

Applying carbon-isotope stratigraphy using well cuttings for high-resolution chemostratigraphic correlation of the subsurface

J. Garrecht Metzger, David A. Fike, and L. B. Smith

ABSTRACT

Basin-scale correlations in the subsurface generally rely on lithostratigraphic information synthesized from wireline logs, and, in some cases, well cuttings, and cores. However, lithostratigraphic boundaries are often diachronous, and, as such, the correlations based upon them may not provide reliable timelines. In this paper, we use $\delta^{13}\text{C}_{\text{carb}}$ data from well cuttings and a core to generate chronostratigraphic logs of Late Ordovician strata spanning the Black River Group, Trenton Group, and Utica Shale across the subsurface of New York State. Although particular $\delta^{13}\text{C}_{\text{carb}}$ values may be impacted by (primary) variability in local dissolved inorganic carbon reservoirs and/or (secondary) diagenetic alteration, it is possible to identify spatially and stratigraphically coherent patterns in $\delta^{13}\text{C}_{\text{carb}}$, which can be used to effectively correlate time-equivalent strata on a basin-wide (or even global) scale, including across lithologies (e.g., between limestone and calcareous shale). The present study emphasizes the use of well cuttings, as these are commonly collected during drilling and can provide the maximum lateral resolution for subsurface correlation. Parallel geochemical (percent carbonate and total organic carbon) and isotopic ($\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$) data are used to understand the origin of stratigraphic and spatial variability in the $\delta^{13}\text{C}_{\text{carb}}$ signal and to identify diagenetic alteration. Stratigraphically coherent $\delta^{13}\text{C}_{\text{carb}}$ trends across New York were used to identify six isotopically distinct packages of time-equivalent strata within these formations. Pairing chemostratigraphic and lithostratigraphic data improves our ability to document the diachronous nature of

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lithologic contacts, including the base of the Utica Shale, which is progressively younger moving west through New York.

INTRODUCTION

Several chronostratigraphic tools can be combined with lithostratigraphy for the temporal correlation of strata. Radiometric dating of detrital minerals in ash beds (e.g., U/Pb or Ar/Ar) provides a means for absolute time determination in sedimentary strata (Bowring et al., 1993; Goldman et al., 1994; Berkley and Baird, 2002; Maloof et al., 2005; Ramezani et al., 2007). These approaches, however, are often difficult to apply in the subsurface because ash beds are infrequently deposited, limited subsurface volcanic materials may be available for sampling, and the resulting age resolution may be too coarse for fine-scale correlations. When ash beds are not present, radiometric ages of organic-rich strata can be obtained using rhenium–osmium (Re–Os) isotopes; however, this approach is unlikely to provide sufficient resolution (<1 m.y.) for fine-scale correlations (e.g., Selby and Creaser, 2005; Selby et al., 2009), and the potential impact of diagenesis on the resulting Re–Os ages remains poorly understood. Biostratigraphy is a powerful tool for chronostratigraphic correlation of strata on a local, regional, and global scale (Goldman et al., 1994; Brett, 1995; Patzkowsky, 1995; Kirchner and Brett, 2008). Although biostratigraphy can often be productively applied in the subsurface (Gartner et al., 1983; Gradstein et al., 1988; Gradstein et al., 1992; Armentrout, 1996; Witrock et al., 2003), challenges can arise from the limited sample availability from cores and destruction of larger biostratigraphically relevant fossils during generation of cuttings fragments. These challenges are most pronounced in the Paleozoic before the rise of abundant planktonic microfossils (e.g., foraminifera, coccolithophores) that are so useful for Mesozoic and Cenozoic biostratigraphy (see Witrock et al., 2003).

Isotope chemostratigraphy has the potential to generate high-resolution chronostratigraphic correlations. The stable isotope composition of marine carbonates $\delta^{13}\text{C}_{\text{carb}} = \{({}^{13}\text{C}/{}^{12}\text{C})_{\text{sample}} / ({}^{13}\text{C}/{}^{12}\text{C})_{\text{standard}} - 1\} \times 1,000$ in units of per mil (‰) relative to the Vienna-PeeDee Belemnite [V-PDB] standard) records the coeval carbon isotopic composition of ambient dissolved inorganic carbon (DIC) in the ocean. Changes in $\delta^{13}\text{C}_{\text{DIC}}$ are thought to primarily derive from changes in the global burial flux of organic carbon, which is enriched in ${}^{12}\text{C}$, the lighter stable isotope of carbon, relative to the local DIC pool, and can occur at time-scales greater than 10^3 years (Mitchell et al., 1996; Hayes et al., 1999; Kump and Arthur, 1999; Saltzman, 2003). Increased burial of organic matter with low $\delta^{13}\text{C}$ values, results in a concomitant

increase in $\delta^{13}\text{C}$ of the marine DIC reservoir from which it is derived. Because $\delta^{13}\text{C}_{\text{DIC}}$ is well mixed in the surface ocean on the thousand-year time scale, coeval carbonates from around the globe preserve similar $\delta^{13}\text{C}_{\text{carb}}$ signatures, which enable high-resolution correlation of strata across vast distances. However, the preservation of a global $\delta^{13}\text{C}_{\text{carb}}$ signature can be overprinted either by (primary) environmental variability in the local $\delta^{13}\text{C}_{\text{DIC}}$ composition (Gruber et al., 1999) or by (secondary) diagenetic alteration (Patterson and Walter, 1994); chemostratigraphic data need to be screened to assess these impacts and reconstruct representative $\delta^{13}\text{C}_{\text{carb}}$ records. The resulting time-varying $\delta^{13}\text{C}_{\text{carb}}$ patterns preserved in marine carbonates have been used extensively to correlate both outcrop and subsurface sections from around the globe (Knoll et al., 1986; Burns and Matter, 1993; Hayes et al., 1999; Pancost et al., 1999; Veizer et al., 1999; Saltzman et al., 2000; Herrle et al., 2004; Tsikos et al., 2004; Fike et al., 2006; Hesselbo et al., 2007; Young et al., 2008; Maloof et al., 2010; Jones et al., 2011; Sabatino et al., 2013). Yet, the majority of existing chemostratigraphic work has focused on generating a time-series record of particular paleoenvironmental conditions (e.g., ocean redox) or global (basin-to-basin) stratigraphic correlation; such studies do not often have a sampling density sufficient to generate high-resolution chronostratigraphic tie points within individual basins. Furthermore, with limited sampling locations within a basin, it is difficult to assess local variability in $\delta^{13}\text{C}_{\text{carb}}$ (e.g., arising from spatial gradients in ocean chemistry or subsequent diagenetic alteration) that may be superimposed on the primary temporal signal of interest (Patterson and Walter, 1994; Immenhauser et al., 2003; Swart and Eberli, 2005; Swart, 2008). Diagenetic alteration typically results from precipitation of carbonate cements in pore waters, wherein bacterial processes have altered the local $\delta^{13}\text{C}_{\text{DIC}}$ composition (e.g., through respiration: Coleman and Raiswell, 1981; or methanogenesis: Hein et al., 2006). Alternatively, later-stage recrystallization of carbonates can produce alteration under the influence of meteoric or basinal fluids in which ambient $\delta^{13}\text{C}_{\text{DIC}}$ has been similarly impacted by oxidation of organic matter (Allan and Matthews, 1982; Joachimski, 1994; Swart and Kennedy 2012).

Here, by combining chemo- and lithostratigraphic data from multiple subsurface boreholes, we demonstrate the potential of $\delta^{13}\text{C}_{\text{carb}}$ -based approaches for high-resolution intrabasinal correlations, assessment of diagenetic alteration, and the identification of diachronous lithostratigraphic contacts. The resulting $\delta^{13}\text{C}_{\text{carb}}$ chemostratigraphy can be used to reconstruct how sedimentation and facies varied across a basin as a function of space and time.

The purpose of this study is fivefold: (1) to collect $\delta^{13}\text{C}_{\text{carb}}$ data from a series of core and cuttings samples from multiple subsurface wells; (2) to assess respective impacts of cuttings-sample resolution (vertical) and well density (lateral) on the ability to resolve $\delta^{13}\text{C}_{\text{carb}}$ signals in a single well and across a region; (3) to evaluate diagenetic alteration of $\delta^{13}\text{C}_{\text{carb}}$ in cuttings samples; (4) to produce chemostratigraphic logs suitable for correlation through the Late Ordovician subsurface strata of New York State (Figure 1); and (5) to identify stratigraphic intervals with distinctive $\delta^{13}\text{C}_{\text{carb}}$ character that can be used for basin-wide correlation. By focusing on ubiquitous cuttings samples, we hope to encourage the broad application of these techniques for the correlation of source rock and reservoir strata in basins of varying age from around the world.

GEOLOGIC CONTEXT

The study interval ranges from the Beekmantown Group, which straddles the Cambrian–Ordovician boundary, through the Upper Ordovician Black River Group, Trenton Group, and Utica Shale (Figure 2). The lowermost unit of the study is the Beekmantown Group, composed of the Upper Cambrian Galway Formation, Little Falls Dolomite, and the more limestone-rich Lower Ordovician Tribes Hill Formation (Smith, 2006). The Beekmantown Group is at least partially equivalent with the Knox Group of the southern United States (e.g., Tennessee; Patchen et al., 2006). Beekmantown strata are truncated by the Knox unconformity, a major unconformity that spans most of the Lower Ordovician and all of Middle Ordovician time in the New York area (Patchen et al., 2006).

Overlying the Knox unconformity, the Upper Ordovician Black River Group consists of clean to

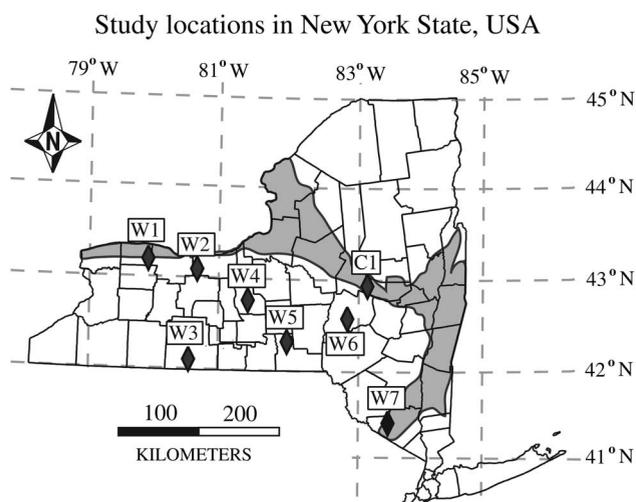


Figure 1. Outcrop map of Late Ordovician sedimentary rocks (gray) and study locations (black diamonds). Map modified from Dicken et al. (2008). For study location information, see Table 1.

argillaceous burrowed limestones, variably dolomitized, that were deposited on a regionally extensive peritidal to subtidal ramp (Keith 1989; Patchen et al., 2006). The Black River Group lithology is uniform over large distances extending as far west as Missouri (Thompson, 1991). The Black River Group is overlain unconformably by the Trenton Group (Mitchell et al., 2004), although in places Trenton Group strata are found directly above the Knox unconformity.

The Trenton Group is primarily composed of limestone and argillaceous limestone and was deposited in a subtidal environment in central and western New York with deeper basinal sections deposited in the east (Brett and Baird, 2002). Lithologies are varied, ranging from muddy, light gray and brown, mostly pure carbonates to dark, organic-rich calcareous shales. Rocks are most often muddy, but do contain shelly lag beds, arenites, and other coarser grained materials (e.g., Brett and Baird, 2002). In the western and central parts of New York, the Trenton Group is capped by the Thruway disconformity (Baird and Brett, 2002; Brett and Baird, 2002), which cuts down into progressively older strata to the south and east. Where present, the Thruway disconformity is overlain by the Utica Shale; where the disconformity is absent in southeastern New York, the Trenton grades upward into the Utica Shale.

In eastern New York, the dark gray to black facies of Mohawkian (Middle Ordovician North American stage) and Cincinnati (Upper Ordovician North American stage) strata are referred to here as the Utica Shale, which comprises the Flat Creek and Indian Castle shale members (after Brett and Baird, 2002). The Utica Shale is composed of variably calcareous shales with infrequent micritic beds, with colors ranging from gray to black. Deposition of the Trenton Group and Utica Shale is concurrent with the last stage of the Taconic orogeny (van Staal and Barr, 2012). At this time, organic-rich strata were deposited in a zone between the shallow marine carbonates of the Trenton to the west and deep-water turbidite facies found in eastern New York (Smith, 2010). The Lorraine Shale overlies the Utica Shale and has upward-increasing sand and silt content.

Despite much study, it remains uncertain how to best correlate the Trenton Group of western New York with the Utica Shale of the eastern part of the state (Figure 2), and multiple different correlations have been proposed (see Brett and Baird, 2002 for an in-depth discussion of correlation history). Outcrop-based correlations using lithostratigraphic, biostratigraphic, and K-bentonite data suggest that the Trenton Group–Utica Shale contact is time-transgressive with a younger Utica Shale base in the west (Brett and Baird, 2002). Specifically, the calcareous and organic-rich Flat Creek, Dolgeville, and lower Indian Castle units are thought to be time-equivalent to the Trenton Group, whereas the upper Indian Castle member (Utica Shale) is younger than the Trenton Group in New York State. Additional work, particularly in the subsurface, is needed to further clarify geographic and temporal relationships of the Trenton Group–Utica Shale interval.

