



Paleo-redox context of the Mid-Devonian Appalachian Basin and its relevance to biocrises

Ruliang He^a, Wanyi Lu^a, Christopher K. Junium^a, Charles A. Ver Straeten^b,
Zunli Lu^{a,*}

^a Department of Earth Sciences, Syracuse University, Syracuse, NY 13244, United States

^b New York State Museum, The State Education Dept., Albany, NY 12230, United States

Received 17 May 2019; accepted in revised form 16 December 2019; available online xxxx

Abstract

The Devonian Period witnessed the expansion of vascular land plants and an atmospheric oxygenation event associated with enhanced organic mass burial. The deposition of organic-rich shales (e.g. black shales of the Marcellus subgroup) and several biotic crises in the marine realm have been linked to Devonian ocean anoxia. However, it is not clear how redox conditions evolved in different parts of the water column in such a context of dynamic changes in the atmosphere-ocean system. To address this problem, we use the bulk carbonate I/Ca proxy on core samples from Yates County, NY, in order to reconstruct the water column redox history through the Onondaga Limestone into the lower Marcellus shale. On the secular scale, the range of I/Ca values support the notion of a Devonian rise in atmospheric oxygen, relative to time intervals earlier in the Paleozoic. In terms of Eifelian Stage stratigraphic trends, I/Ca ratios are generally stable and high in the Onondaga Formation but show large fluctuations in lower Marcellus strata. Low I/Ca ratios are found near the onset of organic-rich shale deposition indicating relatively reducing subsurface waters. The pattern of redox changes resembles that of contemporaneous sea-level changes. Finally, the reconstructed oxygenation changes are correlated to three biotic transitions in Devonian marine systems.

© 2019 Elsevier Ltd. All rights reserved.

Keywords: I/Ca; Devonian; Atmospheric oxygen; Marcellus shale

1. INTRODUCTION

1.1. The Devonian Earth system and Appalachian Basin

The Earth system went through important changes during the Devonian Period. The diversification of vascular land plants during the Mid to Late Devonian and the development of larger and deep root and seed systems significantly altered weathering and sedimentary processes, the hydrologic cycle, and global climate (Gensel and Andrews, 1984, 1987; Algeo and Scheckler, 1998; Meyer-Berthaud

et al., 1999; Stein et al., 2007). Enhanced preservation and burial of biomass decreased the sink of atmospheric oxygen (Kump, 1988; Lenton et al., 2016). The updated GEOCARBSULF model and compilation of inertinite abundance in coal all suggest a rise in atmospheric oxygen pO_2 during Mid Devonian time (Glasspool and Scott, 2010; Krause et al., 2018). A statistical analysis of iron speciation and biotic data (Sperling et al., 2015) suggests that pO_2 might have risen to modern levels during the Devonian. This pO_2 rise is also supported by Mo isotope, I/Ca and Ce anomaly signals recorded in Silurian to Devonian strata (Dahl et al., 2010; Wallace et al., 2017; Lu et al., 2018).

* Corresponding author.

E-mail address: zunlilu@syr.edu (Z. Lu).

<https://doi.org/10.1016/j.gca.2019.12.019>

0016-7037/© 2019 Elsevier Ltd. All rights reserved.

A range of relatively moderate biocrises to well-known extinctions also occurred in Devonian marine ecosystems. At the Frasnian-Famennian stage boundary (372 Ma; Becker et al., 2012), up to 80% of marine species were impacted by a major biotic crisis, namely the Kellwasser event (Hallam and Wignall, 1997). The Hangenberg events, which occurred at the Devonian-Carboniferous boundary (359 Ma), witnessed losses of over 50% vertebrate diversity and is recognized as a “bottleneck” in vertebrate evolution (Sallan and Coates, 2010). The Eifelian-Givetian Kačák biotic event is recorded globally and associated with sea level rise, deposition of anoxic black shales or limestones, and pelagic faunal turnovers (House, 1996; DeSantis et al., 2007). In the eastern U.S. pre-Kačák turnovers, such as the Bakoven and Stony Hollow events, are recorded as well (DeSantis and Brett, 2011) and oceanic anoxia is also linked to these biotic events in association with climate changes (Koch and Boucot, 1982; Algeo and Scheckler, 1998; McGhee et al., 2013; White et al., 2018).

A thick succession of Devonian-age mudrocks in the northern Appalachian Basin, eastern North America, comprises a highly detailed stratigraphic sequence (Baird and Brett, 1986; Griffing and Ver Straeten, 1991; Brett and Baird, 1994; Ver Straeten et al., 1994; Murphy et al., 2000; Werne et al., 2002; Sageman et al., 2003; Ver Straeten, 2007; Brett et al., 2011; Ver Straeten et al., 2011a; Ver Straeten et al., 2011b). It provides an ideal case study region for investigating depositional processes and organic carbon preservation in black shales within a detailed litho- and chronostratigraphic framework, with superb paleontological records, and a growing dataset of geochemical proxies (Arthur and Sageman, 2005; Brett et al., 2011; Ver Straeten et al., 2011b). The dominant controls on the deposition of black shales in Devonian Appalachian Basin have been attributed to rising global sea-level with tectonic contributions (Ver Straeten et al., 1994; Werne et al., 2002; Sageman et al., 2003; Arthur and Sageman, 2005; Brett et al., 2011; Kohl et al., 2014).

The estimates of bottom water redox state were formulated on the basis of various proxies, such as the concentrations and elemental ratios of redox sensitive elements (Mo and U), the degree of pyritization, $\delta^{34}\text{S}$ of syngenetic pyrite, Mo isotopes, and pyrite framboid size distributions (Murphy et al., 2000; Werne et al., 2002; Sageman et al., 2003; Algeo, 2004; Rimmer, 2004; Gordon et al., 2009; Ver Straeten et al., 2011b; Lash and Blood, 2014; Blood and Lash, 2015; Chen and Sharma, 2016). A recent study using a high-resolution chemostratigraphic analysis indicates a close relationship between the microbial sulfate reduction in organic rich layers and the formation of pyrite due to the diffusive flux of H_2S (Liu et al., 2019). The discovery of agglutinated benthic foraminifera in these sequences provides evidence that anoxia was not persistent and that there was at least episodic oxygenation (Schieber, 2009). Fe-speciation data consistent with oxic conditions (Boyer et al., 2011), large pyrite framboids (diameter $>10\text{ }\mu\text{m}$) (Blood and Lash, 2015), and low Fe/Al ratios

<0.55 close to modern oxic sediments (Lash, 2016), are also consistent with episodic benthic oxygenation during deposition of the Marcellus strata.

In the context of this complex history of global/regional paleo-redox, this paper aims to provide new insights into the upper water redox conditions through Onondaga to lower Marcellus strata by I/Ca. We employ the following redox terms and their corresponding oxygen levels: oxic ($>2\text{ ml O}_2/\text{L}$), dysoxic ($\sim 0.2\text{--}2\text{ ml O}_2/\text{L}$), suboxic ($0\text{--}0.2\text{ ml O}_2/\text{L}$), anoxic (no O_2 , no H_2S), and euxinic/sulfidic (no O_2 , with free H_2S present) (Hofmann et al., 2011).

1.2. Iodine paleo-redox proxy

Iodine has a low average concentration of only $\sim 300\text{ ppb}$ in Earth's crust, and $\sim 70\%$ of the global iodine inventory is thought to exist in marine sediments (Muramatsu and Wedepohl, 1998). The average iodine concentration in seawater is nearly constant at $\sim 0.46\text{ }\mu\text{mol/L}$ (Elderfield and Truesdale, 1980). Iodine is an important trace element in biogeochemical and redox reactions (Küpper et al., 2011). The concentrations of iodate (IO_3^-) and iodide (I^-), two thermodynamically stable inorganic species in seawater, are thought to be controlled by primary productivity in the surface ocean (Elderfield and Truesdale, 1980; Chance et al., 2010) and by redox conditions in the water column (Wong and Brewer, 1977; Farrenkopf and Luther III, 2002). Iodate is the main iodine species in well-oxygenated waters (Truesdale and Bailey, 2000), while iodide dominates at depth in anoxic basins (Wong and Brewer, 1977) and in anoxic porewaters (Kennedy and Elderfield, 1987a,b).

Iodate, not iodide, is the only species incorporated into carbonates (Lu et al., 2010) by potential substitution of IO_3^- for CO_3^{2-} (Podder et al., 2017). I/Ca ratios in bulk carbonate have been used as a novel proxy to constrain redox conditions in the upper part of water columns over a range of time scales (e.g. Lu et al., 2010; Hardisty et al., 2014; Zhou et al., 2015; Lu et al., 2016). A decrease in bulk carbonate I/Ca commonly represents development of O_2 -depleted conditions in upper waters, as iodate is converted to iodide. Other factors may partially contribute to changes in I/Ca, such as the upwelling of iodide-rich anoxic waters, iodate loss from mixed-layer waters in high-productivity areas, diagenetic alteration, and mixing with authigenic carbonates (e.g. Zhou et al., 2015). I/Ca ratios of carbonate rocks represent a minimum value at the time of deposition – as understood so far, diagenetic processes can only decrease the original ratio (Hardisty et al., 2017). Recently, this proxy has been applied in studying redox conditions during the Paleozoic (e.g. Edwards et al., 2018; Young et al., 2019). A threshold value of I/Ca ($2.5\text{ }\mu\text{mol/mol}$) was proposed by Lu et al. (2016) to indicate the presence of O_2 -depleted condition in the upper water. However, this threshold value is based on Holocene planktonic foraminifera. Whether it can be used in ancient bulk carbonates remains an open question.

