Stable isotope record of the Eifelian–Givetian boundary Kačák–*otomari* Event (Middle Devonian) from Hungry Hollow, Ontario, Canada

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Abstract: The Kačák Event in the Middle Devonian (Eifelian–Givetian (E–G) boundary) is a period of apparent global anoxia coincident with widespread deposition of black shale in hemipelagic, pelagic, and some neritic facies. Conodont biostratigraphy in the North American Appalachian Basin has proven to be problematic in precisely demarcating the E–G boundary. In this study, we show that the E–G boundary may be defined more accurately through isotope stratigraphy ($\delta^{13}C$) in conjunction with a conodont faunal change across this boundary, identified as the Kačák–*otomari* Event. The Canadian Hamilton Group outcropping in Hungry Hollow, Ontario, is a 22 m sedimentary succession spanning the Middle Devonian. Conodont biostratigraphy for this section makes it difficult to define the E–G boundary, but the *otomari* Event can be detected. High-resolution isotopic analysis of bulk sedimentary carbonate and organic matter for this succession records a significant negative $\delta^{13}C$ excursion ($\delta^{13}C_{carb}$ = up to 2‰; $\delta^{13}C_{org} = \sim 3.0$‰) that is synchronous with total organic carbon (TOC) values up to 12.5%. We identify this negative $\delta^{13}C$ excursion as a result of marine anoxia associated with the Kačák–*otomari* Event and suggest that the excursion is a global event driven by a source of isotopically light carbon, followed by a productivity event, similar to Mesozoic oceanic anoxic events. Such similarities between Devonian and Mesozoic oceanic anoxic events may become more evident with increased high-resolution isotopic and geochemical investigations of Devonian successions.

Résumé : L'événement Kačák au Dévonien moyen (limite Eifélien–Givétien (E–G)) est une période d'anoxie globale apparente qui coïncide avec une déposition étendue de shales noirs dans des faciès hémipélagiques et pélagiques ainsi que dans quelques faciès néritiques. La biostratigraphie des conodontes dans le bassin appalachien de l'Amérique du Nord s'est avérée problématique pour la démarcation précise de la limite E–G. Dans cette étude, nous démontrons que la limite E–G peut être définie de manière plus précise par une stratigraphie des isotopes ($\delta^{13}C$) en conjonction avec des changements dans la faune des conodontes en traversant cette limite, identifiée en tant que l'événement Kačák–*otomari*. Le Groupe canadien Hamilton affleurant à Hungry Hollow, en Ontario, est une succession sédimentaire de 22 m qui recouvre le Dévonien moyen. La biostratigraphie des conodontes dans cette section rend difficile la détermination de la limite E–G, mais il est possible de détecter l'événement *otomari*. Une analyse isotopique à haute résolution de carbonate sédimentaire et de matière organique en vrac de cette succession donne une importante excursion négative $\delta^{13}C$ ($\delta^{13}C_{carb}$ = jusqu'à 2 ‰; $\delta^{13}C_{org} = \sim 3,0$ ‰) qui est synchrone avec les valeurs de carbone organique total jusqu'à des valeurs de 12,5 %. Nous identifions cette excursion $\delta^{13}C$ négative comme étant le résultat d'une anoxie marine associée à l'événement Kačák–*otomari* et nous suggérons que l'excursion soit un événement global poussé par une source de carbone isotopiquement allégé, suivie d'un événement de productivité semblable aux événements anoxiques océaniques au Mésozoïque. De telles similitudes entre les événements anoxiques océaniques au Mésozoïque et au Dévonien pourraient être mieux définies avec plus d'investigations géochimiques et isotopiques à haute résolution des successions du Dévonien.

[Traduit par la Rédaction]

Introduction

Significant global events in Earth history have long drawn the attention of researchers due to their multi-faceted interactions in the global system: the lithosphere, biosphere, atmosphere, and hydrosphere. Within the late Eifelian (Middle Devonian) is the Kačák Event. House (1985) first named and described this event with respect to an ammonoid extinction that was correlated with eustatic sea-level and paleotemperature changes. The Kačák Event is now identified as a period of global anoxia causing the widespread deposition of black shale in hemipelagic, pelagic, and some neritic facies immediately preceding the base of the Givetian stage (Chlupáč and Kukal 1988; Walliser et al. 1995; House 2002). In addition, the Kačák Event is associated with the extinction of 15% of all marine genera (Sepkoski 1996; Racki and Koeberl 2004), but potentially as low as 4% (Bambach et al. 2004). It is now globally identified and chronologically constrained at the Global Stratotype Section and Point (GSSP) in Jebel Mech Irdane, Morocco (Walliser et al. 1995; Walliser 2000). Recently, Ellwood et al. (2003)

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proposed a bolide forcing mechanism for global environmental changes at the Eifelian–Givetian (E–G) boundary; however, the hypothetical bolide has drawn criticism due to a lack of rigorous evidence (i.e., Racki and Koeberl 2004; Ellwood et al. 2003).