METHODS

Geophysical wireline and geological sample logs were obtained from the Empire State Oil and Gas Information system (<http://esogis.nysm.nysed.gov/>). A list of all wells and cores used in this study can be found in Table 1. Hereafter, wells are referred to by a five-digit numerical identifier; the full API 10-digit identifier and well location can be found in Table 1.

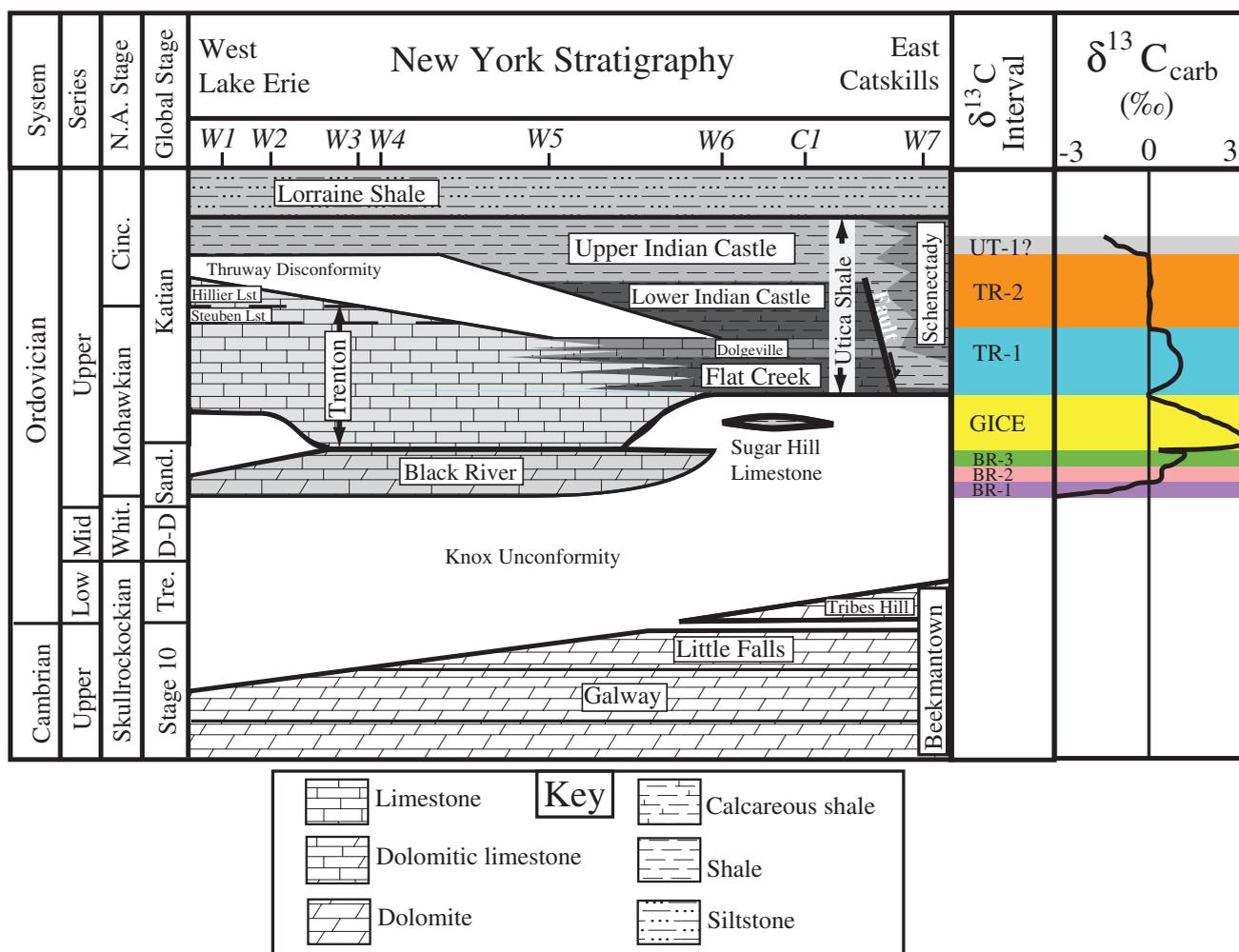


Figure 2. Chronostratigraphic relationships of Upper Ordovician formations in New York (left), generalized $\delta^{13}\text{C}_{\text{carb}}$ intervals and $\delta^{13}\text{C}_{\text{carb}}$ chemostratigraphic profiles (right, see discussion in text). Stage abbreviations are Whit = Whiterockian, Cinc = Cincinnati, Sand = Sandbian, D-D = Darrivilian to Dapingian, Tre = Tremadocian. New $\delta^{13}\text{C}_{\text{carb}}$ intervals (BR = Black River Group, TR = Trenton Group, UT = Utica Shale) are named for lowest formation they are found in. GICE = Guttenberg isotopic carbon excursion (see text). “?” next to UT-1 suggests interval is not suitable for correlation (see Discussion). $\delta^{13}\text{C}_{\text{carb}}$ reference curve with intervals taken from data in this work. Values are in per mil (‰) relative to V-PDB. Study locations (W1–W7, C1) are shown in their approximate position along the west to east transect.

Lithologies for stratigraphic columns were obtained from geologic sampling logs for each well and were described by a geologist soon after the well was completed. Gamma-ray values for core C1 were obtained using a CoreLab Instruments Spectral Gamma Logger Model SGL-300 at the Ohio Department of Natural Resources Division of Geological Survey. Calibration was run each day with American Petroleum Institute (API) standards 0 and 200 (API units).

Cuttings samples were collected from the New York State Geologic Survey and cataloged at

Washington University. A representative subsample of each cuttings sample was collected for analyses. Cuttings were collected into stratigraphic intervals of ~0.5 to 9 m (1.6 to 30 ft) at the borehole and therefore represent a lithologic average over that interval. To help assess the impact of lithologic mixing in the analysis of cuttings samples, several individual carbonate chips were taken from selected intervals in well W7. When picking individual chips, those with macroscopic pyrite, recrystallized material, or macroscopic spar were excluded. Individual chips were powdered for chip-specific analysis, alongside

Table 1. Well and core information

Well ID	Type	AP#	Operator	County	Well Name	Lat. (°)	Long. (°)	S13Ccarb ref.
W1	Cuttings	31-073-09540	Consolidated Gas Supply Corp.	Orleans	Maxon Roger 1	43.1885	-78.0376	Smith, 2006; this paper
W2	Cuttings	31-117-04754	William J. Duscherer	Wayne	Smith Frank 1	43.0824	-77.2696	Smith, 2006; this paper
W3	Cuttings	31-101-03924	Dominion Transmission Inc.	Steuben	Olin 1	42.0631	-77.4303	This paper
W4	Cuttings	31-011-23158	Hensoil Inc.	Cayuga	Carter 1	42.7843	-76.5421	This paper
W5	Cuttings	31-007-05087	Fenix and Scisson Inc.	Broome	Richards 1	42.3235	-75.9474	This paper
W6	Cuttings	31-077-10834	Amoco Production Company	Otsego	Hoose 1	42.9291	-74.7438	This paper
W7	Cuttings	31-071-01001	Croms-Well Inc.	Orange	Fee High Barney 1	41.4246	-74.4539	This paper
C1	Core	NA	National Lead Company	Montgomery	NA	42.9291	-74.7438	This paper

API = American Petroleum Institute.

aggregated subsamples (~0.5 g [~0.02 oz], representing ~10% total cuttings mass) and bulk-homogenized powder. For other samples, cuttings were homogenized by powdering 0.5–10 g (0.02–0.4 oz) of samples. Core samples were microdrilled to collect powders for isotopic and geochemical analysis.

Weight % carbonate minerals (%_{carb}) was determined by gravimetric analyses following the dissolution of 0.1 to 0.5 g (0.004 to 0.02 oz) of powder with 6M HCl at Washington University. Complete dissolution of carbonate fraction was obtained by addition of excess acid and agitation on a shaker table for >12 hours. Total organic carbon (TOC) was measured at Washington University by combustion of homogenized acid-insoluble residues on a Costech ECS 4010 Elemental Analyzer, whereby the emitted CO₂ was quantified and calibrated against standards of known TOC compositions. Additional TOC for well W7 was measured at the New York State Museum on a UIC Coulometrics CM 5130 Acidification module.

Stable isotope analyses were conducted at Washington University. Carbon isotopes are reported as $\delta^{13}\text{C}_{\text{carb}} = \{(^{13}\text{C}/^{12}\text{C})_{\text{sample}} / (^{13}\text{C}/^{12}\text{C})_{\text{standard}} - 1\} \times 1,000$ in units of per mil relative to the V-PDB standard. Oxygen isotopes are reported as $\delta^{18}\text{O}_{\text{carb}} = \{(^{18}\text{O}/^{16}\text{O})_{\text{sample}} / (^{18}\text{O}/^{16}\text{O})_{\text{standard}} - 1\} \times 1,000$ in units of per mil relative to the V-PDB standard. Carbonates ($\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$) were analyzed on a Gas Bench II attached to a ThermoFischer Delta V Plus isotope ratio mass spectrometer. A test set of samples were roasted at 380°C (716°F) for ~12 hours to liberate volatile organic compounds and revealed no systematic offset for $\delta^{13}\text{C}_{\text{carb}}$ and a minor (<~0.3‰) effect on $\delta^{18}\text{O}_{\text{carb}}$ in roasted and unroasted samples. The effect on $\delta^{18}\text{O}_{\text{carb}}$ was too small relative to the magnitude of $\delta^{18}\text{O}_{\text{carb}}$ to impact our interpretations. Therefore, the remaining samples were not roasted prior to $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ analysis. Additional carbonate analyses were done at the University of Albany using a GV Instruments Optima mass spectrometer for well W1 and portions of W2. Calibration of $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ was done by comparison to International Atomic Energy Association standards NBS-19 and NBS-18, National Institute of Standards and Technology standard LSVEC, and in-house standards. Long-term running reproducibility

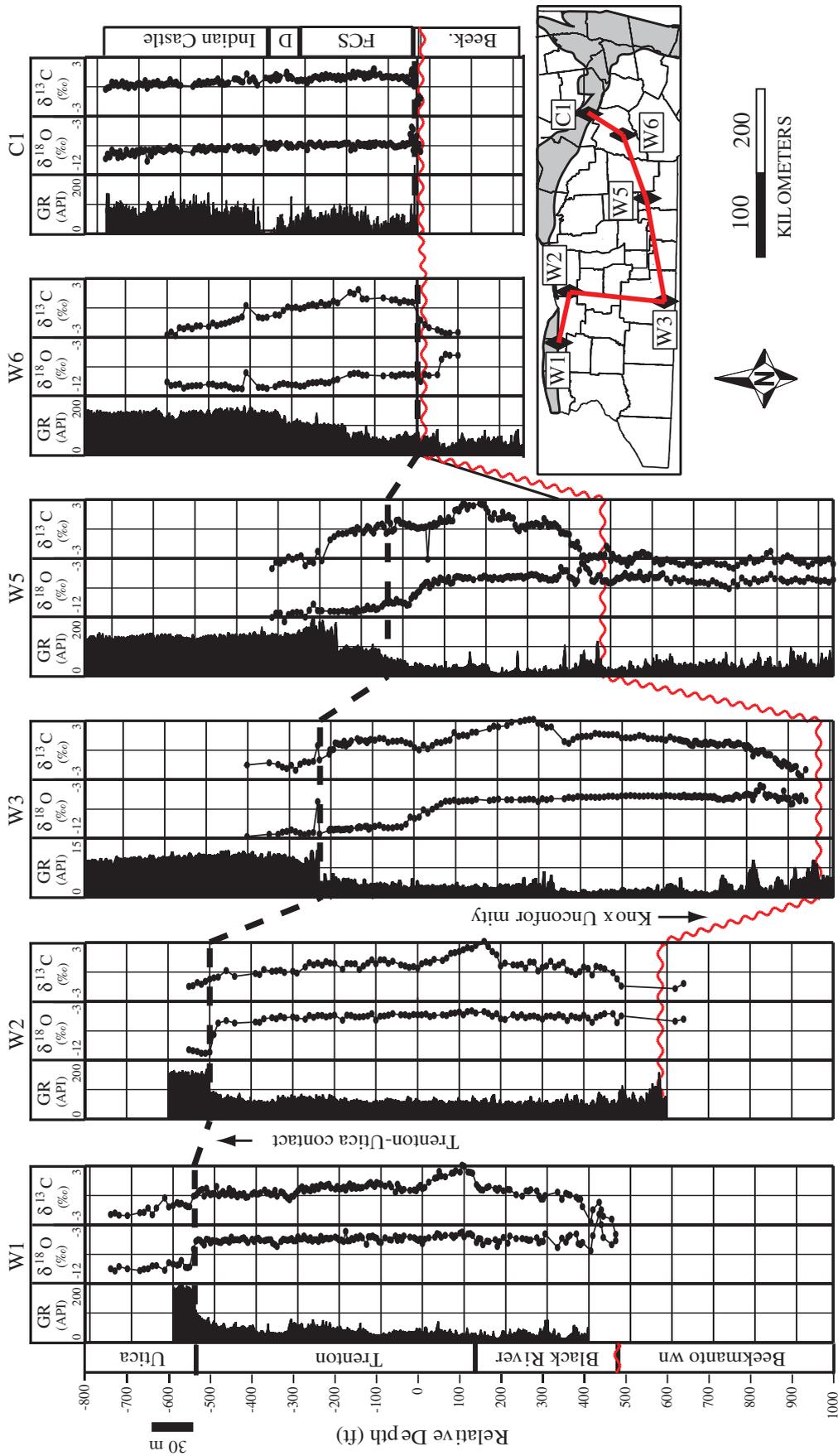


Figure 3. $\delta^{13}\text{C}_{\text{carbr}}$, $\delta^{18}\text{O}_{\text{carbr}}$, and gamma-ray log data for select wells. Isotope values are in per mil (‰) relative to V-PDB. D = Dolgeville, FCS = Flat Creek Shale. Formations unmarked below FCS in core C1 are Sugar River Limestone and Black River Group (see text). Map shows transect through these wells with Trenton–Utica outcrop belt shown in gray. Where gamma-ray logs are truncated, data were not available.