2. GEOLOGICAL BACKGROUND AND SAMPLING

2.1. Study site and stratigraphy

Devonian mudrocks in New York State are part of the Catskill Delta Complex. The development of this sedimentary package was closely related to the Acadian Orogeny, during which the collision of multiple terranes led to the uplift a mountain belt from east Greenland to Alabama, termed the Acadian orogen (Rast and Skehan, 1993; van Staal et al., 2007; van Staal et al., 2009). Paleogeographic reconstruction of North America in the Mid Devonian shows that the Appalachian Basin was a retroarc foreland basin system/epicontinental sea, and was connected to the global open ocean (Rheic Ocean) (Blakey, 2016 and Fig. 1). Water depth at the time of deposition of the black shales was probably tens of meters to two hundred meters maximum, shallowing in the Late Devonian onto arches separating the Appalachian Basin from cratonic basins (Schieber, 1994).

We obtained core samples from a 28 m thick interval of a 5 cm diameter core (Morton Salt Core, API # 31-123-13174-00-00), in the collections of the New York State Museum. The drilled well is located in the town of Starkey, Yates County, western New York State (42.571507°N, 76.934513°W). The strata analyzed in this study comprise lower Middle Devonian rocks of the Eifelian Stage and basal-most Givetian Stage. The classic Onondaga Formation consists of a range of limestone lithologies from grainstone to carbonate mudstone, with minor amounts of chert and shale. In contrast, overlying Marcellus strata in central New York consist primarily of black to dark gray shales. Lower to middle Marcellus strata in the area also feature lesser amounts of limestone, occurring as well-defined beds, laminae of pelagic or low-oxygen adapted benthic shells, and concretions. Upper Marcellus strata are generally very poor in carbonate content.

Since the 1930s (Cooper, 1930) Marcellus strata in New York have been defined as a chronostratigraphic unit,

bounded by time-significant surfaces. In New York the term Marcellus includes all marine strata in the state underlain by the Onondaga Formation and overlain by the Skaneateles Formation, including basal dark/black shales to shoreface sandstones. Associated with a thickness approaching >580 meters in eastern New York, Ver Straeten et al. (1994) and Ver Straeten and Brett (2006) redefined Marcellus Formation of Cooper (1930) as a subgroup of Hamilton Group in New York, and elevated the Union Springs and Oatka Creek members to lower and upper formations within the Marcellus subgroup. Oatka Creek-age strata in eastern New York's thick, basal to shoreface facies are assigned to a Mount Marion Formation. The term Cherry Valley is applied here to strata specifically assigned to that name in New York, which is only correlative with the upper part of the Purcell Member in the central to southern Appalachian Basin.

Stratigraphy of the Morton Salt Core of this study, low to high, comprise the Onondaga Formation (Edgecliff, Nedrow, Moorehouse and Seneca Members), the Union Springs Formation (Bakoven Member) and the lower part of the Oatka Creek Formation (Hurley, Cherry Valley and most of the overlying East Berne Member). The top of the study interval falls at the base of a key marker bed, termed the Dave Elliott Bed (Ver Straeten, 1994). Core samples in this study were obtained from all but a basal phosphatic, sand-rich 0.25 m of the 16.25 m thick Onondaga Limestone, and from overlying 12.35 m of lower Marcellus strata. The Marcellus strata of this study consist of (1) black shales, often calcareous, with thin dacryoconarid shelly limestone laminae and concretionary limestones assigned to the 9.7 m thick Union Springs Formation (Bakoven Member), and (2) lowermost strata of the Oatka Creek Formation, consisting of 1.15 m of bedded limestones of the Hurley and Cherry Valley Members and ~1.5 m of shales of the East Berne Member. The Eifelian-Givetian stage boundary falls within the East Berne Member in the core.

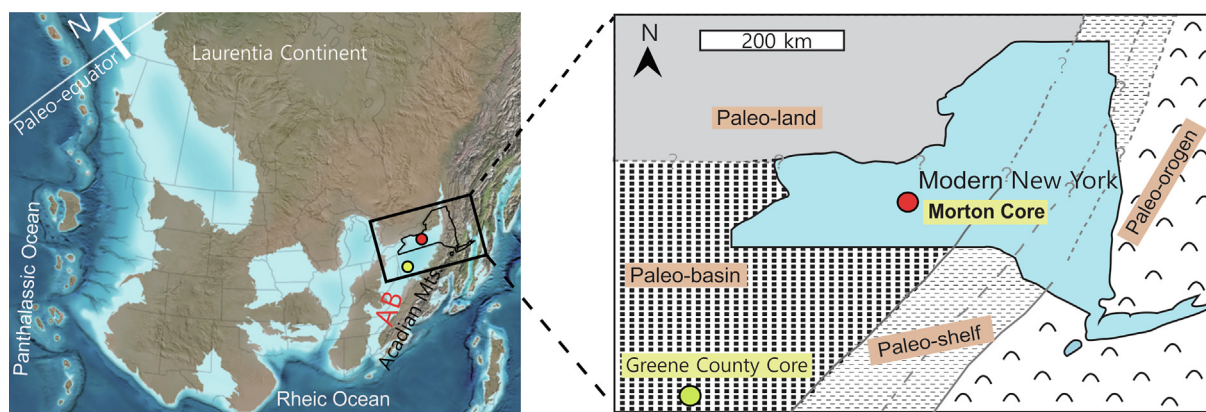


Fig. 1. Paleogeographic maps of North America and New York State in the Mid Devonian Period. North America Map is based on Blakey (2016) and the New York State Map is based on Dennison (1985), Werne et al. (2002), and Sageman et al. (2003). Red circle denotes location of the core used in this study; yellow circle denotes the Greene County core in southwestern Pennsylvania from Lash and Blood (2014) discussed in the text. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.2. Carbonate materials

Union Springs Formation carbonates largely consist of thin limestones of micrite and shelly material of small conical *dacryoconarid*/styliolinid shells, with varying concentrations of thin-shelled brachiopods, bivalves and ostracodes. In central New York, in the study core and three additional sites, [Arroyave \(2014\)](#) described five macro-lithofacies (MLs) in the Union Springs Formation. While ML facies 1–5 predominantly occur low to high through the formation, respectively, the three middle facies interfinger in intervals. Limestone is more prevalent in ML1, ML4 and ML5 facies of [Arroyave \(2014\)](#). Carbonate in ML1, at the bottom of the formation, largely consists of matrix cement and recrystallized microspar mud, and silt-size calcareous sediments ([Fig. S1a](#)). ML4 carbonates consist of generally thin-bedded fossiliferous limestones that occur scattered through relatively organic-rich siliciclastic shales ([Fig. S1b](#)). ML5 carbonates, found in the upper part of the Union Springs in the core and nearby sites, occur as largely concretions which sometimes coalesce to form lenses to continuous knobby beds of limestone. These are less fossiliferous, and are interbedded with silty siliciclastic mudstones ([Fig. S1c](#)).

In contrast, Onondaga Formation limestones are largely bioclastic in character. Coarser grainstones to packstones occur in eastern and western New York, where finer grained facies occur in the upper lower and upper parts of the formation. In the study area of central New York, Onondaga Limestones are overall finer grained, with only minor siliciclastic mudstones in the lower middle part of the unit. Central New York Onondaga strata were deposited in a central trough that extends southward into the deeper central Appalachian Basin. Petrographic studies by [Lindholm \(1967 and 1969\)](#) showed that finest-grained Onondaga carbonates largely consist of silt-size calcareous sediments (“*calcsiltite*”), and not micrite, in contrast with Union Springs limestones. Union Springs carbonates that are most analogous to fine-grained Onondaga limestones are represented by ML1 facies of [Arroyave \(2014\)](#), in the base of the Union Springs ([Fig. S1a](#)). Furthermore, *dacryoconarid* shells were found throughout the Onondaga limestones ([Frappier et al., 2015](#)).

3. METHODS

3.1. Bulk carbonate I/Ca

A total of 92 rock samples were collected at 10–70 cm intervals. Most of the carbonate in shaly samples are fine grain materials. Rock chips containing any visible nodules or fossils were avoided for generating powders. 2–4 mg of powdered samples were weighed out on a microgram balance, and then rinsed with MilliQ water to remove any potential dissolved iodine attached on the surface of the samples. Carbonate fractions in the samples were dissolved with 3% (v/v) HNO_3 and separated from residuals immediately after samples stop bubbling. This sample dissolution procedure only exposes non-carbonate phases to diluted acid for <5 minutes. 0.5% tertiary amine was added to help

stabilize iodate. Measurements of iodine were performed on a quadrupole inductively coupled plasma-mass spectrometer (ICP-MS, Bruker M90) at Syracuse University. The precisions are typically better than 1% for ^{127}I , and they are not reported individually for each sample. The detection limit of I/Ca is usually better than 0.1 $\mu\text{mol/mol}$. The long-term accuracy is guaranteed by frequently repeated measurements of the standard reference material JCP-1 ([Lu et al., 2010](#)).

3.2. TOC and $\delta^{13}\text{C}$ analyses

Stable isotope analyses for $\delta^{13}\text{C}_{\text{org}}$ were performed using an Elementar Isotope Cube elemental analyzer coupled to an Isoprime 100 stable isotope mass spectrometer. Decarbonated samples were weighed and sealed in tin boats for isotopic analysis and combusted at 1100 °C (oxidation furnace) and 650 °C (reduction furnace). Reference gases were calibrated relative to international reference standards IAEA-C6 sucrose (−10.80‰) and NIST-1547 peach leaves (−26.0‰). Standard reproducibility was better than $\pm 0.1\text{‰}$ and reported as $\pm 0.1\text{‰}$ to reflect reported precision from known isotopic values of reference materials. Calibration of samples to reference data was performed using the two-point calibration method described in [Coplen et al. \(2006\)](#). The EA peak area response factors were determined using replicates of NIST-1547 peach leaves (47.79 wt.% C and 2.98 wt.% N) distributed throughout sample analysis runs and bracketing the quantity of C and N in the samples. Reproducibility of the N and C content of NIST-1547 peach leaves is 0.5% (relative error) and $\pm 0.1\text{ wt.\%}$ (1σ). C/N values are reported as atomic ratios.

