

Late Cambrian (Steptoean) sedimentation and responses to sea-level change along the northeastern Laurentian margin: Insights from carbon isotope stratigraphy

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ABSTRACT

Carbon isotopes are applied as tools for stratigraphic correlation of poorly fossiliferous Upper Cambrian carbonate strata in the northern U.S. Appalachians. Upper Cambrian (Steptoean) marine carbonate rocks record a significant global positive carbon isotope excursion ($\delta^{13}\text{C} = +4\text{‰}$ – 5‰ Vienna Pee Dee belemnite [VPDB]), the timing of which is well documented in fossiliferous sections elsewhere. The Steptoean excursion peaks at a sea-level lowstand that produced the Sauk II–Sauk III sequence boundary on the North American craton. In this study, this excursion is documented for the first time in the northern U.S. Appalachians in poorly exposed limestone debris flow and olistolith deposits interbedded within 20 m of continental slope shales of the Schodack Formation. These deposits contain the only reported pre-*Elvinia* zone Steptoean fauna in New York and record $\delta^{13}\text{C}$ values of up to $+3\text{‰}$. The slope carbonate sediment was mainly derived from the shelf margin and is mixed with common coarse-grained siliciclastic material. These deposits reflect a seaward migration of the siliciclastic source area (exposed craton), suppressed carbonate platform sedimentation, and shelf bypassing during the Sauk II–Sauk III sea-level fall. Nonfossiliferous dolostones and dolomitic marbles of the proposed carbonate platform correlatives (the Pine Plains Formation in southeastern New York and the Stockbridge Formation from western Massachusetts) also contain common coarse siliciclastics; however, sampled sections do not record elevated

$\delta^{13}\text{C}$ values, indicating that these strata are probably not of Steptoean age. This suggests that Steptoean time is represented in the carbonate platform to slope succession of the northeastern (present-day) Laurentian margin by an extremely condensed stratigraphic interval or even a hiatus.

Keywords: Schodack Formation, Pine Plains Formation, Stockbridge Formation, Upper Cambrian, northern Appalachians, carbon isotopes.

INTRODUCTION

The primary goal of this study is the correlation of Upper Cambrian carbonate strata in the northern U.S. Appalachians, the precise age of which is poorly constrained due to scanty fossil

preservation, diagenetic and metamorphic modifications, and structural complications. In the absence of fossils, we apply carbon isotopes as a stratigraphic tool. Sparse fossil evidence from the Schodack (Germantown or Hatch Hill) Formation and from strata overlying and underlying the Pine Plains Formation in southeastern New York suggests that parts of these units, and thus also proposed correlative strata of the Stockbridge Formation in western Massachusetts, may be Steptoean (Upper Cambrian; or upper Dresbachian to lower Franconian) in age (Knopf, 1962; Bird and Rasetti, 1968; Fisher, 1977; Fig. 1). Globally, Steptoean marine carbonate rocks record a significant positive carbon isotope excursion ($\delta^{13}\text{C} = +4\text{‰}$ – 5‰ Vienna Pee Dee belemnite [VPDB]), which peaks at a sea-level lowstand associated with the Sauk

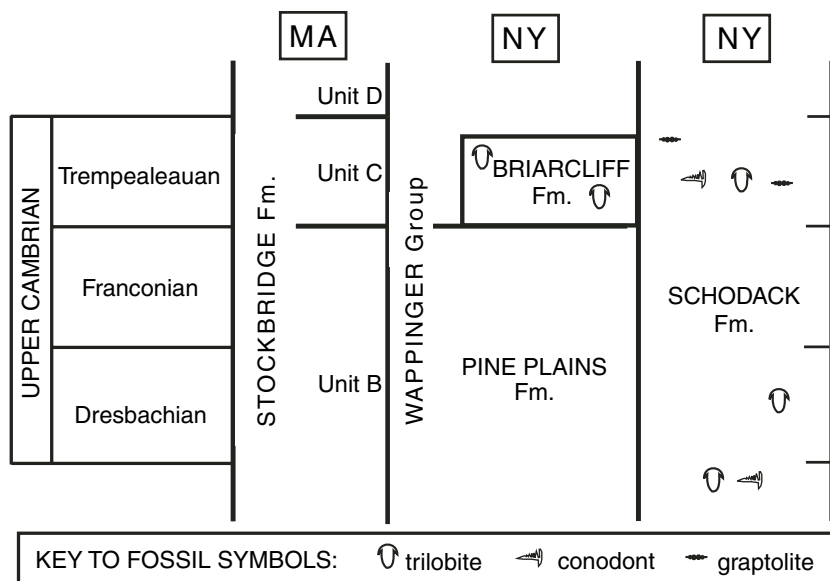


Figure 1. Proposed correlation and established biostratigraphy of the Upper Cambrian strata of the Stockbridge, Schodack, and Pine Plains Formations in the northern Appalachian region of southeastern New York (NY) and western Massachusetts (MA) (after Fisher, 1977).

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II–Sauk III sequence boundary in North America (Brasier, 1993; Glumac and Walker, 1998; Saltzman et al., 1998, 2000, 2004; Fig. 2). This excursion represents a large-scale perturbation in the global carbon cycle that occurred ~500 Ma and lasted for ~3.5 m.y. (Saltzman et al., 2004). Such perturbations are interpreted to be a result of enhanced rates of organic carbon removal from oceanic surface water, which may have been related to increases in primary biogenic productivity, sedimentation rates, or preservation of organic matter in anoxic bottom waters (Arthur et al., 1987; Weissert, 1989; Derry et al., 1992; among numerous others). The association of maximum $\delta^{13}\text{C}$ values with the sea-level fall suggests that the Steptoean excursion may have been caused by an increase in the rate of organic carbon burial in siliciclastic deposits in response to increased rates of weathering and erosion during the regression (Brasier, 1992; Glumac and Walker, 1998; Saltzman et al., 2004).

A consistent relationship between the Steptoean excursion and biostratigraphic markers has been documented from China, Kazakhstan, Australia (Saltzman et al., 1998, 2000), and from several localities in North America (Laurentia), including the Great Basin of Nevada (Brasier, 1993), the Cordilleran passive margin of Utah, the Upper Mississippi Valley of Iowa, and the passive margin of the northern Appalachians in Newfoundland (Saltzman et al., 2004) and the southern Appalachians in Tennessee (Glumac and Walker, 1998). The onset of the excursion coincided with the beginning of the Steptoean Stage, the Pteroceraphaliid biomere, and the *Aphelaspis* trilobite zone (Fig. 2). The excursion maximum in the *Dunderbergia* trilobite zone of the late Steptoean corresponds with the Sauk II–Sauk III sequence boundary on the Laurentian craton, while the excursion ends in the *Elvinia* trilobite zone (Fig. 2). Such good biostratigraphic control on the timing of the excursion allows us to apply carbon isotopes to stratigraphic studies of successions proposed to be of Steptoean age but for which detailed biostratigraphic determinations cannot be made because fossil assemblages either are absent or may not be directly comparable, as in cross-facies correlations. Therefore, carbon isotope stratigraphy is applied here in an across-platform and platform-to-slope study of carbonate depositional patterns of the northern U.S. Appalachians following the approaches successfully used previously in other areas (e.g., Kaufman et al., 1992; Föllmi et al., 1994; Narbonne et al., 1994; Pelechaty et al., 1996; Vahrenkamp, 1996; Saylor et al., 1998; Cozzi et al., 2004; Saltzman et al., 2004).

The Schodack Formation yielded the only documented pre-Franconian Late Cambrian

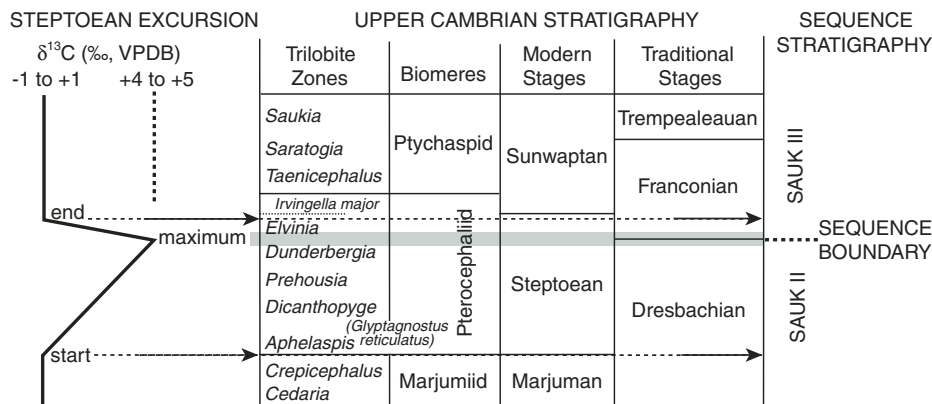


Figure 2. The large global Steptoean positive carbon isotope excursion is defined as an increase in $\delta^{13}\text{C}$ values of marine carbonate above their background value of -1‰ to $+1\text{‰}$ to a maximum of $+4\text{‰}$ to $+5\text{‰}$ (relative to Vienna Pee Dee belemnite [VPDB] standard). Timing of the onset, the maximum, and the end of the excursion was determined by Brasier (1993) and Saltzman et al. (1998, 2000). Note the association of the excursion maximum with the Sauk II–Sauk III sea-level fall, which produced an unconformity on the Laurentian craton (Lochman-Balk, 1971; Palmer, 1981); it also marks a major sequence-bounding interval (Kozar et al., 1990; Osleger and Read, 1991; Glumac and Walker, 2000).