W6

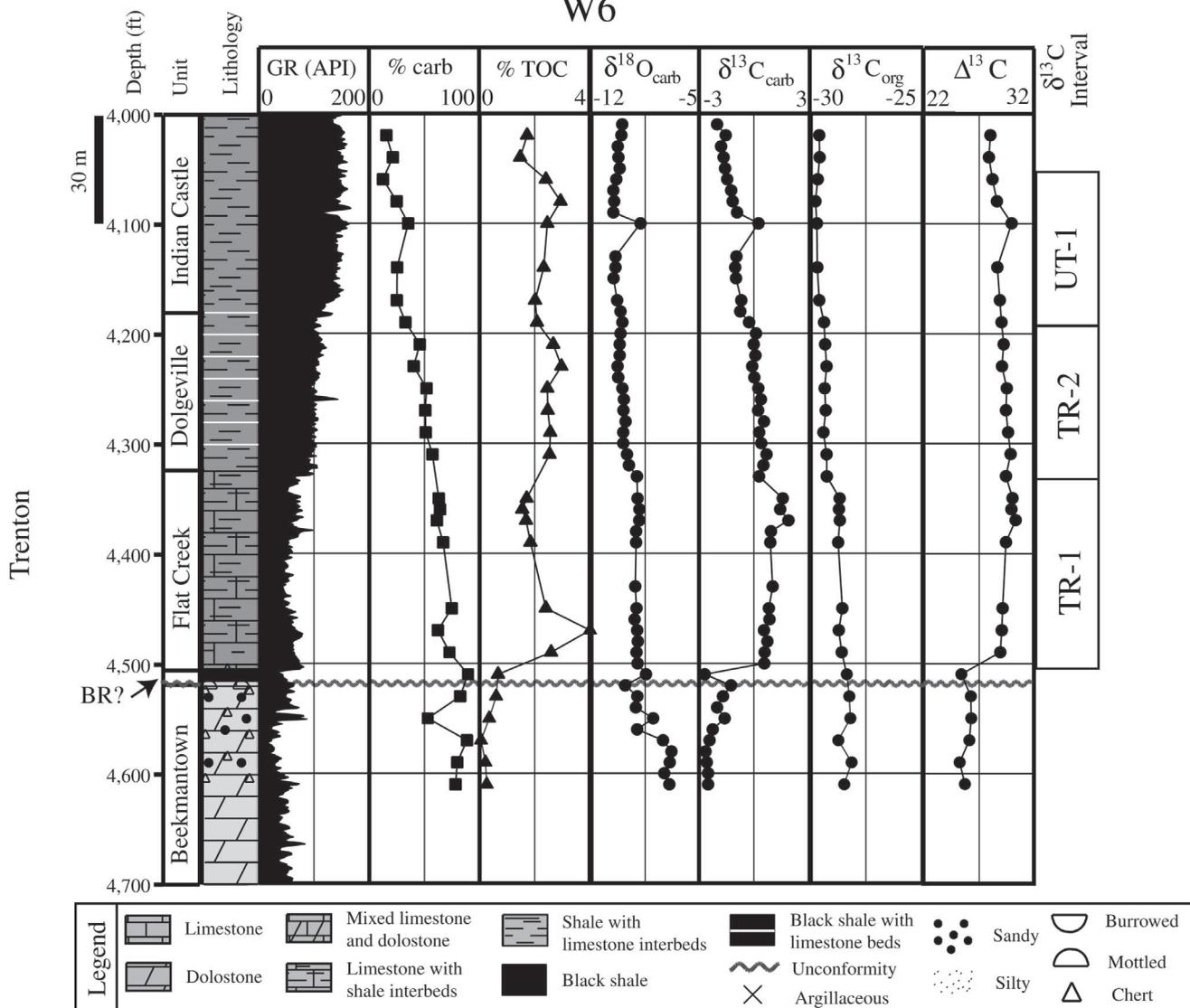


Figure 4. Geologic, geophysical, and geochemical results for well W6. %_{carb} and % TOC are given as mass percent. Isotope values are in per mil (‰) relative to V-PDB. Symbol size is >1σ long-term average analytical error. Knox unconformity marked by thick wavy line. Flat Creek, Dolgeville, and Indian Castle are all part of the Utica Shale group (see text). BR = Black River. Lithological color corresponds to general shade of rocks.

(1σ = 1 standard deviation) for multiple-day replicates for δ¹³C_{carb} and δ¹⁸O_{carb} was 0.09‰ and 0.12‰, respectively.

Cuttings samples for organic carbon analyses were washed prior to processing to reduce contamination from organic carbon in the drilling fluid. Organic carbon isotopes (δ¹³C_{org}) were measured from the acid-insoluble organic matter (see TOC and % carbonate [%_{carb}] methods discussed previously) and were analyzed by combustion to CO₂ on a Costech

ECS 4010 Elemental Analyzer attached to a Delta V Plus mass spectrometer. Values for δ¹³C_{org} were calibrated against international standards from the United States Geological Survey, USGS 24 (graphite), and International Atomic Energy Association standards IAEA CH-6 (sucrose) and IAEA CH-3 (cellulose). During this study, typical precision (1σ) for δ¹³C_{carb} and δ¹⁸O_{carb} replicates of NBS-19 for a single run was 0.04‰. Typical multi-day reproducibility (1σ) for δ¹³C_{org} standards was 0.13‰.

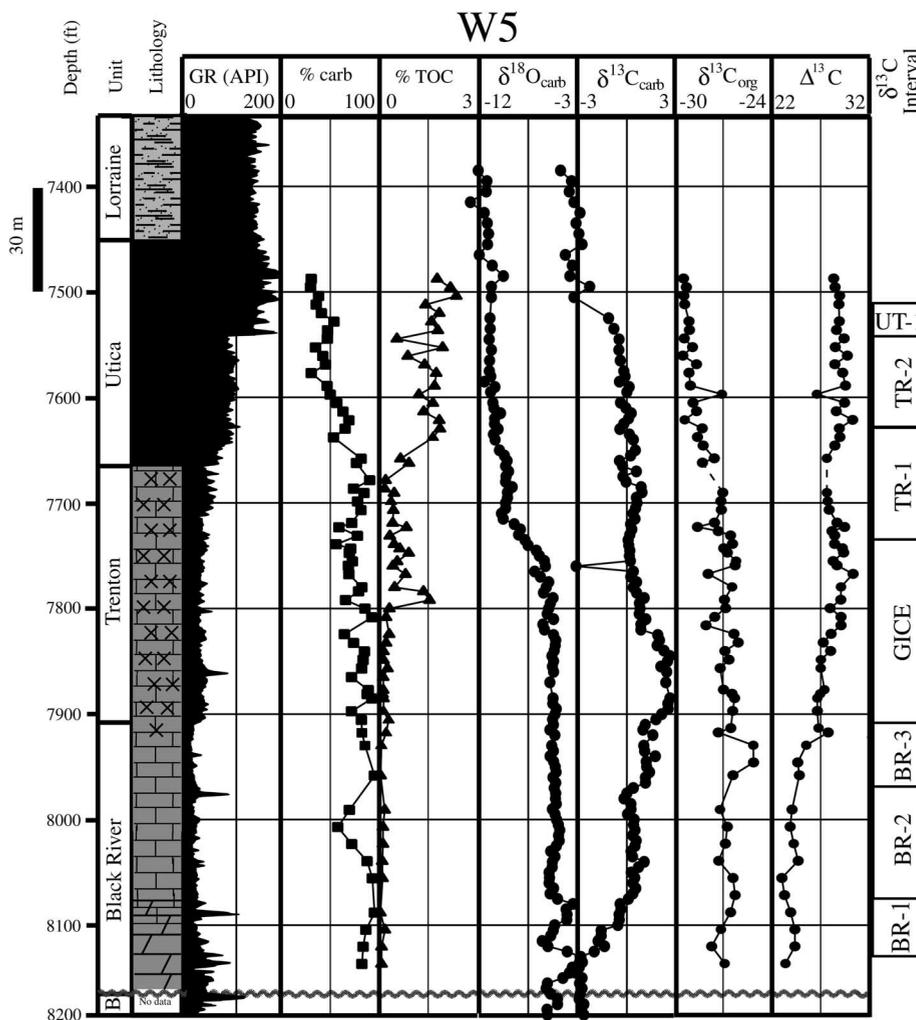


Figure 5. Geologic, geophysical, and geochemical results for well W5. %carb and %TOC are given as mass percent. Isotope values are in per mil (‰) relative to V-PDB. Symbol size is $>1\sigma$ long-term average analytical error. One outlier ($\delta^{13}\text{C}_{\text{org}} = -22.68\text{‰}$, $\Delta^{13}\text{C} = 22.83$) at depth 7765 ft (2367 m) was removed for clarity. Knox unconformity marked by thick wavy line. See Figure 4 for lithology and symbol legend.

RESULTS

Stratigraphic Trends

The $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ data are presented alongside gamma-ray logs in Figure 3. Clear stratigraphic $\delta^{13}\text{C}_{\text{carb}}$ trends are apparent in the sections. A rise in $\delta^{13}\text{C}_{\text{carb}}$ is observed from ~ -3 to 1‰ above the Knox unconformity to the top of the Black River Group. A conspicuous interval in which $\delta^{13}\text{C}_{\text{carb}}$ changes from 0 to 3‰ and returns to 0‰ is observed in the four westernmost wells above the top of the Black River Group. This interval thickens toward the center of the transect. Above this interval, $\delta^{13}\text{C}_{\text{carb}}$ values average around 1‰ in all wells, thickening toward the eastern and western edges of the transect. Above the 1‰ interval, $\delta^{13}\text{C}_{\text{carb}}$ values

average $\sim 0\text{‰}$ in all but the two central wells, W3 and W5. The $\delta^{13}\text{C}_{\text{carb}}$ values fall below 1‰ where the gamma-ray values are highest in the uppermost parts of the wells.

The $\delta^{18}\text{O}_{\text{carb}}$ values vary between -2 and -13‰ . Highest values are found in the Beekmantown Group. Lowest $\delta^{18}\text{O}_{\text{carb}}$ values are found in the Utica Shale and upper Trenton Group. Variation in $\delta^{18}\text{O}_{\text{carb}}$ is lowest in the Black River Group and lower to mid-Trenton Group.

Gamma-ray values are intermediate and variable in the Beekmantown Group. Upsection, gamma-ray readings are lowest in the Black River, intermediate in the Trenton Group, and highest in the Utica Shale. The gamma-ray values increase gradually from the Trenton Group to the Utica Shale in the easternmost wells. Conversely, in the three westernmost wells, the