4. RESULTS

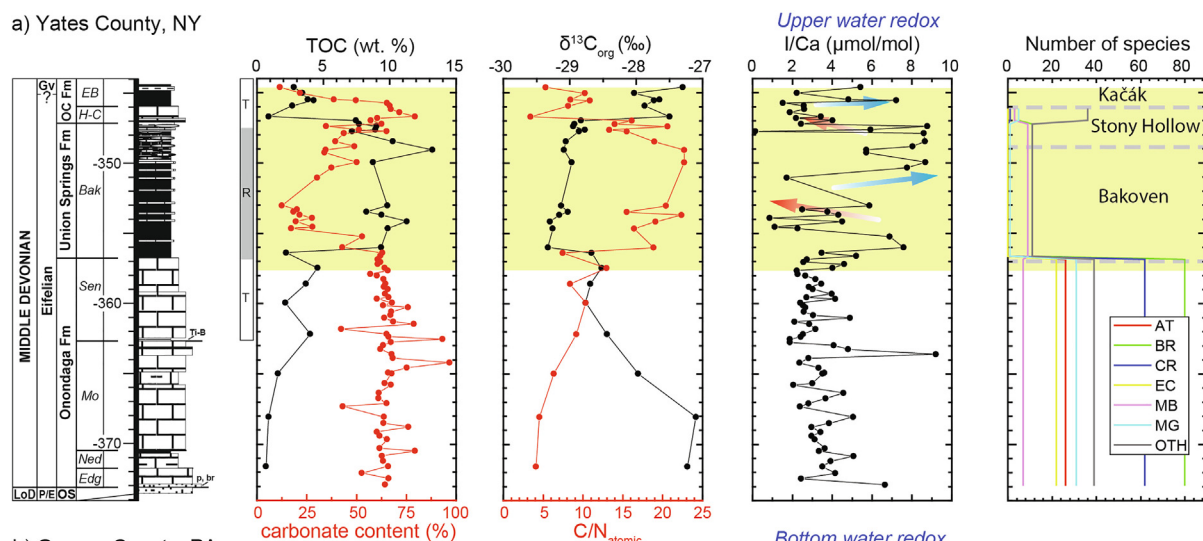
4.1. Bulk carbonate I/Ca

I/Ca shows relatively stable background values ($\sim 2\text{--}4\text{ }\mu\text{mol/mol}$) for most of the Onondaga Limestone ([Fig. 2a](#)). However, passing from the Onondaga Limestone to lower Marcellus strata, I/Ca starts to fluctuate from underlying background values ($\sim 2\text{--}4\text{ }\mu\text{mol/mol}$) to a wider range of values (0.86–7.57 $\mu\text{mol/mol}$). From the lower to middle part of the Union Springs Formation, I/Ca decreases from $>7\text{ }\mu\text{mol/mol}$ to $<1\text{ }\mu\text{mol/mol}$. I/Ca ratios rise to $\sim 8\text{ }\mu\text{mol/mol}$ towards upper part of the Union Springs, except for one very low value most likely representing concretionary carbonate. I/Ca decreases to $<2\text{ }\mu\text{mol/mol}$ within the Hurley and Cherry Valley Members of the Oatka Creek Formation. Then, I/Ca ratios increase again in the East Berne Member to values as high as 7.22 $\mu\text{mol/mol}$.

4.2. TOC and carbon isotopes

The Onondaga Formation contains mostly limestone, with carbonate content in most samples exceeding 60% and TOC content in the range of 0.67% to 4.56% ([Fig. 2a](#)). $\delta^{13}\text{C}_{\text{org}}$ values in the Onondaga Formation start at -27.2‰ , and show a gradual decrease to -28.8‰ and

a) Yates County, NY



b) Greene County, PA

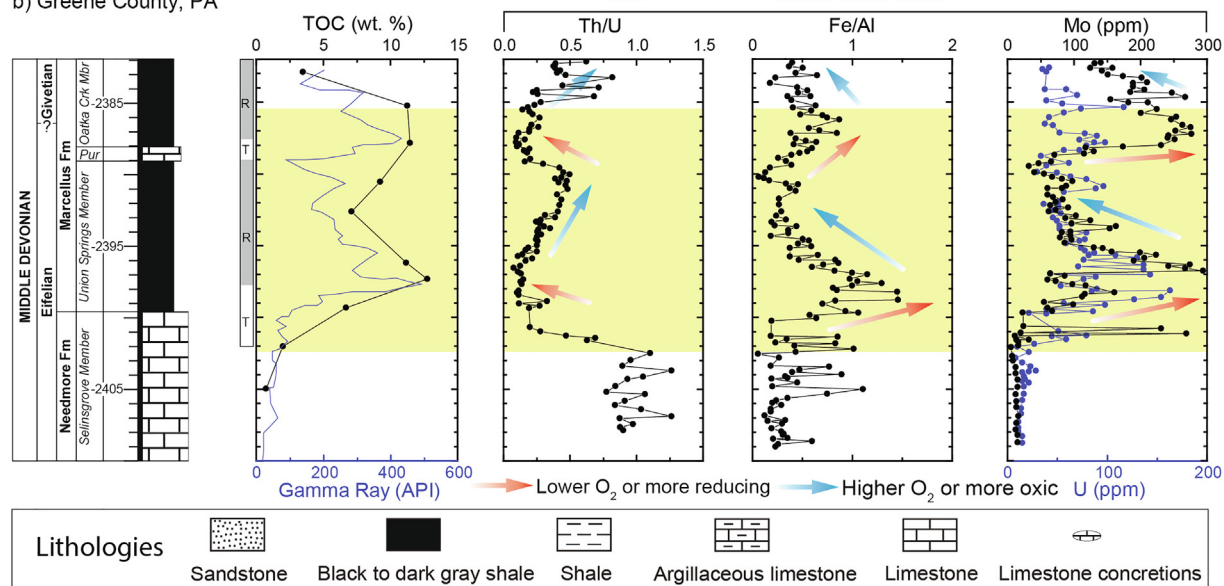


Fig. 2. (a) Chemostratigraphic profiles in the Morton Salt core from Yates County (NY) showing TOC, carbonate content, C/N_{atomic} , $\delta^{13}C_{\text{org}}$, I/Ca ratios, and biotic data. Grey boxes with R indicate regression, and white boxes with T indicate transgression. Yellow boxes mark redox fluctuations in the lower Marcellus subgroup. Biotic data are from DeSantis (2010). Stratigraphy abbreviations (members is italics): Bak = Bakoven; EB = East Berne; Edg = Edgecliff; Fm = Formation; H-C = Hurley and Cherry Valley Members; LoD = Lower Devonian; Mo = Moorehouse; Ned = Nedrow; OC = Oatka Creek; OS = Oriskany and/or Schoharie Formation; p.br = phosphate, brachiopods; P/E = Pragian and/or Emsian Stage; Sen = Seneca; Ti-B = Tioga B, and altered airfall volcanic tephra/K-bentonite. Paleontology abbreviations: AT = trilobites, BR = brachiopods, CR = Corals, EC = crinoids, MB = bivalves, MG = gastropods, OTH = other. b) TOC and redox proxy data in Greene County core (PA) from Lash and Blood (2014). Abbreviations: Crk = Creek; Pur = Purcell Member. Depths are in meters in both cores.

remain relatively constant through the upper ~3.5 m to the base of the Union Springs Formation. TOC content shows a sharp increase from the base of the Union Springs Formation to around 7–13% throughout most of the formation, whereas $\delta^{13}C_{\text{org}}$ shows a rapid decrease to -29.3‰ and maintains a constant value of $\sim -29\text{‰}$ (Fig. 2a). The Hurley and Cherry Valley Members of the Oatka Creek Formation show a rapid drop in TOC content from 7.47% to 0.88%, and $\delta^{13}C_{\text{org}}$ of these members exhibit a sharp increase to -27.50‰ . Then, within the East Berne Member,

TOC values remain below $<5\%$, and $\delta^{13}C_{\text{org}}$ is in the range of -28.03‰ to -27.30‰ .

5. DISCUSSION

5.1. Preservation of redox signals

The Devonian carbonates in the Appalachian Basin, especially in the organic-rich Marcellus strata, may be influenced by diagenetic alteration (Sageman et al., 2003;

Lash and Blood, 2014; Chen and Sharma, 2016). We do not argue that our carbonate I/Ca record is exempt from the effects of diagenesis. However, since authigenic/diagenetic carbonate precipitation occurs in anoxic porewaters where iodide is the dominant iodine species and iodide does not get incorporated into carbonate structure, addition of diagenetic carbonate and recrystallization of primary carbonate can only lower bulk carbonate I/Ca signals (Hardisty et al., 2017). No diagenetic mechanisms considered thus far are able to artificially increase I/Ca values. In addition, I/Ca values show no correlation with Mn/Sr and Mg/Ca ratios, although higher I/Ca values are more frequently found in samples with relatively lower Mn/Sr (Fig. 3). Comparing the average I/Ca in the relatively organic-lean Onondaga Limestone and organic-rich Union Springs and Oatka Creek formations, I/Ca is not significantly lower in the organic-rich intervals where precipitation of authigenic carbonate is more likely to occur (Fig. 2a). Therefore, it is not obvious that the I/Ca trend is universally biased by the presence of diagenetic carbonates in the high TOC intervals. Without diagenesis, the primary I/Ca values in some of the shaly samples theoretically could be even higher.

