SEDIMENTOLOGY AND CARBON ISOTOPE (δ¹³C) STRATIGRAPHY OF SILURIAN–DEVONIAN BOUNDARY INTERVAL STRATA, APPALACHIAN BASIN (Pennsylvania, USA)

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ABSTRACT: Silurian–Devonian boundary interval strata deposited during the expansion of land plants record a major perturbation of the carbon cycle, the global Klonk Event, one of the largest carbon isotope excursions during the Phanerozoic. In the Appalachian Basin, these marine strata record the regional buildup to the Acadian Orogeny. This study reports new sedimentologic, paleontologic, ichnologic, and carbon isotope data from an exceptional quarry exposure in central Pennsylvania, USA, a historically understudied area between better-documented outcrops (>500 km away) to the southwest (West Virginia, Virginia, Maryland) and northeast (New York). Facies spanning the continuous 113-m thick outcrop are dominantly carbonate and fine-grained siliciclastic strata interpreted as being deposited in supratidal through subtidal environments, including oxygen-limited environments below storm wave base. They record parts of three transgressive-regressive cycles, in the (1) upper Silurian Tonoloway Formation, (2) upper Silurian–Lower Devonian Keyser Formation through lower Mandata Member of the Old Port Formation, and (3) Lower Devonian Mandata through Ridgeley Members of the Old Port Formation. Micrite matrix δ¹³C values (δ¹³C_carb) document a positive carbon isotope excursion as much as 7% in amplitude. Outcrops of this interval in the Appalachian Basin occur in two belts, between which correlation has been historically challenging. The regional correlation presented herein is based on carbon-isotope trends and is more consistent with published conodont biostratigraphy and volcanic ash ages, an improvement over published correlations based on lithostratigraphy. Transgressive-regressive trends at the central Pennsylvania study site are not consistent with regional trends, indicating that local controls (tectonics, sediment supply) rather than global (eustasy) dominated depositional patterns in the Silurian–Devonian boundary interval in the Appalachian Basin.

INTRODUCTION

The Silurian–Devonian transition was a time of major change in the global biosphere. Vascular land plants had evolved by the late Silurian and diversified rapidly in the Devonian. In the late Silurian–Early Devonian, arthropods transitioned to land and impacted soil development (Kenrick et al. 2012). These changes coincided temporally with an overall increase in atmospheric oxygen that led to a peak in atmospheric oxygen content (Lenton et al. 2016; Lu et al. 2018). In the Appalachian Basin, the Silurian–Devonian boundary interval has recently been the focus of renewed interest as the advent of modern techniques (uranium-lead geochronology, carbon isotope chemostratigraphy) allows for more advanced, quantitative analysis (Kleffner et al. 2009; Husson et al. 2016; McAdams et al. 2017).

A major perturbation to the carbon cycle, the Klonk Event, is also recorded at the Silurian–Devonian boundary, as a significant carbon isotope excursion. Carbon isotope analyses of bulk marine carbonates (δ¹³C_carb) document a positive carbon isotope excursion as much as 7% in amplitude, making it one of the largest such excursions during the Phanerozoic. The excursion has been documented in sections around the world: the United States in the Great Basin of Nevada and Utah (3.0‰; Saltzman 2002, 2005) and the Arbuckle Mountains of Oklahoma (3.3‰; Saltzman 2002); the Czech Republic and France (3.8–4.0‰; Buggisch and Mann 2004; Buggisch and Joachimski 2006); and Ukraine (>6‰; Malkowski et al. 2009). The similar shape and magnitude of the δ¹³C_carb excursions has led previous workers to argue that it represents a perturbation to the global carbon cycle, with rising values in δ¹³C_carb representing the evolving isotopic composition of global dissolved inorganic carbon (δ¹³C_DIC). Proposed drivers of the Klonk Event include global regression and the weathering of exposed, isotopically heavy Silurian carbonate platforms (Saltzman 2002) or enhanced burial of organic carbon from newly evolved terrestrial biota (Malkowski and Racki 2009). However, coupled chemostratigraphic-sedimentologic studies spanning Silurian–Devonian strata needed to evaluate these potential drivers are generally lacking.

The carbon isotope excursion has been of recent interest in the Appalachian Basin, where it was originally documented in West Virginia (7‰; Saltzman 2002; Husson et al. 2016) and more recently in New York (Husson et al. 2016). However, there still exists a geographic gap of >500 km between Appalachian Basin sites (Fig. 1). The Silurian–Devonian boundary interval has been understudied in most of Pennsylvania, particularly with regards to modern methods, for a number of reasons. Temporally, the period boundary is a natural stopping point, and many studies are restricted to either Silurian (e.g., Smosna and Patchen 1978; Brett et al. 1990; Bell and Smosna 1998; McLaughlin et al. 2012) or Devonian strata (e.g., Diedrich and Wilkinson 1999; Ver Straaten 2007, 2008; Ver Straaten et al. 2011). Geographically, outcrops occur in two belts, a northern belt in New York and parts of New Jersey and northeastern-most Pennsylvania, and a southern belt spanning the Virginia-West Virginia border, the western tip of Maryland, and southern and central Pennsylvania (Fig. 1). Outcrops in central Pennsylvania are generally poor...
since they are less resistant to weathering. Many previous studies are restricted to either the New York-New Jersey part of the northern outcrop belt (e.g., Epstein et al. 1967; Kleffner et al. 2009) or the Virginia-West Virginia-southernmost Pennsylvania part of the southern outcrop belt (e.g., Dorobek and Read 1986); herein, the terms ‘northern outcrop belt’ and ‘southern outcrop belt’ refer to these areas that have been historically well studied. Regional correlations have been published for the southern outcrop belt (Dorobek and Read 1986) and for the northern outcrop belt (Rickard 1962; Epstein et al. 1967; Laporte 1969). Nomenclature and facies changes between the two outcrop belts make correlation difficult, and no basin-wide correlation scheme has been universally adopted (e.g., Smosna 1988).

An exceptional, continuous quarry exposure of Silurian–Devonian boundary interval strata near the town of Winfield in central Pennsylvania (herein referred to as Winfield Quarry; Figs. 1, 2) provides a unique opportunity to fill the temporal and geographic gap. The purpose of this study is to (1) document the sedimentology, paleontology, and lithostratigraphy of Winfield Quarry strata in order to reconstruct depositional environments and relative sea-level change, (2) document the chemostratigraphy and carbon isotope excursion in the context of that detailed sedimentology, paleontology, and stratigraphy, and (3) use the chemostratigraphic-lithostratigraphic framework to improve regional stratigraphic correlations and provide additional constraints on a major perturbation to the ancient geologic carbon cycle.

GEOLOGIC SETTING

Paleogeographic and Tectonic Setting

The Appalachian foreland basin, shaped by plate convergence, spanned much of eastern North America throughout most of the Paleozoic. During the late Silurian–Early Devonian, the basin was at ~30°S latitude (Kent and Van Der Voo 1990; Witzke 1990), making it an environment conducive to carbonate deposition. The foreland basin first formed in the Middle Ordovician, when the Taconic orogeny marked initial closure of the Iapetus Ocean and collision of an island arc with eastern Laurentia. Taconic deformation in New England was most intense from ~496 to ~428 Ma, with metamorphism and roughly coincident development of the foreland basin ranging from ~480 to ~455 Ma in the southern Appalachians and New England (Hatcher 2010 and references therein).

The Silurian–Devonian transition in the Appalachian Basin was a time of diminished clastic input that allowed marine organisms to flourish, resulting in a variety of carbonate facies throughout the basin (e.g., Laporte...
In the central Appalachians, where this study focuses, the late Silurian through Early Devonian historically has been considered a time of tectonic quiescence between the Taconic and Acadian orogenies (Rodgers 1967; Johnson 1971; Dorobek and Read 1986). However, some researchers have suggested that Acadian orogenesis began as early as the late Silurian and would therefore have coincided with deposition of the strata discussed herein (Ebert and Matteson 2003; Ver Straeten 2007).