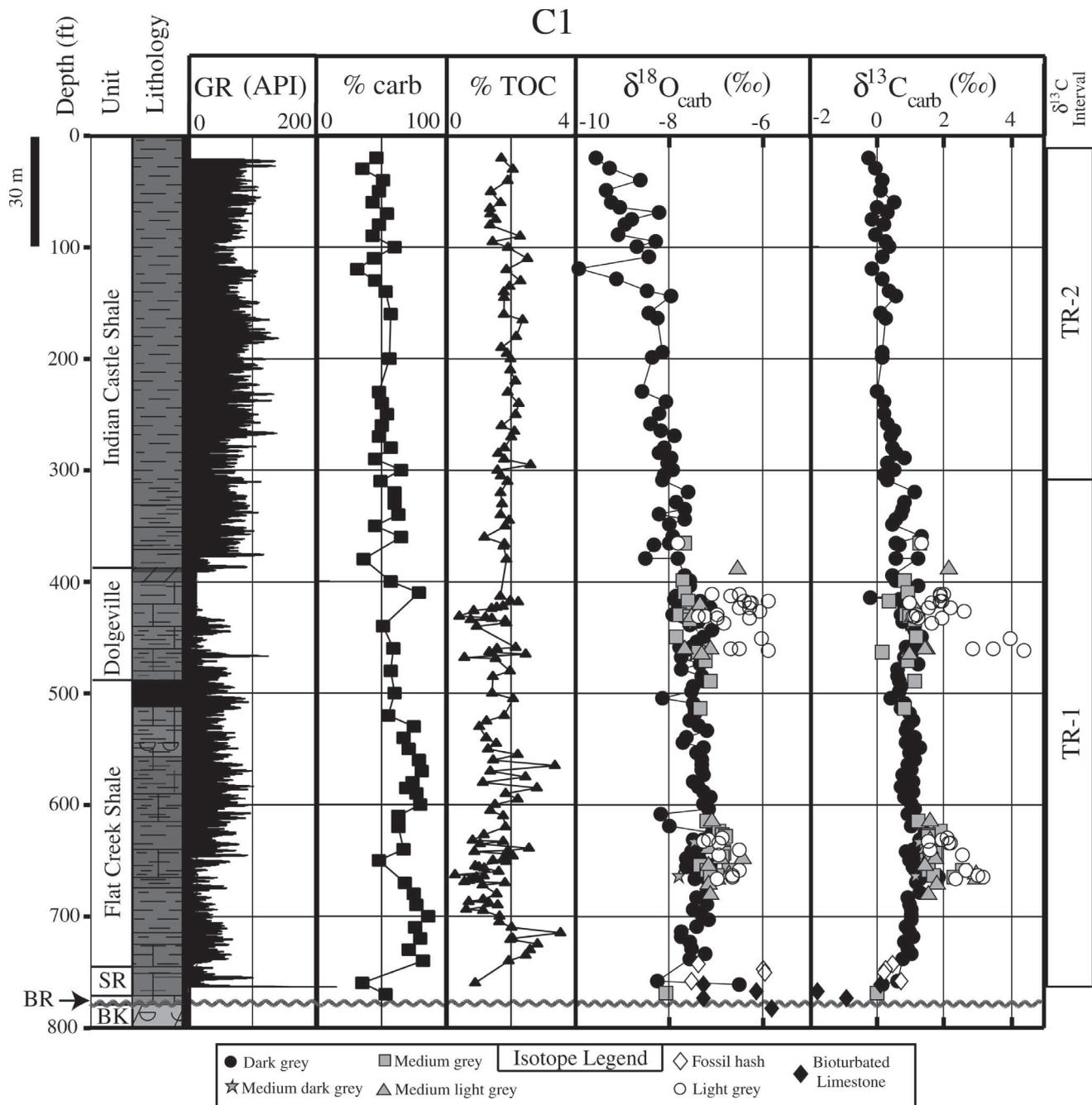


Figure 6. Geologic and geochemical results for core C1. Isotope values are in per mil (‰) relative to V-PDB. Symbol size is $> 1\sigma$ long-term average analytical error. Isotope legend refers to $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ logs, in which colors refer to color-specific sampling of lithologies (see text). Knox unconformity marked by thick wavy line. BK = Beekmantown Group, BR = Black River Group, SR = Sugar River Limestone of Trenton Group. See Figure 4 for lithology and symbol legend.

gamma-ray values sharply increase at the Trenton-Utica contact.

Figures 4–6 show lithologic and geochemical trends of locations W5, W6, and C1. The Beekmantown Group is dolomitized and locally sandy with high $\%_{\text{carb}}$ and low TOC. The Black

River Group (where present) has a high $\%_{\text{carb}}$ and very low TOC and can be variably dolomitized in the lower portions near the contact with the Beekmantown Group (Smith, 2006). The overlying Trenton Group carbonates are argillaceous with increasing clay content upsection. The Utica Shale is

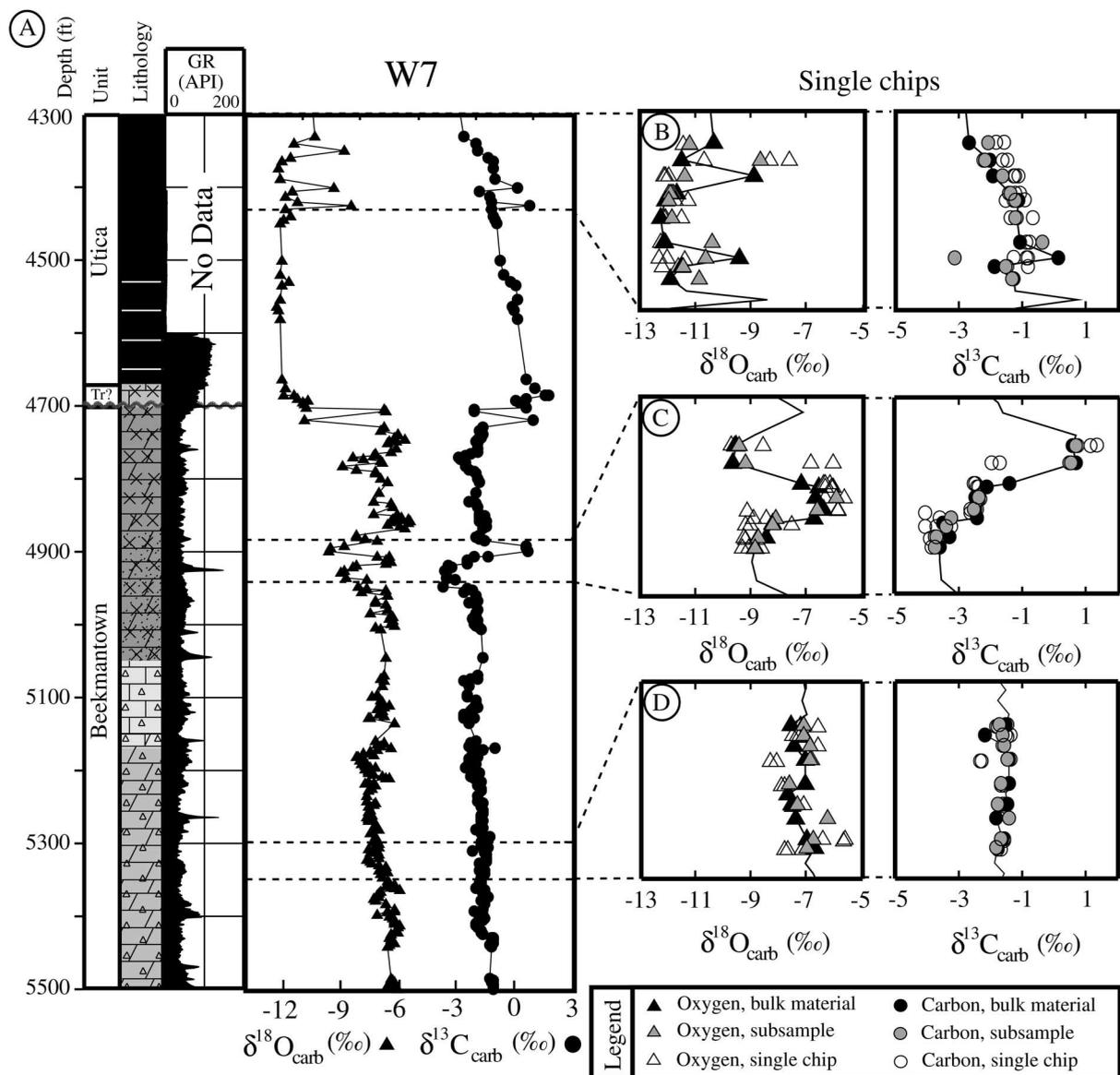


Figure 7. Comparison of isotopic results of bulk material (black symbols), multi-chip subsamples (gray symbols), and single chips (empty symbols) for well W7. Three intervals from the entire well (A) were chosen for their distinct $\delta^{13}\text{C}_{\text{carb}}$ patterns; upward declining (B), upward increasing (C), and constant (D). Isotope values are reported in per mil (‰) relative to V-PDB. In subplots B, C, and D, bulk material values are shown only when single chips were analyzed at the same depth. Bulk material values are connected by a solid line. Up to three single chips were analyzed for a given depth. Symbol size is $>1\sigma$ long-term average analytical error. One outlier ($\delta^{13}\text{C}_{\text{carb}} = 5.13$, $\delta^{18}\text{O}_{\text{carb}} = -6.69$ ‰) from bulk carbonate at depth 4540 ft (1384 m) was removed for clarity.

dominated by dark carbonate strata with dark shale interbeds in the eastern locations (W6, C1) and is more correctly described as marl in much of the section due to its relatively high carbonate content. The Utica Shale in the western sections (W1–4) is exclusively carbonate-poor black shale.

Percent carbonate slowly declines through the Utica Shale in the easternmost locations W6

(Figure 4) and C1 (Figure 6) and the Trenton Group in W5 (Figure 5). The $\%_{\text{carb}}$ is higher in the Utica Shale of eastern locations W6 and C1. TOC averages $\sim 2\%$ the Utica Shale of eastern locations W6 (Figure 4) and C1 (Figure 6), whereas it is more varied in W5 (Figure 5). In this well, TOC is $\sim 0\%$ Black River and lower Trenton strata, $\sim 0.75\%$ in the upper Trenton, and $\sim 1.5\%$ in the Utica.

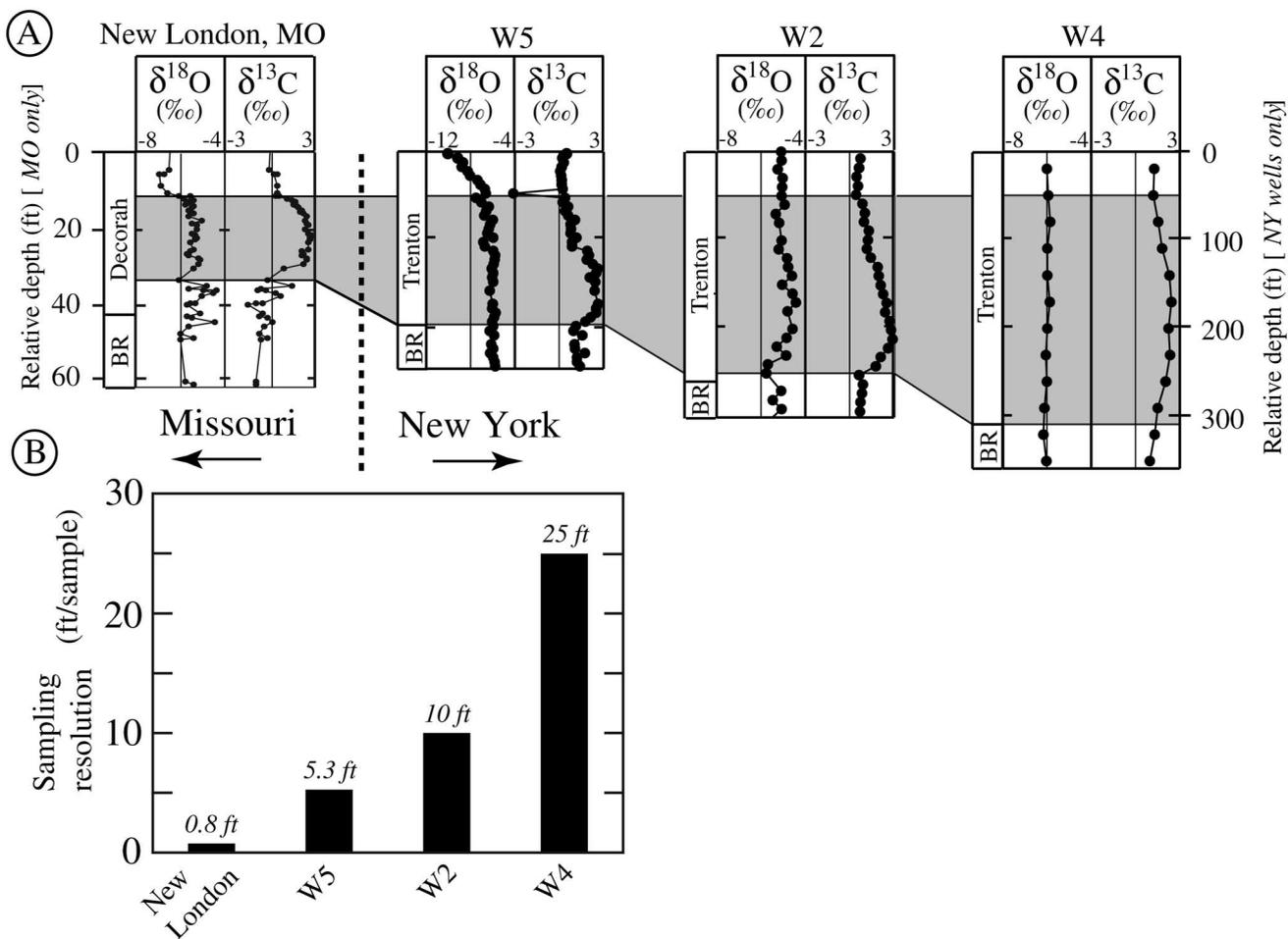


Figure 8. Comparison of sampling resolution for wells and outcrop during the Guttenberg excursion interval (shaded). (A) Correlations between age-equivalent outcrop in Missouri, (Metzger and Fike, 2013) and New York wells presented here. Sampling resolution is coarser moving to the right, associated with decreasing resolution of the GICE interval. Missouri outcrop y axis (left) is exaggerated relative to the three subsurface sections. (B) Bar graph of sampling resolution for the different locations showing number of feet per sample. High values correspond to low sampling resolution.

In general, $\delta^{13}\text{C}_{\text{org}}$ is relatively constant in the highest $\%_{\text{carb}}$ strata where post-Black River Group gamma-ray values are lowest (Figures 4, 5). The $\delta^{13}\text{C}_{\text{org}}$ averages $\sim -27\text{‰}$ in W5 and declines to ~ -30 in the Utica Shale. The $\delta^{13}\text{C}_{\text{org}}$ averages -28.5‰ in W6 (Figure 4) and declines to $\sim -30\text{‰}$ in the Indian Castle Member of the Utica Shale. $\Delta^{13}\text{C}$ ($\Delta^{13}\text{C} = \delta^{13}\text{C}_{\text{carb}} - \delta^{13}\text{C}_{\text{org}}$) averages 28.5‰ in W6 and very closely matches the pattern of $\delta^{13}\text{C}_{\text{carb}}$ because $\delta^{13}\text{C}_{\text{org}}$ has little variability. In W5, $\Delta^{13}\text{C}$ increases from ~ 23 to 30‰ from the Black River Group to the upper Trenton Group values, then varies 29‰ upsection. The large-scale changes in $\Delta^{13}\text{C}$ are not dominantly controlled by $\delta^{13}\text{C}_{\text{carb}}$ or

$\delta^{13}\text{C}_{\text{org}}$, but rather a combination of changing values in both.