The middle-upper Union Springs Formation is known to contain concretionary carbonates of diagenetic origin. We avoided concretions during sampling but the lowest I/Ca value of this study indeed was found in that interval (Fig. 2a). Furthermore, clay, igneous rocks and terrestrial sediments commonly have very low iodine concentration (Muramatsu and Wedepohl, 1998; Fehn, 2012; Lu et al., 2015). For example, bulk rock iodine content in a clay formation is demonstrated to be dominated by carbonate minerals (Claret et al., 2010). We found no covariation between I/Ca values and Al content (Fig. 3c), which is an indicator for silicate contamination. Thus, detrital materials are unlikely to contaminate marine carbonate I/Ca signal. Best examples of lithology changes are near the formation boundaries (Onondaga to Union Springs Formation and Union Springs to Oatka Creek Formation), where carbonate content dropped sharply (Fig. 2a). There is no systematic or consistent correlation between I/Ca and the gradient of carbonate content across these two lithological boundaries (Fig. 3d). I/Ca also does not correlate with carbonate content for the study formation as a whole (Fig. 3d). This indicates influence of lithology on the I/Ca record is weak, if any.

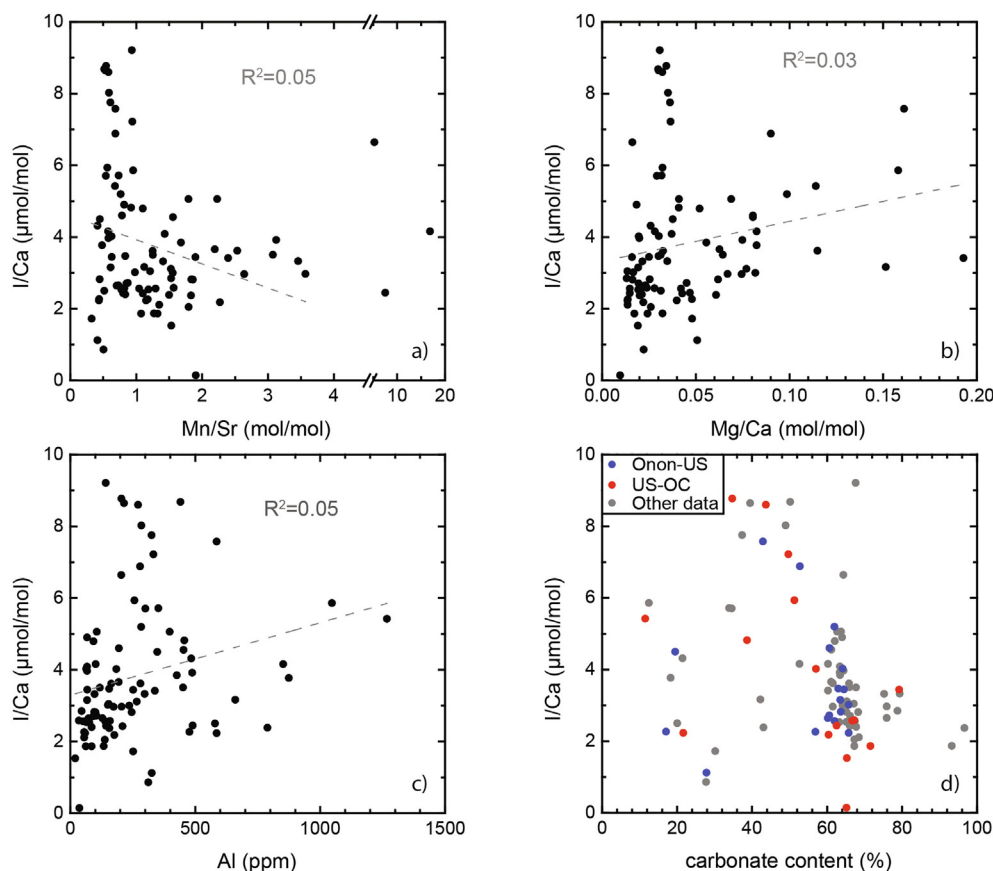


Fig. 3. Diagenesis evaluation using (a) I/Ca vs Mn/Sr and (b) I/Ca vs Mg/Ca cross-plots; (c) I/Ca and Al concentration relation in carbonate fractions showing the influence from detrital input; (d) I/Ca and carbonate mineral content relation showing the influence of lithological change. Onon-US and HC-EB mark two intervals where the carbonate content shows large variations. Abbreviations: Onon-US = Onondaga to Union Springs Formation boundary (354–359 m), US-OC = Union Springs to Oatka Creek Formation boundary (344–348 m), other data = other core samples measured in this study.

Organically-bound iodine theoretically can contaminate carbonate associated I/Ca signals. Our sample dissolution and solution preparation methods were used in many previous studies and no sign of contamination by organic matter was observed. For example, relatively low I/Ca values were more frequently found in high-TOC and low-carbonate rocks, compared to relatively high I/Ca in organic-lean and pure carbonate rocks (e.g. Zhou et al., 2015). In this study, we can't isolate any correlation convincingly indicate that organic matter has major influence on this I/Ca record, after examining samples from intervals with large TOC variations (1%–13% at boundaries of Onondaga to Union Springs Formation and Bakoven to Hurley and Cherry Valley Members) (Fig. 4). It should be noted that different analytical methods are developed for extracting carbonate associated iodine signal (I/Ca) and organically-bound iodine signal (I/TOC) in previous studies about OAEs, the interpretations and rationales for these two proxies are very different (Zhou et al., 2015; Zhou et al., 2017).

5.2. Comparison to secular records in a global context

The I/Ca compilation throughout Earth's history shows low background values (0.5–1 $\mu\text{mol/mol}$) from the Proterozoic Eon into the Paleozoic Era (Lu et al., 2018). High I/Ca values above this generally low background are often found in time intervals with increases in atmospheric $p\text{O}_2$ suggested by other proxies and models (Hardisty et al., 2014; Lu et al., 2017; Wei et al., 2019). The majority of I/Ca values from Middle Devonian strata of this study are above 2 $\mu\text{mol/mol}$ (Fig. 5), within the range of I/Ca in Mesozoic

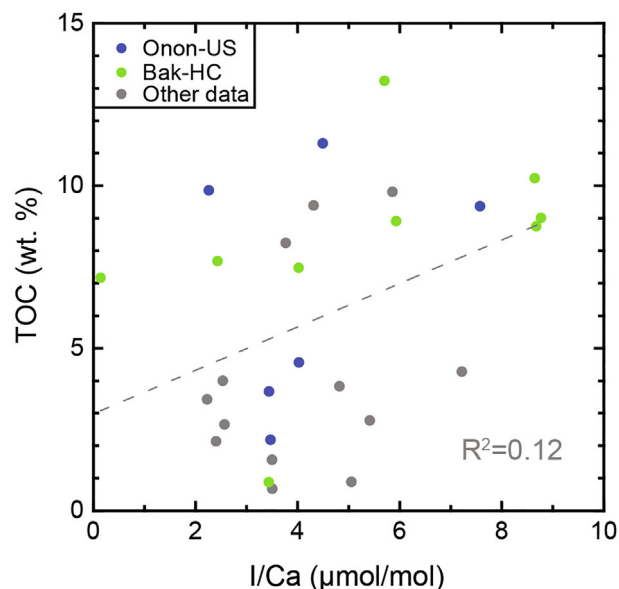


Fig. 4. Correlation between I/Ca and TOC for Morton Salt core samples. Onon-US and Bak-HC mark two intervals where TOC shows large variations. Linear regression includes samples across the whole core. Abbreviations: Onon-US and other data are same as Fig. 3. Bak-HC = Bakoven to Hurley and Cherry Valley Members boundary (346–350 m).

and Cenozoic carbonates (Lu et al., 2018). This contrasts with the low I/Ca baseline in the sections surveyed from the Proterozoic and during Paleozoic extinction events (Edwards et al., 2018; Young et al., 2019). There is no proxy development for the absolute values of I/Ca in long-term records to quantitatively and reliably indicate specific $p\text{O}_2$ values, since the I/Ca proxy is highly dependent on local oceanographic conditions. Independent marine redox proxies (e.g. Fe speciation, Ce anomaly and $\delta^{98}\text{Mo}$), and atmospheric $p\text{O}_2$ trends from several box model studies are converging towards the scenario of an oxygen increase in the atmosphere-ocean system during the Devonian, likely related to the expansion of land plants (Dahl et al., 2010; Sperling et al., 2015; Lenton et al., 2016; Wallace et al., 2017; Krause et al., 2018). As summarized in Meyer-Berthaud et al. (2010), paleobotany studies support a diversification of vascular land plants from the Early Devonian (Fig. 5). Plant maximum axis diameters, related to the height of a self-supporting tree, also show an increase through the Mid to Late Devonian (Fig. 5). Therefore, based on this whole set of proxy data and models, Onondaga to lower Marcellus strata were deposited during a time period featuring overall well-oxygenated atmosphere and at least some parts of global oceans.

This scenario is potentially supported by Ce anomaly measured from Morton Salt Core, since (Figs. S2–S5) these values fit reasonably well into the secular record of decreasing Ce anomaly reported by Wallace et al. (2017), in terms of timing and absolute values. These carbonate Ce anomaly values may not represent ambient seawaters during the deposition of our sample materials, but the primary seawater Ce signal are more likely to indicate more oxic environment (see more discussions in the supplementary materials). No evidence suggests that the I/Ca pulse in the Devonian sections are due to exceptionally better preservation comparing to other Paleozoic sections (Lu et al., 2018), but future studies are required to explain detailed mechanisms for how atmospheric and oceanic conditions might have driven these long-term trends in I/Ca.