Can biostratigraphy isolate the Eifelian–Givetian (E–G) boundary in North America?

Using biostratigraphy to delineate the E–G boundary in North America is problematic. Ammonoid and conodont zonations currently provide the most precise biostratigraphical scales for comparison of Devonian events (House 2002; Kaufmann 2006). Ideally, the E–G boundary is characterized by the ammonoid zonal transition from *Pinacites* to *Maenioceras* and the synchronous appearance of the conodont *Polygnathus hemiansatus* and extirpation of *Polygnathus xylus ensensis* (House and Gradstein 2004). The E–G boundary in European and African (i.e., GSSP) sections has been readily identified using the aforementioned biostratigraphy (e.g., Struve 1982; Walliser et al. 1995; Hladíková et al. 1997; Buggisch and Mann 2004).

In contrast, the E–G boundary in sediments deposited in the Appalachian Basin of North America has proven more difficult to isolate. Ammonoid preservation is often limited to flattened internal molds (Brett et al. 1991) and conodont biostratigraphy is not ideally conformable to European sections (Sparling 1999). Multiple researchers use question marks to demarcate the E–G boundary when illustrating biostratigraphic results from the Appalachian Basin (e.g., see fig. 3 in Klapper and Barrick 1983; see fig. 2 in Sparling 1999; see fig. 1 in Werne et al. 2002; see fig. 5 in Sageman et al. 2003). Additionally, the lack of a conodont change in North America conformable with that in Europe continues to draw debate in dating and correlating stratigraphic sections in identifying the E–G boundary (i.e., Hamilton Group in southern Ontario, Canada: Landing and Brett 1987; Rigby 1991; Sparling 1992, 1999). Conodont biostratigraphy allows researchers to key in on a “lithologic window” potentially containing the E–G boundary, but isolating the boundary to a horizon such as at the Jebel Mech Irdane, Morocco, GSSP has currently been problematic due to minimal recovery of diagnostic specimens. Of no fault to the cited research groups, the inherent nature of biostratigraphy has problems associated with selective preservation, the lack of similar global morphotypes, and globally nonconformable biostratigraphic changes.

Walliser (1983) coined the term “*otomari* Event” to coincide with a facies transition to black sediments from lighter units marking the onset of the Kačák Event. Walliser (2000) expanded the term *otomari* Event to include information about the contemporary conodont faunal transitions occurring at the onset of the Kačák Event in the latest Eifelian. Hereafter, we refer to this interval in stratigraphic time as the Kačák–*otomari* Event. Archetypal Eifelian conodonts, *Polygnathus robusticostatus*, *Po. trigonicus*, and *Tortodus kockelianus* become absent at the Kačák–*otomari* Event and are superseded by species such as *Icriodus* sp., *Ic. obliquimarginatus*, *Po. linguiformis*, *Po. pseudofoliatus*. The decline and subsequent rapid evolution of these species across the Kačák–*otomari* Event suggests that the chemical structure of the oceans and, in particular, dissolved oxygen levels (i.e., dysoxia) played a pivotal role (Schöne 1997). Again, in the absence of diagnostic index fossils, these associated assemblages only allow for keying into the onset of the Kačák–*otomari* Event, but are obviously limited in their ability for direct positioning of the E–G boundary.

The objective of this study was to generate a high-resolution stable isotope profile to (1) identify the Kačák–*otomari* Event in the Canadian part of the Appalachian Basin of ancient Laurentia; (2) investigate the reliability of chemostratigraphy as a viable method in the identification of the Eifelian–Givetian boundary in North America; and (3) to determine whether any perturbation occurred in the carbon cycle in association with the Kačák–*otomari* Event.