During the Acadian orogeny, a series of terranes collided with the northern part of the eastern margin of Laurentia. This transpressional, zippered collision progressed southward through time, affecting areas from present-day Newfoundland through Georgia. It culminated in the closure of the Rheic ocean when Baltica (present-day Europe) collided with Laurentia in the early part of the Mississippian (~345 Ma) (Ver Straeten 2009; Hatcher 2010 and references therein).

**Stratigraphy**

The exposure at Winfield Quarry includes the upper Silurian Tonoloway Formation, upper Silurian to Lower Devonian Keyser Formation, and Lower Devonian Old Port Formation (Fig. 3). These formation designations have been adopted from Inners (1997), the most detailed existing study of upper Silurian–Lower Devonian strata in central Pennsylvania. The Keyser Formation is divided into the Byers Island, Jersey Shore, and La Vale Members (Head 1969). The Old Port Formation is divided into the New Creek-Corriganville, Mandata, and Ridgeley Members (Inners 1997). Stratigraphic nomenclature used in Pennsylvania for this interval is broadly similar to that used throughout the southern outcrop belt but differs significantly from that used in the northern outcrop belt (Fig. 3).
In the southern outcrop belt, the Byers Island Member is termed the lower Keyser Formation (Fig. 3) and is aggradational open-marine carbonates with skeletal banks around the basin edges and bioturbated, nodular carbonates toward the basin center. Skeletal banks consist of coral-stromatoporoid mud mounds and framestones. The middle part of the Keyser Formation in West Virginia is regressive Clifton Forge sandstones on the eastern basin margin and grades basinward into the Big Mountain shale and correlative skeletal carbonates (Dorobek and Read 1986). These clastic units do not extend into Pennsylvania (Head 1969) and their correlation to the carbonate succession there is ambiguous (e.g., compare Head 1969 and Dorobek and Read 1986). The La Vale Member is equivalent to the upper Keyser Formation in the southern outcrop belt, which consists of transgressive skeletal carbonates and contains coral-stromatoporoid mud mounds and framestones (Dorobek and Read 1986).

Outside of Pennsylvania, the term Old Port Formation is not used and its members correspond to named formations. In Maryland, the New Creek Formation interfingers with the uppermost Keyser Formation and is equivalent to the Elbow Ridge sandstone at the eastern edge of the basin. The Corriganville Member is equivalent to the Healing Springs sandstone at the eastern edge of the basin in Virginia. The Mandata and Shriver Members are equivalent to cherty carbonates of the Licking Creek Formation nearer the basin margin in the southern outcrop belt. Outside of central Pennsylvania, the Ridgeley Member is equivalent to the Oriskany Formation.

The northern outcrop belt is oriented parallel to depositional dip, with more proximal facies to the west. Facies are time transgressive and timelines typically span multiple formations or members (Rickard 1962; Laporte 1969; Husson et al. 2016). The Cableskill Formation (Fig. 3) consists of massive, fossiliferous carbonates, including stromatoporoids and corals, and grades westward to lesser fossiliferous, thin-bedded dolomites. The Rondout and Manlius Formations represent a transgressive-regressive cycle consisting of shallow-water stromatolites and stromatoporoid-coral biostromes and bioherms and associated lagoonal facies (Rickard 1962; Laporte 1969; Belak 1980). The Coeymans, Kalkberg, and New Scotland Formations are progressively deeper water facies, transitioning to open marine by the Kalkberg and New Scotland Formations (Laporte 1969).

**Regional Stratigraphic Correlations**

The units discussed above have been correlated thus far mainly using lithostratigraphy (Fig. 3). The Keyser Formation is typically correlated in the northern outcrop belt to portions of the Cableskill, Rondout, and Manlius Formations, and the Old Port Formation is typically correlated to portions of the Manlius, Coeymans, Kalkberg, and New Scotland Formations (Head 1969; Laporte 1969).

Conodont biostatigraphy, volcanic ashes, and carbon isotope stratigraphy have also aided correlation of this complicated stratigraphy. Based on the first occurrence of the conodont *Icriodus woschmidti*, the Silurian–Devonian boundary has been placed in the upper Keyser Formation in Virginia and West Virginia (Helfrich 1978; Denkler and Harris 1988). In the northern outcrop belt, it has been variously placed in the Rondout Formation (Denkler and Harris 1988), the lower Coeymans Formation (Tucker et al. 1998), and either within the Manlius Formation or between the Coeymans and Kalkberg Formations (Kleffner et al. 2009, using combined biostratigraphy and carbon isotope stratigraphy).

Volcanic ashes (bentonites) have been used to correlate the Silurian–Devonian strata over limited distances (e.g., Rickard 1962; Smith and Way 1988). In the southern outcrop belt, Smith and Way (1988) first described a set of three ash beds that occur in the Corriganville (Bald Hill Bentonites A and B) and Mandata (Bald Hill Bentonite C) Members of the Old Port Formation at the type section near Hollidaysburg, Penn., 84 miles west-southwest of Winfield Quarry. In the northern outcrop belt, the Kalkberg Bentonite, an ash bed in the New Scotland Formation, has been dated by McAdams et al. (2017) using U-Pb analysis of zircons, placing it in the middle Lochkovian (Early Devonian) at 417.6 ± 0.12 Ma. Smith and Way (1988) correlated this bed to their Bald Hill Bentonite A in the Corriganville Member of the southern outcrop belt. McAdams et al. (2017) note, however, that the number of volcanic ash beds in the Lower Devonian of the Appalachians makes correlation of individual beds potentially problematic.

Carbon isotope stratigraphy was recently used by Husson et al. (2016) to correlate between a section in West Virginia and four sections in New York. Their correlation shows that facies and the stratigraphic packages based on them are diachronous across the basin, that the Keyser Formation is correlative with the Rondout, Manlius, and parts of the Coeymans Formations of New York, and that the New Creek-Corriganville Members are correlative with the Kalkberg, New Scotland, and Bectraft Formations of New York. The Winfield Quarry section provides an opportunity to refine this correlation between the northern and southern outcrop belts.

**Field Site**

The field site for this study is a quarry approximately 2 km west of Winfield, Pennsylvania, in Union County (N 40.89816°, W 076.89307°) (Fig. 2). It was active a few years prior to the data collection phase, providing a fresh rockface. It was inactive during the data collection phase of this project (2007) and has since been reopened; the base of the original section has been removed. A well-exposed stratigraphic section (WQ1) was measured on a bed-by-bed basis using a Jacob’s staff at the west end of the quarry. Refer to Hess (2008) for an additional, less extensive section spanning only the Old Port Formation. The stratigraphic section and geochemical data from the western exposure are discussed herein.

**Geochemical Methodology**

A total of 63 micrite samples were analyzed from the lower 88 m of the WQ1 section, spanning the Tonoloway Formation through the Shriver Member of the Old Port Formation. Only samples devoid of fossil fragments, fractures, and veins were selected. Rock samples were broken using a rock hammer in a cleaned room to provide a fresh surface. Powder was extracted from this surface using a Dremel drill with a diamond-dust-coated drill bit, while continually monitoring to ensure no material other than micrite was sampled. Powder was deposited and sealed directly into glass vials. Between samples, the rock hammer and drill bit were sanitized using a solution of 10%-diluted hydrochloric acid.

