) and ultimately leads to the dissolution of preexisting carbonate phases or (2) escapes from the sediments (in Zones 1 and 2). Its consumption during methanogenesis favors the precipitation of authigenic carbonates. The second important trend is the reduction of sulfate and iron to sulfide and bivalent iron, which may lead to the formation of pyrite, and removes SO_4^{2-} ions, which appear to inhibit the precipitation of dolomite (Baker and Kastner, 1981).

Carbon isotopes of authigenic carbonates precipitated within the various zones of microbial metabolic processes reflect the $\delta^{13}C$ of the carbon species in those zones (Table II and Figure 37, Pisciotto and Mahoney, 1981). The pore fluids of each diagenetic zone record the signature of $\delta^{13}C$ of the CO_2 produced and dissolved within each zone. Zones 1 and 2 are characterized by negative $\delta^{13}C$ values, since its carbon is dominantly derived from organic carbon, which is generally depleted in ^{13}C (Claypool and Kaplan, 1974; Irwin et al., 1977). Interstitial waters in the zone of methanogenesis show progressive enrichment with respect to ^{13}C, since the preferential incorporation of ^{12}C in methane (CH_4) leaves a reservoir of residual heavy carbon

Reaction	Tracer
aerobic oxidation	
1) $O_2 + CH_2O \quad CO_2 + H_2O$	increase TDC, NO_3^-, PO_4^{3-}
anaerobic oxidation	
2) $4NO_3^- + 5\ CH_2O + 4H^+ \quad 2N_2 + 5CO_2 + 7H_2O$	increase TDC, decrease NO_3^-
3) $2MnO_2 + CH_2O + 4H^+ \quad 2Mn^{2+} + CO_2 + 3H_2O$	increase Mn^{2+}
4) $2Fe_2O_3 + CH_2O + 8H^+ \quad 4Fe^{2+} + CO_2 + 5H_2O$	increase Fe^{2+}
5) $CH_2O + SO_4^{2-} \quad 2HCO_3 + H_2S$	decrease SO_4^{2-}, increase S^{2-}
$(SO_4^{2-} : HCO_3^- = 1:2)$	increase TDC, decrease ^{13}C
6) $CH_4 + SO_4^{2-} \quad HCO_3^- + HS^- + H_2O$	decrease SO_4^{2-}, increase S^{2-}
$(SO_4^{2-} : HCO_3^- = 1:1)$	increase TDC, decrease ^{13}C
	TDC : ^{13}C/TDC larger than for (5)
7) $CH_2O + H_2O \quad CO_2 + 4e^- + 4H^+$	
8) RCHO + H_2O RCOOH + $2e^- + 2H^+$ aldehyde organic acid	electron flow for continued methanogenesis
Thermal decarboxylation	
9) RCOOH RH + CO_2 organic molecule hydrocarbon	increase TDC, increase ^{13}C
Carbonate dissolution	
10) $CaCO_3 + CO_2 + H_2O \quad Ca^{2+} + 2HCO_3$	increase Ca^{2+} and TDC, no ^{13}C
Total CO_2 outputs	
11) $Co_2 + 8e^- + 8H^+ \quad CH_4 + 2H_2O$ methanogenesis/CO_2 reduction	decrease TDC, increase ^{13}C TDC increase CH_4
12) $(Ca^{2+}, Fe^{2+}, Mg^{2+}) + 2HCO_3^-$ (Ca, Fe, Mg) $(CO_3) + CO_2 + H_2O$ authigenic carbonate precipitation	decrease TDC (Ca, Mg, Mn, Fe) no ^{13}C

TDC = Total dissolved carbon

Figure 36. Reactions and tracers of diagenetic processes (modified from Anderson and Arthur, 1983).

Table II. Diagenetic zones and characterizing chemical reactions during burial of organic-rich matter (modified from Pisciotto and Mahoney, 1981).

Diagenetic Zones and Oxidation-Reduction Reactions		Temperature at base of Zone (^{o}C)[a]	Observed or Estimated $\delta^{13}C$ Range (‰ PDB)		
			CO_2	CH_4	Carbonate
Microbial oxidation (aerobic respiration):		2	- -18 to -28	---	No ppt. (Curtis, 1978)
$CH_2O + O_2 \quad CO_2 + H_2O$	(1)				
Microbial sulfate reduction (anaerobic):		2.5	- -15 to -30	---	- 0 to -25
$CH_2O + SO_4^{2-} \quad S^{2-} + 2CO_2 + 2H_2O$	(2)				
Methanogenesis: methane production and carbonate precipitation (anaerobic):		75	- -20 to +10	- -47 to -90	- -10 to +15
$Me^{2+} + 2HCO_3^- + 8H^+ \quad CH_4 + MeCO_3 + 3H_2O$					
where Me = Ca, Mg, Fe, etc.	(3)				
Thermocatalytic decarboxylation:		< 150	- -10 to -20	- -60 to -80	- 0 to -10 (-25?)
fatty acids n-alkanes + fatty acids + CO_2	(4)				

[a] for water/sediment interface temperature of $2^{o}C$.

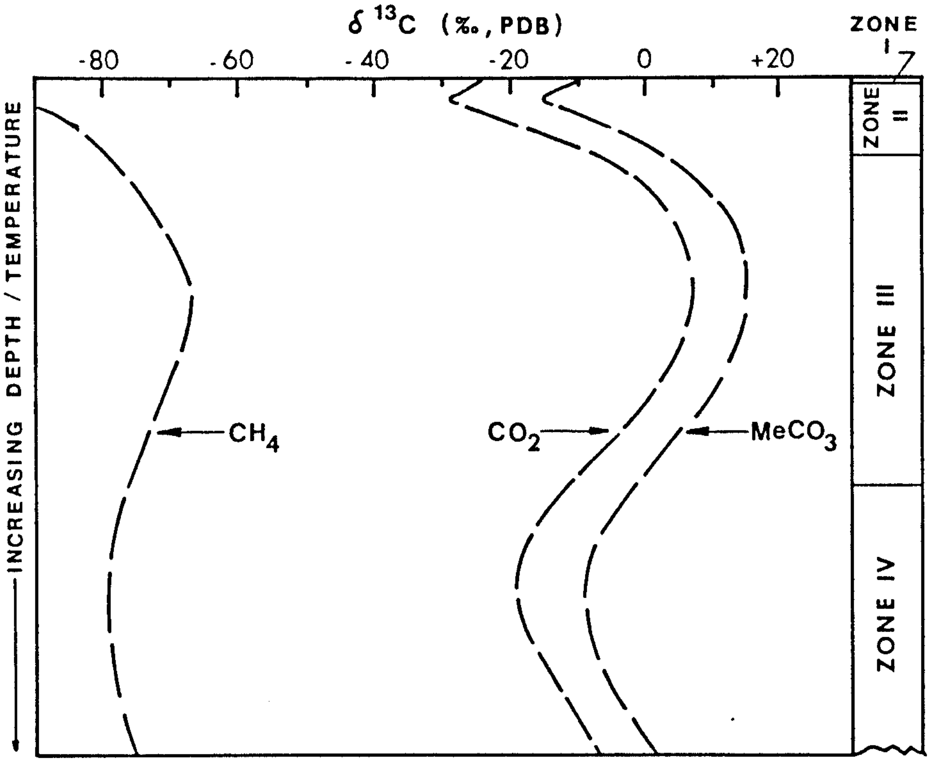

Figure 37. Diagenetic trends of $\delta^{13}C$ (from Pisciotto and Mahoney, 1981)

Me = Ca^{2+}, Mg^{2+}, Fe^{2+}

bicarbonate (Rosenfeld and Silverman, 1959; Claypool and Kaplan, 1974). This trend reverses at greater burial depths, perhaps because of the input of thermocatalytic CO_2 from Zone 4 (Kelts and McKenzie, 1982; Irwin et al., 1977), which would ultimately derive from decarboxylation of organic molecules (see also Table II), and hence be depleted in ^{13}C, or perhaps because of the imbalance between the rates at which light carbon is added and removed in methane production (Claypool, 1974). Even though the explanation for this trend towards negative ^{13}C in the lower part of the zone of methanogenesis is still under discussion, it has been observed at DSDP sites 467, 468, 471 and 479 (Pisciotto and Mahoney, 1981; Kelts and McKenzie, 1982), and in other places (Irwin et al., 1977; Curtis, 1978).

From the discussion so far, it becomes clear that each diagenetic zone has a very characteristic $\delta^{13}C$ signature and very distinct trends that can be compared with isotopic signatures of recent and ancient organic rich sediments that have undergone diagenesis. Sediments that contain the isotopic signature described above should furthermore have some constraints; that is, that they were organic rich to start with and have been buried deep enough to allow organic matter to decompose. Authigenic minerals of those sediments might then record one or more diagenetic zones.

The primary prerequisite for all processes described so far is the incorporation of organic matter into the sediments deposited. The arenites of the Hatch Hill Formation show little direct evidence that they contained abundant organic matter to start with. But, the carbonate shelf adjacent to the Taconic sequence documents a whole variety of biological activity (Fisher, 1985). It is most likely that at least microbiological activity in surface waters extended further seaward and contributed organic matter to the muds of the sea floor, which today are preserved as the gray-black slates of the Hatch Hill Formation. Black shales are usually interpreted to have been deposited under anoxic conditions and to have contained a fair amount of organic matter, as documented for the Paleozoic black shales of Britain (Leggett, et al., 1981). Therefore, it is reasonable to assume that the shales of the Hatch Hill Formation originally contained a fair amount of organic carbon, even though no analyses for their present carbon content have been published.

If these sediments have been buried sufficiently, they should have passed through the diagenetic zones described before, and cements of the sandstone sequence (Curtis, 1978) might preserve the isotopic signature associated with each sequence, or at least parts of one zone. The isotopic trend recorded in the Hatch Hill arenites satisfies this prediction. If the curve for isotopic changes with depth by Pisciotto and Mahoney (1981; Figure 37) is used to estimate the diagenetic zone in which the Hatch Hill arenites formed, the negative trend of the carbon isotopes, and their absolute values, fall into the lower part of Zone 3, where heavy isotopic carbon trends back to lighter values that might be produced by the thermocatalytic reactions in Zone 4. This implies that the cements of the Hatch Hill sandstones should have formed close to the temperature of termination of methane generation (75°C; Rice and Claypool, 1981), since it clearly postdates the main pulse of methane genesis that produced heavy carbon isotopes. A crude depth of pre-orogenic burial can be inferred from calculations by Rowley et al. (1979), who estimated that, after restoring the tectonic thinning, the Taconic sequence (from the top Bomoseen Formation to the bottom Pawlet Formation) had an approximate thickness of 2000 m. This estimate is based on observations in the Granville area. The Taconic sequence in this area is now approximately 600 m thick. Wood (1973, 1974) estimated approximately 75% shortening perpendicular to slaty cleavage, using ellipsoidal reduction spots as finite strain markers. This would indicate a burial of 1100-1500 m for the Hatch Hill Formation before tectonic loading. This depth of burial would imply that the dolomite cements formed at a temperature between 20° and 40°C, if a geothermal gradient of 20-25°C/km is assumed for the Taconic sequence. However, oxygen isotope values indicate higher temperatures and hence a greater depth of formation.

Oxygen isotopes can be used as a thermometer to estimate the temperature of formation for dolomites. However, unlike the well known calcite-water fractionation, the isotopic fractionation between dolomite and water at low temperatures is still uncertain. This can be seen in Table III, where four of the equations are shown that can be used to

Table III. Paleotemperatures determined from cements at the Poultney River section.