Geological setting

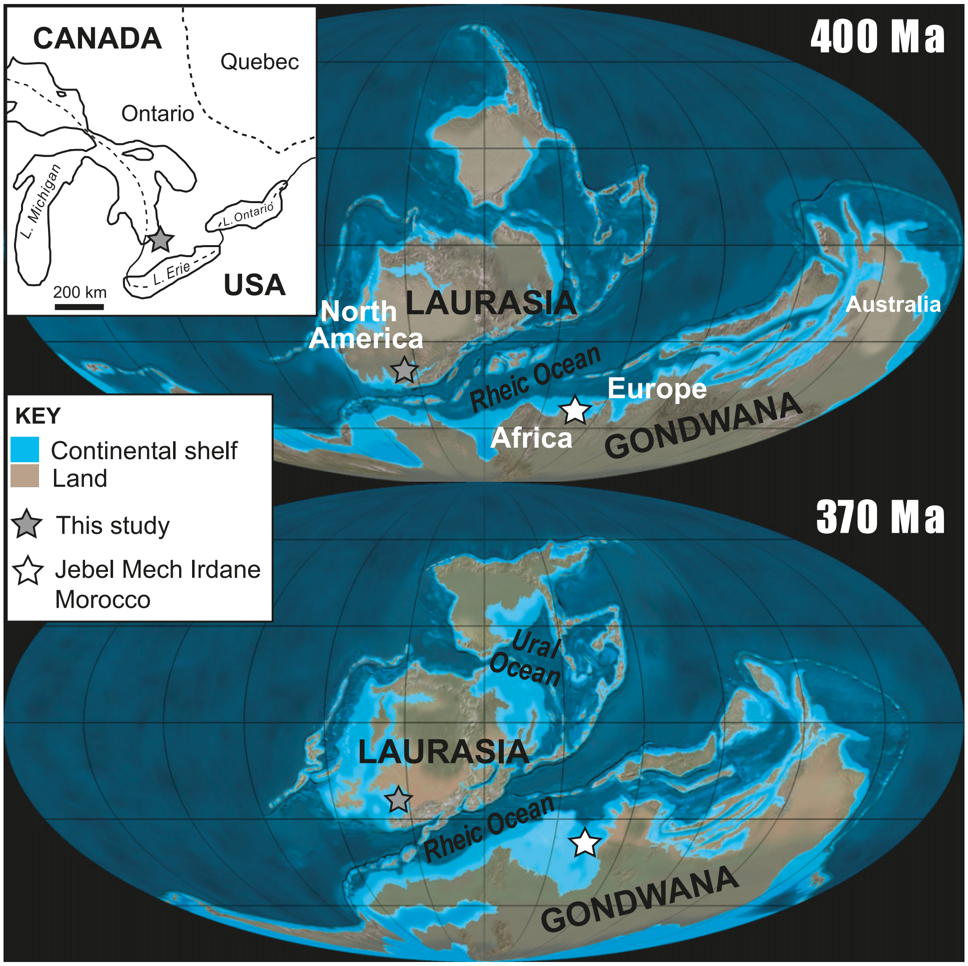
The arrangement of global landmass in the Middle Devonian was grossly divided into the two landmasses Gondwana and Laurasia, which were separated by the Rheic and Proto-Tethys oceans (Fig. 1). Small visceral terranes drifted from north of Gondwana and collided with Laurasia through the Devonian and into the Carboniferous. These collisions caused the Acadian Orogeny in the Appalachian mountain range of eastern North America. The Appalachians provided a significant source of sediment, which was transported northwestwardly into the Appalachian Foreland Basin and the Michigan Basin (Droste et al. 1975). The Hamilton Group in southern Ontario, Canada, represents an accreted clastic wedge sequence within a small waterway that connected the Appalachian Foreland Basin with the Michigan Basin.

Local stratigraphy

Exposed along the Ausable River at Hungry Hollow, Canada, is an ∼22 m section of the Canadian Hamilton Group chosen for this study (Fig. 1). Known widely as “Hungry Hollow,” this locale has been famous for paleontological collection since 1857 (Fig. 2). The exposed Hamilton Group at Hungry Hollow includes the topmost section of the Arkona Shale Formation (11 m), the Hungry Hollow Formation (1.6 m), and a basal portion of Widder Formation (9 m). The Arkona Shale Formation is laminated, medium-grey calcareous shale. Calcareous nodular horizons are present as well, and have been interpreted as early subsurface cementation or storm beds (Landing and Brett 1987). Notably, at the top of the Arkona Shale Formation are regionally variable, brown-black lenticular interbeds within the grey shale. Between the Arkona Shale and Hungry Hollow Formation is a hardground, previously interpreted as a time of submarine nondeposition.

Next is the Hungry Hollow Formation, which exhibits significant lithological variability in comparison to the other formations. Mitchell (1967) subdivided the Hungry Hollow Formation into nine units based on detailed sedimentological and paleontological changes: unit 1 (U1) is the basal limestone ledge, units 2–5 (U2–U5) are black laminated shale, units 6–8 (U6–U8) define another limestone ledge (encrinal limestone), and unit 9 (U9) is a coral biostrome, recently interpreted as earliest Givetian (Donato 2003). In this study, we retain this nomenclature to remain consistent with other published literature. Finally, the outcropping Widder Formation is another massive grey shale, containing abundant bra-

Fig. 1. (Inset) Modern location map of Ausable River at Hungry Hollow, southern Ontario, Canada (grey-filled star). Global paleogeography at 400 Ma and 370 Ma (maps modified after Blakey 2005). Note the global transgression occurring through the Middle Devonian and the migrations of Laurasia southwards and Gondwana northwards. An isotopic comparison between this study and the GSSP site, Jebel Mech Irdane, Morocco (open star) will be conducted.



chiopods (Mucrospiriferids) and calcareous bedding within 1 m of the base. For additional details, the reader is directed to extensive local paleontological and lithological reviews completed by Landing and Brett (1987) and Sparling (1999) for a regional correlation of the southern Ontario Hamilton Group to northern USA sections.