Isotope analyses were conducted in the Stable Isotope Ratios in the Environment, Analytical Laboratory (SIREAL) in the Department of Earth and Environmental Science at the University of Rochester. Samples were pretreated with 30% H2O2 to remove organic material, followed by three rinses with deionized water and a final rinse with methanol. Analyses were run on a Thermo Electron Corporation Finnegan Delta plus XP mass spectrometer in continuous-flow mode via the Thermo Electron Gas Bench peripheral and a GC-PAL autosampler. Samples were loaded into 4mL tubes with pierceable, self-healing rubber septa with PTFE liners. Tubes were then flushed with UHP helium at about 100 mL/minute for 10 minutes.
100% phosphoric acid was injected through the septum manually with a 16-gauge needle and syringe. All samples were vortexed to ensure complete mixing of the sample and the acid. Tubes were loaded into a block heated to 70°C. Samples reacted for at least 45 minutes but never more than 12 hours before they were analyzed. Carbon dioxide gas evolved from the reaction with the acid was then drawn into the instrument for analysis. Carbon and oxygen isotopic results are reported in permil relative to VPDB (Vienna Pee-Dee Belemnite) and normalized (Coplen 1994) on scales such that the carbon and oxygen isotopic values of NBS-18 are -5.01 and -2.2 permil, respectively, carbon and oxygen isotopic values of NBS-18 are -5.01 and -23 permil, respectively, and the carbon isotopic value of L-SVEC is -46.6 permil. Average precision (1-sigma) is 0.06 and 0.10 for carbon and oxygen isotopes, respectively. For repeat analyses, the average of the carbon and oxygen isotope values is discussed herein.

**SEDIMENTOLOGY**

**Facies**

Sedimentary facies are defined on the basis of lithology, sedimentary structures, paleontology, and ichnology, particularly as they relate to the interpretation of depositional environments. Winfield Quarry strata consist of four lithologies: micrite, biomicrite and biosparite, sandy intrabiosparite, and shale. Seven sedimentary facies representative of different depositional environments are identified on the basis of lithology, sedimentary structures, ichnofabrics, and fossils (Table 1, Figs. 4, 5). See Hess (2008) for additional photographs of facies and fossils.

**Massive Micrite Facies (F1a).**—The massive micrite facies is characterized by a lack of fossils and physical sedimentary structures, though some instances contain low-diversity, high-abundance ichnologic assemblages of Chondrites and Zoophycos trace fossils (Fig. 4A, 4B). The majority of this facies is interpreted as having been deposited in low-energy, subtidal environments below storm wave base. The lack of body fossils indicates an inhospitable environment. Zoophycos has been linked to low-oxygen, though not entirely anoxic, conditions (Marintsch and Finks 1978; Bromley and Ekdale 1984), especially when they occur in high abundance and low diversity, as here. While Chondrites and Zoophycos traces in more recent deposits occur in deep water, Paleozoic strata with these traces can have formed in a variety of water depths, from lagoonal to below storm wave base (Ekdale 1988; Frey et al. 1990). On the basis of its thickness (~20 m) and association with relatively deep water under- and overlying units, the package of this facies with Chondrites and Zoophycos traces is interpreted as having been deposited below storm wave base, in oxygen-limited conditions (Fig. 6). For micrites lacking trace fossils, their environmental interpretation is based on the sedimentology and paleontology of interbedded lithofacies, with some units deposited in waters potentially as shallow as the intertidal zone. Refer to the Inferred Depositional Setting and Relative Sea-Level Fluctuations section for more details.

**Micrite with Sedimentary Structures Facies (F1b).**—The micrite with sedimentary structures facies is characterized by the presence of physical and organic sedimentary structures including mudcracks, evaporites, heterolithic bedding, intraclasts, sparse fenestrae, stromatolites, and cryptalgal laminae (Fig. 4C–4F). Stromatolites and cryptalgal laminae are domal on a millimeter to decimeter scale. In one instance, stromatolites form a continuous layer of laminated, low-domal mounds. Laminae thicken toward the crests of mounds (Fig. 4G), a key indicator of microbial origin (Riding 1999), and these are interpreted as in situ stromatolite mounds under Riding's (1999) definition. They are the “laterally linked hemispheroids” type of Logan et al. (1964), which in the modern of Shark Bay, Australia, form in protected, low-energy, intertidal settings. A similar environment is inferred for in situ stromatolites at Winfield Quarry.

This facies contains a low-diversity assemblage of unbranched fossils, chiefly eurypterids, gastropods, and ostracods. This suite of sedimentary structures indicates deposition in an environment that was above fair-weather wave base (symmetrical ripple laminae), within the photic zone (stromatolites and cryptalgal laminae), within the tidal range (heterolithic bedding), with intermittent subaerial exposure (mudcracks) and more extended periods of exposure in the supratidal zone (evaporites). Not all sedimentary features are present in all instances of this facies, and specific depositional environments are interpreted for units on a case-by-case basis (refer to Inferred Depositional Setting and Relative Sea-Level Fluctuations section).

**Biomicrite to Biosparite Facies (F2a).**—The biomicrite to biosparite facies is characterized by the presence of megascopic fossils or fossil fragments in a micrite matrix (Fig. 4H, 4I). Fossils are open-marine fauna consisting of gastropods, brachiopods, bivalves, bryozoans, rugose corals, crinoids, and sparse ostracods. In many instances, fossils are concentrated in pods likely formed by bioturbation or winnowing of fines. In some instances, weathered surfaces appear mottled (Fig. 4H), also possibly resulting from bioturbation. The varying degrees of abrasion and orientation of fossils indicate deposition in open marine settings from subtidal but above fair-weather wave base, for beds with highly abraded fossils, to lower energy environments between fair-weather and storm wave base, for beds with abundant unbranched fossils. Some instances contain symmetrical ripples (Fig. 4J), indicating deposition above fair-weather wave base.

Some beds contain cm-scale fining-upwards successions, which form under waning-flow conditions, and could be interpreted as either tidal channels near to where the fossils were abraded or as turbidity flows formed below normal wave base and distal to the environment in which the fossils were abraded. From the association of these beds with relatively shallow facies and their lack of definitive deep-water indicators, they are interpreted as tidal-channel deposits (refer to Inferred Depositional Setting and Relative Sea-Level Fluctuations for more details).

**Sponge-Coral-Crinoid Biomicrite to Biosparite Facies (F2b).**—The sponge-coral-crinoid biomicrite to biosparite facies is characterized by the presence of sponges (stromatoporoids) and/or corals (Fig. 4K, 4L). Stromatoporoids are discontinuous, overturned, and abraded, in some places including oncolites with concentric growth strata (Fig. 4L). These deposits also contain tabulate and rugose coral, crinoids, and highly abraded, unidentifiable fossil fragments. These are interpreted as reef-flank deposits formed in an environment with sufficient wave energy to rotate oncoids and abrade fossils, above fair-weather wave base and within the photic zone. Some intervals contain shale partings, which may indicate slack water suspension fallout associated with tides or lulls in wave energy. While no framework reefs are present in Winfield Quarry strata, they have been documented in correlative strata (e.g., Cole et al. 2015).

**Sandy Intrabiosparite Facies (F3).**—The sandy intrabiosparite facies consists of coarse-sand- to granule-size quartz and calcareous clasts with sparse disarticulated brachiopods and crinoid ossicles (Fig. 5A). The lack of finer grained sediments indicates that wave energy was sufficient to winnow away mud-sized particles from the depositional environment. This facies is interpreted as having been deposited in an open marine, above fair-weather wave base environment.

**Shale with Fossils and Ichnofabrics Facies (F4a).**—The shale with fossils and ichnofabrics facies is a medium to dark gray shale and

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**SEDIMENTOLOGY AND ISOTOPE STRATIGRAPHY OF SILURIAN–DEVONIAN STRATA**

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**Zoophycos**
TABLE 1.—Summary of facies documented in stratigraphic section WQ1.