fauna in New York (at the Elizaville locality of Bird and Rasetti, 1968), but the ages of the non-fossiliferous Pine Plains and Stockbridge strata are much more poorly constrained (Fig. 1). The sparse Schodack fossils are “undoubtedly of Late Cambrian, post-*Crepicephalus* and pre-*Elvinia* age” (Bird and Rasetti, 1968, p. 38), and the Steptoean positive carbon isotope excursion began directly following the *Crepicephalus* zone and ended in the *Elvinia* trilobite zone (Fig. 2). Knopf (1962) proposed a Middle to Late Cambrian age for the Pine Plains Formation on the basis of Middle Cambrian brachiopods and trilobites in the upper part of the underlying Stissing Dolomite and Late Cambrian (Trempealeauan) trilobites in the lower part of the overlying Briarcliff Dolomite (Fig. 1). No fossils have been identified in the entire Stockbridge Formation. The correlation of unit b of the Stockbridge, as defined by Zen (1966), with the Pine Plains is based on their shared relative position within the Lower Paleozoic sedimentary succession and on their lithology—impure dolomites to dolomitic marbles containing abundant detrital quartz. Ages proposed for the Pine Plains Formation and unit b of the Stockbridge Formation have ranged from Early to Middle Cambrian (Ratcliffe, 1969; Fisher and McLelland, 1975) to Late Cambrian (Fig. 1; Fisher, 1977).

The main hypotheses of this study are: (1) on the basis of Bird and Rasetti’s (1968) interpretation of its fossil content, the Schodack Formation at the Elizaville locality in New York should record the Steptoean positive carbon isotope excursion; and (2) siliciclastic input in the Pine

Plains and Stockbridge Formations, coupled with other shallow-water indicators might reflect a sea-level lowstand associated with the Sauk II–Sauk III unconformity, and thus with the record of the maximum Steptoean carbon isotope excursion. Locating this record would be the first documentation of the Steptoean excursion in the northern U.S. Appalachians, and it would provide new information about sedimentation patterns and stratigraphy of this important time period characterized by large global paleoenvironmental perturbations. This new information would build upon and nicely complement previous detailed investigations of this stratigraphic interval elsewhere (e.g., Saltzman et al., 2004) and the studies of the Lower Paleozoic passive-margin stratigraphy and sedimentation in the Appalachian region summarized by Read (1989) and James et al. (1989).

GEOLOGIC SETTING

The Schodack and Pine Plains Formations are exposed in the Taconic Mountains of southeastern New York, and the Stockbridge Formation crops out in the Berkshire Mountains of western Massachusetts, northwestern Connecticut, and southwestern Vermont (Fig. 3). The Schodack and Pine Plains Formations were studied at localities in northern Dutchess County, the former at the Elizaville locality of Bird and Rasetti (1968), and the latter at its type locality near the town of Pine Plains, where the most continuous and best-documented exposure of nonmetamorphosed Pine Plains Formation is available

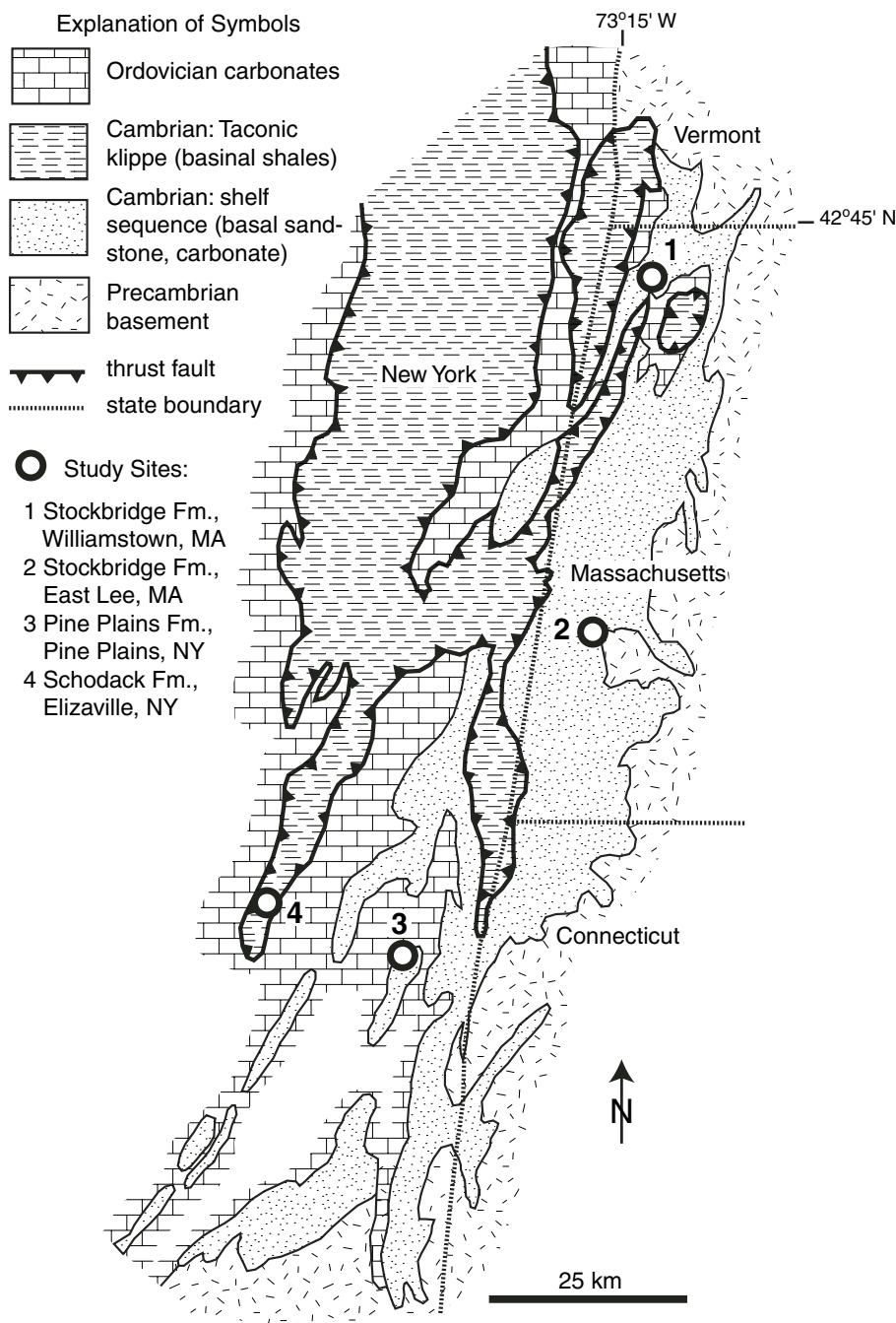


Figure 3. Generalized geologic map showing location of the study sites in southeastern New York and western Massachusetts (modified from Palmer, 1971).

(Knopf, 1962; Fig. 3). The Stockbridge Formation, with the focus on unit b, which consists of impure dolostone to dolomitic marble with significant detrital quartz (Zen, 1966), was examined at two localities in western Massachusetts (Fig. 3). Unit b occurs above pure dolostone/dolomite marble (unit a) and below pure limestone/calcite marble (unit c; Zen, 1966). Two sections representing the lowermost part of unit

b were studied near the town of Lee in the East Lee Quadrangle in southwestern Massachusetts (Ratcliffe, 1985; Fig. 3). The rest of unit b was studied in the Stone Hill Slice south of Williamstown in northwestern Massachusetts (Ratcliffe et al., 1993; Fig. 3). Detailed locality maps are included in Mutti (2002).

The Pine Plains Formation, the underlying Stissing Dolomite, and the overlying Briarcliff

Dolomite comprise the lower part of the Cambrian–Ordovician Wappinger Group. The Wappinger Group and the Stockbridge Formation, its proposed correlative (Fig. 1), represent carbonate platform successions deposited on the passive continental margin of eastern Laurentia. These carbonate strata directly overlie sandstone deposited unconformably on Precambrian basement rocks (Fisher, 1977). The shale-dominated Schodack Formation, on the other hand, represents deeper-water deposition on the continental slope to the east (present-day) of the original carbonate shelf (Fig. 4A). Today, parts of the Lower Paleozoic basinal deposits, such as the Schodack Formation, are exposed to the west and on top of contemporary platform carbonate successions, where they were transported along large-scale thrust faults during the Taconic orogeny (Fig. 3). Accordingly, the Pine Plains and Stockbridge Formations are interpreted as a parautochthonous succession and the Schodack Formation as an allochthonous succession (Fisher, 1977).

Extensive large-scale thrust faulting and folding complicate stratigraphic interpretations, correlations, and determinations of thickness and lateral distribution of Cambrian strata in the northern Appalachians. Significant weathering and soil and vegetative cover contribute to poor exposure of the carbonate succession throughout the region. In addition, regional metamorphism accompanied both the Taconic and Acadian orogenies in the northern Appalachians. Metamorphic grade in the study region increases to the east-southeast (Ratcliffe, 1969), and the Stockbridge Formation consists mainly of marble, particularly in southwestern Massachusetts. Also, Fisher and McLelland (1975) mapped strata of medium metamorphic grade (containing diopside and tremolite) in southern Dutchess County, south of our study area, as the Pine Plains Formation. Since metamorphism may reset carbon isotope signatures, this study focuses on sections that have experienced little or no metamorphism, and it also evaluates the degree of metamorphism and its potential effect.