Sample No.	PDB	SMOW	A	B	C	D
5020	-7.14	23.55	84°C	79°C	74°C	71°C
5049	-6.97	23.72	83°C	78°C	73°C	70°C
5073	-7.39	23.29	86°C	81°C	76°C	73°C
5076	-7.49	23.19	87°C	82°C	76°C	74°C
5080	-7.60	23.08	88°C	83°C	77°C	75°C
Range			4°C	4°C	3°C	4°C

A: $1000 \ln \alpha_{dolomite-water} = 3.2 \times 10^6 T^{-2} - 1.50$ (Northrup and Clayton, 1966)

B: $1000 \ln \alpha_{dolomite-water} = 3.34 \times 10^6 T^{-2} - 3.34$ (O'Neil and Epstein, 1966)

C: $1000 \ln \alpha_{dolomite-water} = 3.23 \times 10^6 T^{-2} - 3.29$ (Shepard and Schwarcz, 1970)

D: $1000 \ln \alpha_{dolomite-water} = 2.78 \times 10^6 T^{-2} + 0.11$ (Fritz and Smith, 1970)

1) This equation is used to transfer PDB values into SMOW values:

$$\delta^{18}O_{SMOW} = 1.03091\, \delta^{18}O_{PDB} + 30.91$$ (from Hoefs, 1980)

2) This equation is used for an approximation of $10^3 \ln \alpha_{dolomite-water}$

$$\delta^{18}O_{dol} - \delta^{18}O_{water} \approx 10^3 \ln \alpha_{dol-water}$$ (in SMOW) (from Hoefs, 1980)

Assumption: $\delta^{18}O$ pore fluid = 0 (SMOW) determine the temperature of formation for a given $^{18}O_{dolomite}$ and $^{18}O_{water}$. The $\delta^{18}O_{dolomite}$ can be measured directly from the carbonate cement phase, but the $\delta^{18}O_{water}$ has to be assumed. The temperature calculations in Table III are based on the assumption that all carbonates have equilibrated with fluids having $\delta^{18}O$ = 0.0‰ SMOW. This assumption yields maximum temperatures if the pore fluids were not affected by meteoritic or brine waters, because many $\delta^{18}O$ profiles of interstitial waters at DSDP sites begin at 0‰, near the sediment-water interface, and gradually decrease with burial (Lawrence et al., 1975; Pisciotto and Mahoney, 1981). The temperatures calculated from four different equations (see Table III) for samples collected at the Poultney River yield temperatures from 71°-88°C, with a narrow range of 3°-4°C for calculations using the same equation. However, regardless of which equation is used, all samples have temperatures close to 75°C, the preclusion temperature of methane generation (Rice and Claypool, 1981), and therefore fall into the temperature interval predicted. The narrow range of oxygen isotope composition of the samples analyzed is probably due to rather constant temperatures in this stratigraphic portion of the Hatch Hill Formation during dolomite formation.

However, if the dolomite cements of the Hatch Hill Formation formed either from meteoritic water ($\delta^{18}O_{H_2O}$: -50‰ to +10‰, SMOW; Hoefs, 1980), brine water ($\delta^{18}O_{H_2O}$: -10‰ to + 8‰, SMOW; Clayton et al., 1966) or a mixture of seawater with either phase, then different temperatures of formation would result, if the equiations of Table III (A-D) are used for estimating temperature. The influx of meteoritic water (depleted in $\delta^{18}O$ with respect to seawater) lowers the actual temperature of formation, while pore fluids enriched in $\delta^{18}O$ by brine waters would result in higher temperatures. Figure 38 shows the effect of the $\delta^{18}O$ composition on the actual temperature of formation for a dolomite phase (curves A and D) and a calcite phase (curve C). Curves A and D are calculated to show the largest paleotemperature difference for dolomite cements that have been determined at the Poultney River section. Curve A is calcualted for a $\delta^{18}O_{dolomite}$ value of 23.55‰ (SMOW), which corresondes to the value measured for sample 5080 using equation A by Northrup and Clayton (1966; see also Table III and Figure 38). Curve A shows the highest paleotemperature for any sample of the Poultney River section at a given $\delta^{18}O$ composition of the pore fluid. Curve D is calcualted for a $^{18}O_{dolomite}$ value of 23.08‰ (SMOW), which corresponds to the value measured for sample 5020, using equation D by Fritz and Smith (1970; see also Table III and Figure 38). Curve D shows the lowest paleotemperature for any sample of the Poultney River setion at a given $\delta^{18}O$ composition of the pore fluid. Curve E is calcualted for an $\delta^{18}O_{calcite}$ value of 18‰ (SMOW), which corresponds to sample 2054 from the Judson Point section, using equation E by Friedman and O'Neil (1977; see also Figure 38).

The temperatures that can be calculated for the calcite

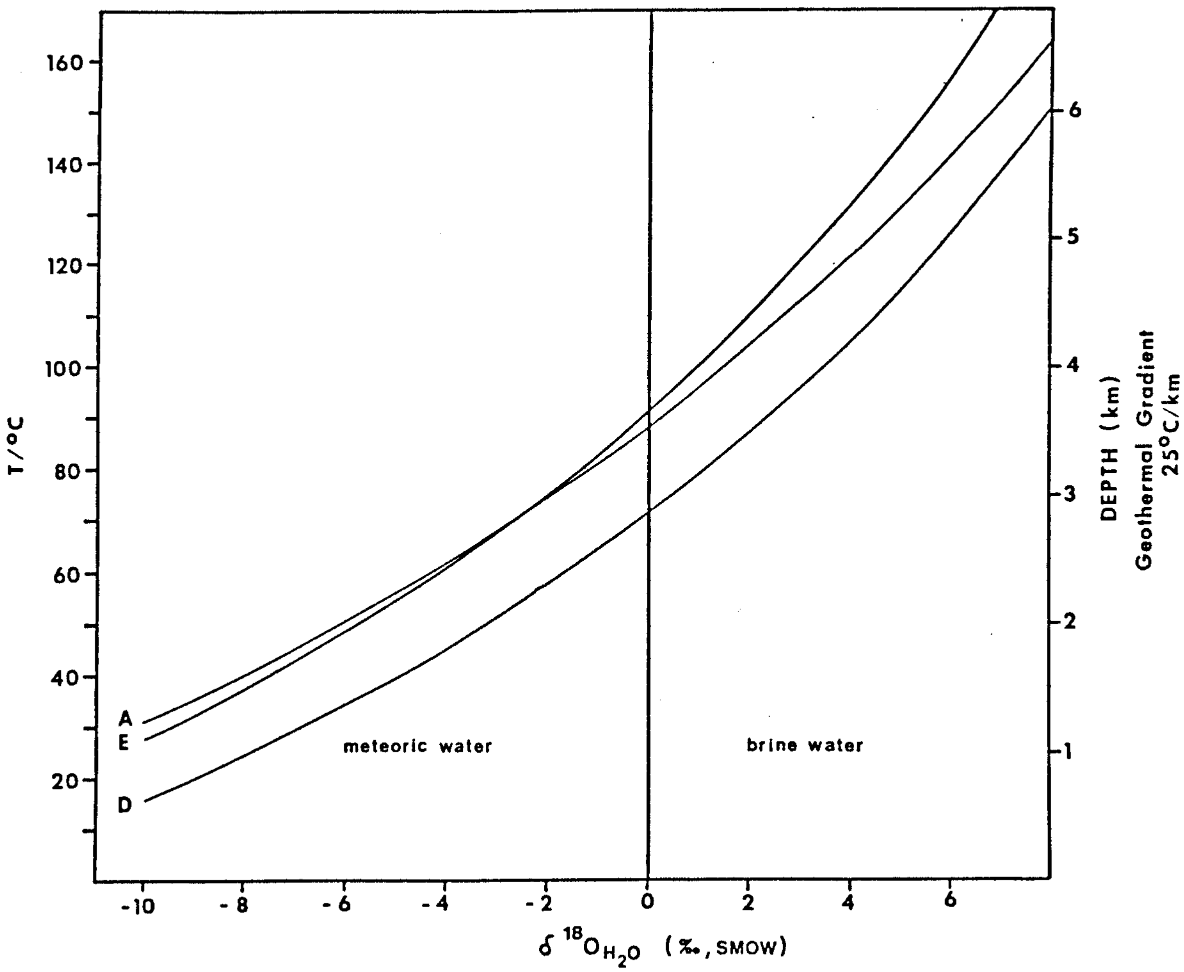

Figure 38. Paleotemperatures versus $\delta^{18}O$ of pore fluids (see also text).

A: $10^3 \ln\alpha_{\text{dolomite-water}} = 3.2 \times 10^6 T^{-2} - 1.5$
(Northrup and Clayton, 1966)

D: $10^3 \ln\alpha_{\text{dolomite-water}} = 2.78 \times 10^6 T^{-2} + 0.11$
(Fritz and Smith, 1970)

E: $10^3 \ln\alpha_{\text{calcite-water}} = 2.78 \times 10^6 T^{-2} - 2.89$
(Friedman and O'Neil, 1977)

Curve A is calculated for a dolomite with $\delta^{18}O$ = 23.08‰ (SMOW).

Curve D is calculated for a dolomite with $\delta^{18}O$ = 23.55‰ (SMOW).

Curve E is calculated for a calcite with $\delta^{18}O$ = 18‰ (SMOW).

phase (sample 2054) overlap and are only slightly higher than the temperatures determined for the dolomite phase. The similar temperatures of formation, and the fact that the $^{18}O_{dolomite-calcite}$ (4.4‰ -5.8‰) lies within the previously known ranges of coexisting calcite and dolomite (3‰-6‰ at 25°C) (Land, 1983) could indicate that both formed under similar conditions. The absolute temperature of formation, however, is dependent on the pore fluid composition at the time of formation.

Since it is not possible to determine the $\delta^{18}O$ composition of the pore fluids during the time of dolomite cement development, the precise temperature of formation cannot be calculated. However, the trend of carbon isotopes with depth suggests that the dolomite cements of the Poultney River section formed in the lower part of the zone of methanogenesis, and hence at temperatures close to 75°C. Therefore, if the equilibration of the oxygen and carbon isotopes took place at the same time and the oxygen isotopes did not reequilibrate at a later stage of diagenesis or metamorphism, then it seems likely that they formed from a pore fluid of a composition close to 0‰ (SMOW).

The temperatures calculated on the assumption that the dolomite cements formed from a pore fluid with $\delta^{18}O = 0$ ‰ (SMOW) can then be used to estimate the depth of burial at the time of cement formation, if a reasonable geothermal gradient is assumed. Present day passive continental margins (e.g. older than 80 million years) such as the shelves of Nova Scotia and Labrador have geothermal gradients of approximately 23°C km^{-1} (Keen, 1979). Hence, to reach a sediment temperature of 75°C, a burial depth of approximately 3 km would be required. This implies that the development of dolomite cements took place during or after the flysch sequence (Pawlet Formation) was deposited on the continental margin sequence.

The dolomite formation within one bed probably occurred over a relatively short time interval, and was not strongly affected by the original form in which the carbonate was deposited. In sample 6008 (Figures 39 and 40), both the dolomite cement that developed between detrital minerals (6008CE) and the dolomite that replaced what was probably originally a calcite clast (6008CL) have very similar isotopic values and vary only by 0.63‰ (PDB) for $\delta^{18}O$ and 0.45‰ for $\delta^{13}C$ composition. This is considerably less variation than observed for the range of the ^{13}C values recorded in the cements of the 60 m stratigraphic interval of the Poultney River section.

As reported before, the $\delta^{13}C$ values of the cements of the Hatch Hill arenites document a formation in diagenetic Zone 3, the zone of methanogenesis. Information about the other diagenetic zones is only recorded in one other authigenic phase, pyrite. Pyrite most likely formed in Zone 2 after the reduction of sulfate to sulfide and its reaction with iron minerals. The formation of pyrite predates dolomite genesis, since pyrite can be found as inclusions in dolomite minerals. Isotopic values for the other carbonate

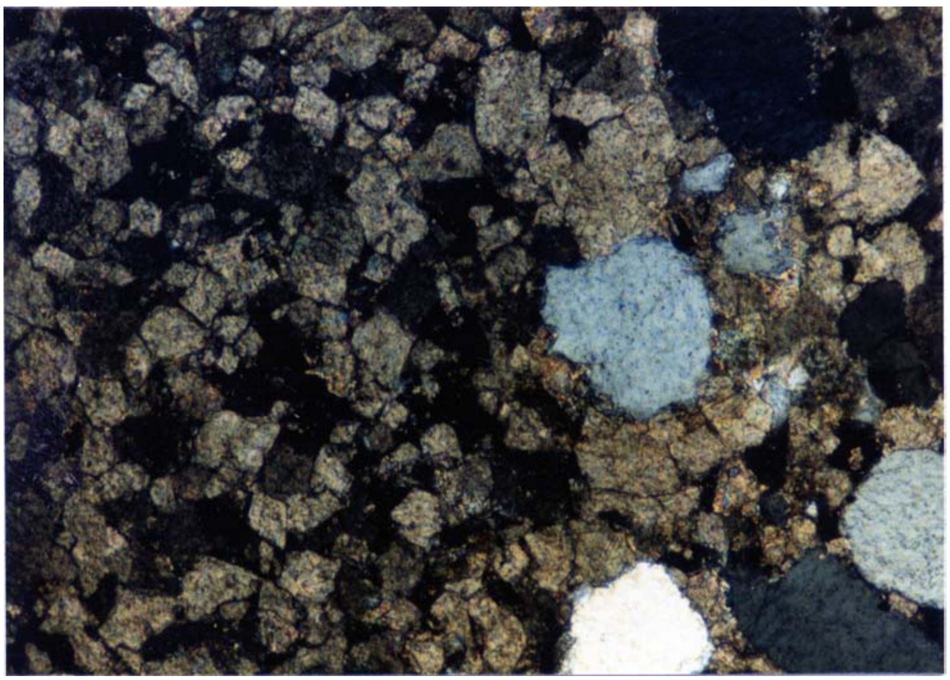

Figure 39. Relatively fine grained dolomite mosaic. On the left is part of a clast (Sa 6008CL). The coarser grained dolomite on the right associated with the detrital quartz is cement (Sa 6008CL) (Mettawee River). (Field of View: 2 mm wide)