5.3. Regional-scale redox changes

The stratigraphic I/Ca trends in our NY core are in general agreement with trace metal data from another core from Greene County, Pennsylvania (PA) (Lash and Blood, 2014), approximately 400 kilometers southwest of the Morton Salt Core of this study (Fig. 1). They broadly show two stages of redox change: relatively stable redox conditions during the deposition of the Onondaga Formation and redox fluctuation from the uppermost Onondaga Formation into overlying Marcellus strata (Fig. 2). These basin scale redox changes are likely associated with relative sea-level oscillations (Brett and Baird, 1996; Ver Straeten, 2007; Brett et al., 2011), which impacted the accumulation of organic matter and faunal turnover. Some high I/Ca ratios are found in relatively organic-rich intervals. We speculate that iodide accumulated in anoxic water might have been oxidized due to rising $p\text{O}_2$ and recorded as the high I/Ca. The exact ocean-atmospheric dynamics for such a scenario will be an interesting topic for future studies.

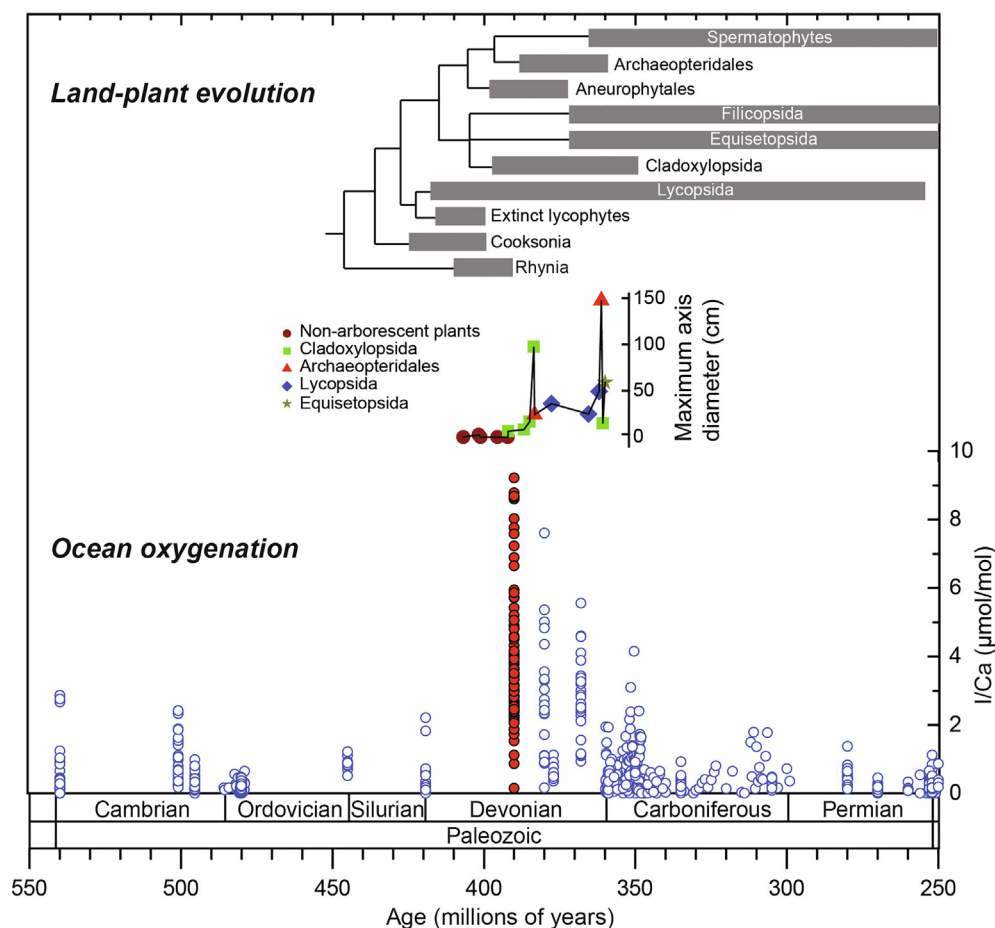


Fig. 5. Secular trend of I/Ca shows marine oxygenation condition coinciding with land-plant evolution. I/Ca values are from Lu et al. (2018) and red dots mark samples discussed in this study. Paleozoic vascular land plants phylogeny and maximum axis diameter are modified from Meyer-Berthaud et al. (2010). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Background I/Ca ratios throughout the Onondaga Formation are in the range of 2–4 $\mu\text{mol/mol}$ (Fig. 2a), comparable to the background ratios of Mesozoic and Cenozoic strata in well-oxygenated settings (Lu et al., 2010; Zhou et al., 2015; Lu et al., 2018). This suggests a stable and well-oxygenated upper water column in this part of the Appalachian Basin during the early Eifelian Stage, as expected from fossil abundance of the Onondaga Limestone. The Greene County core shows relatively high Th/U, low Fe/Al, and low Mo and U concentrations in this interval, consistent with I/Ca results (Fig. 2b). Higher Th/U ratios suggest relatively oxic bottom water conditions since reducing conditions favor U fixation and Th is generally immobile in oxic environments (Wignall and Myers, 1988; Wignall and Twitchett, 1996). Elevated Fe/Al ratios are indicative of reducing bottom water conditions because of the accumulation of Fe during the precipitation of Fe sulfide minerals (e.g. pyrite) that is favored under euxinic conditions (Canfield et al., 1996; Lyons and Severmann, 2006; Algeo and Maynard, 2008). Anoxic/euxinic benthic conditions result in strongly enriched Mo and U owing to their removal from seawater and precipitation as insoluble

forms in sediments ($\text{MoO}_{4-x}\text{S}_x^{2-}$ for Mo; UO_2 , U_2O_7 and U_3O_8 for U) (Zheng et al., 2000; Algeo and Maynard, 2008; Algeo and Tribouillard, 2009; Algeo and Rowe, 2012).

In the lower part of the Union Springs Formation, I/Ca ratios show transient increases to nearly 8 $\mu\text{mol/mol}$. These shifts are followed by decreases of I/Ca ratios to slightly below 2 $\mu\text{mol/mol}$, indicating deoxygenation in subsurface waters close to the onset of black shale deposition (Fig. 2a). These redox changes in the upper water column, inferred from I/Ca trends in the NY core, are generally consistent with the trends in bottom water conditions based on trace metal concentrations in the Greene County core (Fig. 2b). This redox evolution appears to correlate with sea level changes: deoxygenation during overall transgression and re-oxygenation during overall regression (Fig. 2a) (Brett and Baird, 1996; Brett et al., 2011; Ver Straeten et al., 2011b).

The organic matter geochemistry lends further support for a transition from relatively well-oxygenated to more poorly ventilated conditions. Coincident with increasing organic matter content, C/N ratios increase and $\delta^{13}\text{C}$

decreases (Fig. 2a). Assuming a primarily marine source for organic matter, increases in C/N ratios are broadly attributed to more a reducing water column and benthic zone (Meyers and Bernasconi, 2005; Junium and Arthur, 2007). Sources of high C/N organic matter from the incipient terrestrial biosphere was possible, but the organic matter found in Appalachian Basin black shales is of predominantly marine origin (e.g. Jaminski et al., 1998; Kelly et al., 2019). The decrease in $\delta^{13}\text{C}$ with increasing TOC is a hallmark of Appalachian Basin black shales (Sageman et al., 2003; Lash, 2017; Uveges et al., 2018). The specific mechanism of the ^{13}C -depletion is debated but the most likely mechanisms, methane oxidation (Lash, 2017), sources of ^{13}C -depleted DIC from a shallowed chemocline or significant contributions of anaerobe biomass (e.g. Uveges et al., 2018) all rely upon at least episodically reducing water column conditions.

5.4. Local faunal turnovers

We further compare the reconstructed redox history to evidence of faunal turnovers in the Eifelian-Givetian Appalachian Basin. Water column redox changes correlate with at least three well-resolved faunal shifts, which are recorded in coeval formations in adjacent areas of Eastern North America and to some degree globally (DeSantis et al., 2007; DeSantis and Brett, 2011). The Bakoven and Stony Hollow faunal turnovers occurred following the shift from the Onondaga Limestone to the overlying Union Springs Formation. The Bakoven Event in the Bakoven Member of the Union Springs marks a loss of 80% of the Onondaga fauna. Of the diverse Onondaga fauna (276 species), only 5 species (1.8%) carried over into the lower Union Springs Bakoven fauna (32 species) (DeSantis, 2010 and Fig. 2a). Reducing bottom water conditions during sea level rise might have contributed to this rapid decrease of benthic diversity in the lower part of the Union Springs Formation (Fig. 2).

Following the Bakoven event, the Stony Hollow Event marks an influx of taxa migrating chiefly from paleoequatorial waters in western Canada, including benthic fauna of brachiopods, bivalves, *Straparollus* gastropods and aulopod corals (DeSantis et al., 2007; DeSantis and Brett, 2011). In the Appalachian Basin it is best developed in eastern New York, where mid-Marcellus strata represent relatively intermediate depth biofacies, in the Stony Hollow, Hurley and Cherry Valley Members. The Stony Hollow Member, in the upper part of the Union Springs Formation, laterally shifts to dark gray to black shales of the Bakoven Member in eastern New York (Griffing and Ver Straeten, 1991). However, across central to western New York, the Hurley and Cherry Valley Members still retain elements of the Stony Hollow fauna (50 species in total, Fig. 2a) with a greater percentage of pelagic fauna relative to a more limited benthic fauna (DeSantis, 2010). This westward decreasing trend of relative benthic assemblage diversity corresponds to a relatively poorly oxygenated water column, most notably in the Cherry Valley (Fig. 2a).