<table>
<thead>
<tr>
<th>Facies</th>
<th>Lithology</th>
<th>Bed thickness</th>
<th>Bed geometry</th>
<th>Sedimentary structures</th>
<th>Ichnology$^a$</th>
<th>Megafossils$^b$</th>
<th>Associated shale</th>
<th>Interpreted depositional environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a: Massive micrite</td>
<td>micrite-argillaceous micrite</td>
<td>thin to thick</td>
<td>tabular to nodular</td>
<td>none</td>
<td>Chondrites and Zoophycos (in some units prevalent)</td>
<td>none</td>
<td>shale partings to interbedded shales</td>
<td>intertidal–subtidal below storm wave base; some units oxygen limited</td>
</tr>
<tr>
<td>1b: Micae with sedimentary structures</td>
<td>micrite-argillaceous micrite</td>
<td>finely laminated to thick</td>
<td>nodular, tabular, or lenticular</td>
<td>mudcracks, evaporites, heterolithic bedding, convolute, ripple or cryptagal laminae, intratidal to intertidal, sparse hummocks, sparse fenestrae</td>
<td>none</td>
<td>sparse ostracodes where not laminated, sparse fossil fragments, bryozoans, eurypterids, stromatolites</td>
<td>shale partings to interbedded shales</td>
<td>intertidal–supratidal</td>
</tr>
<tr>
<td>2a: Biomicrite to biosparite</td>
<td>(intra)biomicrite to (intra)biosparite or packed (intra)biomicrite, non- to very argillaceous</td>
<td>thin to thick</td>
<td>nodular to tabular</td>
<td>pods and discontinuous bands of micrite, rare evaporites, sparse micrite intraclasts, laminae, symmetrical wave ripples, or hummocky cross-stratification and fining-upwards sequences; chert nodules abundant in some layers</td>
<td>sparse Chondrites; motting and concentration of fossils in pods possibly resulting from bioturbation</td>
<td>sparse–packed, highly abraded–unabraded gastropods, brachiopods, bivalves, ostracodes, bryozoans, rugose corals, crinoids$^c$</td>
<td>sparse–packed, highly abraded–unabraded gastropods, brachiopods, bivalves, ostracodes, bryozoans, rugose corals, crinoids</td>
<td>subtidal, dominantly above fair-weather wave base</td>
</tr>
<tr>
<td>2b: Sponge-coral-crinoid biomicrite to biosparite</td>
<td>(intra)biomicrite to biosparite</td>
<td>medium</td>
<td>nodular to stromatolitic</td>
<td>oncolites and soft-sediment deformation in some units, thrombolites</td>
<td>none</td>
<td>stromatoporoids, tabulate and rugose corals, crinoids, sparse ostracodes, unidentifiable fossil fragments</td>
<td>none to shale partings to thin shales</td>
<td>subtidal above fair-weather wave base, within the photic zone</td>
</tr>
<tr>
<td>3: Sandy intrabiosparite</td>
<td>coarse-sand to granule</td>
<td>thick</td>
<td>massive</td>
<td>centimeter-scale fining upwards sequences</td>
<td>none</td>
<td>sparse disarticulated brachiopods, crinoids</td>
<td>none</td>
<td>subtidal above fair-weather wave base</td>
</tr>
<tr>
<td>4a: Shale with fossils and ichnofabrics</td>
<td>dark gray shale and calcareous siltstone</td>
<td>thin</td>
<td>tabular and fissile</td>
<td>generally none, one 2-cm thick layer with chert nodules</td>
<td>Chondrites, nondescript ichnofabrics</td>
<td>sparse ostracodes, sparse mollusks and brachiopods$^d$</td>
<td>N/A</td>
<td>low energy, subtidal below storm wave base, oxygen limited</td>
</tr>
<tr>
<td>4b: Barren shale</td>
<td>black shale</td>
<td>thin</td>
<td>tabular and fissile</td>
<td>none</td>
<td>none</td>
<td>abundant lingulid brachiopods in one interval</td>
<td>N/A</td>
<td>low energy, subtidal below fair-weather wave base, oxygen limited</td>
</tr>
</tbody>
</table>

$^a$ Dr. Tony Eldale identified many trace fossils.
$^b$ Dr. Carl Brett identified many megafossils.
$^c$ Identifiable fossils include Discomyorthis, Acospirifer cf. murchisoni, Schuchertella cf. brachyprion, Costellirostrapectuaria, Leptocoelea flabellites, possibly Meristella kuevi, Pentamerus cf. glyptidula, and “Schuchetella” woolworthiana.
$^d$ Identifiable fossils include Coelospira dichotoma, Actinopteria cf. communis, Dalegina oblata, Coelospina, and possibly a small, narrow rhynchonellid (Stenorhynchus), Chonostrophiella, Leptaena rhomboidalis, Orbiculosidea cf. duca, Tyersella perelegans, and Discomyorthis.
siltstone with fossils, including ostracods and very sparse mollusks and brachiopods, and in many instances intense *Chondrites* bioturbation (Fig. 5B, lower three-quarters of Fig. 5C). Fossils include *Orbiculoides* and nuculid bivalves, which can indicate an oxygen-limited environment (Brett et al. 1991). The *Chondrites* ichnofacies is also common in oxygen-limited areas, even exceeding *Zoophycos* in the degree of dysoxia it can tolerate (Bromley and Ekdale 1984). This facies therefore represents deposition in an environment below storm wave base in oxygen-limited waters (Fig. 6).

**Barren Shale Facies (F4b).—**The barren shale facies is characterized by dark gray to black shale lacking macrofossils and biogenic and
sedimentary structures (upper quarter of Fig. 5C). The dark color of this facies is likely due to high concentrations of organic material, and it may therefore represent oxygen-limited conditions that would have precluded the presence of bacteria able to break down this organic matter. The lack of fossils and biogenic structures supports this interpretation (Bromley and Ekdale 1984), and this facies is interpreted to represent the most oxygen-deprived environment preserved in the WQ1 section (Fig. 6). The lack of sedimentary structures indicates deposition in a low-energy environment. While these conditions can occur in both lagoonal and offshore settings well below the influence of fair-weather and storm wave base, regional correlation of the Mandata Member, in which a large part of the facies occurs, indicates that it is a deep-water equivalent of sands being shed from the mountains to the east (Smosna 1988).
Instances of this facies outside of the Mandata Member are thin (<2 m) and are associated with shallower-water facies. One contains abundant lingulid brachiopods, which are associated with nearshore dysaerobic environments (Kammer et al. 1986), and the low-diversity, high-abundance assemblage indicates a stressed environment, perhaps due to changes in oxygenation or salinity. These units are interpreted as representing dysaerobic, below-fair-weather wave base environments, shallower water than for the bulk of this facies.

![Photographs of key features of facies F3, F4, and F5 used in identifying depositional environments, in order of facies listed in Table 1. A) Coarse sand- to granule-size quartz clasts and abraded brachiopod fragments (bf), New Creek-Coriganville Members of Old Port Formation F3. B) Chondrites burrows on bedding-plane surface, Mandata Member of Old Port Formation F4a. C) Compacted Chondrites burrows (c) and brachiopod fragments (bf) of facies F4a, overlain by dark, barren shale of facies F4b at top quarter of frame, Mandata Member of Old Port Formation. D) Bentonite (altered volcanic ash) (orange), Mandata Member of Old Port Formation.](https://pubs.geoscienceworld.org/sepm/palaios/article-pdf/34/9/405/4837048/bi0883-1351-34-9-405.pdf)

**Fig. 5.** Photographs of key features of facies F3, F4, and F5 used in identifying depositional environments, in order of facies listed in Table 1. A) Coarse sand- to granule-size quartz clasts and abraded brachiopod fragments (bf), New Creek-Coriganville Members of Old Port Formation F3. B) Chondrites burrows on bedding-plane surface, Mandata Member of Old Port Formation F4a. C) Compacted Chondrites burrows (c) and brachiopod fragments (bf) of facies F4a, overlain by dark, barren shale of facies F4b at top quarter of frame, Mandata Member of Old Port Formation. D) Bentonite (altered volcanic ash) (orange), Mandata Member of Old Port Formation.