METHODS

Our search for Steptoean strata in the carbonate platform successions of the Pine Plains and Stockbridge Formations was based on a large amount of data collected from numerous measured sections, coupled with best estimates of the extent of stratigraphic gaps from regional stratigraphic and structural relationships. Samples for petrographic and stable isotope analyses were collected at approximately 1 m intervals, as constrained by quality of exposure. All of the Pine Plains samples collected were further

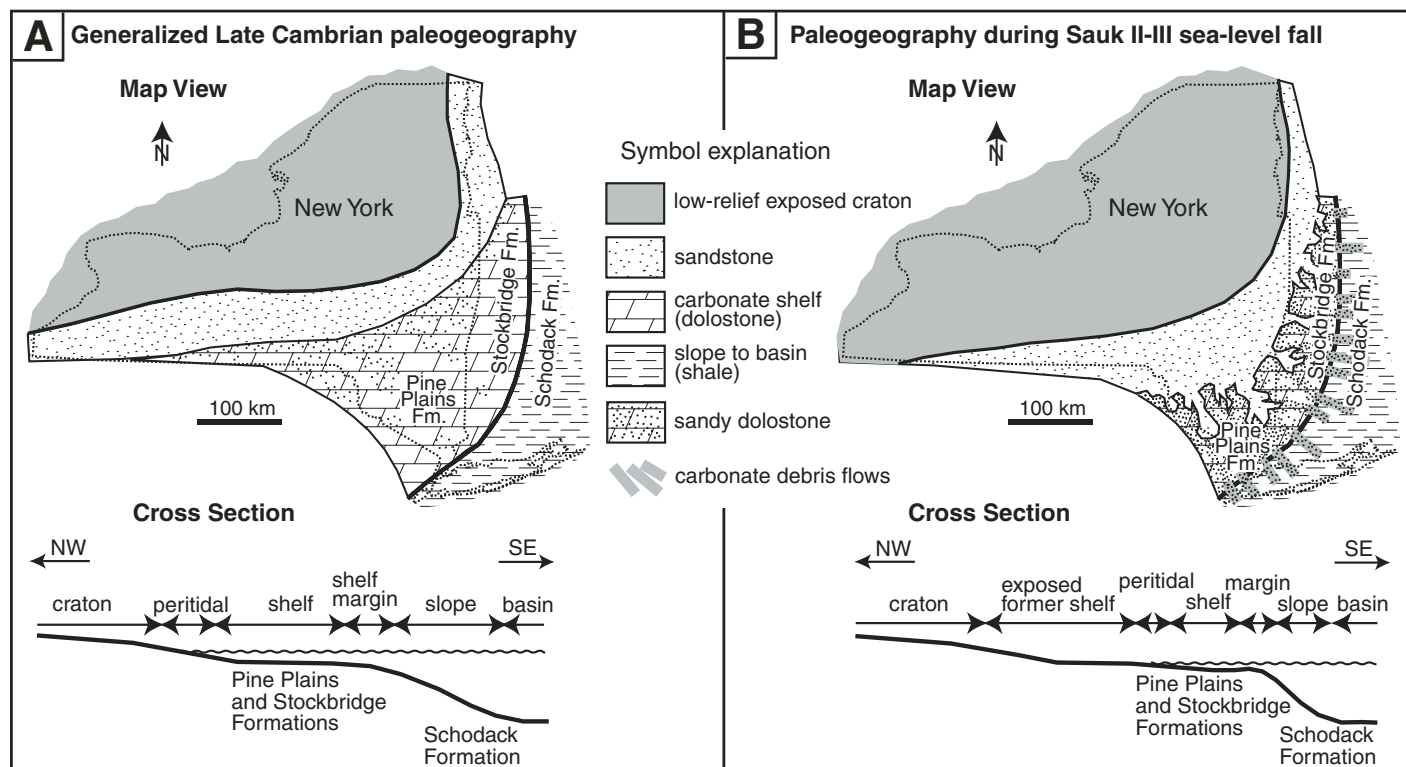


Figure 4. Late Cambrian paleogeography of the northeastern (present-day) Laurentian margin (adopted from Fisher, 1977). (A) Generalized Late Cambrian paleogeography. (B) Paleogeography during Sauk II–Sauk III sea-level fall.

described and analyzed (Table DR1).¹ A subset of the Stockbridge samples, representing an ~5 m sampling interval, was selected for this study (Table DR2, see footnote 1). Sampling of the small Schodack Formation outcrops was much more extensive. All of the Schodack Formation samples containing sufficient carbonate component were analyzed for stable isotopes (Table DR3, see footnote 1).

Following petrographic examination, small amounts (2–3 mg) of powder for stable isotope analysis were obtained from cut, polished, and stained slabs or thin section billets using a microscope-mounted microdrill. Drilled material as much as possible represented micritic, homogeneous, monomineralic, and nonweathered carbonate matrix. In several cases, it was necessary to drill micritic carbonate clasts and “whole rock” material in ooid grainstones and recrystallized samples (Tables DR1–DR3). Stable isotope analysis was performed at the University of Massachusetts–Amherst and at Syracuse University, using a Kiel III online

automated carbonate preparation system coupled directly to Finnegan-MAT DeltaXL+ and Finnegan MAT 252 mass spectrometers, respectively. After roasting for 1 h at 400 °C to remove any volatile organic components, dolomite samples were reacted at 70 °C with 100% anhydrous phosphoric acid (H_3PO_4) for 10 min and calcite samples were reacted for 5 min. Standard isobaric and phosphoric acid fractionation corrections were applied to all data. Internal analytical precision, monitored through daily analysis of carbonate standards, was better than or equal to 0.1‰ for both carbon and oxygen isotope values. Stable isotope results are expressed as $\delta^{13}C$ and $\delta^{18}O$ values in ‰ relative to the Vienna Pee Dee belemnite standard (VPDB).

FIELD AND PETROGRAPHIC OBSERVATIONS AND INTERPRETATIONS

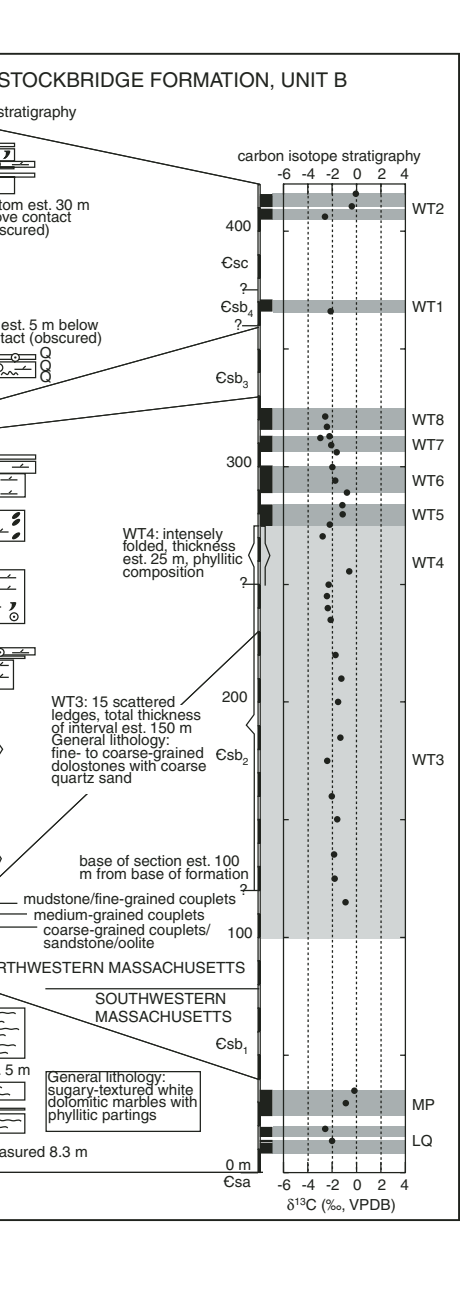
Schodack Formation

Observations

Two limestone-bearing outcrops of the shale-rich Schodack Formation were examined (Fig. 5). The stratigraphically lower outcrop (OFW) is most likely the source of the Steptoean fossils described by Bird and Rasetti

(1968). The lower 4 m of this outcrop consist of slightly metamorphosed (slaty) shale with centimeter-scale limestone interbeds (Fig. 6A). Some of these interbeds are normally graded or have cross-bedded quartz silt- or fine- to coarse-grained sand-rich lower parts (Fig. 6B). Above these strata, there are several massive limestone units (upper part of outcrop OFW; Figs. 5 and 6C), which show no apparent evidence of metamorphism and retain distinctly preserved original fabric of micritic matrix and carbonate grains. The massive limestone units are laterally discontinuous and irregular to lenticular in shape (Fig. 6C), though poor quality of exposure hampers observations of their true extent. The stratigraphically higher exposure (outcrop OFE) is a small limestone ledge, mostly composed of similar lithologies to those observed in the underlying massive limestone units, but its uppermost part contains shale similar to that at the base of the section (Fig. 5). The massive units contain two distinct lithologies: (1) sandy to conglomeratic limestones with closely packed and randomly oriented centimeter-scale micritic carbonate clasts, coarse detrital quartz sand, and ooids in a micritic matrix (Figs. 5, 6D, 6E); and (2) thrombolitic limestones with patchy-mottled micritic texture and well-preserved *Epiphyton* (Figs. 5 and 6F).