Location C1

Location C1, the northeasternmost study section and the only core, is dominated by dark calcareous shales and shaley carbonates. The strata above the Knox unconformity are all part of the Utica Shale except for a very thin (tentative) Black River Group and Sugar River Limestone of the Trenton Group in the ~ 10 m (33 ft) of section immediately above the unconformity (Figure 6). Some lithologies contained lighter and darker beds (e.g., the Flat Creek Member of the Utica Shale). The lighter beds were dominantly

fine-grained with occasional coarse sand-sized grains composed of fossil debris. Lighter beds sometimes displayed a diffuse contact with surrounding beds. Evidence of cm-scale scouring was present in the Utica Shale members.

Additional samples were taken at cm-scale resolution in select intervals to investigate possible lithology-dependent variability in the $\delta^{13}\text{C}_{\text{carb}}$ signal. Samples were split into five different categories based upon a qualitative assessment of their color. In general, the two darkest shades are stratigraphically coherent (i.e., have little scatter) in their isotopic trends. In contrast, the two lightest, most carbonate-rich layers displayed high degrees of scatter in both $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{carb}}$, in which the $\delta^{13}\text{C}_{\text{carb}}$ scatter is skewed toward heavier values relative to the overlying and underlying strata.

Stratigraphic Summary

We focus on the stratigraphic trends observed in the strata of the Black River Group, Trenton Group, and Utica Shale. Gamma-ray logs show similar patterns across formation boundaries with the Utica Shale having highest gamma-ray emission. Percent carbonate is highest in the Beekmantown and Black River Groups and decreases up section. Trends in $\%_{\text{carb}}$ and gamma-ray values are roughly opposite one another. The inverse relationship between $\%_{\text{carb}}$ and gamma-ray logs suggests that the gamma-ray signatures predominantly track potassium-rich siliciclastic input (e.g., from detrital clay minerals), rather than organic carbon. TOC is highest in Trenton Group and Utica Shale. The $\delta^{18}\text{O}_{\text{carb}}$ is generally highest in the formations with highest $\%_{\text{carb}}$ (i.e., Beekmantown Group to Trenton Group). The $\delta^{18}\text{O}_{\text{carb}}$ is not stratigraphically consistent between sections from the middle Trenton upward and is most variable in dolomitized zones (as described in the cuttings geologic sampling logs) and zones with low $\%_{\text{carb}}$. Consistent patterns in $\delta^{13}\text{C}_{\text{carb}}$ are apparent across multiple wells. These include (stratigraphically ascending) (1) a rise from -3 to 0% in the Black River, (2) a stable interval of 0.5% in the Black River, (3) a rise from ~ 1 to $\sim 1.5\%$ in the Black River, (4) a peak at 3% in the Trenton, (5) a stable interval of 1% in the Trenton and Utica, (6) a stable interval of 0% in the Trenton and Utica, and

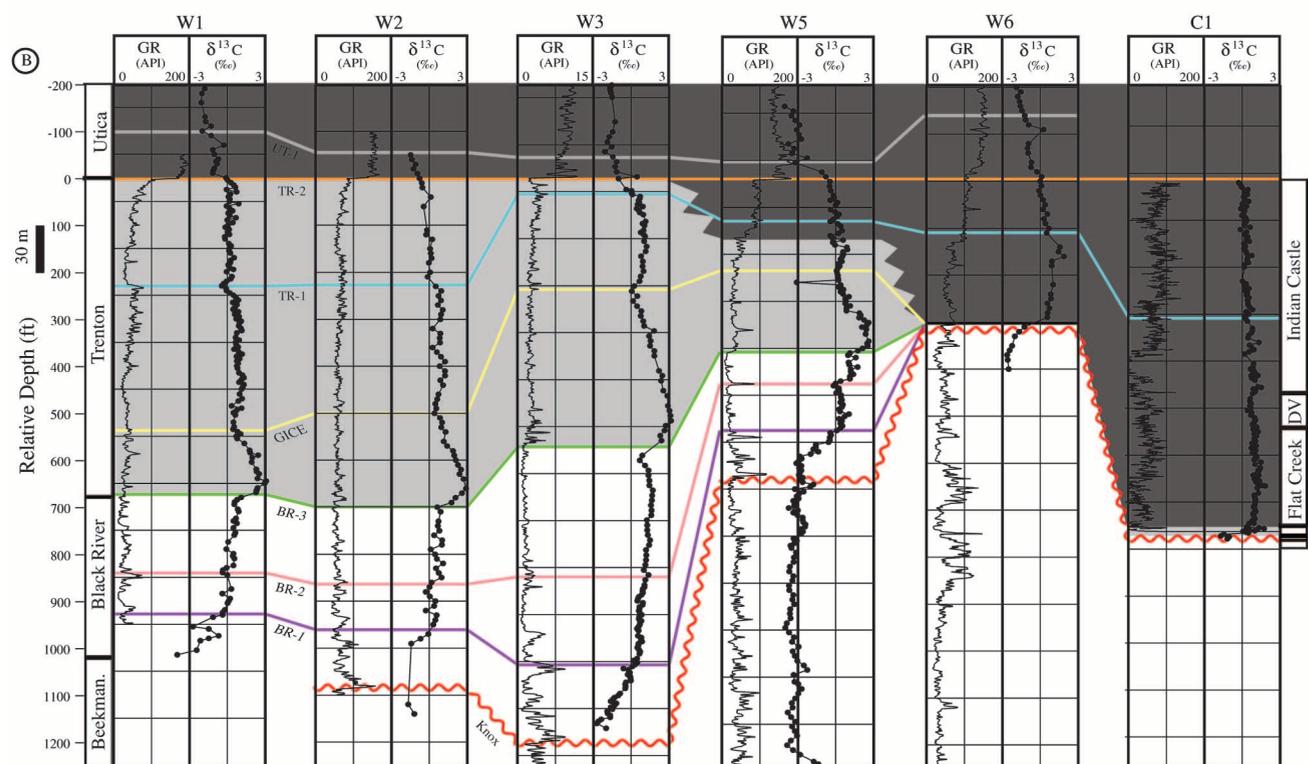
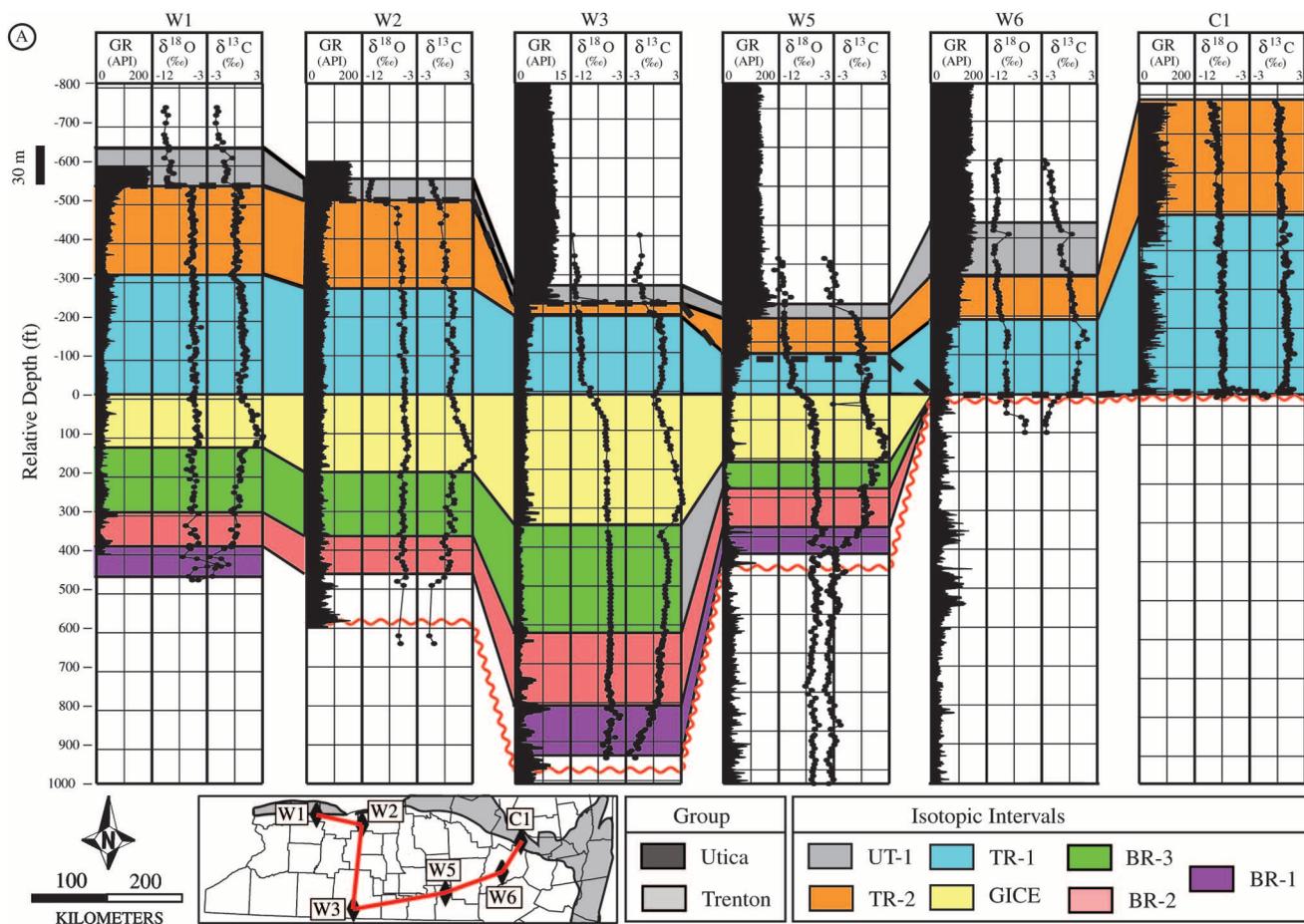
(7) a drop to -1.5% in the Utica. This drop in $\delta^{13}\text{C}_{\text{carb}}$ below 0% is coincident with a decline in $\%_{\text{carb}}$ as well as a parallel decrease in $\delta^{13}\text{C}_{\text{org}}$.

Impact of Lithologic Mixing on $\delta^{13}\text{C}_{\text{carb}}$ in Cuttings

A series of tests were conducted on select cuttings samples from well W7 to evaluate the impact of lithologic mixing in analysis of cuttings samples. Three stratigraphic intervals were investigated in well W7 (Figure 7), each containing a different background $\delta^{13}\text{C}_{\text{carb}}$ trend (declining, increasing, or constant) with decreasing depth as defined by data from bulk-homogenized cuttings. For each sample investigated, several carbonate chips (single chips) were individually analyzed for $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$, as well as a powder representing ~ 0.5 g (subsample). These were compared with the $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ data from the homogenized bulk sample (bulk). A comparison of these results is shown in Figure 7, with the intervals comprising the distinct $\delta^{13}\text{C}_{\text{carb}}$ trends represented in Figure 7B–D. Single chip data are characterized by increased variability in $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ when compared with bulk samples or the subsamples. Single chip $\delta^{13}\text{C}_{\text{carb}}$ scatter increases when the baseline bulk $\delta^{13}\text{C}_{\text{carb}}$ signal is increasing or decreasing. Single chip $\delta^{13}\text{C}_{\text{carb}}$ scatter is low when the bulk $\delta^{13}\text{C}_{\text{carb}}$ signal is not changing. Although single chips reasonably track the bulk $\delta^{13}\text{C}_{\text{carb}}$ signal (albeit with increased variability), the ~ 0.5 g (~ 0.02 oz) subsample more closely tracks the $\delta^{13}\text{C}_{\text{carb}}$ signal of the bulk signal.

Impact of Sampling Resolution

A comparison of $\delta^{13}\text{C}_{\text{carb}}$ profiles sampled at different resolutions through the same interval is shown in Figure 8. The variable vertical sampling resolution between locations results in differing stratigraphic morphologies of the same $\delta^{13}\text{C}_{\text{carb}}$ signal, where a lower sampling resolution results in a smoother isotopic record. The interval of elevated $\delta^{13}\text{C}_{\text{carb}}$ (gray) is ~ 30 ft (~ 9 m) at the New London outcrop in Missouri (see Metzger and Fike, 2013 for discussion of locality), whereas the same interval is >300 ft (>91 m) in New York well W4. The sampling resolution in well W4 is



30 ft (9 m); a similar sampling resolution in New London would reduce the entire interval of elevated $\delta^{13}\text{C}_{\text{carb}}$ values to a single data point.