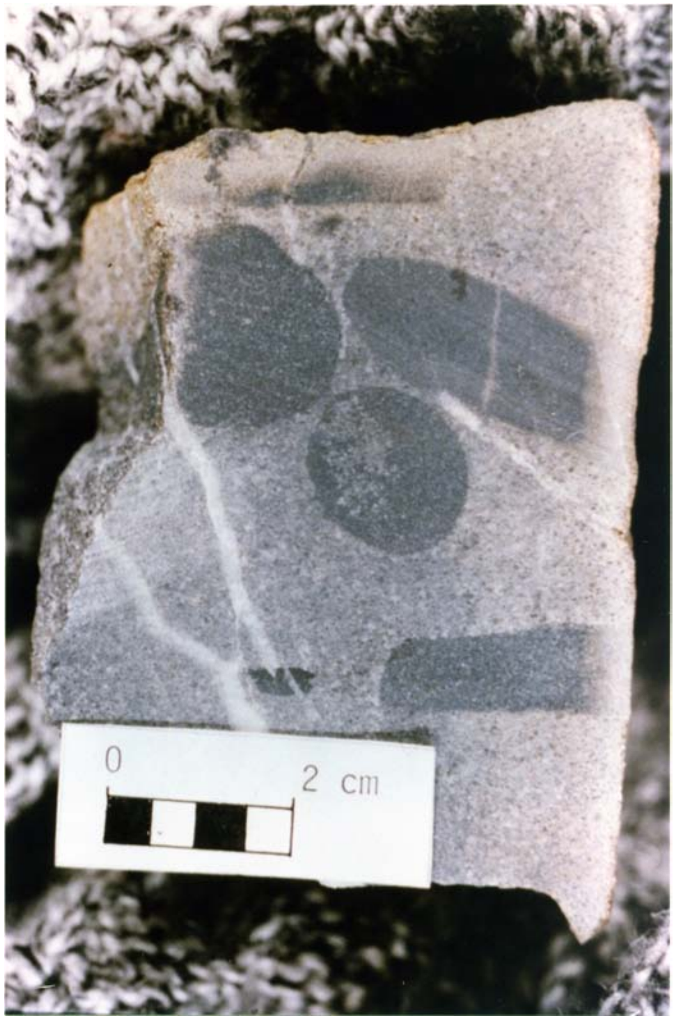

Figure 40. Sample 6008. 6008CE is taken from the cement of the matrix. 6008CL is taken from the clasts. (Mettawee River).

phases have not been determined for coexisting calcite and dolomite, but only for limestone beds within the Hatch Hill Formation. The petrological evidence (cross cutting relationships) show that calcite formation predates dolomite formation, if both carbonate cements coexist in one sample. However, since the limestones contain no dolomite, it is not possible to determine paragenetic relationships for the calcite of the limestones and dolomite cements. The isotopic evidence alone (Table I, sample 997 and 2054) is inconclusive.

SUMMARY AND CONCLUSIONS

The initial purpose of this study was to determine the nature and origin of the dolomite in the Hatch Hill Formation. Two competing hypotheses stood out at the beginning of the study: (1) the dolomite was formed on the shelf adjacent to the depositional environment of the Hatch Hill Formation and dolomitized carbonate material was reworked and redeposited in the Hatch Hill arenites, and subsequently recrystallized to a large extent, or (2) the dolomite formation was a product of processes that took place after deposition of the Hatch Hill arenites, either very shortly after the deposition of the arenites, when free exchange occurred with seawater that had access to the sediments, or at a later stage of burial, under conditions that are dominantly triggered by the sediment composition. In each hypothesis, the carbonate phase should contain clues identifying the environment of deposition.

PETROGRAPHIC RECORD:

The petrographic record shows that the most abundant phase of dolomite is not detrital, dolomitized carbonate grains, but dolomite cements. These cements show no signs of reworking or transportation and grew under conditions that favored the development of euhedral to subhedral crystals. They contain, in a few cases, inclusions of pyrite and postdate the formation of silica cement, since they replace both detrital quartz and authigenic quartz overgrowths. Therefore, the mass of dolomite clearly formed after the deposition of detrital material. The formation of dolomite was probably not a one-stage process, but happened in several stages, as documented by the stages of overgrowth and different extinction patterns. No final conclusion can be drawn from the petrologic data to unambiguously determine the dolomitization of detrital carbonate grains. Both hypotheses, dolomitization and later redeposition, and deposition of micritic calcite grains and later dolomitization, are equally possible. Nevertheless, the formation of dolomite in the detrital carbonate grains clearly predates the formation of dolomite rhombs, since the rhombs replace detrital grains. Hypothesis (1) can therefore clearly be excluded for the formation of the dominant phase of dolomite, the dolomite cements, but might be possible for the minor volume of detrital phases. Dolomitization therefore at least largely, and perhaps entirely, took place after the deposition of the detrital phases of the Hatch Hill arenites.

ISOTOPIC RECORD:

Since at least most, if not all of the dolomitization occurred after the deposition of the Hatch Hill arenites, the isotopic record should yield some information about the environment or diagenetic zone in which the dolomitization took place. Two trends could be extracted from the isotopic record: (1) the variation of the oxygen values is less than 1% for one distinct mineral phase, and (2) the carbon isotopes show a trend towards lighter isotopic values with increasing depth. Very similar trends with respect to the carbon isotopes have been observed by various workers for depth related diagenetic reactions linked with the decay and fermentation of organic material. The carbon isotope trends and their relative values allow the distinction of diagenetic zones in which carbonates that carry those signatures have formed. The isotopic record of the Hatch Hill arenites measured at an outcrop section along the Poultney River matches the isotopic signature that would be predicted for the lower part of diagenetic Zone 3, the zone of methane formation. The isotopic trend is further supported by the fact that paleotemperatures for cement formation are close to the temperatures predicted for this diagenetic zone, and that the Hatch Hill arenites experienced sufficiently deep burial to promote the chemical reactions that are probably responsible for the isotopic trend. In addition, the fact that pyrite formation predates dolomitization, because of its formation in diagenetic Zone 2, supports this interpretation. A slight weakness of this interpretation is the fact that nothing is known about the composition of the gray-black shales that surround the Hatch Hill arenites. These shales are needed as the carrier of organic matter that has subsequently undergone decay and fermentation to produce the isotopic signature, and, at least in part, acted as a donor for ions (Mg^{2+}, Fe^{2+}, CO_3^{2-}, or HCO_3^{-}) that are now documented in the dolomite cements of the Hatch Hill formation. Hence, greater confidence in this interpretation could be provided by study of the Hatch Hill shales. The shale mineralogy and chemical analyses could provide information about whether the Hatch Hill shales are depleted in Ca^{2+}, Fe^{2+} and Mg^{2+}, and thus could have functioned as donators of these ions for the development of dolomitic cements in the sandstones. Carbon isotope data might show similar trends to those observed in the Hatch Hill arenites. Furthermore, the data base of isotopic values for the Hatch Hill Formation ought to be enlarged and extended to other Hatch Hill outcrops of the Taconics. Until this is accomplished, every interpretation has to be somewhat speculative and must extrapolate data that have been collected from a very few sections towards the overall development of the Hatch Hill Formation.

CONCLUSIONS:

Based on the data collected so far, I draw the conclusion that most of the dolomite assemblage is not the product of dolomitization on the carbonate shelf adjacent to the depositional environment of the Hatch Hill formation, but rather took place after deposition and during subsequent burial of the sediment package. Even though it cannot be excluded that some of the detrital carbonate grains might have been dolomitized prior to their final deposition in the Hatch Hill arenites, the majority of the dolomite is a product of diagenetic processes that led to the cementation of the arenites. The diagenesis and its products indicate that depth-related decay and fermentation of organic matter, presumably that deposited in the gray-black shales of the Hatch Hill Formation, played an important role in the cementation process. The isotopic composition suggests that the dolomite cements formed in the lower part of the zone of methanogenesis. This would imply that the cements formed at a depth of approximately 2-3 km, and at temperatures close to 75°C.

Dolomitization, especially in the outcrops of the northern Taconics, was not selective and affected each arenite in the same way. Grain size, packing and clast content of the host rocks only affect the grain size of the dolomite cement, not the degree of dolomitization. Dolomitization postdates the formation of quartz overgrowths and pyrite formation, and was the major contributor to the cementation of the Hatch Hill arenites.

CHAPTER 3

THE BURDEN IRON ORE

INTRODUCTION

The second part of this thesis focuses on the age and nature of the Burden Iron Ore. I use the term Burden Iron Ore following previous workers (e.g. Ruedemann, 1931, 1942; Zen, 1964; Bird and Dewey, 1975) for a sequence of sideritic sandstones, breccias and carbonates that are exposed in Columbia County, New York. In Columbia County, three large areas (up to 11 km long and 3 km wide) of Precambrian-Cambrian to Ordovician rocks of the Taconic sequence can be identified. These areas, although separated by younger rocks from the main Giddings Brook slice, are thought to be parts of this main slice (Zen, 1967). The Burden Iron Ore occurs within the westernmost of these areas (Figure 41). The ore body is exposed along a roughly north-south trending morphological ridge, 0.5 km east of the town of Linlithgo (Hudson South quadrangle, New York). The ridge is approximately 5 km long by 1.5 km wide and dies out to the north.

My interest in the Burden Iron Ore arose from the knowledge, as shown by previous workers (Ruedemann, 1942; Zen, 1967; Bird and Dewey, 1975), that the Burden Iron Ore was very likely part of the Hatch Hill Formation and hence might contribute further information about the dolomitization of the Hatch Hill arenites.

The aim of this study was to determine the

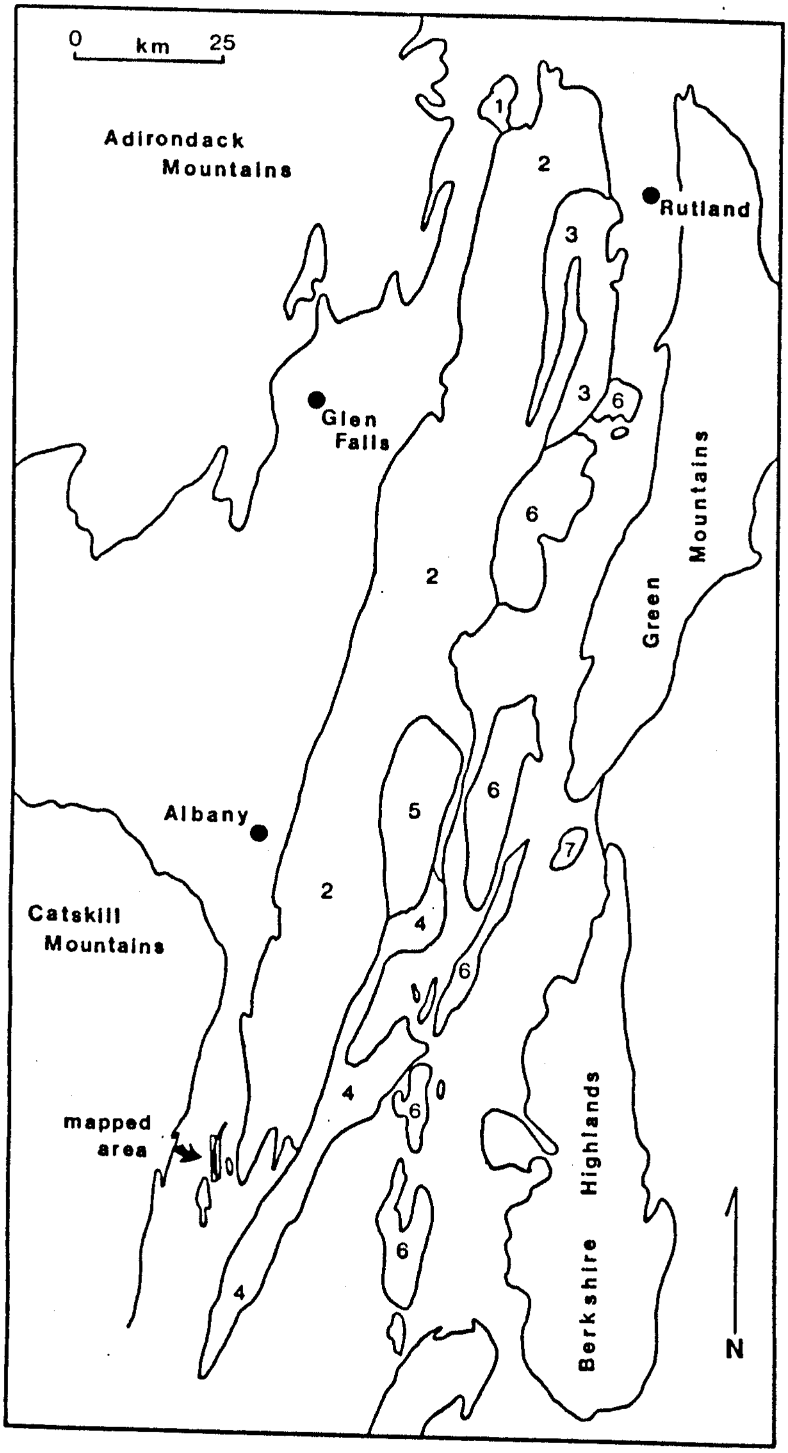

Figure 41. Location of field area.

stratigraphic position, regional distribution and nature of the Burden Iron Ore, which Bird and Dewey (1975) address as "one of the more interesting unsolved geologic problems of the Taconics."