Local biostratigraphy

Researchers have long correlated the Hamilton Group with similar Devonian sediments across Lake Erie into the United States, and a Middle Devonian age is generally accepted. What has been more problematic is identifying the E–G boundary in the North American Middle Devonian sequences due to the aforementioned biostratigraphic problems. Pyritized ammonoid specimens from both the families Agoniatitaceae and Tornoceratacea have been found at the Hungry Hollow study site (Miller 1938; House 1965; Prosh 1990), but specimens are rare and often flattened imprints. Additionally, this only narrows the age of the section to Middle Devonian.

Analysis of conodont biostratigraphy was initiated by Uyeno et al. (1982), expanded by Landing and Brett (1987), and summarized by Sparling (1999), but the exact location of the E–G boundary still remains elusive (Fig. 2). Landing and Brett (1987) found *Icriodus*-dominated conodont assemblages in the uppermost Arkona Shale Formation that included *Ic. obliquimarginatus*; this taxon is accepted as evolving in the latest Eifelian and becoming extinct in the earliest Givetian (Belka et al. 1997). Additionally, the Arkona Shale Formation is securely correlated with the Plum Brook Shale Formation of Ohio, USA (Rickard 1984), which has yielded abundant *Po. xylus xylus* and advanced forms of *Po. xylus ensensis* (Landing and Brett 1987). Based on the described conodonts from the uppermost Arkona Shale Formation and the correlative Plum Brook Shale Formation, Landing and Brett (1987) suggested their conodont assemblages from the Arkona Shale Formation to represent the *Po. xylus ensensis* Zone. The base of the Givetian is defined by the Subcomission on Devonian Stratigraphy to be the lowest occurrence of *Po. hemiansatus* (Fig. 3), which probably evolved from the *Po. pseudofoliatus* group (Walliser et al. 1995). However, the only report of this morphotype is a sole specimen from the uppermost Arkona Shale Formation (Sparling 1999). The Hungry Hollow Formation and Widder Formation contain abundant representatives of *Polygnathus* sp., including *Po. timorensis*, the type specimen