**Fig. 6.** Summary of features observed in the studied stratigraphy and corresponding interpretations of bottom-water oxygenation during deposition. See Table 1 for description of facies.
Possible Volcanic Ash.—In addition to the sedimentary facies, eight beds of what may be bentonites (altered volcanic ash) are also preserved in WQ1. They are thin (<10-cm thick), clay-rich (sticky when wetted), and weather bright orange, often leaching color to underlying beds (Fig. 5D). The thickest horizon, in the Mandata, was sampled and yielded doubly terminated euhedral zircons (see Online Supplemenatal File) indicative of airfall ash.

Inferred Depositional Setting and Relative Sea-Level Fluctuations

This section summarizes the stratigraphic distribution of the facies documented in the previous section (Fig. 7) and relative sea-level fluctuations inferred from the upsection facies changes (Fig. 8A–8C).

Tonoloway Formation.—The base of WQ1 consists of ~7 m of Tonoloway Formation laminated micrite (F1b; Fig. 7). Laminae show the
FIG. 8.—Stratigraphy, relative sea level, transgressive-regressive cycles, and geochemistry for section WQ1, Winfield, PA, and equivalent strata south of Pennsylvania and in New York based on lithologic correlation (Fig. 3). A) Generalized stratigraphy for section WQ1. Silurian–Devonian boundary age is from Cohen et al. (2008); boundary is
convex geometry of crinoidal laminae and stromatolites, evaporites, and mudcracks are also abundant. Laminae are lacking in some portions of this stratigraphic package. Identifiable fossils are for the most part limited to sparse ostracods, with unidentifiable fossil fragments also present. These strata are interpreted to represent deposition in shallow-water intertidal to supratidal environments, including carbonate tidal flats (Fig. 8B).

An exposure ~580 m along strike from the base of section WQ1 along the north wall of Winfield Quarry contains an exceptionally well-preserved eurypterid Lagerstätte ~2 m below the top of the Tonoloway Formation (Vrazo et al. 2014). The exceptional exposure in the quarry allowed for physical tracing of this bed to the WQ1 section. Upon close inspection, two partial eurypterid fossils of the taxa noted by Vrazo et al. (2014; Eurypterus cf. remipes) were found in the Tonoloway Formation of WQ1 and it is likely that the 3.2-m-thick covered section 2 m below the contact between the Tonoloway and Keyser Formations correlates to the Lagerstätte exposed along strike within Winfield Quarry.

In the uppermost 1.5 m of the Tonoloway Formation, sedimentary structures are lacking and the concentration of evaporites gradually decreases. The boundary between the Tonoloway and the Byers Island Member of the Keyser Formation is marked by an increase in fossil abundance and diversity from sparse ostracods in the Tonoloway to bryozoans, brachiopods, bivalves, gastropods, ostracods, and rugose corals typical of F2a in the Keyser. This transition is gradational from 5.9 to 7.6 m and the formation boundary is picked at 7.6 m in WQ1, the point where the rate of increase in fossil abundance slows. The loss of evaporites and mudcracks and the increasing fossil abundance and diversity indicate freshening and minor relative sea-level rise across the contact between the Tonoloway and Keyser Formations.

**Keyser Formation Byers Island Member.**—The Byers Island Member is distinguished by the nodularity of its beds (Head 1969). It is biomictic (F2a) with normal marine fauna and is interpreted to represent deepening to a subtidal above fair-weather wave base environment. The upper contact of this member is chosen at 12.8 m, where consistently nodular strata become more sporadically nodular.

**Keyser Formation Jersey Shore Member.**—Fossils in the nodular biomictic (F2a) of the Jersey Shore Member are fragmentary and randomly oriented. They become less prevalent upsection to about 23 m and are lost entirely from 13 to 15 m where there is a package of massive micrite (F1a). Two stromatoporoid-bearing units (F2b) are at ~17–18 m and ~26–31 m, and the lower contains oncosoids while the upper contains fragmented fossils that become increasingly abundant and diverse upsection. The covered section at ~23–26 m is exposed in nearby parts of the quarry, where it contains stromatoporoids, *Favosites* corals, and abundant crinoid ossicles; it is inferred to also be facies F2b. The presence of oncosoids and stromatoporoids indicate that these formed in a high-energy environment within the photic zone during continued relative sea-level rise. As the corals and stromatoporoids are mainly not in life position, these units are interpreted as reef-margin deposits that would have formed adjacent to reefs. Above the covered section in WQ1, stromatoporoids are present up to 31 m and other fossils are fragmentary and increasingly abundant and diverse. The top of the stromatoporoid-bearing strata at 31 m was chosen as the boundary between the Jersey Shore and overlying La Vale Member.

**Keyser Formation La Vale Member.**—The La Vale Member is biomictic, biosparite, and argillaceous biomictic (F2a). A return to non-reef margin biomictic stratiographically above the reef margin unit may indicate a relative sea-level fall and a return to environments similar to those inferred from strata below the reef-margin package. Alternatively, sea level may have continued to rise, as depositional environments would have been broadly similar both landward and seaward of the reef. Starting at ~45 m, fossils are gradually more abraded upsection and cm-scale fining-upwards successions are noted at ~50 m. Based on the stratigraphic context and lack of definitive deep-water features, they are interpreted as having formed by waning flow in tidal channels and bars, indicating that by this point relative sea level had begun to fall. Upsection, strata grade into laminated micrite (F1b), argillaceous micrite (F1a), and finally a package of micrite and interbedded shales from ~61 to 64 m in which the micrites exhibit mudcracks, cm-scale cut-and-fill structures, sparse fenestrae, and heterolithic bedding with silt-sized particles showing ripple-scale multidirectional planar cross-bedding (F1b). The variations observed in the La Vale Member are consistent with tidally influenced nearshore environments and indicate an overall regressive trend culminating with interbedded micrites and shales at the top of the unit deposited in an intertidal environment frequently subject to subaerial exposure and tidal influence.

**Old Port Formation New Creek and Corriganville Members.**—A distinct contact separates the Keyser and Old Port Formations at 64 m above the base of the section. Interbedded micrites and shales of the uppermost Keyser Formation occur below ~1 m of *in situ* mounded stromatolites (F1b) of the New Creek-Corriganville Members of the Old Port Formation. It is an apparently conformable contact with shallow marine facies above and below and no evidence of erosion or prolonged exposure. *In situ* stromatolites are interpreted to have formed in a protected intertidal environment.

Above the *in situ* stromatolites is a ~1-mm-thick cross-bedded, sandy intrabiosparite (F3) representing siliciclastic input into the basin and similar to that described by Inners (1981) ~1 m above the contact in the Bloomsburg and Mifflinville Quadrangles ~15 km to the east. The sandy unit is overlain by a series of biosparite, micrite, and biomictic strata with moderate to sparse, dominantly abraded fossils, which indicate a deepening to a shallow subtidal environment above fair-weather wave base.