For this reason, the area was mapped during the 1985 field season. Mapping was conducted on a topographic map (1:10,000). The focus of the field work was the stratigraphic position of the Burden Iron Ore, and to collect samples of the ore bearing lithologies for petrographic studies. Structural work was conducted primarily to determine disturbances within the area that might have led to an incorrect stratigraphic interpretation. The overall structural history of the field area was not under consideration.

The general approach was to use an updated and more detailed stratigraphy that was developed most recently in the northern part of the Taconics (Rowley *et al.*, 1979; Fisher, 1985). The advantages of the new stratigraphy over the older stratigraphy, for example that used by Ruedemann (1942), lie in the better stratigraphic resolution for detailed mapping of the area. The new stratigraphy was especially helpful for the subdivision of the Schodack shales and limestones into three distinct formations, the Browns Pond Formation, the Middle Granville slate and the Hatch Hill Formation. This was particularly important for my own field work, since the Burden Iron Ore is closely associated with the Schodack shales and limestones. The new

PREVIOUS WORK

The area under discussion received considerable interest in the last century. The focus of interest from 1880 to 1901 lay in the then commercial exploitation of the natural resource provided by the ore body. Partially filled mine entrances and a number of outcrops are remnants of the early mining activity. These outcrops provide an excellent opportunity to study the Burden Iron Ore today.

The term Burden Iron Ore dates back to the end of the last century, when the mining business on Mt. Tom was the property of the Burden family. Today the old mine is used as a private storage facility, which prohibits free access to the outcrops in this area. The name is still kept alive in the village of Burden, 0.25 km east of Mt. Tom.

The first scientific interest is documented by publications by Dana (1884), Smock (1889), Kimball (1890) and Eckel (1905). Each of these workers focused on the nature and origin of the Burden Iron Ore, and failed to discuss the stratigraphic position of the ore in detail. A summary of previous work that concentrated on the origin and nature of the ore body is given later in this chapter.

The first attempt to determine the stratigraphic position of the Burden Iron Ore was conducted by Ruedemann (1930, 1942). Ruedemann (1942) mapped the area as part of the Catskill quadrangle and presented the first geological map. The major accomplishment of his work was the determination of the thrust contact between the Austin Glen (medial Ordovician) and the overlying Nassau beds

(Precambrian-Cambrian) in the Mt. Tom area, and the recognition of three areas that contained Taconic rocks west of the main Giddings Brook slice. He placed the Burden Iron Ore between the Nassau beds and the Schodack shales and limestones (lower Cambrian to early Ordovician). Unfortunately, the term Schodack shales and limestones includes several formations of the modern Taconic stratigraphy, and hence functions only as a crude indicator for the age of the Burden Iron Ore.

The large scale structural relations between the Giddings Brook slice and the western klippen of Taconic rocks and their tectonic implications have been discussed by Zen (1967), Bird (1969), and Bird and Dewey (1975). Zen (1967) discusses them under his description of "isolated areas of low Taconic rocks" (p. 95) and suggests that they might represent submarine slides that have "broken off from the main Giddings Brook slice and moved farther west into the sea of Trenton mud." Bird (1969) was also influenced by the concept of gravity sliding and interprets the areas as "huge blocks in the Forbes Hill." The Forbes Hill conglomerate is, in the interpretation of Bird (1969), a wildflysch (melange) that resulted from sedimentary slumping and sliding on the slope of a rising tectonic element. Bird and Dewey (1975) go even further and suggest a connection between the genesis of the Burden Iron Ore and the tectonic mechanism that led to the emplacement of the isolated areas of Taconic rocks in the Catskill quadrangle.

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"It is possible that the ferruginous quartzite and carbonate beds, and local carbonate and sand conglomerate, originated in a fringing reef and shore environment where the upper portions of the supposed slide-blocks in the wildflysch were exposed as islands in the Normanskill sea. Such an environment would produce quartz and carbonate sand, and conglomerates, along the slopes of the blocks. Possibly, the ferruginous carbonates formed by reaction of carbonate precipitates with the iron-rich, deep-water facies sediments of the allochthonous blocks. It is interesting to note that the ferruginous carbonate blocks seen in the wildflysch at [a roadcut on Route 151 just south of Rysedorph Hill, 1.7 miles southeast of City Hall, Rensselaer, New York] are very similar to carbonate beds exposed here. Also, the Austin Glen facies is quite carbonate-rich in the region west of these hills. Perhaps some of the enigmatic carbonate conglomerates of the wildflysch, such as the Rysedorph, also had their origins in carbonate-reef and shore environments of moving islands of separated blocks in front of, and on tectonic salients along the leading edge of the advancing Giddings Brook slice." (Bird and Dewey, 1975)

This idea must be strongly questioned based on the data provided in the following chapters.

STRATIGRAPHY

INTRODUCTION:

As already mentioned before, the main aim of the stratigraphic work was to locate the exact position of the Burden iron ore within the established Taconic stratigraphy. To accomplish this aim, stratigraphic units of the northern part of the Taconics were applied to this area, which is located in the southern part of the Taconics. The use of the formation names is based on descriptions by Rowley *et al*. (1979), with one exception, the Middle Granville slate (Kidd *et al*., 1985). This formation includes material that in some places was previously included in the Mettawee slate formation, and because the Browns Pond formation was confused with the West Castleton formation, in other places it was included in of the West Castleton formation. Zen's (1961) West Castleton formation is now largely included in the Hatch Hill formation.

Applying the northern Taconic formation names to the area under observation was very helpful for the field work, but also caused many problems. The major problem was incompleteness of the mapped section, as only five formations could be clearly identified: the Bomoseen formation, the Browns Pond formation, the Hatch Hill formation, the Poultney formation and the Mount Merino formation. The Truthville slate, the Middle Granville slate and the Indian River formation appeared to be absent, or not observable in the outcrops present.

BOMOSEEN FORMATION:

The lowest lithostratigraphic unit in the area is referred to as the Bomoseen Formation (Jacobi, 1977; Bomoseen Graywacke of Zen, 1961). It is a hard, massive, olive green-gray, micaceous, poorly-cleaved wacke, with minor amounts of interbedded fine to medium grained quartz arenites.

The wacke weathers to reddish-brown. Its texture is heterogeneous and depends on grain size, which ranges from silt to sand size. A typical variety of the wacke contains lenses of coarser grained material (1-2 cm) within a generally fine grained matrix, producing an anastamosing cleavage that is present everywhere in this unit (Figure 42).

The quartz arenites form clean, white to greenish weathering beds up to 20 cm thick. Neither sedimentary features nor cleavage have been observed in them. The beds are generally continuous on an outcrop scale; only a few beds pinch out.

The thickness of the formation is limited in this area (210 + m) since the lower contact is not seen and is fault-bounded (see Ruedemann, 1942).

Dale (1899) called this unit the olive grit; Ruedemann (in Cushing and Ruedemann, 1914) renamed it the Bomoseen grit after exposures near Lake Bomoseen. Most recent workers treat it as part of the Nassau Formation (e.g. Fisher, 1985) or its equivalent the Bull Formation (e.g. Zen, 1961). Ruedemann (1942), in his original description

Figure 42. Outcrop of the wackes of the Bomoseen Formation.

of the area, subdivides two units, his Nassau beds and the stratigraphically higher Bomoseen grit. Both units are here included in the Bomoseen Formation because little difference was observed.

Jacobi (1977) suggested giving the Bomoseen a formation status because of its definite stratigraphic position and lithological differences with the overlying and underlying units. Both criteria also apply for this area. The Bomoseen is therefore treated as a formation.

BROWNS POND FORMATION:

The term Browns Pond Formation was introduced by Jacobi (1977). It is a heterogeneous assemblage of lithologic types all lying within a predominantly black shale matrix. The lithologies present in this area are dolomitic calcarenites, a carbonate conglomerate, and a carbonate breccia.

The dolomitic micrites occur as dense, microcrystalline, black, grayish-weathering beds up to 10 cm thick, typically dissected by calcite and dolomite veins. A faint parallel lamination due to compositional differences is sometimes present. Individual beds are up to 10 cm thick and separated by thin layers of black shale. It is overlain locally by a carbonate conglomerate (Figure 43). The matrix of the conglomerate is made up of dense, dark dolomite. The clasts consist of jumbled blocks of carbonate that weather a distinctive grayish color. The block size varies from 4-40

Figure 43. Carbonate clast breccia with dolomite matrix.

cm. The individual blocks are mostly rectangular and are oriented parallel to bedding with respect to their longest axis. Small blocks with rounded edges are also present. The stratigraphically highest lithology is a matrix-supported carbonate breccia. Its minor constituents are carbonate and sandstone clasts. They are swimming in a sandy, coarse-grained, carbonate cement matrix. The individual clasts are chaotically distributed, up to 15 cm thick, angular sandstone and limestone or dolostone fragments. A variety of this breccia can be observed in the area where the formation pinches out southward. It is a monomict, clast supported dolomite breccia with minor amounts of carbonate cemented matrix (Figure 44).

This unit was not mapped as an individual formation by Ruedemann (1942). He included it within the Schodack shales and limestones. This Schodack formation includes, if the modern stratigraphy is applied, three formations: the Browns Pond Formation (BP), the Middle Granville Slate (MGS)and the Hatch Hill Formation (HH). The subdivision of the individual formations is based on color changes of the shales from black to green (BP/MGS) and green to black (MGS/HH). These changes are not present in the area mapped as the Middle Granville Slate is not present. The separation of the Browns Pond Formation and the Hatch Hill Formation is therefore based on lithological differences. The sequence of layered calcarenites, carbonate conglomerate and carbonate breccia is not present in the lower part of the Hatch Hill Formation, the only other Taconic formation

Figure 44. Dolomite breccia with sandy matrix.

that contains lithologies similar to the Browns Pond. This alone does not justify classifying these units as Browns Pond, since local developments of these lithologies could occur in the Hatch Hill. But, if the sequence is compared with outcrops of Browns Pond (or its equivalents) further north, especially those at Schodack Landing (Figures 3 and 4), similarities are obvious. The sequence at Schodack Landing, consisting of layered micritic limestones, a limestone conglomerate and a limestone breccia, is very similar to the one observed here. Therefore, using Schodack Landing (the type locality of the Schodack shales and limestones) as a reference locality of the Browns Pond for the southern Taconics, it is justified to treat this sequence as part of the Browns Pond Formation.

In the Mt. Tom area, the Browns Pond formation is only present as a small band that pinches out towards the north (see Geological Map of Mt. Tom Area). The thickness of the formation therefore varies between 0-30 m. An outcrop of the lower contact with the Bomoseen Formation has not been seen in this area, but the map pattern does not indicate an unconformable or fault-bounded contact and since the Burden Iron Ore is observed to conformably overlie the Bomoseen (see below), the Browns Pond is thought to do so, also. The laminated dolomitic calcarenites appear to conformably overlie a somewhat coarse grained variety of the Bomoseen wacke.

The age of the Browns Pond formation is Lower Cambrian, as determined at Schodack Landing, where an Elliptocephala asaphoides fauna (Ford, 1884; Goldring, 1943; Bird and Rasetti, 1968) was recovered from the clasts of the limestone conglomerate. To verify the age of the unit mapped as Browns Pond, I collected a sample of the dolomitic calcarenite at an outcrop 550 m southeast of the intersection of Woodchuck Road and White Birch Road, and dissolved approximately 2.5 kg for conodont determination, since no other fossils are apparent in hand specimen. Unfortunately, no conodonts are present in the sample processed.

HATCH HILL FORMATION:

The term Hatch Hill Formation is used in the sense of Theokritoff (1964) with the restrictions applied by Kidd et al. (1985). It consists of carbonate cemented quartz arenites, polymict breccias and carbonates interbedded with well-cleaved black shales.