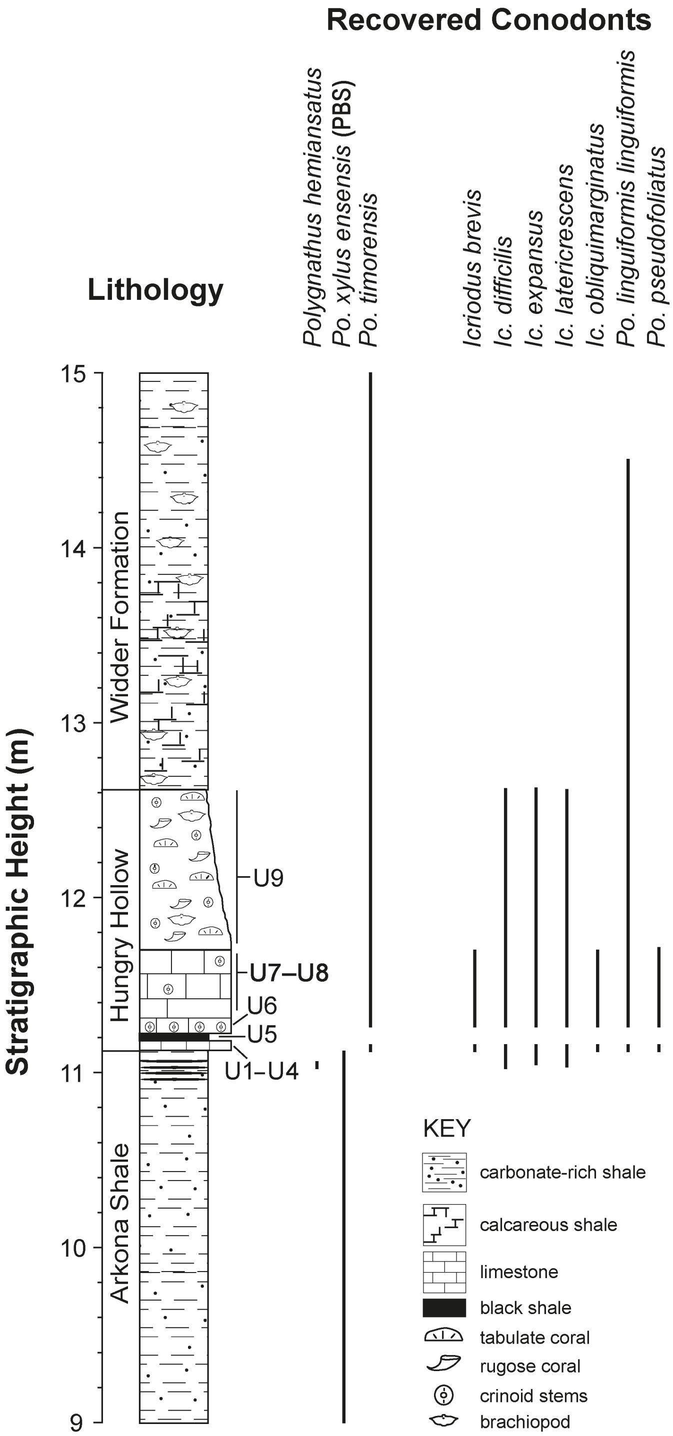


Fig. 2. Recovered conodont biostratigraphy from 6 m of the central Hamilton Group exposed in southern Ontario (after Uyeno et al. 1982; Landing and Brett 1987). Index fossils are arranged on the left. The *Polygnathus xylus ensensis* is recovered from the Plum Brook Shale (PBS), Ohio, USA, which is securely correlated to the Arkona Shale Formation (Rickard 1984) and provides corroborative evidence for the presence of the Eifelian–Givetian boundary at this site. Mitchell (1967) divided the Hungry Hollow Formation into nine units (U1 to U9).

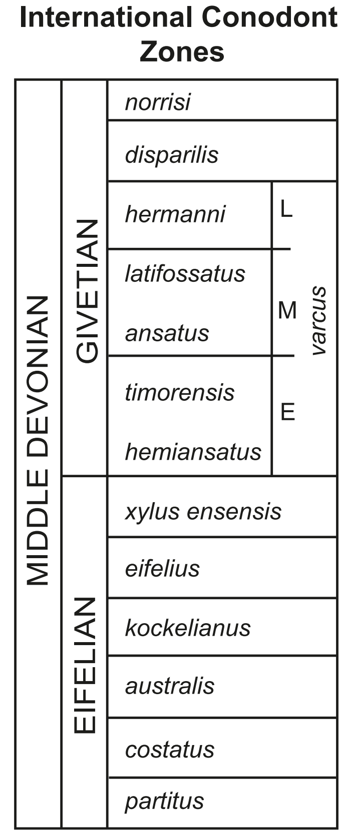


Fig. 3. International conodont zones for the Middle Devonian, as proposed by Kaufmann (2006), used in this study. E, early; M, middle; L, late.

for the early *timorensis* Zone. The recovered conodont biostratigraphy from this section of the Hamilton Group suggests that the E–G boundary is present in the study section (Fig. 2).

Methods

At Hungry Hollow the entire stratigraphic section was sampled to accurately characterize the long-term isotopic curve in bulk sedimentary carbonate and organic matter. The base of the outcropping Arkona Shale Formation in the Ausable River was used as the 0 m datum, and the sampling strategy varied to encompass the lithologic variability throughout the exposed section. Above 21.75 m the construction of a reliable mid-Devonian carbonate and organic record was deemed impossible due to advanced Holocene pedogenesis.

Prior to stable-isotope analysis, sediment samples were washed to remove adhering clays, desiccated in a 60 °C drying cabinet for 24 h, then ground to a homogenous powder. Stable isotope analysis of bulk sedimentary carbonate was performed using an online carbonate system (ISOCARB) connected to a VG OPTIMA isotope-ratio mass spectrometer. Analytical precision on international standard NBS-19 was better than ± 0.1‰ for both $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$.

Bulk sedimentary organic matter ($\delta^{13}C_{org}$) and total organic content (TOC) analysis was performed on finely ground samples that were treated with 10% HCl for 12 h to remove the carbonate component. Following the acid treatment, the samples were rinsed to neutrality and dried before being re-ground to a homogenous powder. Isotopic analysis was performed on a sub-sample with a Costech elemental analyzer connected to a Thermo-Finnigan DeltaPlus XP. Carbon isotope ratios were measured against several internal and international standards (NBS-21, USGS-24, ANU-Sucrose, Urea, Spar calcite). Isotopic ratios are all expressed in the standard delta (δ) notation in per mil (‰) against Vienna Pee Dee Belemnite (VPDB). Reproducibility for organic and carbonate isotope analysis were within ± 0.2‰ and ± 0.1‰, respectively (Table 1).