Lastly, the East Berne shale in Oatka Creek strata is linked to the Late Eifelian global biocrisis known as the

Kačák Event, defined by total loss of the Stony Hollow fauna and abrupt conodont turnovers (DeSantis et al., 2007; DeSantis and Brett, 2011). Hypoxic-anoxic conditions were suggested for the Kačák Event, often based on the presence of black shale. Both I/Ca and metal concentrations (Fig. 2) show slightly more improved oxygenation conditions from basinward Hurley-Cherry Valley strata upwards into the East Berne. The Kačák Event in this region is apparently represented by the migration of the classic Hamilton Group fauna into the Appalachian Basin in the oldest well oxygenated facies within the lower 1/3 of the Oatka Creek Formation and equivalent strata (Brett and Baird, 1995). These observations suggest that sea-level changes and climate conditions might have played important roles in these biotic turnovers (House, 2002; DeSantis et al., 2007; Brett et al., 2009; DeSantis and Brett, 2011).

5.5. Reconciling $p\text{O}_2$ rise and marine anoxia

A broader and important question for the paleo-redox community is how to reconcile a growing body of evidence for atmospheric $p\text{O}_2$ rise and the traditional view of frequent anoxia in global oceans during the Devonian. On one hand, the timing of $p\text{O}_2$ change needs to be more precisely pinned down for comparison with the occurrences of marine black shale and faunal turnovers, which will then reveal whether the rise of atmospheric $p\text{O}_2$ was coeval with widespread ocean anoxia. On the other hand, estimates on the spatial extent of Devonian ocean anoxia also need to be improved, since new proxies (e.g. U isotope) start to indicate a surprisingly low percentage of global anoxic seafloor during episodes of widespread black shale deposition (Clarkson et al., 2018). It is also important to consider the vertical O_2 gradient in the water column. In this study, the Devonian global redox context (Fig. 5) and local proxy trends (Fig. 2) appear to indicate that organic-rich Devonian shales might have been formed with a relatively well-oxygenated upper water column but anoxic bottom waters. Future studies providing a more nuanced picture of spatial and temporal evolutions of Devonian redox conditions may lead to new insights into how the Earth system responded to major changes in the biosphere.

6. CONCLUSIONS

In the northern Appalachian Basin, I/Ca ratios recorded in the Onondaga Formation and lower to middle Marcellus subgroup (Union Springs and lower part of the Oatka Creek formations) are consistent with the rising atmospheric $p\text{O}_2$, most likely due to the proliferation of vascular plants during the Devonian Period. At a shorter timescale (Eifelian to lower Givetian Stages), the I/Ca signal shifted from a persistently well-oxygenated conditions in the upper water column in the Onondaga Formation to fluctuating redox in the lower Marcellus subgroup. I/Ca ratios echo the variations in redox-sensitive metal data indicating anoxic bottom water conditions during the onset of organic-rich shale deposition. These variations are broadly consistent with regional fauna turnovers and sea-level

changes. Our results also point to the need to further disentangle the nuanced dynamics between changing atmosphere oxygen level, ocean redox conditions and biotic responses.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

ACKNOWLEDGEMENTS

This work was supported by NSF EAR-1349252, OCE-1232620, and OCE-1736542 to Z.L. and NSF EAR-1455258 to C.K.J. We thank three anonymous reviewers and guest editor Tom Algeo for constructive criticisms and suggestions.

RESEARCH DATA

Data associated with this article can be accessed at <https://doi.org/10.17632/m9xdvpjygh.1>.

APPENDIX A. SUPPLEMENTARY MATERIAL

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.gca.2019.12.019>.

REFERENCES

- Algeo T. J. (2004) Can marine anoxic events draw down the trace element inventory of seawater? *Geology* **32**, 1057–1060.
- Algeo T. J. and Maynard J. B. (2008) Trace-metal covariation as a guide to water-mass conditions in ancient anoxic marine environments. *Geosphere* **4**, 872–887.
- Algeo T. J. and Rowe H. (2012) Paleooceanographic applications of trace-metal concentration data. *Chem. Geol.* **324–325**, 6–18.
- Algeo T. J. and Scheckler S. E. (1998) Terrestrial-marine teleconnections in the Devonian: links between the evolution of land plants, weathering processes, and marine anoxic events. *Philos. Trans. R Soc. London. Ser. B Biol. Sci.* **353**, 113–130.
- Algeo T. J. and Tribovillard N. (2009) Environmental analysis of paleoceanographic systems based on molybdenum–uranium covariation. *Chem. Geol.* **268**, 211–225.
- Arroyave A.Z., 2014. Geological Characterization of the Union Springs Formation, Lower Marcellus Shale in the Appalachian Basin, Central New York. Unpublished M.S. Thesis. Brooklyn College, p. 203.
- Arthur M. A. and Sageman B. B. (2005) Sea-level control on source-rock development: perspectives from the Holocene Black Sea, the mid-Cretaceous Western Interior Basin of North America, and the Late Devonian Appalachian Basin. *Soc. Sediment. Geol. Special Publ.* **82**, 35–59.
- Baird, G.C., Brett, C.E., 1986. Submarine erosion on the dysaerobic seafloor: Middle Devonian corrasional disconformities in the Cayuga Valley region. In: 58th Annual Meeting Guidebook. New York State Geological Association, Ithaca, New York. pp. 23–80.
- Becker R. T., Gradstein F. M. and Hammer O. (2012) The Devonian Period. In *The Geologic Time Scale, 2012* (eds. F. M. Gradstein, J. G. Ogg, M. Schmitz and G. Ogg). Elsevier, New York, pp. 559–601.
- Blakey, R., 2016. Paleogeography and Geologic Evolution of North America. <http://www2.nau.edu/rcb7/nam.html> (accessed at October 15, 2016).
- Blood D. R. and Lash G. G. (2015) Dynamic redox conditions in the Marcellus Shale as recorded by pyrite framboid size distributions. *Geol. Soc. Am. Spec. Pap.* **515**, 153–168.
- Boyer D. L., Owens J. D., Lyons T. W. and Droser M. L. (2011) Joining forces: Combined biological and geochemical proxies reveal a complex but refined high-resolution palaeo-oxygen history in Devonian epeiric seas. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **306**, 134–146.
- Brett, C.E., Baird, G.C., 1994. Depositional sequences, cycles, and foreland basin dynamics in the late Middle Devonian (Givetian) of the Genesee Valley and western Finger Lakes region. In: Brett, E., Scatterday, J. (Eds.), 66th Annual Meeting Guidebook. New York State Geological Association. pp. 505–585.
- Brett C. E. and Baird G. C. (1995) Coordinated stasis and evolutionary ecology of Silurian to Middle Devonian faunas in the Appalachian Basin. In *New Approaches to Speciation in the Fossil Record* (eds. D. H. Erwin and R. L. Anstey). Columbia University Press, New York, pp. 285–315.
- Brett, C.E., Baird, G.C., 1996. Middle Devonian sedimentary cycles and sequences in the northern Appalachian Basin. In: Witzke, B.M., Ludvigson, G.A., Day, J. (Eds.), *Paleozoic Sequence Stratigraphy: Views from the North American Craton*. Geological Society of America Special Paper 306, Boulder, CO. pp. 213–242.
- Brett C. E., Baird G. C., Bartholomew A. J., DeSantis M. K. and Ver Straeten C. A. (2011) Sequence stratigraphy and a revised sea-level curve for the Middle Devonian of eastern North America. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **304**, 21–53.
- Brett C. E., Ivany L. C., Bartholomew A. J., DeSantis M. K. and Baird G. C. (2009) Devonian ecological-evolutionary subunits in the Appalachian Basin: a revision and a test of persistence and discreteness. *Geol. Soc. Lond. Spec. Publ.* **314**, 7–36.
- Canfield D. E., Lyons T. W. and Raiswell R. (1996) A model for iron deposition to euxinic Black Sea sediments. *Am. J. Sci.* **296**, 818–834.
- Chance R., Weston K., Baker A. R., Hughes C., Malin G., Carpenter L., Meredith M. P., Clarke A., Jickells T. D. and Mann P. (2010) Seasonal and interannual variation of dissolved iodine speciation at a coastal Antarctic site. *Mar. Chem.* **118**, 171–181.
- Chen R. and Sharma S. (2016) Role of alternating redox conditions in the formation of organic-rich interval in the Middle Devonian Marcellus Shale, Appalachian Basin USA. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **446**, 85–97.
- Claret F., Lerouge C., Laurieux T., Bizi M., Conte T., Ghestem J. P., Wille G., Sato T., Gaucher E. C., Giffaut E. and Tournassat C. (2010) Natural iodine in a clay formation: Implications for iodine fate in geological disposals. *Geochim. Cosmochim. Acta* **74**, 16–29.
- Clarkson M. O., Stirling C. H., Jenkyns H. C., Dickson A. J., Porcelli D., Moy C. M., von Strandmann P. A. P., Cooke I. R. and Lenton T. M. (2018) Uranium isotope evidence for two episodes of deoxygenation during Oceanic Anoxic Event 2. *Proc. Natl. Acad. Sci.* **115**, 2918–2923.
- Cooper G. A. (1930) Stratigraphy of the Hamilton Group of New York Part I. *Am. J. Sci.* **19**, 116–134.
- Coplen T. B., Brand W. A., Gehre M., Gröning M., Meijer H. A., Toman B. and Verkouteren R. M. (2006) New guidelines for $\delta^{13}\text{C}$ measurements. *Anal. Chem.* **78**, 2439–2441.
- Dahl T. W., Hammarlund E. U., Anbar A. D., Bond D. P., Gill B. C., Gordon G. W., Knoll A. H., Nielsen A. T., Schovsbo N. H. and Canfield D. E. (2010) Devonian rise in atmospheric oxygen