¹GSA Data Repository item 2007116, Tables DR1–DR3, sample descriptions and stable isotope data, is available on the Web at <http://www.geosociety.org/pubs/ft2007.htm>. Requests may also be sent to editing@geosociety.org.



d. PP0 through PP7 indicate outcrops of the tops of the Schodack Formation; sa, sb, and sc through 8 indicate Lee Quarry and William-DB—Vienna Peedee belemnite.

Paleozoic dep

be the product of storms, and can be deposited in a variety of settings, ranging from peritidal to slope (Sepkoski, 1982; Demicco, 1985; Whisonant, 1987; Myrow et al., 2004). Ooids form in shallow, high-energy environments, commonly located along carbonate platform margins. The thrombolitic limestones associated with debris-flow deposits in massive limestone units

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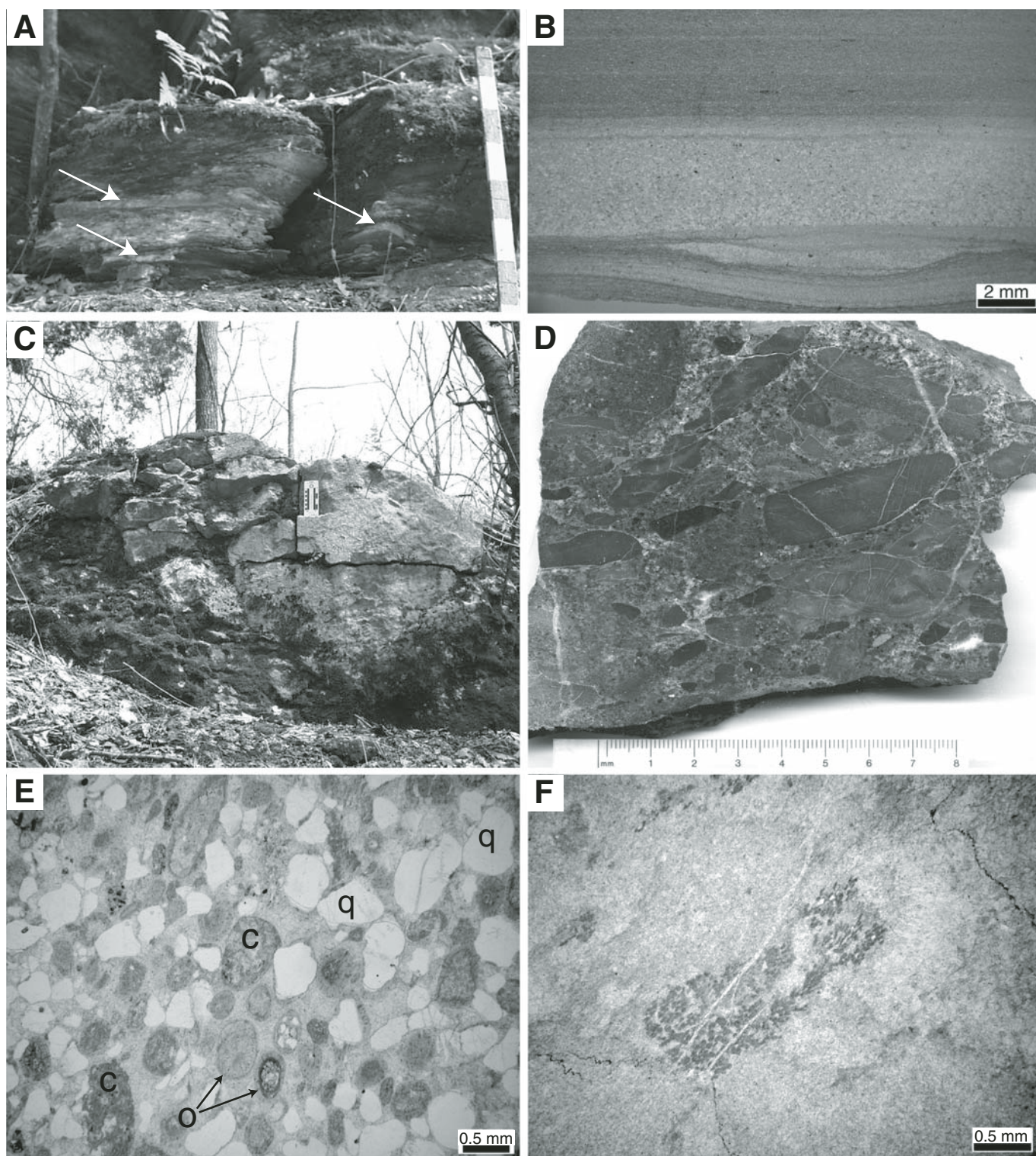


Figure 6. Photographs of characteristic features of the Schodack Formation. (A) Field photograph of the shaly strata interbedded with centimeter-scale limestone layers (arrows) in the lowermost part of the succession examined (outcrop OFW; Fig. 5). Jacob's staff is marked in 10-cm increments. (B) Photomicrograph of one such silty limestone interbed (shown in A) characterized by normal grading and cross-bedding at the base. (C) Field photograph of a lenticular limestone body (from the upper part of OFW outcrop; Fig. 5). Photo-scale is 16 cm tall. (D) Polished slab and photomicrograph (E) of a sample from one such limestone body (shown in C) characterized by closely packed and randomly oriented cm-scale micritic carbonate clasts (labeled c), coarse-grained quartz sand (labeled q), and ooids (labeled o) in micritic matrix. (F) Photomicrograph of a thrombolite from a limestone body (such as the one shown in C) with characteristic patchy-mottled micritic texture and well-preserved cyanobacteria *Epiphyton* (central part of the photograph).

(Fig. 5) are interpreted here as olistoliths, or blocks of partially lithified sediment transported downslope by submarine gravity sliding or slumping. *Epiphyton*, a common component of Cambrian thrombolites (Fig. 6F), is likely calcified coccoid cyanobacteria, which commonly formed microbial buildups or reefs on the carbonate platform rim (Pratt, 1984; Coniglio and James, 1985). Thus, the Schodack Formation strata are interpreted to have been deposited on a slope seaward of a shallow shelf, which may have been at least partially rimmed by thrombolitic bioherms and ooid sand accumulations (Fig. 4). The same setting was proposed by James and Stevens (1986) for the Upper Cambrian Cow Head Group strata in western Newfoundland, Canada, which consist of lithologies (sandy conglomeratic limestones, olistoliths, and thrombolites including *Epiphyton*) very similar to those of the Schodack Formation.

Pine Plains Formation

Observations

The Pine Plains Formation consists of non-metamorphosed dolostone with common detrital quartz (Figs. 5 and 7). The lower part of the formation (sections PP6, unfortunately exposed on a highly weathered cliff, and PP7; Fig. 5) contains very light-gray-colored fine-grained dolostones with stromatolitic intervals, centimeter-scale intraclasts, and coarse sand-size detrital quartz (Fig. 7A) interbedded with dark shale-carbonate laminites (Fig. 5). Significant detrital quartz and rare feldspar grains are found throughout the formation but are most prevalent in the middle part (sections PP0–PP3), which contains several sandstone units (Figs. 5 and 7B). This stratigraphic interval is dominated by a carbonate couplet lithology in which coarser-grained bases grade upward into dolomicrite (Figs. 5 and 7C). Couplets are classified as fine-, medium-, or coarse-grained according to the relative thickness of the grainy bases and size of their constituents, which may include intraclasts (“flat pebbles”), peloids, ooids, and quartz sand and/or silt. Grainy intervals commonly show both planar and cross-stratification (Figs. 5 and 7D). Fine-grained micritic couplet tops are often argillaceous, bioturbated, mud cracked, and/or microbially laminated (Figs. 5 and 7C). Microbial laminations are particularly common in the lower and middle Pine Plains Formation (Fig. 5), where several stromatolitic units with both planar and domal morphologies are noted (Figs. 5 and 7E). Coarser-grained couplets and oolites become more common and eventually dominate higher in the succession (upper section PP3 and PP4; Figs. 5 and 7F). Many samples from the middle to upper Pine Plains, and all from the

uppermost part (section PP5; Fig. 5), are recrystallized to a mosaic of medium to coarsely crystalline dolomite, which makes interpretation of their original lithology difficult.