**Old Port Formation Mandata Member.**—An abrupt transition to shale and siltstone at ~71 m marks the contact between the New Creek-Corriganville and Mandata Members. Packages of dark gray bioturbated shale with sparse fossils (F4a) and black, barren shale (F4b) are punctuated by tens-of-centimeter-thick beds of nodular micrite and biomictic. Together, these facies indicate deposition in a subtidal environment below storm wave base following a rapid relative sea-level rise at the base of the Mandata Member. Black shales are interpreted to represent times when bottom waters were the most inhospitable to normal marine fauna, oxygen limited, and conducive to preservation of organic material. Micrite, biomictic, and fossiliferous shale with *Chondrites* bioturbation are interpreted to represent times of oxygen limitation, but to a lesser degree than during deposition of facies F4a (Fig. 6). Precipitated pyrite is common throughout this member, further supporting the interpretation of oxygen-limited, likely euxinic conditions. At a time when global atmospheric and

approximate. See Figure 7 for explanation of symbols. B) Interpreted relative sea-level curve for section WQ1. Gray shading indicates interpreted oxygen limitation during deposition, with darker shading indicating increasing oxygen limitation. C) Transgressive-regressive cycles from section WQ1 (black), south of Pennsylvania (blue, from Dorobek and Read 1986), and New York (red, from Laporte 1969 and Belak 1980). D) Isotope data from section WQ1 (black) and West Virginia (light blue and dark blue, Saltzman 2002 and Husson et al. 2016, respectively) plotted relative to stratigraphic position. Red box indicates peak carbon isotope values in New York (Husson et al. 2016). Abbreviations: Fm. = Formation; Mbr. = Member, FWWB = fair-weather wave base; SWB = storm wave base; VA = Virginia; WV = West Virginia; MD = Maryland; PA = Pennsylvania; NY = New York.
The change from relative sea-level rise to fall is placed at ~75 m, where a minor increase in oxygenation is inferred from the change in facies from mainly F4b to F4a.

**Old Port Formation Shriver Member.**—Above the Mandata Member is an abrupt transition to the Shriver Member, which consists of micrite with interbedded shales (F1a). Zoophycos feeding traces are prevalent on some bedding planes from ~81 to 87 m. Due to the nature of exposure in the quarry it is difficult to directly observe bedding planes in intervals higher than ~87 m, though it appears that Zoophycos permeates the majority of this unit. The lack of fossils and presence of Zoophycos indicate continued deposition under oxygen-limited subtidal below storm wave base conditions, though under slightly more oxygenated conditions than for underlying deposits (Fig. 6); such conditions would have prevented the preservation of as much organic matter as observed in the Mandata Member black shales. As with the underlying Mandata Member, precipitated pyrite is common in this part of the section, providing further support for continued oxygen limitation and likely euxinia.

**Old Port Formation Ridgeley Member.**—The boundary between the Shriver and Ridgeley Members is marked by an abrupt increase in fossil content. From ~99 to 106 m, the Ridgeley Member is biomicrite (F2a) in which fossils are less fragmented than in the Keyser Formation. Argillaceous biomicrite makes up the remainder of the section from ~106 to 113 m, and the fossils in this unit are dominantly unabraded gastropods and robust, abraded to unabraded brachiopods. The presence of fossils indicates the return of normal-marine, subtidal below fair-weather wave base conditions, likely the result of continued relative sea-level fall. The top of the Winfield Quarry outcrop is in the Ridgeley Member and the top of the Old Port Formation is not preserved.

**Possible Volcanic Ash Beds.**—Seven of the possible volcanic ash beds occur in the Keyser Formation, one in the Jersey Shore Member at 15.3 m and six in the La Vale Member at 38.3, 41.1, 43.6, 47.3, 51.1, and 53.5 m. No works have thus far documented volcanic ashes in the Keyser Formation. If these are in fact volcanic ashes, they may be the oldest in the Devonian of the Appalachian Basin and the earliest indication of the beginning of the Acadian orogeny. Alternatively, it is possible that the clay-rich layers recorded here are detrital terrestrial clays. The uppermost bed occurs in the Mandata at 73.5 m; it is this bed that yielded doubly terminated euhedral zircons (see Online Supplemental File) and is therefore considered a confirmed bentonite.

**GEOCHEMISTRY**

Micrite samples from this stratigraphic section show an 8.7‰ increase in $\delta^{13}$C_carb from the base of the section to the upper part of the La Vale Member of the Keyser Formation (Fig. 8D, Table 2). Values rise from a minimum of -4.3‰ in the Tonoloway to a high of +4.4‰ in the upper La Vale. A gap in the data through most of the Jersey Shore and the lower part of the La Vale reflects the high fossil content through this part of the section, as only samples devoid of visible biotic and sparry components were sampled. Carbon isotope values then decrease by >5‰ to a low in the Mandata Member of the Old Port Formation.

Oxygen isotope ($\delta^{18}$O_carb) values range from -7.3 to -4.1‰. From the base of the section in the Tonoloway Formation to the base of the data gap that begins in the Jersey Shore Member of the Keyser Formation, values increase overall from -7.3 to -6.1‰. From the middle of the La Vale Member of the Keyser to midway through the New Creek-Corriganville Members (~66 m), values vary between -6.9 and -5.2‰. Above this to the top of the sampled interval in the Shriver Member of the Old Port Formation, values are overall ~1‰ higher, varying between -6.4 and -4.1‰.

Comparison of the oxygen and carbon isotope compositions permits evaluation of diagenetic overprinting. A plot of carbon versus oxygen isotope values for the entire stratigraphic column (Fig. 9) shows little correlation ($R^2=0.01$). Most individual facies also show little correlation ($R^2<0.15$). Isotope values for facies F1b show some correlation ($R^2=0.39$), but this can be partially explained by two populations of points created by two different stratigraphic occurrences of this facies. Relatively low isotope values are recorded in the Tonoloway Formation and lower part of the Keyser Formation; relatively high isotope values are recorded in the upper part of the Old Port Formation and upper part of the Keyser Formation. When trendlines for those intervals are plotted separately, the correlation in the lower part of the section disappears ($R^2=0.00$) and that in the upper part of the section is substantially reduced ($R^2=0.29$). Thus, the lack of correlation between carbon and oxygen isotope values suggests that the
sampled micrite matrix generally provides a faithful record of primary seawater $\delta^{13}$C values. However, a few anomalously low carbon isotope values in the organic-rich Mandata Member of the Old Port Formation may record early diagenetic cementation. Two carbon isotope values (at 72.24 and 74.49 m above the base of the section) are anomalously low compared to samples from adjacent strata. It is possible that remineralization of organic matter in the sampled shale resulted in an isotopically light early cement (e.g., Weissert et al. 2008). However, carbon isotope values decrease from the peak of the positive carbon isotope excursion beginning \approx 8 m stratigraphically below the Mandata Member, so the stratigraphic position of the positive excursion is well constrained.

Another possible concern is alteration of the isotopic signature by meteoric diagenesis, especially for very shallow-water facies (e.g., at the boundary between the Keyser and Old Port Formations). However, the occurrence and similar magnitude of the positive excursion throughout the Appalachian Basin suggests that any effect is minimal. Finally, restriction in shallow-marine environments can cause the carbon isotope values of the dissolved inorganic carbon in those environments to be lower than those in the open ocean, typically resulting in positive carbon isotope excursions in deep-water facies or during rapid transgression (e.g., Patterson and Walter 1994; Immenhauser et al. 2003; Saltzman and Edwards 2017). This is opposite of the pattern observed here, with the positive carbon isotope excursion recorded in the shallowest-water facies. Nevertheless, caution should be used when comparing the absolute values of the record presented here with data from distant locations.