The formation is somewhat atypical in this map area, since here its basal portion contains a sideritic ore body that is not observed elsewhere in the Taconics.

Although the black shale is probably the most abundant lithology in the area, the quartz arenites form the most abundant outcrops. The black shales are almost never present in individual outcrops if they are not associated with quartz arenites because of their weak resistance to weathering and erosion. The arenites are hard, brownish-weathering, fine to coarse grained, 1-110 cm thick sandstones. They show a sugary surface texture, since the cementing carbonate weathers preferentially and produces a rough surface of sand grains. The sandstone beds show a variety of sedimentological features that are in part overprinted by the ore phase, although they are still present in thin section. The most prominent features are parallel laminations and graded bedding. Incomplete Bouma sequences (A-E or ABE types) are present. Rip-up clasts have been observed in the basal part of coarse grained, massive or graded sandstone beds. Fine grained beds typically show bedding plane parallel laminations. Cross bedding has not been observed.

The carbonate breccias consist of grayish weathering micritic limestone or dolostone clasts embedded in a coarse grained dolomite cemented quartz matrix (Figure 45). The matrix typically weathers brownish-gray. The rock has the same sugary texture as the quartz arenites. Clast sizes range from 1-10 cm; the degree of roundness ranges from angular to subrounded. Clasts of one breccia usually have the same overall degree of roundness and clast size. Breccias with small clasts are matrix-supported while bigger clast sizes tend to clast supported. The breccias are more abundant in the upper part of the formation. Only two carbonate beds, a siderite and a limestone horizon, outcrop in the area. Both are dark gray structureless micrites that weather to light gray and occur as thin (up to 10 cm thick) beds.

Figure 45. Carbonate breccia from the Hatch Hill Formation.

As mentioned above, the lower part of the formation contains an ore body. This stratiform ore body occurs in lenses. It is located in a sequence of arenites that are cemented by siderite, the ore-bearing phase. The ore body, where present, conformably overlies the Bomoseen formation, (see also the section on stratigraphic position) (Figure 46). The lower contact of the Hatch Hill Formation with the underlying Browns Pond and Bomoseen Formations is only very poorly exposed. Three manmade outcrops are present where the containing sandstones conformably overlie the wacke of the Bomoseen Formation. The contact is sharp and marked by the first bed of ferruginous quartz arenite. The contact between the ore-free part of the Hatch Hill Formation and the Bomoseen or Browns Pond Formation has not been observed, because it is not exposed in this area. The thickness of the ore horizon is 0-50 m. The overall thickness of the Hatch Hill Formation ranges from 20-140 m.

Previous workers in the southern part of the Taconics include the Hatch Hill Formation either in the Schodack shales and limestones (Ruedemann, 1942), as discussed above, or in the Germantown Formation (Fisher, 1961). The Germantown Formation covers, according to Zen (1964), the Hatch Hill Formation and the lower parts of the Poultney Formation. In the useage of Fisher et al. (1970), it appears that the Browns Pond Formation and the Middle Granville Slate are also part of the Germantown Formation.

The age of the Hatch Hill Formation is also not completely clear. A probable age bracket can be obtained

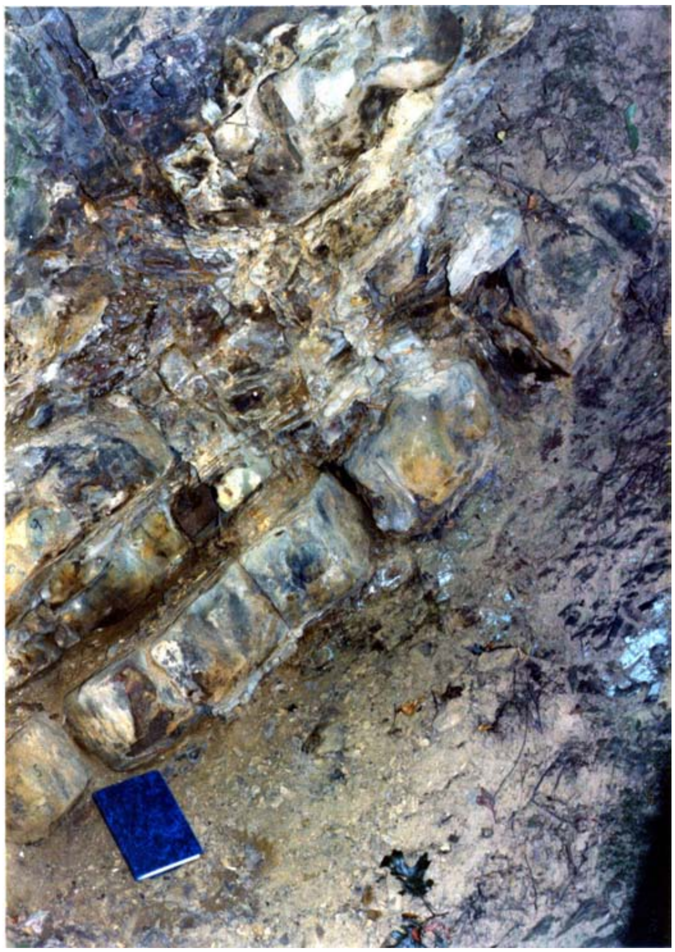

Figure 46. Contact between the Bomoseen and Hatch Hill. Top of field book marks contact (Long Cut).

when the Upper Middle Cambrian _Centropleura_ fauna recovered from Judson Point (Bird and Rasetti, 1968) and Upper Cambrian _Callograptus_ and _Dendrograptus_ faunas from the Germantown Formation at Fishers Quarry (Berry, 1959) are used as upper and lower limits. This would indicate an Upper Middle Cambrian to Lower Upper Cambrian age for the strata containing the Burden Iron Ore. A carbonate breccia 250 m north of outcrop MT2 on the west slope of the hill that closely overlies the orebody did not reveal any conodonts for age determination.

POULTNEY FORMATION:

The Poultney Formation was named by Keith (1932) for outcrops along the Poultney River, Vermont, and originally included the Hatch Hill Formation. In the studied area, the Poultney Formation is very poorly exposed. It consists of a monotonous sequence of fissile, thinly cleaved, olive green shales. The olive green shale is the only lithology present (Figure 47). It varies in grain size from clay to silt. Its only sedimentological features are dark rip-up clasts of black shale embedded in the green matrix. In the upper part of the formation, towards the transition to the Mt. Merino Formation, a few isolated beds of dense green-black chert have been observed.

It is not possible to distinguish members of this formation as was done by other workers (Potter, 1972; Jacobi, 1977), as these determinations are based on

Figure 47. Green slates of the Poultney Formation.

associated lithologies that are not present or not exposed in this area. The lower contact with the Hatch Hill Formation is therefore placed at the first occurrence of green shale. It is not exposed. The average thickness of the Poultney Formation is 140 m.

Partially equivalent terms used for the Poultney Formation are the Deepkill shale (Ruedemann, 1942) and Stuyvesant Falls Formation (Fisher, 1961). Neither of these names exclusively describes the Poultney Formation, and both include parts of the upper Hatch Hill Formation as used here. Fossil ages (graptolites) for the Stuyvesant Falls formation reveal Late Cambrian to early Ordovician ages (Fisher, 1977). The more detailed record in the northern Taconics reveals Upper Canadian to Lowest Llandeilan ages (Fisher, 1977).

MT. MERINO FORMATION:

The type locality of the Mt. Merino Formation is at Mt. Merino, west of the town of Hudson in the southern Taconics. It was named by Cushing and Ruedemann (1914).

This formation is characterized by black chert associated with black shales. The fresh shale is sooty black and ranges from hard, crudely cleaved argillite to softer, thinly cleaved shale. Pyrite is a common constituent and the rock weathers to an orange-brown because of it. The cherts occur in dark, dense, hard bands up to 15 cm thick, separated by thin layers of black shale. When weathered, the chert reveals a typical white color (Figure

48) with small black holes where radiolarians have weathered out. The radiolarians are always present in thin section.

The lower contact with the Poultney formation is characterized by a transition of green shale interbedded with black chert to black shale with more abundant chert.

The thickness of the formation in this area is 210 + m, which is rather anomalous. Typical thicknesses observed in other areas vary between 30-50 m (Potter, 1972, Rowley et al., 1979; Fisher, 1985). It is therefore likely, even though the map pattern does not suggest it, that the Mt. Merino Formation has fault replications within this area.

The age of the Mt. Merino Formation, as determined by graptolites, ranges from Berry's Zones 11 to 12, which correspond to Upper Middle Ordovician to Lower Late Ordovician (Caradocian and perhaps late Llandeilan).

Figure 48. White weathering cherts of the Mt. Merino Formation.

DISCUSSION

STRATIGRAPHIC POSITION:

The ore body has always attracted attention since, like the Hatch Hill dolomites, it is a rather anomalous feature within the Taconic sequence. The stratigraphic position of the ore body was under considerable discussion, but this problem was finally resolved by detailed mapping of the Catskill and Kaaterskill quadrangles by Ruedemann (1942). In his description, Ruedemann used the stratigraphic names developed earlier in the 19th and 20th centuries. This stratigraphy has been updated considerably since 1942. Many units that were once mapped as one formation have been subdivided into several subunits with formational character. This development allows better resolution for field geologists mapping on the formational level.

Ruedemann (1942) mapped the rocks containing the Burden Iron Ore as an independent unit, and placed them between the Nassau beds and the Schodack shales and limestones. Unfortunately, he does not explain the criteria he used to separate this unit from the underlying and overlying formations. As explained above, both the Nassau beds and the Schodack shales and limestones can be subdivided into several units with formational character. The Nassau beds are equivalents of the Bomoseen Formation and the Truthville slate; the Schodack shales and limestones correspond to the Browns Pond Formation, the Middle Granville Slate, the Hatch Hill Formation, and at least part of the Poultney Formation.

These formations cover a time interval from Precambrian or Cambrian to early Ordovician. The stratigraphic position of the Burden Iron ore proposed by Ruedemann would translate into modern stratigraphic terms as lying between the Bomoseen and Browns Pond Formations. This indicates an age somewhere between the Precambrian-Cambrian boundary, which might be present in the Bomoseen Formation, and the early Cambrian, the age of the Browns Pond Formation.

My approach to the Burden Iron ore was different, and hence leads to controversial conclusions. Besides the fact that I used a modern stratigraphy, I tried to find common features between the ore body and the formations that are associated with it. I included the Burden Iron Ore in one of the formations observed, instead of separating it just because of its anomalous nature.

The chapter on stratigraphy already shows my conclusions. The Burden Iron Ore is placed in the lower part of the Hatch Hill Formation. Criteria used for this placement are based strictly on lithological comparisons and could not be backed up by fossil ages, since no fossils have been found in lithologies carrying the ore body, or other lithologies in this area. The formations that can be distinguished within the mapped area, and are equivalent to Ruedemann's Nassau beds and Schodack shales and limestones, are the Bomoseen Formation, the Browns Pond Formation and the Hatch Hill Formation. The Bomoseen Formation consists predominantly of wackes and arenites, is typically mica spangled, and contains a relatively high amount of detrital quartz and feldspar with almost no carbonate present. The Browns Pond Formation is characterized by black shales that are interbedded with micritic limestone or dolostone beds and a carbonate clast breccia. No quartz arenites have been observed, and detrital quartz, with the exception of the carbonate clast breccia, is only present in silt and finer grain sizes. The Hatch Hill Formation consists of a variety of quartz arenites, breccias and a minor amount of limestone. Lithic fragments are a minor constituent of the arenites, which are cemented by dolomite.

The ore phase is present as siderite cement, and contained in quartz arenites. The rusty weathering of this rock in outcrop obliterates sedimentary structures, but the high quartz content is already detectable on this level of observation. If slabs and thin sections are cut, the similarities to the Hatch Hill Formation become even more obvious. Thin sections and polished slab of the beds containing the ore phase show that there are fine to medium grained bedding parallel laminated sandstones, graded beds topped with thin shale and siltstone layers, medium to coarse grained sandstones with rip-up clasts, medium grained structureless arenites and micritic carbonates. The mineralogy of the arenites consists of bimodally distributed rounded to subrounded quartz grains with minor amounts of pyrite and heavy minerals cemented by euhedral to subhedral siderite cements. The overall sand to shale ratio is usually very high and approximately comparable with the ratio at Judson Point. These are typical features observed in the Hatch Hill Formation in the area studied, and elsewhere in the Taconics. Hence, it appears to be justified to treat the Burden Iron Ore as an anomalous subunit of the basal part of the Hatch Hill Formation. The age of the rocks containing the ore phase (which is not necessarily the age of the ore-carrying phase) is therefore probably upper middle Cambrian to upper Cambrian.