Interpretations

Carbonate lithologies and sedimentary structures in the Pine Plains Formation suggest deposition in shallow-marine environments (Knopf, 1962; Ervilus and Friedman, 1991; Friedman et al., 2002). Restricted peritidal to shallow subtidal carbonate shelf environments protected from fair-weather waves are probable given the abundance of micrite, the absence of fossils, and the presence of mud cracks and stromatolites (Fisher and Warthin, 1976; Coniglio and James, 1985; Riding, 2000). Intraclastic or flat-pebble conglomerates likely record periodic storms. Common coarse quartz sand throughout the succession suggests that exposed cratonic siliciclastic source areas were nearby (Fig. 4). Coarse- and medium-grained couplets characterized by cross-bedding and ripple marks also represent deposition in intertidal to subtidal settings dominated by tides and storm waves and currents (Hardie and Ginsburg, 1977; Glumac and Walker, 2000). The presence of ooids indicates deposition on higher-energy shoals, which could have created a barrier protecting the restricted Pine Plains environments. Pervasive dolomitization of the Pine Plains Formation strata likely occurred during early diagenesis or as penecontemporaneous dolomitization of carbonate sediment deposited in shallow, restricted marine environments (Morrow, 1982; McKenzie, 1991). Early diagenetic dolomitization is indicated by the preservation of primary sedimentary textures and structures in most of the Pine Plains deposits (Friedman et al., 2002). The coarse crystalline dolomite mosaic, common in the uppermost sections examined (Fig. 5), on the other hand, may reflect original coarse-grained texture in these rocks. Ghost ooids in some coarsely crystalline samples suggest that, originally, these deposits were likely oolites. This confirms the predominance of oolite in the upper sections (PP3 and PP4; Fig. 5) and indicates a general deepening upward trend throughout the Pine Plains Formation from restricted peritidal and shallow subtidal settings into an environment dominated by ooid shoals.

Stockbridge Formation

Observations

In southwestern Massachusetts (Fig. 3), unit b of the Stockbridge Formation consists of a medium to coarsely crystalline, very light-gray dolomitic marble with prominent planar phyllitic partings (Figs. 5 and 8A). On the other

hand, the strata in northwestern Massachusetts (Fig. 3) appear to be nonmetamorphosed dolostones (or metamorphosed to a low degree) that have mostly fine to medium crystalline texture (Figs. 5 and 8B), even though they are associated with one intensely folded phyllitic interval (section WT4; Fig. 5). The lowermost exposures in northwestern Massachusetts (section WT3; Fig. 5) are substantially weathered and contain significant coarse quartz sand in the upper part (Fig. 8C). Strata overlying the phyllite (sections WT5–WT8; Fig. 5) are fine-grained, light-colored, and relatively pure dolostones with carbonate intraclasts (Fig. 8D), ooids, and rare quartz sand. The quartz grains commonly show recrystallization fabrics, such as undulose extinction, jagged grain boundaries, and polymineralic character (Fig. 8C), but their distribution reflects detrital origin with deposition in layers or reworking into burrows. Outstanding preservation of primary physical sedimentary structures, including planar stratification, microbial lamination, cross-bedding, and ripple marks (Figs. 8E and 8F), characterizes these and the overlying strata (section WT1; Fig. 5), which also contain abundant quartz sand. The uppermost exposure (section WT2; Fig. 5) includes an oolitic layer interbedded between bioturbated dolomitic mudstones. This outcrop has been mapped as unit c of the Stockbridge Formation (Ratcliffe et al., 1993), which is defined as limestone to calcitic marble (Zen, 1966). Strata at this outcrop, however, consist of dolostone, and thus most likely represent the uppermost part of unit b.

Interpretations

The depositional environment for the Stockbridge Formation unit b is proposed to have been similar to that interpreted for the Pine Plains Formation, a shallow-marine shelf setting (Fig. 4; Fisher, 1977), judging from many shared characteristics, including common coarse quartz sand (Fig. 8C) derived from the exposed craton (Fig. 4), the absence of fossils, the abundance of muddy deposits interbedded with cross-bedded intervals, the presence of microbial laminations, intraclasts and ooids, as well as pervasive dolomitization. In general, the finely crystalline dolomite texture of the Stockbridge Formation unit b strata in northwestern Massachusetts argues against major recrystallization during late diagenesis or metamorphism, which has allowed these strata to retain primary sedimentary features such as cross-bedding and ripple marks to a remarkable extent (Figs. 8E and 8F). The presence of extensively folded phyllitic strata (section WT4; Fig. 5), directly underlying dolostones with essentially no internal deformation, indicates that micaceous intervals

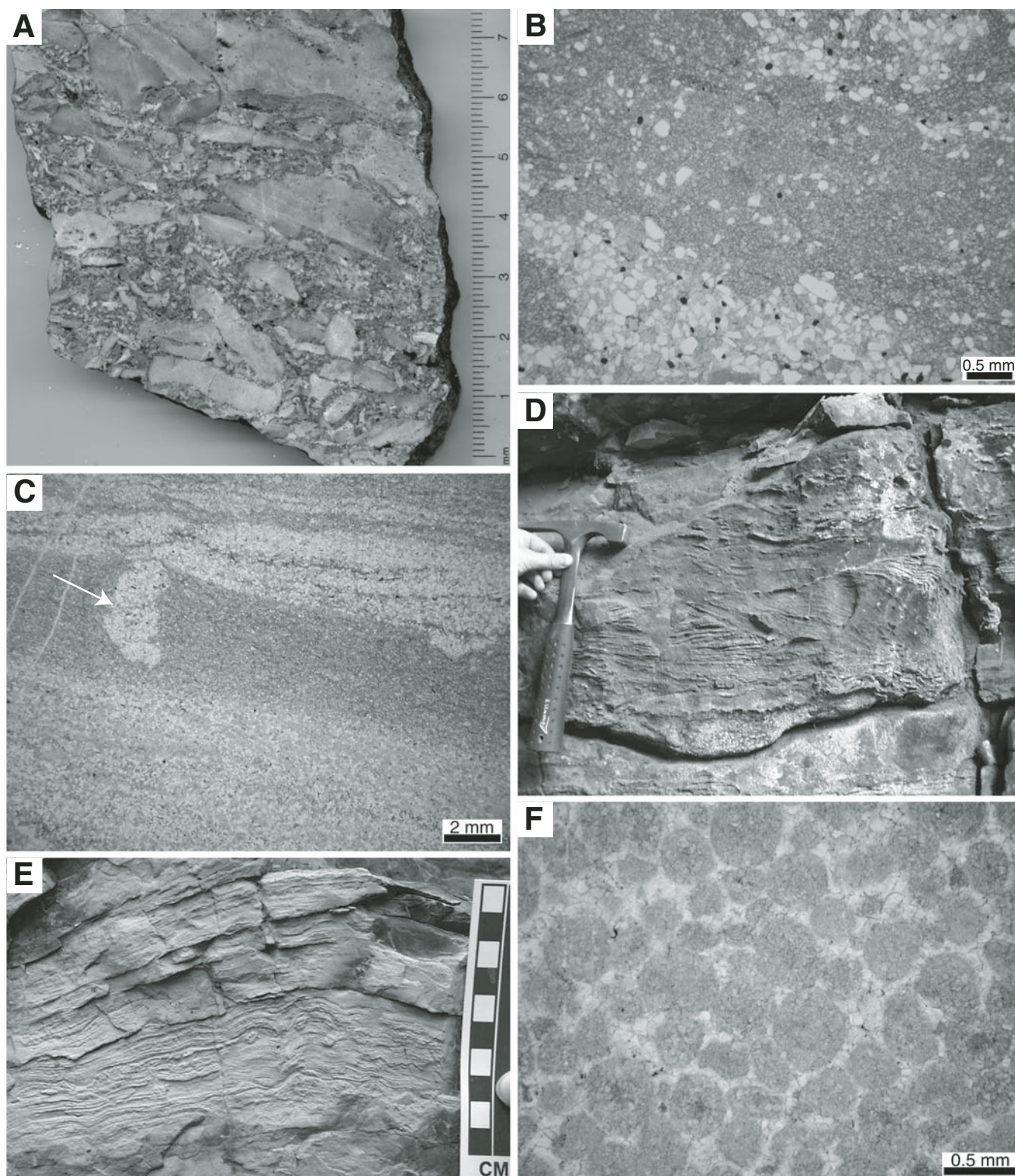


Figure 7. Photographs of characteristic features of the Pine Plains Formation. (A) Polished sample from the lower part of the succession examined (see Fig. 5) showing centimeter-scale dolostone intraclasts and coarse-grained quartz sand in dolomicritic matrix. (B) Photomicrograph of sandy dolostone (common in the middle part of the succession) showing quartz grains in dolomicrosparitic matrix. Dark grains are pyrite. (C) Photomicrograph of carbonate couplets (also from the middle part of the succession) with cross-laminated quartz silt- and sand-rich couplet bases and argillaceous (bioturbated or mud cracked?; arrow) dolomicritic couplet tops. Field photographs of cross-bedding (D) and stromatolites (E) from the middle part of the succession. (F) Photomicrograph of an ooid grainstone (from the upper part of the succession) recrystallized to dolomicrosparite and medium-crystalline dolomite.