DISCUSSION

The $\delta^{13}\text{C}_{\text{carb}}$ can be used to chronologically correlate strata because the $\delta^{13}\text{C}_{\text{DIC}}$ value synchronously changes across any well-mixed portion of the ocean. Stratigraphically meaningful correlations require preservation of the original $\delta^{13}\text{C}_{\text{carb}}$ signal, and various post-depositional processes may alter $\delta^{13}\text{C}_{\text{carb}}$ values. Sampling methods (e.g., vertical sampling resolution and sample selection) are additional controls on the resolution and accuracy of $\delta^{13}\text{C}_{\text{carb}}$ logs. Here, we identify seven intervals with distinctive $\delta^{13}\text{C}_{\text{carb}}$ signatures that can be used for correlation. We then examine evidence of alteration of the original $\delta^{13}\text{C}_{\text{carb}}$ signal and the impact of sampling resolution on the morphology of $\delta^{13}\text{C}_{\text{carb}}$ logs.

Seven discrete $\delta^{13}\text{C}_{\text{carb}}$ intervals, bounded by correlation points in the carbon isotope logs, have been identified within the stratigraphic interval examined (Figure 9): three in the Black River Group (BR-1, BR-2, and BR-3) and four in the Trenton Group and Utica Shale (GICE, TR-1, TR-2, and UT-1). These are defined as follows:

- BR-1: an interval of increasing $\delta^{13}\text{C}_{\text{carb}}$ from -3 to 0‰ in the Black River Group.
- BR-2: a stable interval of $\sim +0.5\text{‰}$ in $\delta^{13}\text{C}_{\text{carb}}$ in the Black River Group above BR-1.
- BR-3: an interval starting at $\sim 1\text{‰}$ in $\delta^{13}\text{C}_{\text{carb}}$ and increasing to $\sim 1.5\text{‰}$ in the Black River Group above BR-2.
- GICE: a positive excursion in $\delta^{13}\text{C}_{\text{carb}}$, increasing from ~ 0.5 to 3‰ before decreasing to

$\sim 0\text{‰}$. Known as the Guttenberg isotopic carbon excursion (GICE), this positive $\delta^{13}\text{C}_{\text{carb}}$ excursion has been identified in much of central and eastern Laurentia (e.g., Ludvigson et al., 2004; Young et al., 2005; Bergström et al., 2010; Metzger and Fike, 2013) as well as Sweden (Bergström et al., 2004), China (Young et al., 2005; Bergström et al., 2009), and Malaysia (Bergström et al., 2010). In this paper, it begins near the base of the Trenton Group.

- TR-1: a stable interval of $+1\text{‰}$ in $\delta^{13}\text{C}_{\text{carb}}$ in the Trenton Group (western-central New York) and Utica Shale (eastern New York) that post-dates the Guttenberg excursion.
- TR-2: a stable interval of $\sim 0\text{‰}$ in $\delta^{13}\text{C}_{\text{carb}}$ above TR-1.
- UT-1: an interval of decreasing $\delta^{13}\text{C}_{\text{carb}}$ from ~ 0 to -1.5‰ .

Figure 2 shows a $\delta^{13}\text{C}_{\text{carb}}$ reference curve (divided into seven $\delta^{13}\text{C}_{\text{carb}}$ intervals) for the New York region and its relationship to formation boundaries across the state.

Evaluating Diagenetic Alteration

Diagenetic (postdepositional) processes can alter original $\delta^{13}\text{C}_{\text{carb}}$ values in marine carbonates (Allan and Matthews, 1982; Patterson and Walker, 1994; Melim et al., 2004; Metzger and Fike, 2013), giving rise to apparent spatial heterogeneities in $\delta^{13}\text{C}_{\text{carb}}$ values and limiting the ability to use $\delta^{13}\text{C}_{\text{carb}}$ for correlations. Several recognized mechanisms exist by which diagenesis can alter $\delta^{13}\text{C}_{\text{carb}}$. The most common is oxidation of organic matter ($\delta^{13}\text{C}_{\text{org}} \sim -30\text{‰}$),

Figure 9. Proposed correlations of the New York subsurface based on $\delta^{13}\text{C}_{\text{carb}}$. Red line (map) shows sampling transect for both (A) and (B). GR = gamma ray (in API units). (Note that API range is 0–200 API units for all locations except for W3 for which the range was 0–15 API units due to a different gain setting during analysis. The 0–15 API unit range in this well is roughly equivalent to the 0–200 units in other wells.) $\delta^{13}\text{C} = \delta^{13}\text{C}_{\text{carb}}$ given in per mil (‰) relative to V-PDB, $\delta^{18}\text{O} = \delta^{18}\text{O}_{\text{carb}}$ given in ‰ relative to V-PDB, BK = Beekmantown Group, BR = Black River Group, SR = Sugar River Limestone. (A) Isotopic intervals (colored zones) show shift in the sediment depocenter from western and central New York from $\delta^{13}\text{C}_{\text{carb}}$ to eastern New York following the GICE. Isotopic intervals are defined and discussed in text (see Discussion). Generalized $\delta^{13}\text{C}_{\text{carb}}$ curve for New York region and chronostratigraphic relationships are found in Figure 1. The basal contact of the Utica Shale is marked by a thick dashed red line. Wells are hung on base of $\delta^{13}\text{C}_{\text{carb}}$ interval TR-1. (B) Sampling transect showing time-equivalent nature of lower Utica (dark gray) and upper Trenton (light gray) facies. Wells hung on top of $\delta^{13}\text{C}_{\text{carb}}$ interval TR-2.

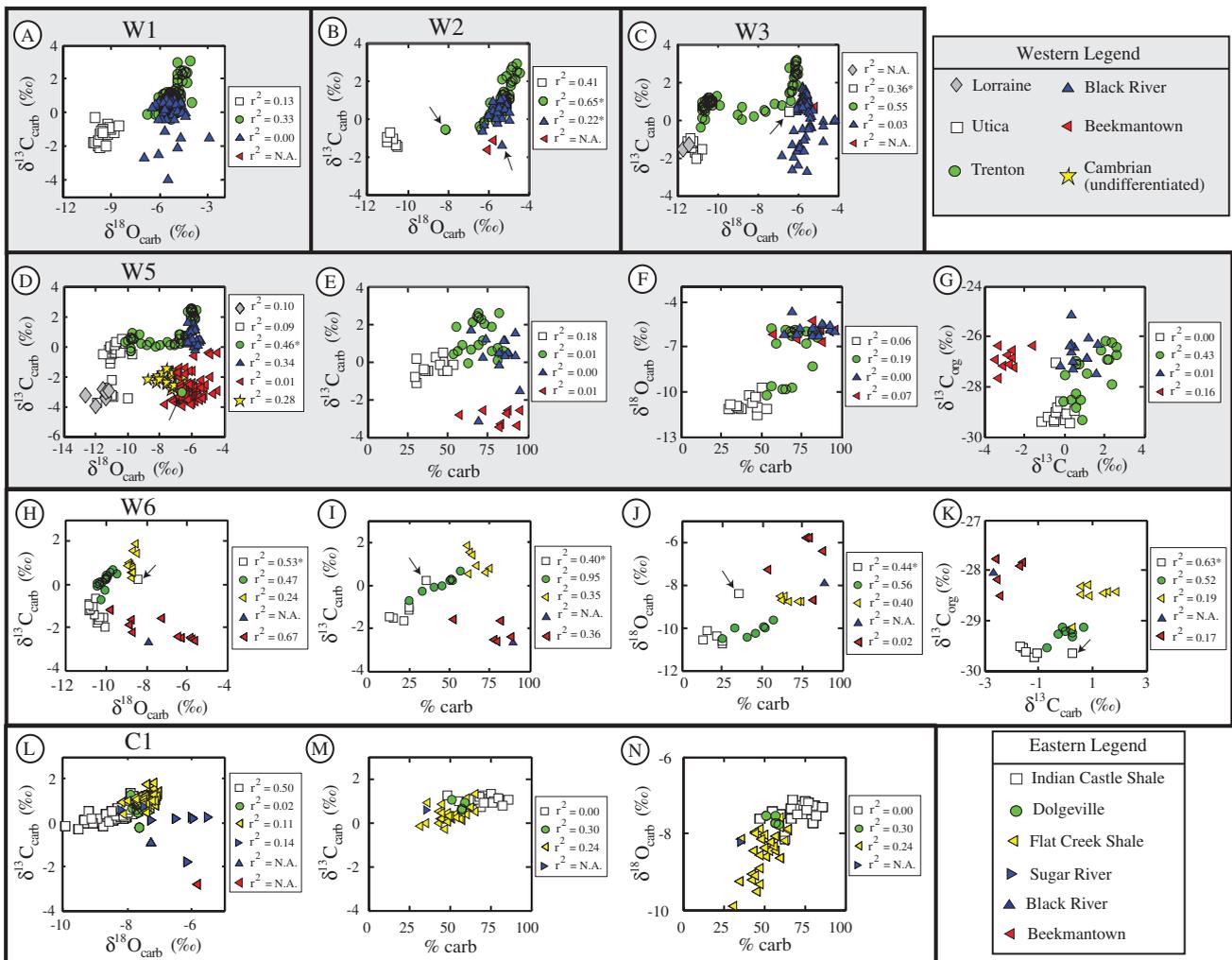


Figure 10. Geochemical cross-plots of well (A) W1, (B) W2, (C) W3, (D-G) W5, (H-K) W6, and (L-N) core C1. Western sections have gray background. Eastern sections have white background. * indicates outliers omitted from r^2 calculation. These outliers are shown by arrows. For all isotope values, symbols are larger than 1σ long-term average analytical error. No r^2 is given for data sets with $n < 3$.

which results in a decrease in $\delta^{13}\text{C}_{\text{DIC}}$ of pore fluids and subsequently a decrease in $\delta^{13}\text{C}_{\text{carb}}$ of any strata that re-equilibrate with such pore fluids. This can happen either as meteoric diagenesis, in which soil carbon is the source (e.g., Knauth and Kennedy, 2009; Swart and Kennedy, 2012), or during burial diagenesis (e.g., Derry, 2010), in which oxidation results from thermal breakdown of migrating hydrocarbons or in situ organic matter.

Covariation in $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{18}\text{O}_{\text{carb}}$, and $\%_{\text{carb}}$

Geochemical crossplots can provide context for identifying possible postdepositional alteration. An examination of covariation between geochemical

parameters and $\delta^{13}\text{C}_{\text{carb}}$ can constrain possible diagenetic pathways. Often, covariation in $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ is examined, because changes in $\delta^{18}\text{O}_{\text{carb}}$ are largely or entirely independent of changes in $\delta^{13}\text{C}_{\text{carb}}$ prior to alteration, and therefore covariation between these two parameters is not expected. However, in meteoric fluids both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are low (e.g., Bathurst, 1975; Allan and Matthews, 1982; Lohmann, 1988), and covarying $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ can indicate isotopic alteration by meteoric diagenesis (we note that although covariation can indicate diagenetic alteration, the absence of covariation cannot be taken as evidence of primary $\delta^{13}\text{C}_{\text{carb}}$ values being retained). For example, covariation in $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ is observed in formations that have

undergone visible karstification (e.g., Lohmann, 1988). When considering diagenetic alteration of $\delta^{13}\text{C}_{\text{carb}}$, two important points must be considered: (1) most diagenetic mechanisms decrease $\delta^{13}\text{C}_{\text{carb}}$; and (2) $\delta^{18}\text{O}_{\text{carb}}$ is easier to reset than $\delta^{13}\text{C}_{\text{carb}}$ during diagenesis because of the relative abundance of O relative to C in any diagenetic fluid (e.g., Banner and Hanson, 1990). This offset in oxygen and carbon concentrations in diagenetic fluids allows quantitative description of the volume of diagenetic fluid required to change the rock's $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ values. This is normally described in terms of fluid to rock ratios (fluid:rock). Most relevant here is the molar ratio of the cumulative flux of pore fluids migrating through a sample to the volume of carbonate material within the sample. Under a low fluid:rock ratio, the $\delta^{18}\text{O}_{\text{carb}}$ is vulnerable to change, whereas the $\delta^{13}\text{C}_{\text{carb}}$ is less susceptible due to the lower carbon content of the fluids (Banner and Hanson, 1990). For a given flux of diagenetic fluids, siliciclastic-dominated strata with low percent carbonate will have their $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ signatures more easily altered compared to the same volume of carbonate-rich strata. However, the low porosity/permeability of fine-grained siliciclastics (e.g., shales) results in decreased fluid flux, thereby increasing preservation potential of a primary isotopic signature in lower $\%_{\text{carb}}$ strata. Bulk rock $\delta^{13}\text{C}_{\text{carb}}$ signatures can also be altered by the addition of pore-filling secondary cement, which adds secondary material to void spaces, rather than sequential equilibration of the bulk rock itself with the diagenetic fluid. These factors must be considered when interpreting $\delta^{13}\text{C}_{\text{carb}}$ records in fine-grained lithologies with low carbonate contents.