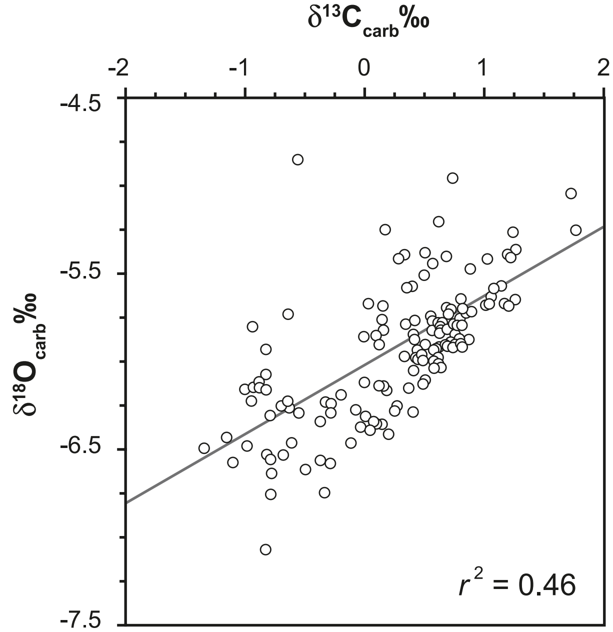
Isotopic results

To accurately interpret the isotopic ratios derived from whole-rock samples, the integrity of the data must be evaluated to determine whether a primary signal of marine chemistry has been preserved or whether there has been secondary diagenesis. This study employed the isotopic analysis of inorganic as well as organic carbon components preserved in bulk sediments. Currently, there is no known mechanism to simultaneously alter the carbonate and organic carbon isotope signals in magnitude or direction (Holser et al. 1996). The simultaneous negative isotope excursions in both $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ support a lack of significant diagenetic overprinting in the carbonate isotope record. Furthermore, the $\delta^{13}C_{carb}$ values of the investigated material fall within the range of values for the best-preserved carbon isotope signatures for the Eifelian–Givetian time interval (see Veizer et al. 1999). In addition, $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ cross plots have been routinely used to evaluate diagenesis in sedimentary sequences (Weissert 1989). Although almost half of the results co-vary ($r^2 = 0.46$; Fig. 4), we can assume that the $\delta^{13}C_{carb}$ record has maintained a primary or near primary signal. However, the $\delta^{18}O_{carb}$ values have been shifted from realistic seawater values that would be expected for the Devonian, since diagenetic fluids in many cases do not contain much CO_2 to severely reset the carbon isotope signature of carbonates. The $\delta^{18}O_{carb}$ curve is presented, although it does not merit further discussion in this paper.

The carbonate and organic isotope data are shown graphically in Fig. 5 (see Table 1). The $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ data generally follow the same gross pattern. From 0 to 8 m the $\delta^{13}C_{carb}$ value fluctuates between –1.4‰ and +0.2‰ (average = –0.6‰). From 8 to 11 m the fluctuation ceases and the values generally trend in a positive direction. At 10.82 m a rapid negative shift occurs from +0.8‰ to –0.3‰, followed by another of larger magnitude from +0.7‰ to –0.8‰ (see Fig. 6). These shifts occur just prior to the onset of laminated black shale deposition in the uppermost Arkona Shale and Hungry Hollow formations. At 11.12 m, the $\delta^{13}C_{carb}$ curve shifts positive from –0.6‰ to a maximum of +1.8‰, but gradually returns to relatively pre-excursion values by 11.8 m.

The $\delta^{13}C_{org}$ curve displays a slightly different pattern. From 0 to 10.8 m the $\delta^{13}C_{org}$ values exhibit little variation and range from –27.0‰ to –26.1‰ (average = –26.5‰). After 10.8 m, there is a rapid negative $\delta^{13}C_{org}$ excursion from –26.6‰ to –29.5‰ that occurs just prior to the onset of black shale deposition in the Arkona Shale Formation. After this initial negative $\delta^{13}C_{org}$ excursion, the isotopic values stabilize around –29‰ through the next black shale horizon in the Hungry Hollow Formation, before rapidly returning towards pre-excursion values. However, no positive excursion is recorded in $\delta^{13}C_{org}$ in comparison to the $\delta^{13}C_{carb}$ record. In fact, the $\delta^{13}C_{org}$ value trend towards more negative values from ~11.6 to ~13 m, after which the values fluctuate around –28.5‰ for the remainder of the sampled interval.

Fig. 4. Scatter plot of bulk-sediment $\delta^{13}C_{carb}$ versus $\delta^{18}O_{carb}$ (see text for discussion).



Total organic carbon (in wt.%) remains relatively constant at <1% for the entire section, except during two intervals. At 11.1 m, TOC rises concurrently with the lithologic transition to black shale, where it reaches a maximum of 12.45%. The second TOC shift occurs within the coral biostrome between 11.5 and 12.85 m and reaches a maximum of 3.1% at 12.45 m. Following this second rise in TOC, values return to <1% throughout the remainder of the section.

Similar regional or global trends are a strong argument for global changes in the carbon system (Buggisch and Mann 2004), and a $\delta^{13}C$ negative excursion has been found at the GSSP for the E–G boundary (Ellwood et al. 2003), Laurasia (Sageman et al. 2003) and Gondwana (i.e., Buggisch and Joachimski 2006; Hladíková et al. 1997). Thus, we interpret this negative $\delta^{13}C$ excursion as a time-stratigraphic marker.