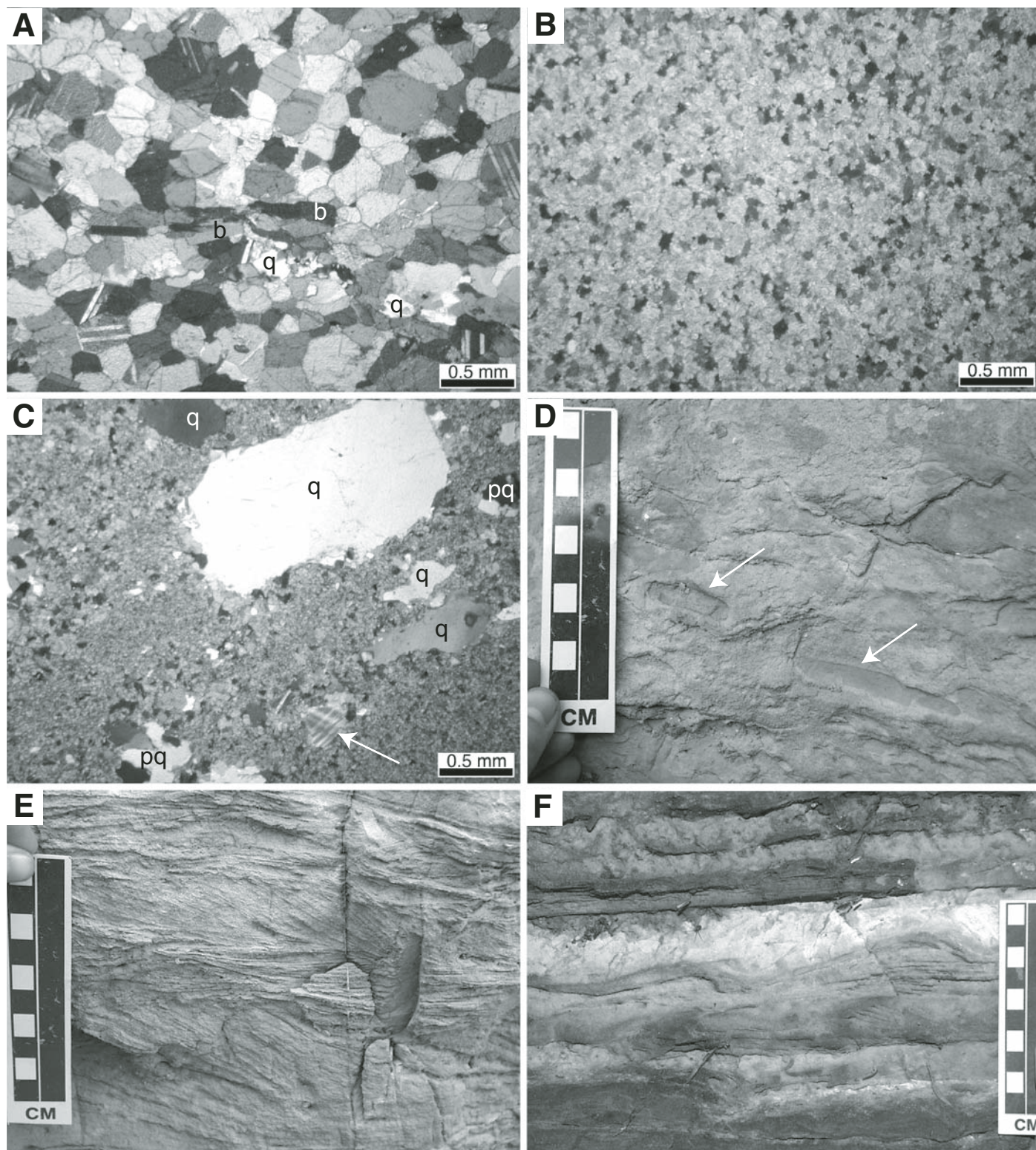


Figure 8. Photographs of characteristic features of the Stockbridge Formation. (A) Cross-polarized light photomicrograph of coarse-crystalline dolomitic marble with quartz (labeled q) and biotite (labeled b) grains (from southwestern Massachusetts). (B) Cross-polarized light photomicrograph of fine-crystalline dolostone (from northwestern Massachusetts). (C) Cross-polarized light photomicrograph of coarse-grained quartz sand (labeled q) in dolostones from northwestern Massachusetts. Note the angular shape and jagged boundaries of quartz grains and the presence of polymineralic quartz (labeled pq). Feldspar grains are also present (arrow). Field photographs of centimeter-scale carbonate intraclasts (D; arrows), cross-bedding (E), and asymmetrical ripple marks (F) in dolostones from northwestern Massachusetts.

accommodated much of the structural deformation in this section. Fluid pathways preferentially follow zones of weakness, and rocks are typically weakest where they have been deformed. Consequently, it is possible that the Stockbridge dolostones in northwestern Massachusetts may not have interacted extensively with late diagenetic and metamorphic fluids, the flow of which through these strata may have been chiefly contained to deformed noncarbonate intervals. In fact, Ratcliffe et al. (1993) documented a dolomite-quartz assemblage for carbonate rocks of the Stockbridge Formation and only low-temperature (chlorite-grade) assemblages in pelitic rocks in northwestern Massachusetts. Burger (1975) reported dolomite with quartz and phlogopite in unit b of the Stockbridge Formation in southwestern Massachusetts, but the absence of metamorphic minerals talc and tremolite indicates that none of these rocks evolved significant carbon dioxide in metamorphic decarbonation reactions (Spear, 1993). Therefore, these rocks may preserve their primary or close to primary marine carbon isotope signatures.

STABLE ISOTOPE ANALYSIS

Theoretical Considerations

Physicochemical precipitation of marine carbonates occurs in isotopic equilibrium with seawater, and there is essentially no temperature effect on carbon isotope fractionation within the near-surface temperature range (Anderson and Arthur, 1983; Romanek et al., 1992). Thus, the primary carbon isotope signature of marine depositional and diagenetic carbonate components closely reflects that of the seawater from which they precipitated, unless it has been subsequently modified during diagenesis or metamorphism. Massive alteration of $\delta^{13}\text{C}$ values of carbonate phases is usually hindered by small concentrations of carbon in diagenetic and metamorphic fluids. Carbon isotope signatures can become significantly reset only if the rocks experience either: (1) extensive flow of carbon-rich fluids through open-system exchange (Banner and Hanson, 1990); or (2) decarbonation reactions during metamorphism, in which isotopic fractionation accompanies the formation of carbon dioxide that is expelled from the rock (Shieh and Taylor, 1969). The record of the Steptoean carbon isotope excursion is readily preserved in extensively altered rocks that consist of fabric-obliterated and coarsely crystalline dolomite and that interacted with Mississippi Valley-type hydrothermal brines (Glumac and Walker, 1998), which suggests that carbon isotope stratigraphy can be applied to highly dolomitized, deformed, and even metamorphosed strata.

The majority of samples used in this study are homogeneous micrite and dolomicrite, without visible cements and skeletal fragments (Tables DR1–DR3). Various petrographic (including cathodoluminescence) and geochemical (major- and trace-element compositions) criteria have been used to demonstrate the potential of using shallow-water micrite and dolomicrite for the reconstruction of seawater carbon isotope evolution (e.g., Fairchild et al., 1990; Marshall, 1992; Schidlowski and Aharon, 1992; Brasier et al., 1994; Kaufman et al., 1993; Narbonne et al., 1994; Kaufman and Knoll, 1995; Knoll et al., 1995). Extensively dolomitized carbonate successions likely experienced dolomitization during early diagenesis (Morrow, 1982; McKenzie, 1991), under conditions similar to those during deposition, and therefore commonly retain their primary or close to primary marine carbon isotopic signatures.

Examples of diagenetic alteration of the deposits examined here include neomorphism and recrystallization of micrite to microsparite, and dolomitization of fine-grained carbonate to dolomicrosparite and coarse-crystalline replacement dolomite (Tables DR1–DR3). Diagenetic modifications are substantiated by oxygen isotope compositions that are more negative than the predicted oxygen isotopic composition of Upper Cambrian to Lower Ordovician marine calcites of -5‰ to -3‰ (Lohmann and Walker, 1989; Gao and Land, 1991; Fig. 9). In such altered deposits, the presence of tightly constrained carbon isotope variation curves showing no significant scatter of $\delta^{13}\text{C}$ values and the lack of systematic covariance between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are commonly cited as evidence that the carbon isotope signal is not strongly influenced by diagenetic modifications (Hudson and Anderson, 1989; Derry et al., 1992; Brasier et al., 1994).

RESULTS

In the shaly interval that makes up the lower part of the measured section of the Schodack Formation (lower OFW strata), $\delta^{13}\text{C}$ values in calcite samples from limestone interbeds range from -0.69‰ to -1.83‰ , with only one value near $+1\text{‰}$ (Fig. 5). In the overlying massive limestone deposits, the $\delta^{13}\text{C}$ values first increase upsection from -1.14‰ to reach $+2.91\text{‰}$, followed by a slight decrease, but the values remain above $+1\text{‰}$ (Fig. 5). The $\delta^{13}\text{C}$ values from the stratigraphically higher outcrop (OFE) generally decrease upsection from $+1.74\text{‰}$ to -0.56‰ (Fig. 5). Oxygen isotope compositions are quite negative for all samples analyzed, varying between -15‰ and -11‰ (Fig. 9; Table DR3).

Uniformly negative $\delta^{13}\text{C}$ values (-2‰ – 0‰) with little stratigraphic scatter characterize dolomitic samples from the middle to upper Pine Plains Formation sections, with the exception of section PP4, which shows slightly positive values (up to $+0.5\text{‰}$; Fig. 5; Table DR1). Dolomitic samples from the lower part of the succession (sections PP6 and PP7) show the greatest scatter of $\delta^{13}\text{C}$ values, with samples from the base of the section yielding the lowest $\delta^{13}\text{C}$ values (at -5.5‰ to -2‰ ; Fig. 5). These low and variable $\delta^{13}\text{C}$ values are associated with rather constant $\delta^{18}\text{O}$ values (-8‰ to -6‰ ; Fig. 9), even though oxygen isotope compositions throughout the succession range between about -9.5‰ and -5.5‰ (Fig. 9; Table DR1).