Most of the formations in this study do not show strong covariation in $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ (Figure 10), and, therefore, we find no formation-scale evidence of meteoric diagenesis. However, in Trenton Group strata, $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ show moderate to strong correlation in all wells ($r^2 = 0.33$ to 0.65). Understanding the origin of the covariation in the Trenton Group requires closer examination, and we will look at well W3 as an example. There are three $\delta^{13}\text{C}_{\text{carb}}$ intervals present in the Trenton Group: the GICE, TR-1, and TR-2. These intervals are all characterized by minimal stratigraphic variability (i.e., scatter) and relatively high values of $\delta^{13}\text{C}_{\text{carb}}$, both

inconsistent with the variably decreasing $\delta^{13}\text{C}_{\text{carb}}$ expected from alteration by diagenetic fluids with low $\delta^{13}\text{C}$ values. Examining $\delta^{18}\text{O}_{\text{carb}}$ values in these three intervals, we see a general trend toward decreased $\delta^{18}\text{O}$ values. This trend, however, is not consistent from well to well. Thus, whereas the uppermost GICE, TR-1, and TR-2 show consistent $\delta^{13}\text{C}_{\text{carb}}$ signatures between sections, they are characterized by variable $\delta^{18}\text{O}_{\text{carb}}$ profiles. The low and spatially variable $\delta^{18}\text{O}_{\text{carb}}$ values and spatially reproducible $\delta^{13}\text{C}_{\text{carb}}$ profiles support diagenetic alteration to $\delta^{18}\text{O}_{\text{carb}}$, but not $\delta^{13}\text{C}_{\text{carb}}$ (Figure 9). This is consistent with low water:rock ratio (because $\delta^{18}\text{O}_{\text{carb}}$ is more easily reset), suggesting that the low scatter $\delta^{13}\text{C}_{\text{carb}}$ did not result from homogenization during diagenesis. The simultaneous decrease in both $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ in the uppermost GICE is merely coincidental, because the GICE shows the same decline in other wells (wells W2 and W1) with no change in $\delta^{18}\text{O}_{\text{carb}}$ (Figure 9). It is the combination of variably altered $\delta^{18}\text{O}_{\text{carb}}$ values against a changing primary $\delta^{13}\text{C}_{\text{carb}}$ trend, rather than diagenetic alteration of $\delta^{13}\text{C}_{\text{carb}}$ itself, that produces a moderate degree of covariance in each of the three isotopic intervals in Trenton Group strata (e.g., Figure 10, well W5: $r^2 = 0.55$). Further evidence of a low water:rock ratio can be seen in TR-1 of wells W1, W2, and W3 (Figure 9), in which $\delta^{13}\text{C}_{\text{carb}}$ is consistent whereas $\delta^{18}\text{O}_{\text{carb}}$ shows great disparity between wells.

Another interval of possible isotopic alteration is UT-1. The $\delta^{13}\text{C}_{\text{carb}}$ interval UT-1 shows an upward decrease in $\delta^{13}\text{C}_{\text{carb}}$ from 0 to -1.5‰ , a parallel decrease in $\%_{\text{carb}}$, and constant, but low, $\delta^{18}\text{O}_{\text{carb}}$ (Figures 4, 5). Because $\delta^{18}\text{O}_{\text{carb}}$ can be reset under low water:rock ratios (in this case "rock" is equivalent to carbonate content), then UT-1 can plausibly be the result of (1) meteoric diagenesis under a fixed flux of fluid in which strata with lower $\%_{\text{carb}}$ have lower $\delta^{13}\text{C}_{\text{carb}}$, or (2) differential fluid:rock ratios across the strata with a fixed $\%_{\text{carb}}$ where $\delta^{13}\text{C}_{\text{carb}}$ is lower in strata where fluid flux was higher. If $\delta^{13}\text{C}_{\text{carb}}$ interval UT-1 is diagenetic in origin, then this unit may not represent coeval strata, but instead capture a regionally extensive diagenetic event or episode, information which may be useful for other purposes (e.g., reservoir development) beyond chronostratigraphic correlation.

$\delta^{13}\text{C}_{\text{org}}$ and $\Delta^{13}\text{C}$

Another isotopic parameter, $\delta^{13}\text{C}_{\text{org}}$, can be used to identify potential alteration of $\delta^{13}\text{C}_{\text{carb}}$. This is because organic matter is derived from the local dissolved inorganic carbon (DIC) reservoir and is isotopically offset from DIC as a result of biological carbon fixation (e.g., Hayes et al., 1999). The offset is relatively constant when the conditions controlling the source (e.g., growth rate, $[\text{CO}_2]_{\text{aq}}$; Popp et al., 1997) and preservation (e.g., thermal maturity, Des Marais, 1997) of organic matter are stable, so any variation in $\delta^{13}\text{C}_{\text{DIC}}$ (i.e., what is eventually recorded in $\delta^{13}\text{C}_{\text{carb}}$) should appear as a parallel variation in $\delta^{13}\text{C}_{\text{org}}$. This, in turn, leads to a constant $\Delta^{13}\text{C}$ ($= \delta^{13}\text{C}_{\text{carb}} - \delta^{13}\text{C}_{\text{org}}$; e.g., Kump and Arthur, 1999). Variations in $\delta^{13}\text{C}$ can provide constraints on possible processes that change $\delta^{13}\text{C}_{\text{carb}}$ or $\delta^{13}\text{C}_{\text{org}}$ signatures. For example, in the middle of the GICE interval of well W5 (Figure 6), $\Delta^{13}\text{C}$ increases for ~90 ft (~27 m) up section before returning to a relatively stable value of 29‰. This results from a larger decrease in $\delta^{13}\text{C}_{\text{org}}$ than $\delta^{13}\text{C}_{\text{carb}}$. Meteoric diagenesis should not affect $\delta^{13}\text{C}_{\text{org}}$, and the stable and high $\delta^{18}\text{O}_{\text{carb}}$ values in this interval provide further evidence that meteoric diagenesis is unlikely the source of the change in $\Delta^{13}\text{C}$. Rather, a short-term change in organic carbon source or composition (with a different isotopic fractionation from DIC and therefore a different $\delta^{13}\text{C}_{\text{org}}$ value) could explain the pattern, and this explanation has been proposed for strata of similar age in Iowa (Pancost et al., 1999) and elsewhere (Pancost et al., 2013).

Stratigraphic Reproducibility

Consistent $\delta^{13}\text{C}_{\text{carb}}$ patterns across multiple locations in a region are deemed stratigraphically reproducible. The lack of regional stratigraphic reproducibility can reveal local (diagenetic or primary) overprints on the $\delta^{13}\text{C}_{\text{carb}}$ signals. A primary oceanic $\delta^{13}\text{C}_{\text{carb}}$ signal will be consistent over a large area, whereas the isotopic composition of diagenetic fluids (or a local deviation in $\delta^{13}\text{C}_{\text{DIC}}$) are inherently variable over large distances. To have stratigraphically reproducible diagenetic $\delta^{13}\text{C}_{\text{carb}}$ patterns means all locations must have been modified in such a way that the combination of (1) the degree of diagenesis and (2) the isotopic signature of the diagenetic fluid(s) resulted

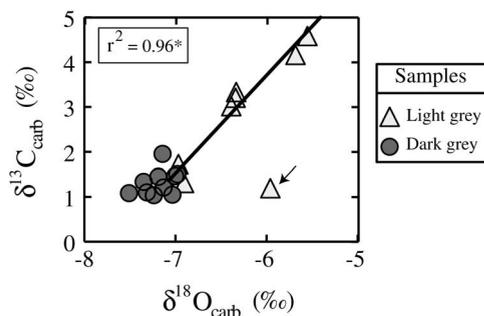


Figure 11. Isotopic cross-plots for light (concretionary) and dark samples from core C1. r^2 refers to linear least-squares fit. * = one outlier (arrow) omitted from regression calculation.

in the same alteration of the $\delta^{13}\text{C}_{\text{carb}}$ signal. The large local range in O and C isotopic signatures of diagenetic fluids and the differing lithological properties of the rocks in different areas will tend to produce scatter in $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ of altered rocks. The inverse, low scatter (particularly in $\delta^{13}\text{C}_{\text{carb}}$) is consistent with a primarily oceanic signal, which should produce a smoothly changing isotopic record through time. Intervals BR-2, BR-3, GICE, TR-1, and TR-2, show very consistent, smoothly changing $\delta^{13}\text{C}_{\text{carb}}$ patterns between sections, strong evidence for a primary signal. Some $\delta^{13}\text{C}_{\text{carb}}$ intervals show minor discrepancies between wells (TR-1 of W2, BR-1 of W1), but the overall trends are clear enough to distinguish between $\delta^{13}\text{C}_{\text{carb}}$ intervals.

All but one of the $\delta^{13}\text{C}_{\text{carb}}$ intervals in this work are characterized by stable, high $\delta^{13}\text{C}_{\text{carb}}$ values or during positive rather than negative trends. The single negative interval, UT-1, does not carry a stratigraphically reproducible morphology and is found in strata with low carbonate abundance and low $\delta^{18}\text{O}_{\text{carb}}$, suggesting this interval is the product of alteration. However, the stable $\Delta^{13}\text{C}$ values in UT-1 suggest alteration is minimal. There are stratigraphic arguments arguing against UT-1 being a correct chronostratigraphic correlation. The base of the Utica Shale is younger in the west (Ruedemann, 1925; Kay, 1937), because of this we would predict that the isotopes would not align. At this time, the primary nature of this interval is unlikely.

Absence of covariation in geochemical parameters and stratigraphic reproducibility cannot prove alteration did not occur, they merely provide no evidence for alteration. Conversely, covariation and lack

of stratigraphic reproducibility can show areas where alteration most likely did occur (e.g., UT-1), an important distinction. Minor differences in $\delta^{13}\text{C}_{\text{carb}}$ for a given isotope interval do exist between wells (e.g., small negative shifts in TR-1 of W2) and may be the result of primary or secondary overprints to the $\delta^{13}\text{C}_{\text{carb}}$ trend, but the larger $\delta^{13}\text{C}_{\text{carb}}$ patterns (at the scale of 10s–100s of feet) in each interval are sufficient to distinguish them from the other $\delta^{13}\text{C}_{\text{carb}}$ intervals.

Relationship between Color and Isotopes in Core C1

Centimeter-scale sampling of light and dark layers (Figures 6, 11) in core C1 reveals significant color-specific covariation between $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$. Stratigraphically, the intervals TR-1 and TR-2 are clearly defined in the darkest layers of core C1, whereas interbedded lighter layers showed high isotopic scatter as well as $\delta^{13}\text{C}_{\text{carb}}$ values higher than observed in other wells (Figure 6). Although data from the dark layers cluster together in a $\delta^{13}\text{C}_{\text{carb}}$ versus $\delta^{18}\text{O}_{\text{carb}}$ crossplot (Figure 11), the lighter layers are arranged along a line that intersects the centroid of the samples from the darker layers, a pattern consistent with a linear mixture of two isotopically distinct components: a dark primary carbonate phase and a lighter colored diagenetic carbonate component. Therefore, $\delta^{13}\text{C}_{\text{carb}}$ values obtained from the lighter layers are not representative of global (or even basin-wide) $\delta^{13}\text{C}_{\text{carb}}$ and should not be used for chemostratigraphic correlation.

One possible source for the higher $\delta^{13}\text{C}_{\text{carb}}$ values observed in the lighter component is precipitation in fluids that were impacted by microbial methanogenesis. Because methane carries a low $\delta^{13}\text{C}$ value relative to the surrounding dissolved inorganic carbon (DIC) reservoir (e.g., Conrad, 2005), methane production leads to an increase in local $\delta^{13}\text{C}_{\text{DIC}}$ if the methane is not re-oxidized and returned to the DIC reservoir. Methanogenesis has been argued to be the source of high $\delta^{13}\text{C}_{\text{carb}}$ values in septarian concretions of the Devonian Marcellus Shale of central New York (Siegel et al. 1987). Some of the lighter beds in core C1 are fossil-poor micrite in thin section, display diffuse contacts with darker beds, and appear concretionary in outcrop (G. C. Baird, 2013, personal communication) suggesting that some of the lighter

bands may be concretionary or impacted by in situ carbonate precipitation during lithification and/or diagenesis. Widespread, abundant concretions have been observed in the Kope Formation of Kentucky and Ohio (Brett et al., 2008), which is partially contemporaneous with the Utica Shale of New York. The high degree of scatter, lack of regionally reproducible $\delta^{13}\text{C}_{\text{carb}}$ values or vertical trends, and petrographic characteristics of some of the lighter-colored layers is consistent with a significant secondary overprint of isotope values and suggests these materials should be avoided when correlating.

The higher $\delta^{13}\text{C}_{\text{carb}}$ values in the lighter carbonate layers may explain the origin of the heavier than expected $\delta^{13}\text{C}_{\text{carb}}$ values in depths 5350–5370 ft (1631–1637 m) of well W6 (Figure 4) as the lighter colored layers correlate lithologically to the higher than expected $\delta^{13}\text{C}_{\text{carb}}$ values in W6. Although cuttings samples were screened for obvious alteration (e.g., macroscopic spar or pyrite), they were not screened by color, so it is possible that these three samples contain the lighter material with higher $\delta^{13}\text{C}_{\text{carb}}$ values as seen in core C1. Alternatively, the higher $\delta^{13}\text{C}_{\text{carb}}$ values in W6 could be explained by a local $\delta^{13}\text{C}_{\text{DIC}}$ signal. Grain-specific $\delta^{13}\text{C}_{\text{carb}}$ analyses and an increased well density could test this hypothesis.