Discussion

The Kačák–*otomari* Event, as identified and described by Walliser et al. (1995) using the term "*otomari* Event," is represented by the lithologic transition from a limestone to black shale sedimentary facies at the E–G boundary. In addition to the lithologic change, Walliser (2000), also using the term "*otomari* Event", described the loss of well-established Eifelian conodont species (e.g., *Tortodus kockelianus*, *Po. trigonicus*, and *Po. robusticostatus*), rapid evolution of the polygnathid group members (*pseudofoliatus*, *ensensis*, and *Icriodus*), and to *Ic. obliquimarginatus* directly near the E–G boundary. Although these species are not directly in-

Fig. 5. Geochemical trends through the Hamilton Group, Ontario, Canada. Bulk sediment carbonate ($\delta^{13}C_{carb}$), organic carbon ($\delta^{13}C_{org}$), and total organic carbon (TOC in wt.%) profiles for the entire sampled interval (see text for discussion). HH, Hungry Hollow Formation.

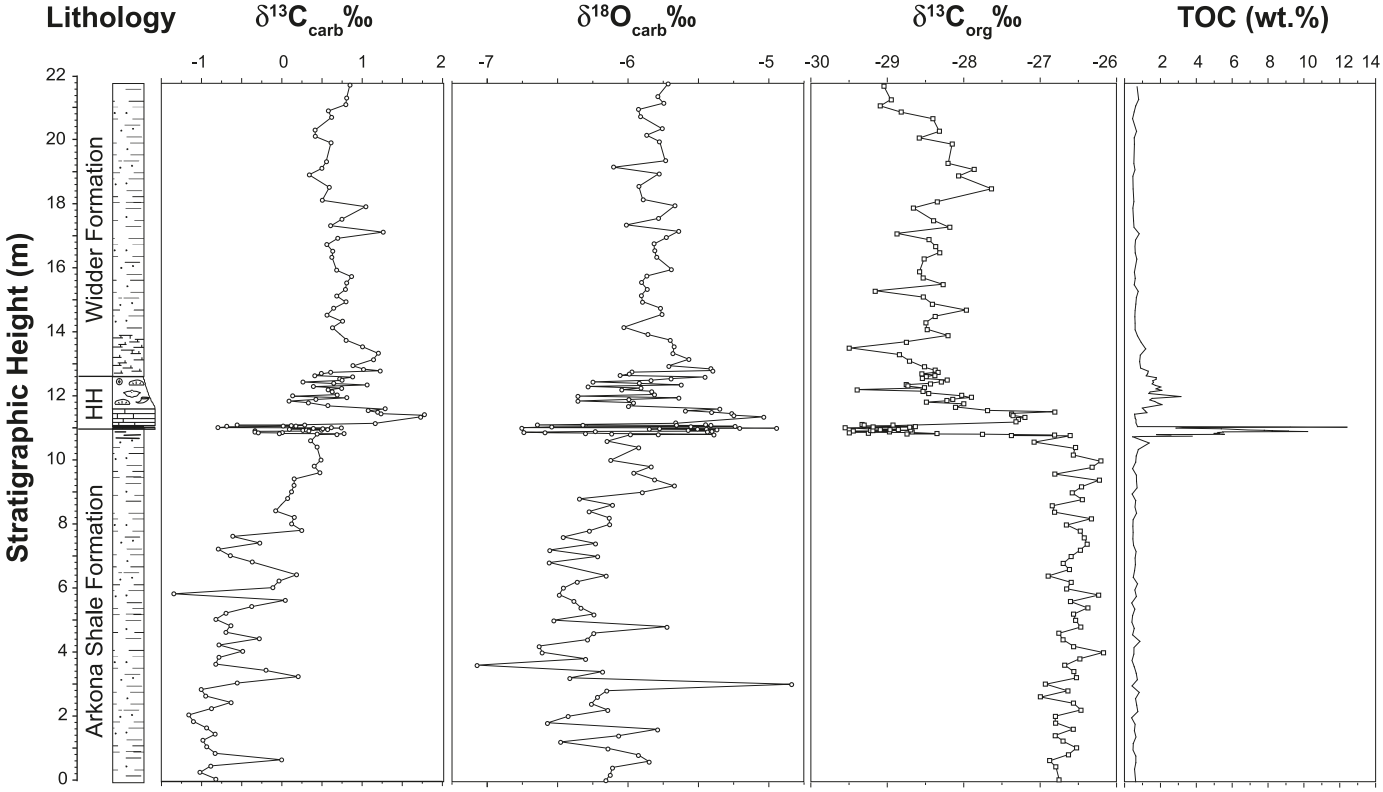
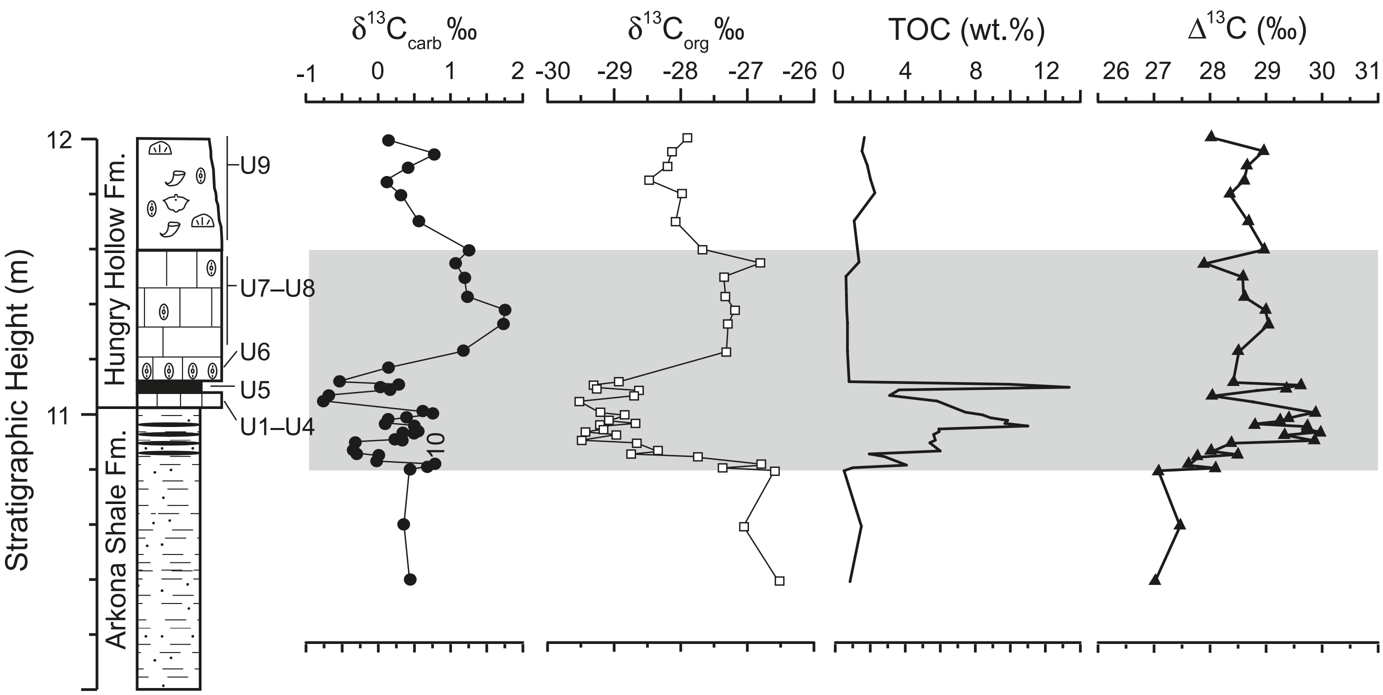