REGIONAL DISTRIBUTION:

The ore body occurs in four distinct podiform bodies striking roughly north-south (map). The lenses are up to 30 m thick and several hundred meters long. The ore bodies always overlie the Bomoseen Formation (Figure 49). This contact is exposed in three outcrops (map and profiles). The contact itself is sharp (Figure 50) and structurally conformable. It is defined by the first iron bearing bed that overlies the wackes of the Bomoseen Formation. This first bed may consist of various lithologies. In the three outcrops that expose the contact between the Bomoseen and iron-bearing sandstones, the contact is marked by a fine grained arenite bed at MT2, a siderite-replaced carbonate bed at LC and a medium grained sandstone with quartz pebbles at WH. These changes within the lowest bed of the ore body are not very suprising, because most of the beds of the Hatch Hill Formation pinch out, even though some might extend laterally for several hundred meters. The upper

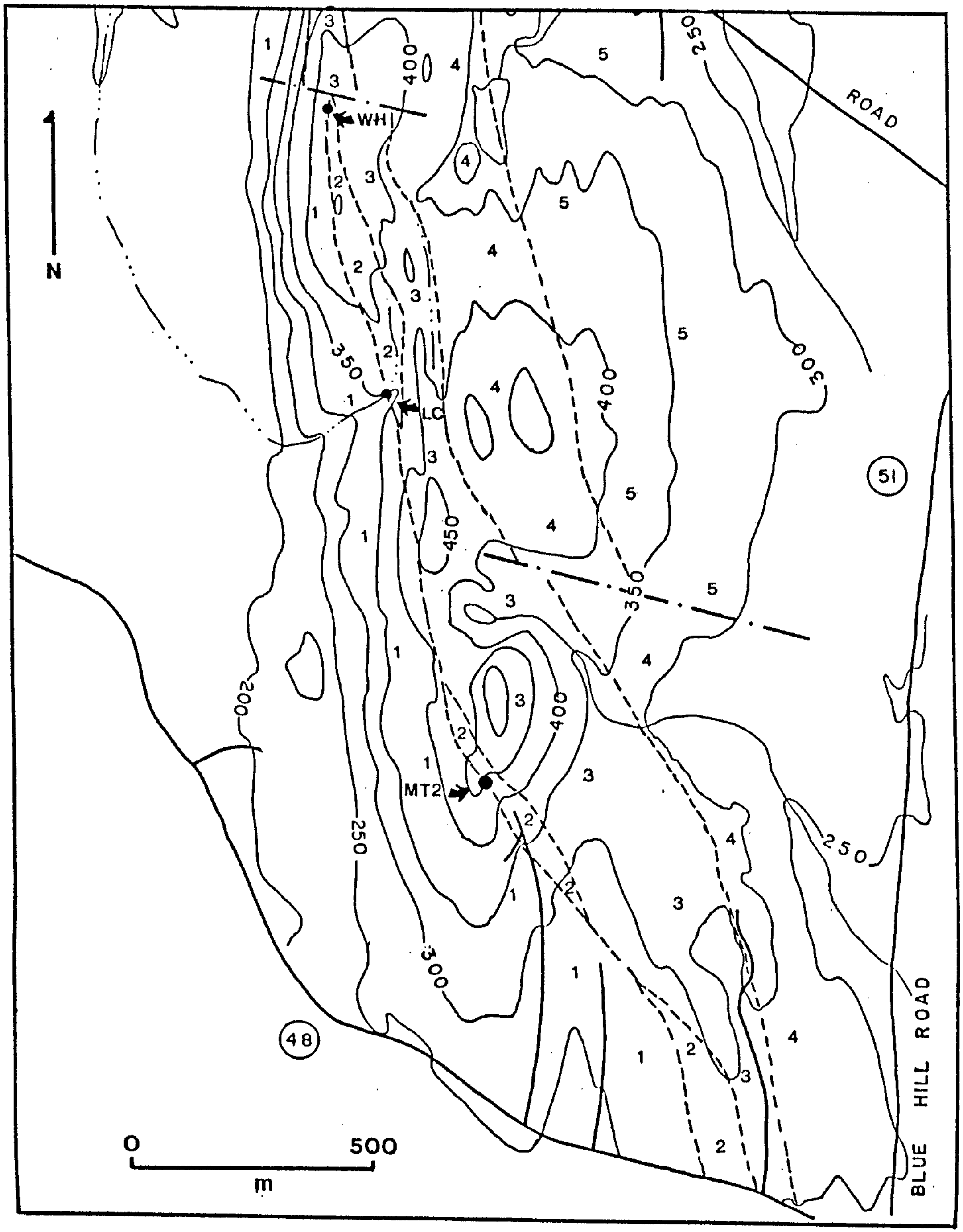

Figure 49: Outcrops showing the contact between the Bomoseen and Hatch Hill Formations.

(1) Bomoseen Formation
(2) Hatch Hill Formation (ore body)
(3) Hatch Hill Formation (ore free)
(4) Poultney Formation
(5) Mt. Merino Formation
MT2 = Mt. Tom
LC = Long Cut
WH = Whitcomb's House

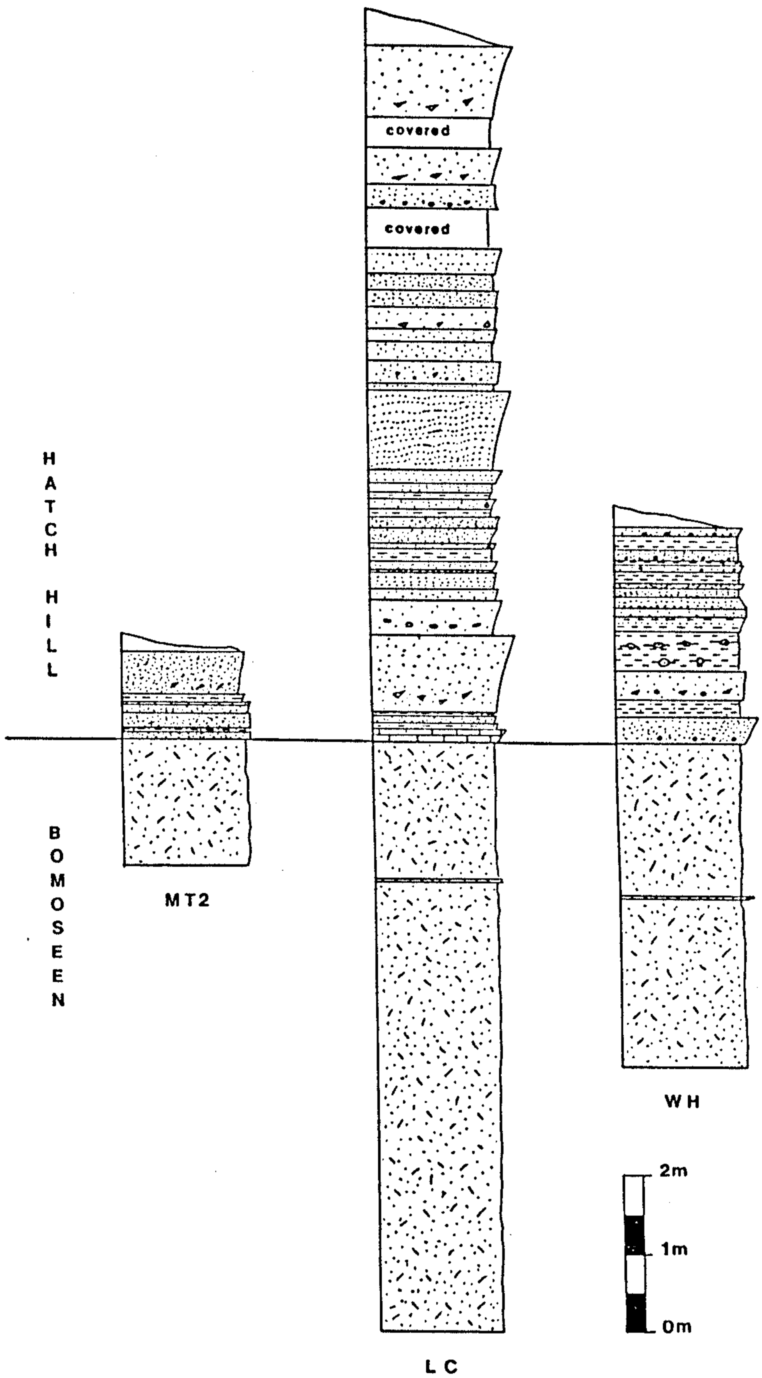

Figure 50. Profiles of the Bomoseen/Hatch Hill contact. The Hatch Hill Formation contains the ore body.

contact with the "ore free" part of the Hatch Hill Formation is not exposed in outcrop.

To my knowledge, this is the only place in the Taconics where the Hatch Hill Formation disconformably overlies the Bomoseen Formation. Therefore, if the unit that I mapped as the Hatch Hill Formation is the same age as identical lithologies further north in the Taconic allochthon, it would imply that in this area there was a period of deposition followed by erosion, and/or non-deposition during lower Cambrian to upper middle Cambrian time.

PETROGRAPHY AND MINERALOGY:

The rock lithologies containing the iron phase are to a large extent quartz-bearing arenites and breccias, with minor amounts (less than 2%) of pure carbonates. All lithologies are strongly affected by weathering and are stained brownish-red by the ore phase.

Arenites

The arenites are the most abundant rock type observed. They are usually cemented by carbonate, with up to 50% of the rock volume consisting of cements. The detrital minerals are dominantly quartz with minor amounts of rock fragments, carbonate clasts, chert and zircon. The quartz grains are usually rounded to subrounded. The degree of roundness increases with increasing grain size; grains over 250 um are typically well rounded. Bimodal distribution can be observed, but the grain size fractions that define its bimodality may vary. Most of the quartz grains show undulose extinction, but clear grains and a few grains showing recrystallization mosaics are also present. Quartz overgrowths are almost absent and only a few grains contain fluid inclusions.

Rock fragments are usually fine grained and consist of silt sized quartz grains. They are probably fragments of siltstones. The carbonate clasts are typically completely replaced by the siderite cements; the original clast shapes are rounded to subrounded. The grains can be identified since the surrounding cements are usually coarser grained than the replacement minerals (Figure 51). Even very delicate structures, such as the shape of what were probably oolites, are still preserved and outlined by the growth of the siderite rhombs (Figure 52).

The outer rims of the original carbonate clasts are often coated with a red-brown stain, which is probably caused by the weathering of siderite to limonite and other iron hydroxides.

Siderite is the dominant cement within the ferruginous sandstones. The cements consist of individual siderite grains that appear to be "squeezed" with respect to their shortest extension if compared with dolomite rhombs. The siderite rhombs form a mosaic that cements the detrital phases. Individual grains are usually euhedral to subhedral; anhedral grains are an exception. The siderite grains show a weak pleochroism and several have a cloudy texture. The grain boundaries of individual siderite grains

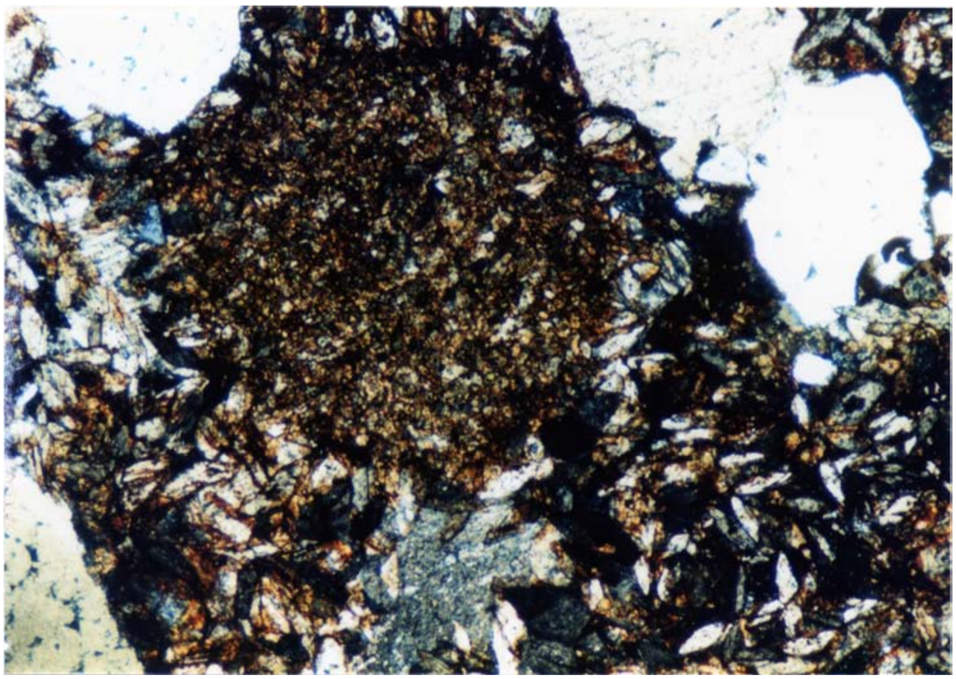

Figure 51. Coarse grained matrix of euhedral siderite and an original carbonate clast, replaced by micritic siderite (Long Cut). (Field of View: 0.85 mm wide).