- correlated to the radiations of terrestrial plants and large predatory fish. *Proc. Natl. Acad. Sci.* **107**, 17911–17915.
- Dennison J. M. (1985) Catskill Delta shallow marine strata. *Catskill Delta: Geol. Soc. Am. Spec. Pap.* **201**, 91–106.
- DeSantis M., Brett C. and Ver Straeten C. (2007) Persistent depositional sequences and bioevents in the Eifelian (early Middle Devonian) of eastern Laurentia: North American evidence of the Kačák Events? *Geol. Soc. Lond. Spec. Publ.* **278**, 83–104.
- DeSantis, M.K., 2010. Anatomy of Middle Devonian faunal turnover in eastern North America: Implications for global bioevents at the Eifelian-Givetian stage boundary. Ph.D. thesis. University of Cincinnati.
- DeSantis M. K. and Brett C. E. (2011) Late Eifelian (Middle Devonian) biocrises: timing and signature of the pre-Kačák Bakoven and Stony Hollow events in eastern North America. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **304**, 113–135.
- Edwards C. T., Fike D. A., Saltzman M. R., Lu W. and Lu Z. (2018) Evidence for local and global redox conditions at an Early Ordovician (Tremadocian) mass extinction. *Earth Planet. Sci. Lett.* **481**, 125–135.
- Elderfield H. and Truesdale V. W. (1980) On the biophilic nature of iodine in seawater. *Earth Planet. Sci. Lett.* **50**, 105–114.
- Farrenkopf A. M. and Luther, III, G. W. (2002) Iodine chemistry reflects productivity and denitrification in the Arabian Sea: evidence for flux of dissolved species from sediments of western India into the OMZ. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **49**, 2303–2318.
- Fehn U. (2012) Tracing crustal fluids: applications of natural ^{129}I and ^{36}Cl . *Annu. Rev. Earth Planet. Sci.* **40**, 45–67.
- Frappier A. B., Lindemann R. H. and Frappier B. R. (2015) Stable isotope analysis of Dacryoconarid carbonate microfossils: a new tool for Devonian oxygen and carbon isotope stratigraphy. *Rapid Commun Mass Spectrom.* **29**, 764–774.
- Gensel P. G. and Andrews H. N. (1984) *Plant Life in the Devonian*. Praeger, New York.
- Gensel P. G. and Andrews H. N. (1987) The evolution of early land plants. *Am. Sci.* **75**, 478–489.
- Glasspool I. J. and Scott A. C. (2010) Phanerozoic concentrations of atmospheric oxygen reconstructed from sedimentary charcoal. *Nat. Geosci.* **3**, 627.
- Gordon G. W., Lyons T. W., Arnold G. L., Roe J., Sageman B. B. and Anbar A. D. (2009) When do black shales tell molybdenum isotope tales? *Geology* **37**, 535–538.
- Griffing, D.H., Ver Straeten, C.A., 1991. Stratigraphy and depositional environments of the lower part of the Marcellus Formation (Middle Devonian) in eastern New York State. In: Ebert, J.R. (Ed.), 63rd Annual Meeting Guidebook. New York State Geological Association. pp. 205–224
- Hallam A. and Wignall P. B. (1997) *Mass Extinctions and their Aftermath*. Oxford University Press, UK.
- Hardisty D. S., Lu Z., Bekker A., Diamond C. W., Gill B. C., Jiang G., Kah L. C., Knoll A. H., Loyd S. J., Osburn M. R., Planavsky N. J., Wang C., Zhou X. and Lyons T. W. (2017) Perspectives on Proterozoic surface ocean redox from iodine contents in ancient and recent carbonate. *Earth Planet. Sci. Lett.* **463**, 159–170.
- Hardisty D. S., Lu Z., Planavsky N. J., Bekker A., Philippot P., Zhou X. and Lyons T. W. (2014) An iodine record of Paleoproterozoic surface ocean oxygenation. *Geology* **42**, 619–622.
- Hofmann A. F., Peltzer E. T., Walz P. M. and Brewer P. G. (2011) Hypoxia by degrees: Establishing definitions for a changing ocean. *Deep Sea Res. Part I Oceanogr. Res. Pap.* **58**, 1212–1226.
- House M. R. (1996) The Middle Devonian Kačák Event. *Proc. Ussher Soc.* **9**, 79–84.
- House M. R. (2002) Strength, timing, setting and cause of mid-Palaeozoic extinctions. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **181**, 5–25.
- Jaminski J., Algeo T. J., Maynard J. B. and Hower J. C. (1998) Climatic origin of dm-scale compositional cyclicity in the Cleveland Member of the Ohio Shale (Upper Devonian), Central Appalachian Basin, USA. In *Shales and Mudstones* (eds. J. Schieber, W. Zimmerle and P. S. Sethi). Schweizerbart'sche, Stuttgart, pp. 217–242.
- Junium C. K. and Arthur M. A. (2007) Nitrogen cycling during the Cretaceous, Cenomanian-Turonian oceanic anoxic event II. *Geochem. Geophys. Geosyst.* **8**.
- Kelly A. A., Cohen P. A. and Boyer D. L. (2019) Tiny keys to unlocking the Kellwasser events: detailed characterization of organic walled microfossils associated with extinction in Western New York State. *Palaia* **34**, 96–104.
- Kennedy H. and Elderfield H. (1987a) Iodine diagenesis in non-pelagic deep-sea sediments. *Geochim. Cosmochim. Acta* **51**, 2505–2514.
- Kennedy H. and Elderfield H. (1987b) Iodine diagenesis in pelagic deep-sea sediments. *Geochim. Cosmochim. Acta* **51**, 2489–2504.
- Koch W. and Boucot A. (1982) Temperature fluctuations in the Devonian Eastern Americas realm. *J. Paleontol.*, 240–243.
- Kohl D., Slingerland R., Arthur M., Bracht R. and Engelder T. (2014) Sequence stratigraphy and depositional environments of the Shamokin (Union Springs) Member, Marcellus Formation, and associated strata in the middle Appalachian Basin. *AAPG Bull.* **98**, 483–513.
- Krause A. J., Mills B. J., Zhang S., Planavsky N. J., Lenton T. M. and Poulton S. W. (2018) Stepwise oxygenation of the Paleozoic atmosphere. *Nat. Commun.* **9**, 4081.
- Kump L. (1988) Terrestrial feedback in atmospheric oxygen regulation by fire and phosphorus. *Nature* **335**, 152.
- Küpper F. C., Feiters M. C., Olofsson B., Kaiho T., Yanagida S., Zimmermann M. B., Carpenter L. J., Luther, III, G. W., Lu Z. and Jonsson M. (2011) Commemorating two centuries of iodine research: an interdisciplinary overview of current research. *Angew. Chem. Int. Ed.* **50**, 11598–11620.
- Lash G. G. (2016) Hyperpycnal transport of carbonaceous sediment – Example from the Upper Devonian Rhinestreet Shale, western New York, U.S.A. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **459**, 29–43.
- Lash G. G. (2017) A multiproxy analysis of the Frasnian-Famennian transition in western New York State, U.S.A. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **473**, 108–122.
- Lash G. G. and Blood D. R. (2014) Organic matter accumulation, redox, and diagenetic history of the Marcellus Formation, southwestern Pennsylvania, Appalachian basin. *Mar. Pet. Geol.* **57**, 244–263.
- Lenton T. M., Dahl T. W., Daines S. J., Mills B. J., Ozaki K., Saltzman M. R. and Porada P. (2016) Earliest land plants created modern levels of atmospheric oxygen. *Proc. Natl. Acad. Sci.* **113**, 9704–9709.
- Lindholm, R.C., 1967. Petrology of the Onondaga Limestone (Middle Devonian), New York. Unpublished Ph.D. dissertation. Johns Hopkins University, p. 188.
- Lindholm R. C. (1969) Carbonate petrology of the Onondaga Limestone (Middle Devonian), New York; a case for calcisiltite. *J. Sediment. Res.* **39**, 268–275.
- Liu J., Algeo T. J., Jaminski J., Kuhn T. and Joachimski M. M. (2019) Evaluation of high-frequency paleoenvironmental variation using an optimized cyclostratigraphic framework: Example for C-S-Fe analysis of Devonian-Mississippian black shales (Central Appalachian Basin, U.S.A.). *Chem. Geol.* **525**, 303–320.