**DISCUSSION**

Parts of three transgression-regression cycles have been identified in Winfield Quarry strata (Fig. 8B, 8C). The first is the final portion of a regressive phase in the Tonoloway Formation. The second is a transgression through the Byers Island and Jersey Shore Members of the Keyser Formation and a regression through the La Vale Member. The third

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$\delta^{13}$C and $\delta^{18}$O values for stratigraphic section WQ1 micrite samples.
includes a transgression through the New Creek-Corriganville Members of the Old Port Formation and part of the Mandata Member and a regression through the remainder of the Mandata, Shriver, and Ridgeley Members. Transgressive-regressive cycles interpreted elsewhere in the basin by other researchers were added to Figure 8C using correlation based on lithology (Formation and Member equivalencies; Fig. 3). They do not, for the most part, coincide with cycles documented here. One exception is the cycle interpreted for Keyser-equivalent strata in New York, though this correlation, with no intervening outcrop, is uncertain. The relative lowstand at the top of the Keyser Formation also roughly coincides with that in the New Creek of the southern outcrop belt, as noted by Saltzman (2002). The overall misalignment of transgressive-regressive cycles across the basin could result from lateral facies changes affecting lithologic correlations, differential tectonic activity affecting accommodation and clastic sediment supply, or both.

The positive carbon isotope excursion at the Silurian–Devonian boundary is a global event and should peak at the same time in strata throughout the Appalachian Basin. The stratigraphic peak of the excursion can therefore be used to test whether the lithologic correlations shown in Figure 3 in fact correlate time-equivalent strata; if they do, lithologic correlation of sections with carbon isotope data should show coincident isotope trends, including the stratigraphic placement of the positive excursion at the Silurian–Devonian boundary. This idea was originally put forth by Husson et al. (2016), who used 206Pb/238U dating of volcanic ashes to show that carbon isotope stratigraphy can result in a viable correlation of the Silurian–Devonian boundary interval across the Appalachian Basin. The excursion was first documented in the Appalachian Basin by Saltzman (2002) at Smoke Hole, West Virginia (Fig. 1), where it peaks at ~5% in the upper Keyser Formation. Husson et al. (2016) resampled that section at higher resolution, confirmed Saltzman’s (2002) trend, and additionally documented the excursion at four sections in New York where it peaks at ~3.5% in the upper Manlius Formation, ~5.3% in the lower Coeymans Formation, and ~3.5% in the lower Kalkberg Formation. To test whether lithology-based correlations (Fig. 3) represent timelines, their carbon isotope data from West Virginia was pinned at stratigraphic unit boundaries and stretched and squeezed uniformly between those boundaries (Fig. 8D). This correlation places the West Virginia excursion about 14 m stratigraphically below its peak in Winfield Quarry (compare blue and black δ13C data in Fig. 8D). Uncertainty in the lithologic correlation between the northern and southern outcrop belts prohibits reliable correlation with the New York data at this level of detail, though the excursion would peak higher in the section than at Winfield Quarry (red bar in Fig. 8D). Husson et al. (2016) also noted that a facies-based correlation results in an apparently diachronous carbon isotope excursion across the basin. They concluded that it is in fact the formation and member boundaries that are diachronous, as originally suggested by Rickard (1962) and Laporte (1969), and therefore correlated instead using carbon isotope stratigraphy.

The Winfield Quarry section has been added to Husson et al.’s (2016) carbon-isotope-based correlation by stretching, squeezing, and cutting the isotope curve and accompanying stratigraphic section relative to the reference curve in New York (Fig. 10), under the assumption that changes in δ13C occurred at the same time throughout the Appalachian basin. The correlation (Fig. 10A) indicates that the Keyser Formation at Winfield Quarry is equivalent to the Keyser and Tonoloway Formations in West Virginia and parts of the Rondout, Manlius, and Coeymans Formations in New York. The New York-Corriganville Members at Winfield Quarry are almost entirely equivalent to the New Creek Formation in West Virginia and parts of the Kalkberg and New Scotland Formations in New York. The Mandata Member is equivalent to at least part of the Corriganville Formation in West Virginia and parts of the Kalkberg, New Scotland, and Becraft Formations in New York. Stretching and squeezing of the section during correlation has implications for relative sedimentation rates between the WQ1 section and the New York reference section. Stretching implies a lower sedimentation rate, periods of nondeposition or erosion, or higher compaction for the WQ1 section relative to the New York reference section, and squeezing implies a higher sedimentation rate or lower compaction. For the correlation to be viable, the relative sedimentation rates implied by the stretching and squeezing factors for the WQ1 section and the reference section in New York must make sense for their depositional environments (e.g., lower sedimentation rates for shale than for reefal carbonates is reasonable, whereas the reverse is not).

The correlation of the lower, biomicrite part of the La Vale Member of the Keyser Formation required squeezing of the WQ1 section and implies a higher sedimentation rate there than in the New York section. As this part of the Keyser Formation contains significant skeletal material, it is reasonable that its sedimentation rate would be higher than that of the thinly bedded, microbiolite, lagoonal limestones described by Husson et al. (2016) for the Manlius Formation. Carbon isotope values in the Tonoloway and lower Keyser Formations are more negative than those at the base of the section reported by Husson et al. (2016), indicating that the values likely correlate with a lower part of the section not sampled by Husson et al. (2016). Lacking data to correlate to, we applied the squeezing factor from the upper Keyser Formation to the data gap and the points from the underlying units, which places these points stratigraphically below the Husson et al. (2016) data. Correlation of the upper, micritic part of the La Vale Member of the Keyser Formation required stretching of the WQ1 section relative to the deeper-water (Laporte 1969) Coeymans Formation of New York. As this part of the section was deposited in very shallow water depths, accommodation is expected to have been limited, leading to slow sedimentation or even bypass and erosion (Pomar 2001), which would result in a thinner package than the Coeymans.

A hiatus between the Keyser Formation and the New Creek-Corriganville Members of the Old Port Formation is necessitated by increasing negative isotope values in the New Creek-Corriganville. This is consistent with the very shallow water depths and limited accommodation for the underlying unit. The New Creek-Corriganville part of the section in WQ1 was not stretched or squeezed during correlation. The implied similar depositional rates for this unit and the Coeymans Formation in New York are consistent with their similar shallow-shelf depositional environments interpreted herein and by Laporte (1969), respectively. Correlation of the Mandata Member, an organic-rich shale, required stretching relative to the New Scotland Formation open-marine carbonates and Becraft sandstones in the reference section. This stretching is reasonable because, while shelfal carbonates, sandstones, and organic-rich shales can have similar sedimentation rates (e.g., Walker et al. 1983; Stein 1986), shales compact more (Baldwin and Butler 1985). Data from the Shriver Member extend above the part of the section sampled by Husson et al. (2016). In the absence of data to correlate to, they were extended without stretching or squeezing.

Note that the correlation presented (Fig. 10) is an interpretation based on the observed carbon isotope trends and that there is some uncertainty inherent in the methodology. Unconformities have been documented in correlative strata, particularly in northern areas (e.g., Ebert and Matteson 2003) and may also complicate interpreted correlations. The Winfield Quarry data extend above and below the available data from New York and West Virginia, and correlations in these parts of the section would benefit from additional regional data. The peak of the excursion, which occurs approximately at the Silurian–Devonian boundary according to Husson et al.’s (2016) preferred interpretation, is better constrained and appears to correlate well.

Compared to lithostratigraphic correlation, this chemostratigraphic correlation is more consistent with a conodont biostratigraphy event observed by other researchers across the Appalachian Basin. The first
appearance datum (FAD) of *I. woschmidti* occurs within 2 m of the Silurian–Devonian boundary and has been used globally to constrain the location of that boundary (Denkler and Harris 1988). In the southern outcrop belt of the Appalachian Basin, this FAD has been documented near the top of the Keyser Formation and in the New Creek Formation (Helfrich 1978; Denkler and Harris 1988). In the northern outcrop belt, it has been documented in the Manlius and Coeymans Formations (Denkler and Harris 1988; Milunich and Ebert 1993; Natel et al. 1996; Kleffner et al. 2009), which lithologic correlation marks as equivalent to units overlying the Keyser Formation in the southern outcrop belt (Fig. 3).