Evaluation of Lithologic Mixing on $\delta^{13}\text{C}_{\text{carb}}$ in Cuttings

Results from the single-chip test in well W7 indicate moderate degrees of isotopic heterogeneity on a scale smaller than the cuttings sampling resolution (i.e., within a single cuttings sampling interval). Variability in $\delta^{13}\text{C}_{\text{carb}}$ of single chips is higher when the baseline $\delta^{13}\text{C}_{\text{carb}}$ values of bulk cuttings is changing. This variability is interpreted to result from the mixture of stratigraphically varying components within the cuttings sample. The $\delta^{13}\text{C}_{\text{carb}}$ values of multiple individual chips approximate the subsample $\delta^{13}\text{C}_{\text{carb}}$ values (~ 0.5 g [~ 0.04 oz]), which in turn approximates the bulk $\delta^{13}\text{C}_{\text{carb}}$ values of the bulk material (except in cases of strongly varying background $\delta^{13}\text{C}_{\text{carb}}$ and/or $\delta^{18}\text{O}_{\text{carb}}$ signals). The range of values in $\delta^{13}\text{C}_{\text{carb}}$ suggests that only a small number of chips (coarse sand and larger) need to be powdered to satisfactorily approximate the total sample values.

In general, the magnitude of $\delta^{18}\text{O}_{\text{carb}}$ variability was higher than that of the stratigraphically equivalent $\delta^{13}\text{C}_{\text{carb}}$. This is consistent with the theoretical prediction that $\delta^{18}\text{O}_{\text{carb}}$ is easier to reset during diagenesis (e.g., Banner and Hanson, 1990). Small-scale variation in porosity and permeability can result in variable $\delta^{18}\text{O}_{\text{carb}}$ over the stratigraphic interval that a single cuttings sample represents (e.g., 10 ft [3 m]). Those materials with higher permeability will have more fluids pass through them and therefore are more susceptible to alteration of the original $\delta^{18}\text{O}_{\text{carb}}$ signal (for fixed carbonate content). When picking material in a given sample, micritic components seem to have the best potential to record a primary oceanic $\delta^{13}\text{C}_{\text{carb}}$ signal (e.g., Metzger and Fike, 2013).

Evaluation of Sampling Resolution

In chemostratigraphic studies, the geographic resolution is set by the lateral well spacing, whereas the temporal resolution is set by the stratigraphic (vertical) sampling resolution. A high stratigraphic sampling density most closely reproduces the evolving marine $\delta^{13}\text{C}_{\text{carb}}$ record. Cuttings typically average lithology over depths of ~ 1 to 10 m (~ 3 to 33 ft), whereas core and outcrop studies only average over the width of the drill bit used for sampling (a few mm). For this reason, at a given sampling resolution, chemostratigraphic profiles from cuttings will be smoother than the equivalent profiles obtained from cores or outcrops. As seen in Figure 8, low sampling resolution in well W4 dampens the magnitude of isotopic variations and can give the appearance of lateral isotopic variability between localities where there is none. Low sampling resolution also obscures the stratigraphic position of distinct isotopic tie points (e.g., the low sampling resolution in well W4 is not appropriate for detailed chemostratigraphic correlation). Similar effects of averaging are present in other geochemical records, such as TOC and $\%_{\text{carb}}$. This stratigraphic averaging is important for calibrating isotopic data against other borehole data such as wireline logs (e.g., gamma ray), which more accurately track true depth. When choosing wells for a study, especially across a large range of sedimentation rates, the sampling resolution must be sufficient to identify, resolve, and correlate geochemical features of interest.

Summary

Covariation in isotopic and geochemical parameters can supply one method for evaluating diagenetic alteration. Pairing of $\delta^{13}\text{C}_{\text{carb}}$ with $\delta^{13}\text{C}_{\text{org}}$ can be used to test for meteoric diagenesis during negative $\delta^{13}\text{C}_{\text{carb}}$ excursions; however, this method is limited by the natural variability in organic carbon sources and should be used in tandem with other screening procedures. Stratigraphic reproducibility of $\delta^{13}\text{C}_{\text{carb}}$ trends in closely spaced wells can discriminate between basin-wide and local $\delta^{13}\text{C}_{\text{carb}}$ signals. This combined approach helped in identifying the diagenetic origin of both high $\delta^{13}\text{C}_{\text{carb}}$ (e.g., core C1) and low $\delta^{13}\text{C}_{\text{carb}}$ values (e.g., TR-1 in well W2, Figure 9). Low degrees of scatter and stratigraphic reproducibility of $\delta^{13}\text{C}_{\text{carb}}$ intervals BR-2, BR-3, GICE, TR-1, and TR-2 strongly suggest these intervals represent a primary basin-wide or global $\delta^{13}\text{C}_{\text{DIC}}$ signal. Analysis within this paper suggests that the vast majority of the rocks within the interval BR-1 retain the original $\delta^{13}\text{C}_{\text{carb}}$ signal, but is variably impacted by local diagenetic processes. The primary nature of the UT-1 $\delta^{13}\text{C}_{\text{carb}}$ values is unlikely.

Geologic Implications

Correlations using $\delta^{13}\text{C}_{\text{carb}}$ intervals reveal stratigraphic relationships not apparent using gamma-ray logs and geologic sampling logs. For example, the Black River Group can be confidently subdivided into three chronostratigraphic units based on $\delta^{13}\text{C}_{\text{carb}}$ logs. These chronostratigraphic divisions are very similar to divisions that would be made using gamma-ray logs (except for the uppermost part of the Black River Group in W3, in which isotopic data suggest variable erosion of the upper Black River strata) and suggest that the environmental change was synchronous across the basin. Conversely, $\delta^{13}\text{C}_{\text{carb}}$ interval TR-1 shows the diachronous nature of environmental change across the basin as the shaley facies form in the eastern portion of the basin first. Further, $\delta^{13}\text{C}_{\text{carb}}$ intervals BR-1, BR-2, and BR-3 show that differences in thickness of the Black River Group between sections result mainly from differences in the thickness of the upper portion of the Black River (i.e., BR-3). The fact that BR-3 is proportionally much thicker in the well W3 may result from non-deposition or erosion of the

uppermost Black River strata in the regions of the flanking wells. In this interpretation, the top of interval BR-3 in wells W1 and W2 is truncated and would correlate to the middle of interval BR-3 in well W3. This correlation is supported by the fact that the highest $\delta^{13}\text{C}_{\text{carb}}$ values in BR-3 are found in the upper part of this interval in well W3 and not observed in BR-3 from adjacent wells with a thinner BR-3 interval. An unconformity between the Black River and overlying Trenton groups is known in outcrop strata north of the western wells near Lake Erie (Mitchell et al., 2004) and the unconformity may extend down to our study area, manifested as variable truncation of the uppermost BR-3 interval.

The $\delta^{13}\text{C}_{\text{carb}}$ interval above BR-3 is the GICE. This interval appears to be fully preserved in the three western wells examined here (W1, W2, and W3) and mostly present in W5. This is evidenced by the gradual thickening and thinning of the GICE interval and the preservation of both the rise and fall in $\delta^{13}\text{C}_{\text{carb}}$ values across the basin. In eastern New York, either non-deposition occurred or erosion subsequently removed GICE strata. This is shown in Figure 9A in which $\delta^{13}\text{C}_{\text{carb}}$ intervals BR-2, BR-3, and the GICE interval pinch out between wells W5 and W6. TR-1 sediment accumulation as encountered in the eastern wells began immediately following the GICE interval, as evidenced by the thick rising limb of interval TR-1 prior to the 1‰ plateau. If more time were missing, the rise in $\delta^{13}\text{C}_{\text{carb}}$ would not be captured and would instead appear as a step change in $\delta^{13}\text{C}_{\text{carb}}$. This places tight chronostratigraphic boundaries on the events and factors that controlled sedimentation across the basin. Assuming that sedimentation was restricted in eastern New York due to insufficient accommodation space, then new accommodation space was created just after the end of the GICE. The increase in accommodation space likely arose from extensional faulting in which eastern New York was rapidly thrust downward following the GICE interval. The tectonic activity shifted the basin depocenter from southwestern New York (near well W3) before the GICE to eastern New York (near core C1) after the GICE.

Coupled lithostratigraphy and chemostratigraphy can be used to reconstruct basin dynamics. Figure 9 shows the relative position of the base of the Utica

Shale contact (lithostratigraphic contact; red wavy line in Figure 9) and top of TR-1 (chemostratigraphic contact; top of blue zone in Figure 9). These lines cross moving from east to west across New York State. This relationship demonstrates the time-transgressive nature of the Utica Shale contact, in which the basal Utica Shale is progressively younger moving west across New York. This is in general agreement with interpretations of Brett and Baird (2002), who used lithostratigraphic, biostratigraphic, and K-bentonite data to construct their chronostratigraphic correlations of outcrops in central and eastern New York.

Figure 9B shows two sets of correlations arising from lithostratigraphic (light and dark gray-shaded backgrounds) and chemostratigraphic methods (colored lines). A detailed chronostratigraphic understanding of the diachronous nature of the lithologic change is made possible using the $\delta^{13}\text{C}_{\text{carb}}$ data and produces a different depositional history than may otherwise be constructed for the Trenton–Utica sequence using gamma-ray logs and geologic sample logs alone. Correlations based upon shifts in gamma-ray logs and lithologic transitions from limestones to shales would suggest more strata missing in eastern New York than the correlations based upon $\delta^{13}\text{C}_{\text{carb}}$ data alone. Although the time-transgressive nature of the Trenton–Utica contact has been identified in previous studies (see Baird and Brett, 2002; Brett and Baird, 2002), these were conducted using outcrops with abundant fossils, event beds, and K-bentonites, materials that are rare or unavailable in the subsurface. This agreement suggests $\delta^{13}\text{C}$ chemostratigraphy is a fruitful way to link together subsurface regions and their correlative outcrop belts within a unified chronostratigraphic framework. This paper demonstrates the power of $\delta^{13}\text{C}_{\text{carb}}$ stratigraphy for understanding chronostratigraphic relationships in the subsurface, especially across different depositional facies and lithologies (Figure 9B) for which biostratigraphy may not be practical or feasible.

CONCLUSIONS

The ubiquity of well cuttings and the ability to rapidly analyze large numbers of samples for $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{18}\text{O}_{\text{carb}}$, and $\delta^{13}\text{C}_{\text{org}}$ have created an opportunity to

enhance chemostratigraphic studies from a few outcrops and cores to a network of wells to obtain the spatial density needed to assemble a high-resolution, basin-wide correlative framework in the subsurface. The sampling of wells in a high spatial density that results in large data sets can be used to resolve small ($\%$ -level) changes in $\delta^{13}\text{C}_{\text{carb}}$ that may otherwise be ascribed to noise when considering single sections alone. Multiple $\delta^{13}\text{C}_{\text{carb}}$ intervals can be found within a single formation or lithology demonstrating the potential high-resolution correlative power of $\delta^{13}\text{C}_{\text{carb}}$ chemostratigraphy from large data sets. We believe this paper demonstrates that $\delta^{13}\text{C}_{\text{carb}}$ can provide robust chronostratigraphic correlations across thick stratigraphic packages and over large lateral distances with small sample volumes and limited labor investments. The $\delta^{13}\text{C}_{\text{carb}}$ chemostratigraphy may be particularly useful in basins where environmental segregation of species during deposition limits the utility of biostratigraphy, such as the Permian Khuff Formation of Saudi Arabia (Dasgupta et al., 2001), the Jurassic Arab Cycles of Saudi Arabia (Alsharhan and Whittle, 1995), and the Silurian of the Michigan basin (Mesolella et al., 1974).

Several points must be kept in mind for a cuttings-based chemostratigraphic study:

1. Wells for cuttings-based studies must be chosen carefully based on their maximum vertical sampling resolution and the number of available wells in a given area needed to create the desired spatial resolution. Wells with coarse sampling intervals can limit the stratigraphic resolutions possible, as well as shift the isotopic values and stratigraphic position of local isotopic minima and maxima.
2. Isotopic analysis of single chips show that only a small fraction (e.g., $<0.5\text{ g}$ [$<0.02\text{ oz}$]) of a standard cuttings sample must be homogenized to obtain representative isotopic values.
3. The resulting data must be screened for diagenetic alteration that could otherwise skew resulting chemostratigraphic correlations. In particular, parallel $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ trends are strong evidence for a primary $\delta^{13}\text{C}$ signal in both phases. Similarly, covariation in $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{18}\text{O}_{\text{carb}}$, TOC, and carbonate abundance can be indicators for diagenetic alteration.

4. Diagenetic alteration of a single location cannot be fully assessed without comparison of isotopic trends (here, $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{13}\text{C}_{\text{org}}$, and $\delta^{18}\text{O}_{\text{carb}}$) from multiple sections within a basin, because traditional techniques for assessing diagenetic alteration (e.g., covariation in $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{18}\text{O}_{\text{carb}}$) can also result from primary environmental signals. Testing for reproducible $\delta^{13}\text{C}_{\text{carb}}$ patterns from closely spaced wells (stratigraphic reproducibility) is a rigorous technique for assessing diagenetic alteration at the basin scale.

Chemostratigraphic study of Upper Ordovician strata of New York has revealed that

1. Consistent with results using biostratigraphic, lithostratigraphic, and event-bed stratigraphic methods from outcrops in central New York State, the Trenton Group–Utica Shale contact is time-transgressive in subsurface regions south and west of the outcrop belt with the basal Utica Shale being progressively younger moving west across New York. This can be observed in the $\delta^{13}\text{C}_{\text{carb}}$ composite presented herein for the New York region of the Middle and Upper Ordovician Mohawkian and Cincinnati Series, respectively.
2. The locus of sedimentation shifted from southwestern New York (during the deposition of the Black River Group to middle Trenton Group) to eastern New York during deposition of the Utica Shale because of local tectonic forces likely related to the Taconic orogeny.

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