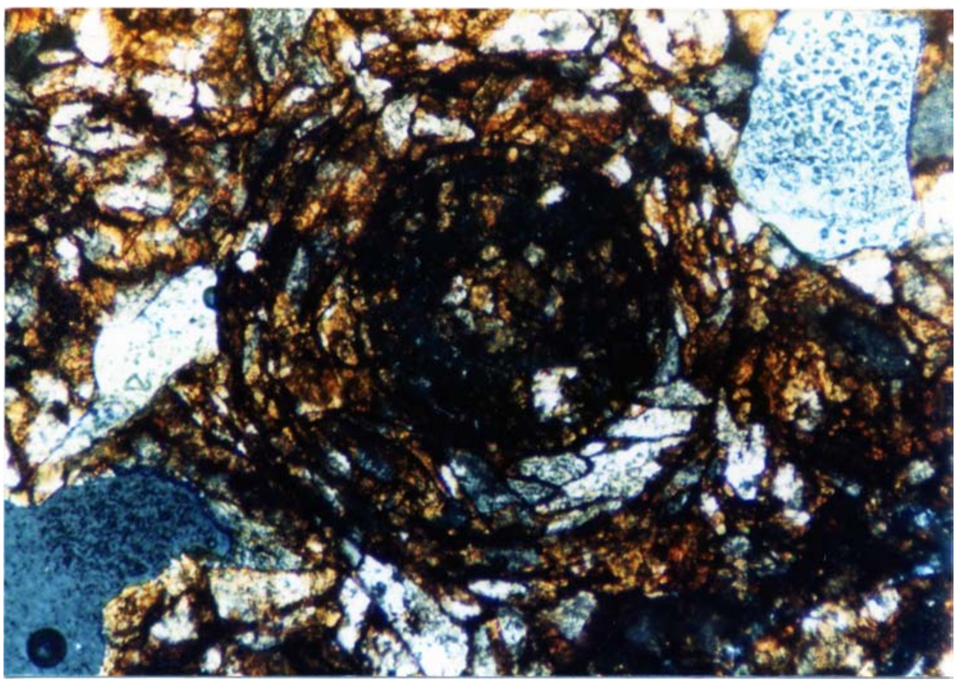

Figure 52. Oolite replaced by siderite grains (Mt. Tom). (Field of View: 0.85 mm wide).

are often outlined by a limonite stain, which is probably a product of later corrosion of the grain. Fresh samples are difficult to obtain, since most of the outcrops are remnants of mining activity during the last century and have undergone intense weathering since then, as indicated by rusty weathering surfaces. In fresher samples, the amount of stain decreases. The grain size of individual siderite rhombs varies from 10-150 um. Their grain size is always finer than that of the detrital phases, but can vary considerably.

The only other authigenic phase, except for later calcite filling of vugs and joints, is pyrite. Pyrite occurs as framboids and as filling between siderite grains.

Carbonates

Carbonates are only a very minor component of the ore bearing lithologies. One bed of carbonate has been observed. It marks the contact between the Bomoseen Formation and the ore body at LC. The bed consists of a mosaic of siderite rhombs (about 10 um in size) and only a very minor amount of silt sized quartz and plagioclase.

Breccias

Breccias are exposed at the entrance to the old Burden Mine at Mt. Tom. Clasts are strongly overprinted by the ore phase. Individual clasts are angular to subangular and consist of sandstone clasts and minor amounts of carbonate clasts (Figure 53). Carbonate clasts can be identified when they contain less detrital quartz than the matrix of the breccia. The matrix consists of quartz grains cemented with

Figure 53. Breccia overprinted by the iron ore. Hatch Hill Formation (Mt. Tom).

siderite. The preferential weathering of the carbonate phase gives the matrix a sugary texture.

ORIGIN OF THE ORE:

Previous Work

There has been considerable discussion about the origin of the Burden Iron Ore. Two contrasting views could be determined from the literature: (1) primary deposition of the ore-carrying mineral siderite, and (2) a secondary replacement under various conditions. The only common point on which most authors agree and which could be proven by Newland (1936) is the fact that the limonite present is the product of weathering of the siderite phase.

In chronological order, the following opinions of the origin of the Burden iron ore have been proposed: Dana (1884) argues for a sedimentary deposition of siderite as the primary mineral. Kimball (1890) believes that a ferric oxide, deposited contemporaneously with the sandy fraction of the sandstones, was later reduced to siderite in the presence of hydrocarbons. Smock (1889) and Eckel (1905) oppose that view and feel that the siderite was deposited as replacement of original limestone. They exclude the possibility of a contemporaneous deposition of the siderite within the enclosing rocks. Hobbs (1907) considers both the siderite and limonite as replacement phases, but argues for different sources for each mineral phase. He assumed that the time of ore formation was post-glacial. Ruedemann (1930) favors a sedimentary solution, by magnetite concentration and through longshore currents and a later alteration process that might produce siderite. Newland (1936) postulates a lagoonal or inshore environment that was periodically supplied with clastic input and received a steady influx of iron solution from PreCambrian terrains. Siderite formed as a primary mineral. Bird and Dewey (1975) speculate about the nature of the ore deposit and propose a fringing reef within a shore environment that formed ferruginous carbonates by the reaction of carbonate precipitates with iron-rich deep water sediments.

Discussion

The question addressing the origin of the Burden Iron Ore could be partially answered, although not completely solved, in this study. However, certain constraints can be used to disprove several theories proposed previously.

As discussed above, it seems to be justified to treat the Burden Iron Ore as part of the Hatch Hill Formation. The depositional environment of the Hatch Hill Formation is the continental rise and/or the continental slope. This implies that the Burden Iron Ore is definitely an ore body that formed either in a deep sea environment or during burial of the deep sea sediment. Hence theories that postulate a continental shelf type of environment, or even a shoreline or lagoonal environment, as the place of formation must clearly be rejected. There is no evidence within the Hatch Hill Formation that can support a continental shelf environment. The mass of arenites are clearly products of turbidites, debris flow deposits and other processes that are active on the continental rise and slope. Every interpretation has to take this into account and must include the fact that the Hatch Hill arenites, and hence the Burden Iron Ore, are included within a deep water sediment sequence.

Further constraints can be drawn from the fact that the siderite is present as cement. Individual siderite grains show no evidence for transportation or multi-stage growth, and hence must have formed after the deposition of the arenites. This leads to the next question: When did the siderite form, and was it the primary iron bearing phase and just recrystallized, or is it a replacement of some type of predecessor? The conditions under which siderite is thermodynamically stable are severely restricted (Curtis and Spears, 1968; Berner, 1971). The formation of siderite requires the presence of dissolved Fe^{2+}, and HCO_3^- in the absence of HS^-, since the presence of dissolved sulfide favors the formation of pyrite instead of siderite (Figure 54). However, reducing conditions are necessary for the formation of siderite, because iron can only be built in the siderite lattice in the Fe^{2+} state. Reducing conditions in natural environments are the product of anaerobic bacterial decomposition (Berner, 1971), and almost always include the reduction of sulfate to H_2S. Hence, to allow siderite formation, reducing conditions must be established, but at the same time the sulfate reduction must essentially be

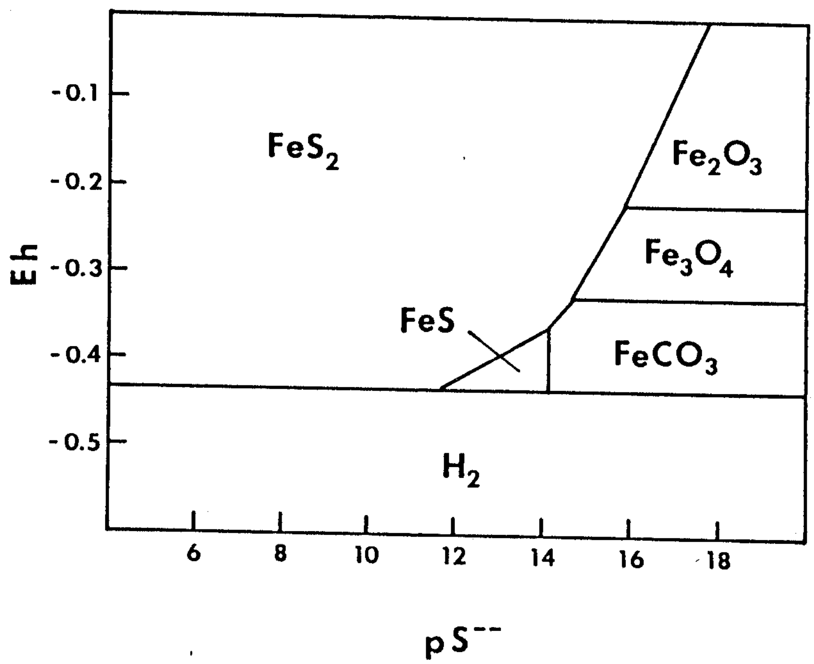

Figure 54. Stability field of iron minerals (from Berner, 1971).
pH = 7.37, log P_{CO_2} = −2.40, T = 25°C, P_{total} = 1 atm.

completed. These conditions have been reported from organic rich, deep water sediments that have undergone some degree of burial (Gautier and Claypool, 1984; Gautier, 1985; Curtis, 1978; Berner, 1981). The burial of organic rich sediments leads to the development of distinct diagenetic zones that are characterized by their chemical conditions, which are subsequently responsible for the formation of chemically distinct authigenic mineral phases. Iron minerals can be used to decipher these conditions since the valence state of Fe^{2+} or Fe^{3+} and its ability to form compounds with O^{2-}, S^{2-} and CO_3^{2-} is very sensitive with respect to changing chemical conditions. Figure 55 shows the stability range of iron minerals with respect to diagenetic zones that develop during the burial of organic rich sediments. In Zone 1, the zone of microbial oxidation, hematite would be the stable iron mineral, and in zone 2, the zone of microbial sulfate reduction, pyrite would be the stable phase. Siderite becomes a stable phase within Zone 3, the zone of microbial fermentation, and can also be present during decarboxylation, liquid hydrocarbon generation and metamorphism. The petrology of the Burden Iron Ore gives no conclusive evidence as to which zone the formation of siderite took place. However, the sediments must have passed through Zones 1 and 2 before the formation of the ore body. Hence the siderite ore is either a diagenetic or metamorphic ore, and not a primary precipitate from an iron saturated solution at the sediment/water interface. A metamorphic origin for the ore seems to be

Zone	Process Description	Base Depth (m)[a]	T/°C at Base[b]	Average Porosity (%)	$\delta^{13}C_{PDB}$ ‰ Carbonate	Carbonate Precipitated	Other Minerals Precipitated
I	Bacterial Oxidation	10^{-2}	2	80	-25	NONE: diffusion of solutes into overlying depositional waters	
II	Bacterial Sulfate Reduction	10	2.5	75	-25	Calcite Low Fe, Mn	Pyrite
III	Bacterial Fermentation	3000	75	30	+15	Ferroan Calcite	Amorphous Carbonate Apatites
IV	Decarboxylation	4000	105	15	-20	Dolomite or Siderite	Kaolinite?
V	Liquid Hydrocarbon Generation	6000	150	10	Variable: may include carbon from primary or early diagenetic carbonates	Calcite Dolomite Ferroan Dolomite Siderite depending upon instability of earlier carbonates	
VI	Gas Graphite Metamorphism	8000	200	10			

Figure 55. Characteristics of diagenetic zones that develop during the burial of organic-rich sediment (modified from Curtis, 1978).
a: for a geothermal gradient of 25°C/km
b: for water/sediment interface temperature of 2°C

hard to envision, since both the sedimentary structures of individual beds and even the textures of rather delicate structures such as oolites, are still preserved.

However, no matter in which diagenetic zone the ore body formed, the question regarding the source of the iron required for siderite formation remains. The ore body occurs in four distinct lenses that are separated from each other by unsideritized portions of the Hatch Hill Formation. Hence the mechanism that led to the sideritization and the source from which the iron is derived must account for this distribution. The processes that lead to the development of diagenetic zones or environments within a sediment package are depth related and triggered by the presence of organic material, but only depend to a minor degree on the type of lithology. Therefore, if the Hatch Hill arenites had had a homogeneous clastic composition, the cement composition would also be homogeneously either siderite or dolomite throughout the Hatch Hill Formation. The only factor that influences the chemical composition of coexisting cements is, therefore, the ions present during precipitation of the cement. The reason for the development of chemically distinct cements must lie in the original composition of the sediment, and in the case of siderite, in the presence of minerals that contained iron and were locally enriched. The iron-bearing phases were probably iron oxides or hydroxides (hematite, magnetite or goethite). Iron-bearing silicates such as glauconite or chlorite contain only minor amounts of iron compared with iron oxides and hydroxides. It seems unlikely that iron-bearing silicates could provide sufficient iron for the sideritization of the Hatch Hill arenites. Furthermore, a by-product of the dissolution of iron-bearing silicates would be the liberation of a large volume of silica. However, the silica phases present in the Burden Iron Ore (chert and quartz overgrowths) account for less than 3% of the total rock volume.