The $\delta^{13}\text{C}$ values of dolomitic samples from the Stockbridge Formation are consistently negative; they vary throughout the section between -3‰ and 0‰ and show great scatter stratigraphically (Fig. 5; Table DR2). The least negative $\delta^{13}\text{C}$ values (between -0.5‰ and 0‰) bracket the large covered interval in the lower part of the succession (at the top of the section in southwestern Massachusetts and at the base of the section in northwestern Massachusetts; Fig. 5). Similar $\delta^{13}\text{C}$ values are also observed at the very top of the measured succession (section WT2), in strata mapped by others as just above the unit b–unit c boundary but assigned in this study to uppermost unit b (Fig. 5). Throughout the section, $\delta^{18}\text{O}$ values are intermediate between the Pine Plains Formation and Schodack Formation values (mostly between -10.5‰ and -6‰ ; Fig. 9; Table DR2). The $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ cross-plots show a random scatter of data points with no apparent covariant or any other trends (Fig. 9).

INTERPRETATIONS

The $\delta^{13}\text{C}$ values documented in carbonate strata from the Schodack Formation reach almost $+3\text{‰}$ and represent the first documentation of the Steptoean positive carbon isotope excursion in the northern U.S. Appalachians. This interpretation is consistent with these strata hosting the only documented pre-*Elvinia* zone Steptoean fossils in New York State (Bird and Rasetti, 1968; Fig. 1). The $\delta^{13}\text{C}$ values show a trend that is consistent with the onset of the excursion documented elsewhere (Brasier, 1993; Glumac and Walker, 1998; Saltzman et al., 1998, 2000, 2004). The slightly elevated $\delta^{13}\text{C}$ value ($+0.93\text{‰}$) of one thin carbonate turbidite sample from below the massive limestone deposits (Fig. 5) may correspond to the small peak observed just before the start of the excursion in the southern Appalachians (Glumac and Walker, 1998). It is possible that the Schodack Formation strata exposed at the lower outcrop

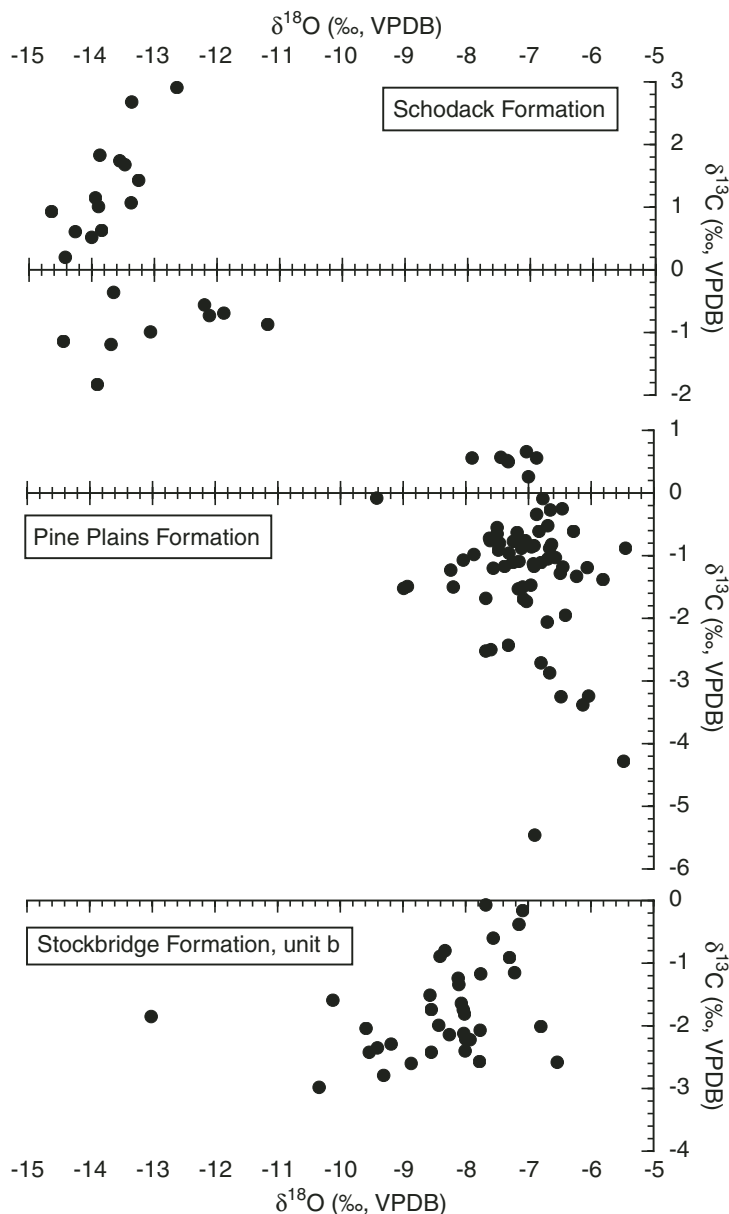


Figure 9. Relationship between carbon and oxygen isotope values for the samples from the successions examined. Note that the Schodack Formation samples are calcitic, whereas the Pine Plains and Stockbridge Formation samples are dolomitic (see also Tables DR1–DR3). VPDB—Vienna Pee Dee belemnite.

(OFW) record the beginning of the excursion and the strata at a stratigraphically higher outcrop (OFE) record its end (Fig. 5). If so, then the thickness of the stratigraphic interval containing the Steptoean positive carbon isotope excursion is condensed within ~20 m (Fig. 5).

Highly negative $\delta^{18}\text{O}$ values observed throughout the section (Fig. 9; Table DR3) indicate significant alteration of the original seawater values. The slaty texture of the shale from the lower part of the Schodack Formation (Fig. 5) suggests low-grade metamorphism of

these strata. Interaction with metamorphic fluids at elevated temperatures would account for the highly negative $\delta^{18}\text{O}$ values (Fig. 9). The range of measured $\delta^{18}\text{O}$ values (–15‰ to –11‰) suggests possible recrystallization temperatures of 75–180 °C (equations after Friedman and O’Neil, 1977), assuming a range for $\delta^{18}\text{O}$ values of 0‰–8‰ SMOW (standard mean ocean water) (Kharaka and Thordsen, 1992). Fractionation of carbon isotopes, however, is not affected significantly by temperature (Anderson and Arthur,

1983; Romanek et al., 1992), and the primary carbon isotope signature of the Schodack Formation strata examined appears not to have been altered much, since stratigraphic trends in $\delta^{13}\text{C}$ are fairly well defined (Fig. 5), and the $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ cross-plot shows the scatter of data points (Fig. 9).

The absence of elevated $\delta^{13}\text{C}$ values in the exposed sections of the Pine Plains Formation, which span substantial stratigraphic thickness of the formation, strongly suggests that these strata are not of Steptoean age (Fig. 5). If recorded at all, the Steptoean positive carbon isotope excursion would have to be present within a condensed interval, which was not sampled due to lack of exposure. The documented carbon isotope compositions, with the exception of those from the lowermost exposure (section PP6; Fig. 5), define a “tight” stratigraphic curve and likely represent primary or close to primary seawater signatures, whereas the consistently depleted oxygen isotope compositions of samples from throughout the Pine Plains Formation reflect alteration during diagenesis (Fig. 9). Primary $\delta^{18}\text{O}$ values predicted for Upper Cambrian dolomites precipitated in equilibrium with normal marine water range between –2‰ and 0‰, judging from marine calcite values of –5‰ to –3‰ (Lohmann and Walker, 1989; Gao and Land, 1991) and a $+3\text{‰} \pm 1\text{‰}$ fractionation factor between calcite and dolomite (Friedman and O’Neil, 1977; Land, 1980). The range of $\delta^{18}\text{O}$ values for dolomitic matrix of the Pine Plains Formation (–8‰ to –6‰) yields recrystallization temperatures of 65–140 °C (equations after Land, 1985; $\delta^{18}\text{O}$ values of formational waters in sedimentary basins after Kharaka and Thordsen, 1992). The calculated temperature range is consistent with maximum burial temperatures of ~150–155 °C proposed previously for the Pine Plains strata (Ervilus and Friedman, 1991).

Highly variable and negative $\delta^{13}\text{C}$ values of marine carbonates, such as those observed in the lowermost Pine Plains exposure (section PP6; Fig. 5), are typical of diagenetic modification in the presence of decaying organic material (e.g., Friedman and O’Neil, 1977; Veizer, 1983; Fairchild et al., 1990; Kaufman et al., 1991; Marshall, 1992). The strata at this exposure are also characterized by a rather narrow range of $\delta^{18}\text{O}$ values, which may indicate diagenetic alteration of marine carbonates in the presence of meteoric fluids (Lohmann, 1988). Since this lowermost examined exposure of the Pine Plains Formation is a highly weathered, lichen-covered cliff, it may have experienced more interaction with rain water and organic material than other exposures.

The strata from the Stockbridge Formation examined in this study also fail to document the Steptoean positive carbon isotope excursion.