- Lu W., Ridgwell A., Thomas E., Hardisty D. S., Luo G., Algeo T. J., Saltzman M. R., Gill B. C., Shen Y., Ling H.-F., Edwards C. T., Whalen M. T., Zhou X., Gutchess K. M., Jin L., Rickaby R. E. M., Jenkyns H. C., Lyons T. W., Lenton T. M., Kump L. R. and Lu Z. (2018) Late inception of a resiliently oxygenated upper ocean. *Science* **361**, 174–177.
- Lu W., Wöhrndle S., Halverson G. P., Zhou X., Bekker A., Rainbird R. H., Hardisty D. S., Lyons T. W. and Lu Z. (2017) Iodine proxy evidence for increased ocean oxygenation during the Bitter Springs Anomaly. *Geochem. Perspect. Lett.* **5**, 53–57.
- Lu Z., Hoogakker B. A., Hillenbrand C.-D., Zhou X., Thomas E., Gutchess K. M., Lu W., Jones L. and Rickaby R. E. (2016) Oxygen depletion recorded in upper waters of the glacial Southern Ocean. *Nat. Commun.* **7**, 11146.
- Lu Z., Hummel S. T., Lautz L. K., Hoke G. D., Zhou X., Leone J. and Siegel D. I. (2015) Iodine as a sensitive tracer for detecting influence of organic-rich shale in shallow groundwater. *Appl. Geochem.* **60**, 29–36.
- Lu Z., Jenkyns H. C. and Rickaby R. E. M. (2010) Iodine to calcium ratios in marine carbonate as a paleo-redox proxy during oceanic anoxic events. *Geology* **38**, 1107–1110.
- Lyons T. W. and Severmann S. (2006) A critical look at iron paleoredox proxies: New insights from modern euxinic marine basins. *Geochim. Cosmochim. Acta* **70**, 5698–5722.
- McGhee G. R., Clapham M. E., Sheehan P. M., Bottjer D. J. and Droser M. L. (2013) A new ecological-severity ranking of major Phanerozoic biodiversity crises. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **370**, 260–270.
- Meyer-Berthaud B., Scheckler S. E. and Wendt J. (1999) *Archaeopteris* is the earliest known modern tree. *Nature* **398**, 700–701.
- Meyer-Berthaud B., Soria A. and Decombeix A. L. (2010) The land plant cover in the Devonian: a reassessment of the evolution of the tree habit. *Geol. Soc. Lond. Spec. Publ.* **339**, 59–70.
- Meyers P. A. and Bernasconi S. M. (2005) Carbon and nitrogen isotope excursions in mid-Pleistocene sapropels from the Tyrrhenian Basin: Evidence for climate-induced increases in microbial primary production. *Mar. Geol.* **220**, 41–58.
- Muramatsu Y. and Wedepohl K. H. (1998) The distribution of iodine in the earth's crust. *Chem. Geol.* **147**, 201–216.
- Murphy A. E., Sageman B. B., Hollander D. J., Lyons T. W. and Brett C. E. (2000) Black shale deposition and faunal overturn in the Devonian Appalachian Basin: Clastic starvation, seasonal water-column mixing, and efficient biolimiting nutrient recycling. *Paleoceanography* **15**, 280–291.
- Podder J., Lin J., Sun W., Botis S. M., Tse J., Chen N., Hu Y., Li D., Seaman J. and Pan Y. (2017) Iodate in calcite and vaterite: Insights from synchrotron X-ray absorption spectroscopy and first-principles calculations. *Geochim. Cosmochim. Acta* **198**, 218–228.
- Rast, N., Skehan, J.W., 1993. Mid-Paleozoic orogenesis in the North Atlantic: the Acadian orogeny. In: Roy, D.C., Skehan, J. W. (Eds.), *The Acadian Orogeny: Recent Studies in New England, Maritime Canada and the Autochthonous Foreland*. Geological Society of America Special Paper 275, Boulder, Colorado. pp. 1–25.
- Rimmer S. M. (2004) Geochemical paleoredox indicators in Devonian-Mississippian black shales, Central Appalachian Basin (USA). *Chem. Geol.* **206**, 373–391.
- Sageman B. B., Murphy A. E., Werne J. P., Ver Straeten C. A., Hollander D. J. and Lyons T. W. (2003) A tale of shales: the relative roles of production, decomposition, and dilution in the accumulation of organic-rich strata, Middle-Upper Devonian, Appalachian basin. *Chem. Geol.* **195**, 229–273.
- Sallan L. C. and Coates M. I. (2010) End-Devonian extinction and a bottleneck in the early evolution of modern jawed vertebrates. *Proc. Natl. Acad. Sci.* **107**, 10131–10135.
- Schieber J. (1994) Evidence for high-energy events and shallow-water deposition in the Chattanooga Shale, Devonian, central Tennessee, USA. *Sediment. Geol.* **93**, 193–208.
- Schieber J. (2009) Discovery of agglutinated benthic foraminifera in Devonian black shales and their relevance for the redox state of ancient seas. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **271**, 292–300.
- Sperling E. A., Wolock C. J., Morgan A. S., Gill B. C., Kunzmann M., Halverson G. P., Macdonald F. A., Knoll A. H. and Johnston D. T. (2015) Statistical analysis of iron geochemical data suggests limited late Proterozoic oxygenation. *Nature* **523**, 451.
- Stein W. E., Mannolini F., Hernick L. V., Landing E. and Berry C. M. (2007) Giant cladoxyploid trees resolve the enigma of the Earth's earliest forest stumps at Gilboa. *Nature* **446**, 904–907.
- Truesdale V. W. and Bailey G. W. (2000) Dissolved iodate and total iodine during an extreme hypoxic event in the Southern Benguela system. *Estuar. Coast. Shelf Sci.* **50**, 751–760.
- Uveges B. T., Junium C. K., Boyer D. L., Cohen P. A. and Day J. E. (2018) Biogeochemical controls on black shale deposition during the Frasnian-Famennian biotic crisis in the Illinois and Appalachian Basins, USA, inferred from stable isotopes of nitrogen and carbon. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*
- van Staal, C.R., Whalen, J.B., McNicoll, V.J., Pehrsson, S., Lissenberg, C.J., Zagorevski, A., van Breemen, O., Jenner, G. A., 2007. The Notre Dame arc and the Taconic orogeny in Newfoundland. In: Hatcher Jr., R.D., Carlson, M.P., McBride, J.H., Martínez Catalán, J.R. (Eds.), *4-D Framework of Continental Crust: Geological Society of America Memoir* 200. pp. 511–552.
- van Staal C. R., Whalen J. B., Valverde-Vaquero P., Zagorevski A. and Rogers N. (2009) Pre-Carboniferous, episodic accretion-related, orogenesis along the Laurentian margin of the northern Appalachians. *Geol. Soc. Lond. Spec. Publ.* **327**, 271–316.
- Ver Straeten, C.A., 1994. Microstratigraphy and depositional environments of a Middle Devonian foreland basin: Berne and Otsego Members, Mount Marion Formation, eastern New York State. In: Landing, E. (Ed.), *Studies in Stratigraphy and Paleontology in Honor of Donald W. Fisher*. New York State Museum Bulletin 481, Albany. pp. 367–380.
- Ver Straeten, C.A., 2007. Basinwide stratigraphic synthesis and sequence stratigraphy, upper Pragian, Emsian and Eifelian stages (Lower to Middle Devonian), Appalachian Basin. In: Becker, R.T., Kirchgasser, W.T. (Eds.), *Devonian Events and Correlations*. Special Publication 278, Geological Society of London, London. pp. 39–81.
- Ver Straeten, C.A., Baird, G.C., Brett, C.E., Lash, G., Over, D.J., Karaca, C., Jordan, T., Blood, R., 2011a. The Marcellus subgroup in its type area, Finger Lakes area of New York, and beyond. In: *83rd Annual Meeting Guidebook*. New York State Geological Association. pp. 23–86.
- Ver Straeten C. A. and Brett C. E. (2006) Pragian to Eifelian strata (middle Lower to lower Middle Devonian), northern Appalachian Basin-stratigraphic nomenclatural changes. *Northeastern Geol. Environ. Sci.* **28**, 80.
- Ver Straeten C. A., Brett C. E. and Sageman B. B. (2011b) Mudrock sequence stratigraphy: a multi-proxy (sedimentological, paleobiological and geochemical) approach, Devonian Appalachian Basin. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **304**, 54–73.

- Ver Straeten, C.A., Griffing, D.H., Brett, C.E., 1994. The lower part of the Middle Devonian Marcellus ‘shale,’ central to western New York State: stratigraphy and depositional history. In: 66th Annual Meeting Field Trip Guidebook. New York State Geological Association. pp. 271–321.
- Wallace M. W., Shuster A., Greig A., Planavsky N. J. and Reed C. P. (2017) Oxygenation history of the Neoproterozoic to early Phanerozoic and the rise of land plants. *Earth Planet. Sci. Lett.* **466**, 12–19.
- Wei H., Wang X., Shi X., Jiang G., Tang D., Wang L. and An Z. (2019) Iodine content of the carbonates from the Doushantuo Formation and shallow ocean redox change on the Ediacaran Yangtze Platform South China. *Precambrian Res.* **322**, 160–169.
- Werne J. P., Sageman B. B., Lyons T. W. and Hollander D. J. (2002) An integrated assessment of a “type euxinic” deposit: evidence for multiple controls on black shale deposition in the Middle Devonian Oatka Creek Formation. *Am. J. Sci.* **302**, 110–143.
- White D. A., Elrick M., Romaniello S. and Zhang F. (2018) Global seawater redox trends during the Late Devonian mass extinction detected using U isotopes of marine limestones. *Earth Planet. Sci. Lett.* **503**, 68–77.
- Wignall P. B. and Myers K. J. (1988) Interpreting benthic oxygen levels in mudrocks: a new approach. *Geology* **16**, 452.
- Wignall P. B. and Twitchett R. J. (1996) Oceanic anoxia and the end Permian mass extinction. *Science* **272**, 1155–1158.
- Wong G. T. F. and Brewer P. G. (1977) The marine chemistry of iodine in anoxic basins. *Geochim. Cosmochim. Acta* **41**, 151–159.
- Young S. A., Kleinberg A. and Owens J. D. (2019) Geochemical evidence for expansion of marine euxinia during an early Silurian (Llandovery–Wenlock boundary) mass extinction. *Earth Planet. Sci. Lett.* **513**, 187–196.
- Zheng Y., Anderson R. F., van Geen A. and Kuwabara J. (2000) Authigenic molybdenum formation in marine sediments: a link to pore water sulfide in the Santa Barbara Basin. *Geochim. Cosmochim. Acta* **64**, 4165–4178.
- Zhou X., Jenkyns H. C., Lu W., Hardisty D. S., Owens J. D., Lyons T. W. and Lu Z. (2017) Organically bound iodine as a bottom-water redox proxy: Preliminary validation and application. *Chem. Geol.* **457**, 95–106.
- Zhou X., Jenkyns H. C., Owens J. D., Junium C. K., Zheng X.-Y., Sageman B. B., Hardisty D. S., Lyons T. W., Ridgwell A. and Lu Z. (2015) Upper ocean oxygenation dynamics from I/Ca ratios during the Cenomanian-Turonian OAE 2. *Paleoceanography* **30**, 510–526.

Associate editor: Thomas Algeo