Therefore, it seems more likely that iron oxides and/or hydroxides were locally enriched in the Hatch Hill arenites. A local enrichment of some type of iron-bearing phase appears to be necessary, since the distribution of siderite cement is not dependent on the grain size or sedimentary structures of a particular bed, but affects a variety of lithologies.

Therefore, the mechanism for the distribution of the siderite bodies has to be the result of a sedimentary process that produced distinct lenses of an iron-bearing phase. A sedimentary process that leads to this kind of distribution pattern is hard to envision. The depositional environment of the Hatch Hill Formation is the continental rise and/or slope. Coarse clastic material that is deposited within this environment is either derived from the continental shelf or upper parts of the slope. The transport of clastic material usually occurs in submarine channels and canyons. Hence, one possible process that could explain the iron ore bodies could be that they were deposited in distinct channels, which were fed by clastic material derived from an iron source on the shelf or continental slope. The unsideritized portions of the Hatch Hill Formation would then require a different channel system that did not receive iron-bearing clastic material. Areas that received sediments from both channel systems should thus show layers of unsideritized and sideritized sandstones. It is not possible to verify this model, because neither the lateral nor the vertical contact between the ore bearing sandstones and the dolomitic arenites is exposed in this area. The generally poor exposure also prevents any detailed study of the large scale depositional structures of the Hatch Hill Formation.

SUMMARY AND CONCLUSIONS:

I showed in the previous chapters that the Burden Iron ore occurs in a stratigraphically and structurally undisturbed slice of the Taconic allochthon. Lithological comparison based on the stratigraphy developed primarily in the northern part of the Taconics allowed the separation of five formations, the Bomoseen Formation, the Browns Pond Formation, the Hatch Hill Formation, the Poultney River Formation and the Mount Merino Formation. Equivalents of the Mettawee Formation, the Middle Granville Slate and the Indian River are not present in this area. The Burden Iron Ore, which was the major target of this study, is included in the Hatch Hill Formation, based on its stratigraphic position, lithology and petrography.

Detailed mapping showed that the Burden Iron Ore occurs in four distinct lenses. Each of these lenses overlies the Bomoseen Formation. The contact between the Bomoseen Formation and the Burden Iron Ore is sharp and shows no signs of structural disturbance. Since the Bomoseen Formation is of Precambrian or lowermost Cambrian age, and the Hatch Hill Formation is of upper middle Cambrian to early Ordovician age, the contact is marked by a disconformity that has not been observed elsewhere in the Taconics.

The Burden Iron Ore is trapped in a sequence of sandstones, limestones and breccias that are interbedded with black shales. Only two formations of the Taconic sequence contain similar lithologies, the Browns Pond Formation and the Hatch Hill Formation. The Browns Pond Formation, as present in this area, is dominantly composed cf micritic limestone and dolostone beds, a carbonate clast breccia and black shales. The Burden Iron Ore, however, consists of sideritic arenites that show graded bedding, bedding parallel laminations, rip-up clasts and Bouma sequences. These are sedimentological features that are also typical of the Hatch Hill Formation, and not the Browns Pond Formation.

The petrological study revealed that both the Burden Iron Ore and the Hatch Hill Formation have several close similarities. The detrital composition of each unit dominantly consists of rounded to subrounded quartz in bimodal distribution and minor amounts of clastic potassium feldspar, plagioclase and micritic carbonate grains. Both units are cemented by carbonate minerals. The only distinction is the chemical composition of the carbonate phase, since the Hatch Hill Formation is cemented dominantly by dolomite and minor amounts of calcite, and the Burden Iron Ore is cemented by siderite.

The origin of the Burden Iron Ore can be related to diagenetic processes that took place after the deposition of the sandstones that contain the ore bearing phase. Two lines of evidence based on petrographic and geochemical data can be used to support this statement. The siderite cements occur as euhedral to subhedral rhombs and show no signs of transportation. They replace clastic grains (oolites), but do preserve the delicate textures of the grains. Geochemical data show that siderite is only stable under very restricted environmental conditions, which can only be obtained by bacterial activity and partial burial of the host sediments. Both lines of evidence clearly indicate that the ore must have formed after the deposition of the host sediments.

One further problem, however, the regional distribution of the ore bodies, remains unsolved. I show that the Burden Iron ore is a diagenetic ore. This requires that the supply of iron to produce siderite was derived from a local source, most likely within the host sandstones, since other portions of the Hatch Hill Formation that occupy the same stratigraphic level are unsideritized. The enrichment of the sandstones with respect to iron most likely occurred during the process of resedimentation. However, a process that led to this type of enrichment is difficult to envision.

CHAPTER 4

SYNTHESIS AND FUTURE RESEARCH

The starting point of this work was two anomalous features: dolomite that occurs in sediments deposited in deep water, and a sideritic ore body trapped in a sandstone sequence. The only common link between both features was that previous workers such as Zen (1964) had speculated that the Burden Iron Ore might be part of the Hatch Hill Formation. During the course of this thesis, I tried to relate both features to each other and attempted to show that they share many distinct characteristics.

STRATIGRAPHY AND SEDIMENTOLOGY

The Burden Iron Ore occurs within a structurally intact sequence of Taconic sediments that includes the Bomoseen Formation, the Browns Pond Formation, the Hatch Hill Formation, the Poultney Formation and the Mount Merino Formation. The iron ore is trapped in a sequence of carbonate cemented sandstones, polymict breccias and micritic carbonates. The sedimentological features that can be observed, even though they are obscured by the weathering of the ore, include incomplete Bouma sequences (A-E), graded beds, rip-up clasts and bedding parallel laminations. Individual beds are not continuous on an outcrop scale, often pinching out. The only formation of the Taconic sequence that shows the same characteristics is the Hatch Hill Formation. Therefore, based on lithological comparisons, I include the Burden Iron Ore in the Hatch Hill Formation.

MINERALOGY

The petrological study of the Burden Iron Ore and the Hatch Hill arenites revealed almost identical mineralogical composition. The detrital minerals of both units are dominated by rounded to subrounded quartz and minor amounts of potassium feldspar, plagioclase and carbonate grains. Lithic fragments are sparse and almost absent. The cement of each unit consists of a carbonate phase: siderite in the Burden Iron Ore and dolomite with minor amounts of calcite in the Hatch Hill Formation. The only distinguishing feature is the chemistry of the carbonate cement.

DIAGENESIS

Based on two different lines of evidence, I believe that both the dolomites of the Hatch Hill Formation and the siderite of the Burden Iron Ore formed as diagenetic minerals during burial. Petrographic evidence shows that the dolomites formed after the formation of authigenic pyrite and the development of quartz overgrowths. Siderite rhombs can be seen to replace oolitic grains because the outlined internal structure of the oolites can be seen. Neither mineral phase shows evidence of reworking or transportation. The second line of evidence is based on isotopic studies and the geochemical stability fields of iron minerals. The isotopic trends of the dolomites of the Hatch Hill Formation suggest that these dolomites record a signal typical for the lower part of the zone of methanogenesis, and hence formed after they passed through the zone of sulfate reduction. Siderite becomes stable only during the progressive burial of organic-rich sediments, after the sulfide phase produced in the zone of sulfate reduction has been almost completely removed from the pore fluids. However, when siderite is formed, it is stable up to low grades of metamorphism. Hence it was not possible to place the formation of siderite within one distinct diagenetic zone without further isotopic information.

In summary, I point out that the features shared by the Hatch Hill dolomite and the siderite of the Burden Iron Ore by far outnumber the differences between both units. They occupy the same stratigraphic level, have almost identical mineralogical and petrological characteristics, and have undergone very similar post-depositional histories. The only distinguishing feature is the presence of iron in the Burden Iron Ore, which was probably derived from a local iron source. Hence the Burden Iron Ore is a local subfacies of the Hatch Hill Formation.

SUGGESTIONS FOR FUTURE RESEARCH

This thesis has only scratched the surface of what the Hatch Hill Formation still has to offer. I only probed a very few outcrops on a very small scale compared to the extensive occurrence of the Hatch Hill Formation within the over 200-km-long Taconic allochthon. A trend for the diagenetic history of the Hatch Hill Formation was established and seems to be promising for future work. More extensive research should be focused along two lines: (1) more isotopic data are necessary to verify the systematic variation of the carbon isotopes, and (2) the influence of reactions that may have occurred during the diagenesis of organic-rich shales and could have affected the authigenic mineralogy of interbedded sandstones needs to be investigated.

ISOTOPIC STUDIES:

Any isotopic study needs to concentrate on two major goals: (1) to verify the carbon isotope trend that has been established for the Poultney River section, and (2) to study cements that coexist within one sample, or in one stratigraphic level.

The verification of the diagenetic trend proposed for the Hatch Hill Formation can best be obtained at three outcrops described in some detail within this thesis, at Schodack Landing, Judson Point and Mettawee River. All of these sections provide extensive outcrops of the Hatch Hill Formation and contain abundant carbonate-cemented quartz arenites. None of these sections is extensively disturbed by later structural features, and hence allows good stratigraphic control. The sections at Schodack Landing and Mettawee River can even provide further information about whether the trends observed in the Hatch Hill Formation extend into lower parts of the Taconic sequence. Sampling of stratigraphically more extensive outcrop sections can also provide information about whether the cementation of carbonate cemented sandstone sequences within the Taconics always occurred within one diagenetic zone, or happened within various zones. This might even be possible within one sample, since coexisting authigenic minerals can form in different diagenetic environments. This has been demonstrated for pyrite and dolomite, and could be extended to calcite. In an ideal case even one grain could record the development of the diagenetic environment in which it formed. If the isotopic composition of one grain could be probed on a μm scale, useful information about the maturation of pore fluids might be obtained.

The isotopic study of siderite is more problematic than the one of dolomite and calcite. The amount of oxygen isotope fractionation during formation of the rock and the fractionation between phosphoric acid (used to dissolve the samples) and siderite are not known. However, carbon isotope studies of the Burden Iron Ore and the surrounding unsideritized parts of the Hatch Hill Formation could provide further information on the diagenetic zone in which siderite formed.

SHALES:

Previous studies (e.g. Boles, 1978; Curtis, 1978) have shown that the diagenetic changes within shales are a major contributor to the formation of sandstone cements. The development of sandstone cements is especially important, since sandstones function as pathways and host rocks for hydrocarbons. If the slates of the Hatch Hill Formation were donators of Mg^{2+}, Fe^{2+} and Ca^{2+} during the cementation of the Hatch Hill arenites, the geochemical signature of the shales should be relatively depleted with respect to these elements. The composition of the mineral assemblage, especially smectite and illite and their degree of ordering, can provide some informaticn about how far the shales of the Hatch Hill Formation were affected by diagenetic processes that would have contributed to dolomitization of the arenites.

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APPENDIX

OUTCROP LOCATIONS

Judson Point: Hudson North quadrangle, New York.
7.5 minute series.
2 km northwest of Columbiaville, at the end of County Road 59A. Outcrop extends approximately 300 m south along the Conrail railroad tracks.

Mettawee River: Granville Quadrangle, New York.
7.5 minute series.
Outcrop is located along the northern bank of the Mettawee River, 500 m northeast of North Granville and 1 km northwest of Truthville.

Nutten Hook: Hudson North quadrangle, New York.
7.5 minute series.
0.5 km west of Newton Hook at the end of Ferry Road. Outcrop extends approximately 250 m northward along a cliff facing the Hudson River (private property).

Poultney River: Thorn Hill quadrangle, New York-Vermont.
7.5 minute series.
Outcrop is located on the eastern bank of the Poultney River, 2.9 km northwest of Fairhaven, Vermont, and 2.4 km northeast of Low Hampton, New York.

Schodack Landing: Ravena quadrangle, New York.
7.5 minute series,
2.5 km south of Schodack Landing along State Route 9J. Outcrop can be reached along a small dirt road off Route 9J, 270 m south of the intersection of Route 9J and Ridge Road. Outcrop extends 300 m along side tracks of Conrail railroad tracks.

Stockport Station: Hudson North quadrangle, New York.
7.5 minute series.
2 km southwest of Columbiaville, at the end of County Roads 59 and 22. Outcrop extends approximately 100 m north along Conrail railroad tracks.