Consistently negative $\delta^{13}\text{C}$ values throughout the section establish that most of the succession is not Steptoean in age (Fig. 5). Similar stratigraphic trends in $\delta^{13}\text{C}$ values (negative and widely oscillating) to those in the middle and upper Stockbridge Formation unit b (-3‰ – 0‰ ; Fig. 5) have been observed in Upper Cambrian post-Steptoean carbonate strata of the upper Conococheague Formation in northern Virginia (-4‰ – 0‰ ; R.L. Ripperdan, 2001, personal commun.). This might suggest that unit b of the Stockbridge Formation is Sunwaptan (middle to late Franconian) and/or Trempealeauan in age (Figs. 1 and 2). If this is true, Steptoean time may be represented in the lower part of unit b or even in the underlying unit a, and the excursion, if recorded at all, would have to be present in a relatively thin, condensed interval as is proposed for the Pine Plains Formation.

The $\delta^{18}\text{O}$ values of the Stockbridge Formation (ranging from -10.5‰ to -6‰) are interpreted to reflect isotopic exchange with fluids at elevated temperatures, calculated as $65\text{--}165\text{ }^{\circ}\text{C}$ (after Friedman and O'Neil, 1977; Land, 1985; Kharaka and Thordsen, 1992). This exchange could have occurred either during deep burial diagenesis or metamorphism. Pervasive alteration of the $\delta^{18}\text{O}$ signature was accompanied by some carbon isotope exchange: the documented negative and widely oscillating $\delta^{13}\text{C}$ values are consistent with alteration by fluids containing variable amounts of carbon derived from decaying organic matter. Metamorphic decarbonation reactions, however, are likely not responsible for alteration of primary carbon isotope signatures in these strata, as constrained by the absence of minerals such as talc and tremolite. Most importantly, the Steptoean positive carbon isotope excursion is of great enough magnitude (up to $+5\text{‰}$) that, if present, the record of the elevated carbon isotope signatures should be recognizable despite alteration of $\delta^{13}\text{C}$ values to the degree observed in the Stockbridge Formation.

DISCUSSION

The $\delta^{13}\text{C}$ values of material in the carbonate debris-flow and olistolith deposits of the Schodack Formation suggest that this sediment formed on a shelf during the onset of the positive carbon isotope excursion in the early Steptoean (Figs. 2 and 5). Since carbonate sediments are commonly lithified early in their diagenetic history, soon after its formation this sediment was transported downslope in a series of debris flows (Fig. 4B). Thus, the sediment in the carbonate debris flows of the Schodack Formation is not much older than the debris flow themselves, which allows us to apply carbon isotope stratigraphy to these allochthonous

slope deposits. In fact, globally, the Steptoean positive carbon isotope excursion is readily documented in deep-water carbonate deposits (Saltzman et al., 2000). In Australia, the excursion is recorded in finely laminated, organic-rich pyritic deposits from a deep-water intracratonic basin. Fine-grained, dark-colored argillaceous limestone and carbonate gravity-flow deposits from a submarine-fan environment on the flank of a seamount record the Steptoean excursion in Kazakhstan. The record of the excursion in China comes from slope deposits at a transition between the shallow-water carbonate platform and a deep-basinal setting. The slope deposits consist of rhythmically bedded argillaceous limestones and calcareous shales with minor dolomitic limestones. Interbedded with these deposits are limestone-clast breccia beds interpreted as debris flows produced by episodic slumping of the upper slope and carbonate-platform margin (Saltzman et al., 2000).

The association of elevated $\delta^{13}\text{C}$ values with quartzose carbonate debris flows and olistoliths deposited on the continental slope (Fig. 5) suggests that this depositional pattern of the Schodack Formation may represent the response to sea-level fall during the late Steptoean that resulted in the Sauk II–Sauk III unconformity on the craton (Figs. 2 and 4B). During the lowstand, parts of the carbonate platform may have been exposed and eroded, and thus little carbonate deposition occurred on the shelf (Fig. 4B). On the parts of the platform that remained submerged, production of carbonate sediment continued at a decreased rate, and, in general, sites of carbonate sediment production and deposition moved seaward (Fig. 4B). Carbonate deposition may have been restricted to the shelf margin area, which could have at least partially been rimmed by microbial (thrombolitic) bioherms and ooid sand accumulations. The sea-level fall also caused the seaward migration of sources of siliciclastic material, which increased siliciclastic input onto the carbonate platform area (Fig. 4B). Already reduced carbonate sedimentation suffered additionally with heavy siliciclastic input. This siliciclastic material joined carbonate sediment in bypassing the shelf to become deposited on the adjacent slope (Fig. 4B). Just such a bypass margin depositional model has been proposed by James and Stevens (1986) for the Upper Cambrian Cow Head Group strata from western Newfoundland, which are time equivalent and share similar lithologies with the Schodack Formation strata examined here.

Since little carbonate deposition was occurring during the late Steptoean sea-level fall, it is not surprising that the carbon isotope excursion might be recorded in a highly condensed,

~20-m-thick interval of the Schodack Formation (Fig. 5). The Cow Head Group strata from Newfoundland, which represent the upper four trilobite zones of the Dresbachian Stage and span approximately the same time period during which the Steptoean positive carbon isotope excursion occurred (Fig. 2), were also condensed into less than 20 m of stratigraphic thickness (James and Stevens, 1986). This biostratigraphic interpretation was recently confirmed by carbon isotope stratigraphy of the Petit Jardin Formation in Newfoundland (Saltzman et al., 2004). These conclusions about highly reduced carbonate deposition along the Upper Cambrian margin of northeastern (present-day) Laurentia are also consistent with information on Upper Cambrian continental slope deposits of the Gorge Formation in northwestern Vermont. Limited biostratigraphy and carbon isotope stratigraphy of the lower Gorge Formation document an unconformity that encompasses most of the late Dresbachian (post-*Crepicephalus* zone) and early Trempealeauan Stages (Gilman Clark and Shaw, 1968a, 1968b; Landing, 1983; Glumac and Spivak-Birndorf, 2002). Thus, lithologic features, fossil evidence where available, and carbon isotope stratigraphy of Upper Cambrian slope deposits from the northern Appalachians consistently indicate severely reduced or arrested carbonate sedimentation during the Sauk II–Sauk III sea-level fall in the late Steptoean (Fig. 4B).

The carbon isotope data indicating non-Steptoean age for strata of the Pine Plains and Stockbridge Formations examined here are consistent with greatly reduced shelf deposition during the Steptoean. Carbonate platform deposition almost certainly slowed and could have even ceased altogether during maximum Sauk II–Sauk III sea-level fall (Fig. 4B). If the carbonate material produced during this time bypassed the shelf, there would be no or very little carbonate sediment deposited on the shelf recording the excursion. Instead, this sediment would be incorporated in Steptoean slope deposits, such as the highly condensed Schodack Formation carbonate strata. Given the general regional patterns in Sauk II–Sauk III deposition along the northeastern Laurentian margin that have emerged from this study (Fig. 4B), it is possible that the entire Steptoean age is represented within the Pine Plains and Stockbridge Formations by only a very thin interval or even a hiatus, which may be very difficult or impossible to locate in the field due to limited exposure. For comparison, the Steptoean positive carbon isotope excursion is recorded in an ~80-m-thick shallow carbonate platform succession in the southern Appalachians (Glumac and Walker, 1998) and in more than 200-m-thick strata in the Great Basin of the

western United States (Saltzman et al., 2000). Thus, the condensation of Upper Cambrian deposition on the northeastern Laurentian carbonate shelf documented in this study provides important new insights into the variable rates of sedimentation and subsidence along the passive continental margins of Laurentia.

The major shift in depositional regime represented by transition from sandy dolomitic marbles in unit b to clean calcitic marbles in the overlying unit c of the Stockbridge Formation (Zen, 1966) could indicate a transition from a shallow-water (restricted peritidal) setting, with pervasive early diagenetic dolomitization, to a slightly deeper, carbonate shelf environment during transgression at the beginning of the Sauk III sequence. The same mechanism may be responsible for the deepening-upward trend observed in this study within the Pine Plains Formation. Thus, it is possible that most, if not all, of the Upper Cambrian carbonate shelf strata from the northern Appalachians are in fact younger than the Steptoean carbon isotope excursion and were deposited during the transgressive stage of the Sauk III sequence (Fig. 2). These strata could therefore be correlative with the post-Steptoean carbonate deposits of the Knox Group from the southern Appalachians and with the Conococheague Formation from the central Appalachians.

CONCLUSIONS

1. The Steptoean positive carbon isotope excursion is documented for the first time in the northern U.S. Appalachians from basinal facies of the Schodack Formation of southeastern New York.

2. Exposures of platform dolomite successions from the Pine Plains Formation in southeastern New York and unit b of the Stockbridge Formation in western Massachusetts do not record the excursion and are thus not likely to be of Steptoean age.

3. The results of carbon isotope stratigraphy support severely reduced carbonate deposition during Steptoean time throughout the northern Appalachians.

4. Deposition on the carbonate shelf of northeastern (present-day) Laurentia was limited during late Steptoean sea-level fall, which resulted in the Sauk II–Sauk III unconformity and sequence boundary on the craton. The shelf was subjected to significant siliciclastic input from the nearby exposed craton. The shelf also became less laterally extensive and may have been partially exposed. Most of the sediment that reached or was produced on the shelf at this time likely bypassed the shelf to become deposited as debris flows or olistoliths on the adjacent slope.

5. The quality and extent of exposure in the northern U.S. Appalachians represent the main challenges to stratigraphic studies that utilize carbon isotopes. Low-grade metamorphism does not appear to alter carbon isotope values enough to compromise interpretation of primary marine signatures.

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