Similarly, ages from volcanic ashes are more consistent with the chemostratigraphic correlation than with lithostratigraphic correlations. An ash bed in the Corriganville of West Virginia has been dated as 417.22 Ma, and a series of ashes in the uppermost Coeymans and Kalkberg in New York have been dated as 418.42–417.56 Ma (Husson et al. 2016). While lithostratigraphic correlation places the New York ashes equivalent to or stratigraphically above the West Virginia ash, chemostratigraphic correlation places these ashes in stratigraphic order consistent with their ages (compare Figs. 3 and 10).

**FIG. 10.**—Correlation based on carbon isotope data. Data from this study is in black; New York (red) and West Virginia (blue) data from Husson et al. (2016), except where otherwise specified. Symbols in legend apply to all colors. Vertical scale is normalized stratigraphic position given relative to Husson et al.'s (2016) section H4a. a) Stratigraphic sections (lithology) and transgressive-regressive cycles. Lithologies for stratigraphic section WQ1 converted to classification scheme used by Husson et al. (2016) to facilitate combination of these data sets. b) Carbon isotope values on which this correlation is based. Gray shading indicates interpreted oxygen limitation during deposition, with darker shading indicating increasing oxygen limitation. Silurian–Devonian boundary and age data from Husson et al. (2016). FAD *I. w. w* is first appearance datum of *Icriodus woschmidti woschmidti*. LAD *O.e.d* is last occurrence datum of *Oulodus elegans detorta*. c) Factors by which data in this figure was vertically stretched or squeezed expressed as 1 divided by the stretching or squeezing factor. H1 through H5 refer to Husson et al. (2016) stratigraphic section names. Abbreviations: WV = West Virginia; PA = Pennsylvania; NY = New York; To = Tonoloway; Corr = Corriganville; NC-C = New Creek-Corriganville; Sh = Shriver; Ro = Rondout; Co = Coeymans.
The transgressive-regressive cycles documented herein record local change in relative sea level from as shallow as supratidal environments to as deep as below storm wave base. Dorobek and Read (1986) estimated the water depth of storm wave base at this time in the Appalachian Basin as 50–60 m or deeper, on the basis of thicknesses of sedimentary packages from which they approximated the slope of the Appalachian Basin ramp (10–15 cm/km). Haq and Schutter (2008) show a maximum of ~80 m of global sea-level change for third-order fluctuations through the latest Silurian and earliest Devonian (Pridolian and Lochkovian). Therefore, from the local record of relative sea-level change alone, it is possible that the transgressive-regressive cycles at WQ1 are the result of eustatic sea-level change. However, if eustasy was the primary driver, relative sea-level cycles would be coincident throughout the Appalachian Basin, and the chronostratigraphic correlation does not support this scenario (Fig. 10A).

Comparing the transgressive-regressive cycles in light of the chronostratigraphic correlation presented herein, a maximum transgression in the Keyser Formation was synchronous through at least the southern outcrop belt. Another maximum transgression in the Mandata Member appears to coincide with that in the Kalkberg-New Scotland Formations of New York. Otherwise, transgressive-regressive cycles do not appear to correlate across the basin. We therefore conclude that local factors such as tectonics and sediment supply were the dominant control on depositional patterns in the Appalachian Basin at this time.

A positive carbon isotope excursion requires either addition of 13C or removal of 12C. As a possible cause of the Klond excursion, Malkowski and Racki (2009) suggested that the expansion of land plants resulted in burial of organic matter rich in 12C in epicontinental seas. The Winfield section records oxygen limitation and enhanced burial of organic matter in the Mandata Member. However, that unit is 9 m above the peak of the positive isotope excursion, having been deposited after rather than before or during the excursion as would be expected for organic-rich units that could have contributed to the positive excursion. Saltzman (2002) noted that the carbon isotope excursion in West Virginia coincides with a relative sea-level lowstand and suggested that the lowered sea level could have exposed and caused increased erosion of 13C-rich Silurian carbonate strata. The correlation presented herein using carbon isotope data does not show a synchronous lowstand throughout the Appalachian Basin (Fig. 10A). However, because transgressive-regressive cycles appear to reflect local rather than regional or global sea-level changes, a finer scale than the forces that would have governed global carbon isotope trends, this does not disprove Saltzman’s (2002) hypothesis. Additional stratigraphic studies reporting high-resolution isotopic, geochronologic, and lithologic data from late Silurian–Early Devonian sections are needed to fully characterize and interpret the Klond excursion.

CONCLUSIONS

At a time when global atmospheric and surface-water oxygen levels were rising, there is evidence for oxygen limitation in the Appalachian Basin. Strata at Winfield Quarry are interpreted to document a range of depositional oxygenation conditions. Normal marine conditions are interpreted for biomicrite with abundant, diverse fauna. Progressively lower oxygenation is interpreted for facies from gray micrite with Zoophycos burrows to gray shale with Chondrites burrows and limited, sparse fauna to black, barren shale.

Facies distribution in the stratigraphic section reveals parts of three transgressive-regressive cycles: (1) The Tonoloway Formation with intertidal to supratidal laminated, mudcracked, evaporitic micrites represents the tail end of a regression; (2) The Byers Island and Jersey Shore Members of the Keyser Formation are biomicrites with sponge-coralline bryostomes that indicate a return to normal marine conditions and overall transgression. The La Vale Member of the Keyser Formation contains fossils that are increasingly abraded upsection and culminates in micrites with mudcracks and tidal bedding, indicating regression and a return to an intertidal to supratidal setting; and (3) The New Creek-Corriganville Members of the Old Port Formation are a variety of shallow-water facies that, above a basal bed of in situ stromatolites, lack indicators of subaerial exposure or tidal influence; this records transgression to a subtidal, above fair-weather wave base setting. An abrupt shift to mainly black, barren shales in the lower Mandata Member indicates rapid deepening to an oxygen-limited environment below storm wave base. Upper Mandata Member mainly gray shales with Chondrites traces and a limited fossil assemblage and Shrimer Member micrites with Zoophycos traces were deposited under continued but decreasing levels of oxygen limitation, likely related to regression. This trend culminates with a return to normal marine conditions, as shown in Ridgeley Member biomicrites deposited below fair-weather wave base.

The Klond Event positive carbon isotope excursion is recorded in central Pennsylvania as a rise from a minimum of ~4.3‰ in the Tonoloway Formation to a high of ~6.4‰ in the upper part of the La Vale Member of the Keyser Formation, then a drop >5‰ to a low in the Mandata Member of the Old Port Formation. Using trends observed in this globally coincident data to correlate regionally, following methodology from Husson et al. (2016) and incorporating their data, shows that the Keyser Formation is equivalent to the Keyser and Tonoloway Formations in West Virginia and parts of the Rondout, Manlius, and Coeymans Formations in New York. The New Creek-Corriganville Members at Winfield Quarry are mostly equivalent to the New Creek Formation in West Virginia and parts of the Kalkberg and New Scotland Formations in New York. The Mandata Member is equivalent to at least part of the Corriganville Formation in West Virginia and parts of the Kalkberg, New Scotland, and Bercraft Formations in New York. This new correlation is more consistent with other time-correlative markers, including conodont biostratigraphy and volcanic-ash chronostatigraphy.

Interpreted transgressive-regressive trends do not match between West Virginia, Pennsylvania, and New York when correlated using existing lithostratigraphic correlation or the carbon-isotope correlation presented here incorporating data from Pennsylvania. It is inferred that local (tectonics, sediment supply) rather than global (eustatic) controls dominated depositional patterns in the Silurian–Devonian boundary interval in the Appalachian Basin.

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SUPPLEMENTAL MATERIAL

Data are available from the PALAIOS Data Archive: https://www.sepm.org/supplemental-materials.

REFERENCES


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