Fig. 6. High-resolution geochemical profile of the Kačák–*otomari* Event at Ausable River, Hungry Hollow. Note, the onset of the negative $\delta^{13}C_{carb}$ excursion occurs just prior to the onset of black shale deposition. The $\delta^{13}C_{org}$ negative excursion also occurs prior to the initiation of black shale formation; however, it does not return back as in the $\delta^{13}C_{carb}$ record. A $\Delta^{13}C$ (= $\delta^{13}C_{carb} - \delta^{13}C_{org}$) record is also presented, which shows fractionation between the carbonate and organic reservoirs, thus showing a clear change across the Kačák–*otomari* Event. Fm., Formation.



dex fossils, collectively they can be used as additional indirect evidence for the time-stratigraphic interval where the E–G boundary exists. At Hungry Hollow, the recovered index fossils appear taphonomically influenced, obscuring the conodont zones and E–G boundary location. However, using the *otomari* Event conodont changes in conjunction with the index fossils provides further biologic evidence that the E–G boundary and Kačák–*otomari* Event are present in the Hungry Hollow section of Ontario.

Isotopic curve at Hungry Hollow

Broad isotopic trends through the studied interval are important in understanding the environmental transition from an Eifelian to Givetian world. The $\delta^{13}C_{carb}$ curve in the Arkona Shale Formation shows a general trend from background values of ~–1‰ to +0.5‰ just prior to the contact with the Hungry Hollow Formation (Figs. 5 and 6). This general trend is interrupted by a sharp negative and positive excursion, which returns to pre-excursion values (~+0.5‰). The Widder Formation begins with slightly more elevated values (~+1.2‰) after the second (minor) TOC enrichment, but fluctuates thereafter between +0.5‰ and +1.0‰. Overall an average $\delta^{13}C_{carb}$ shift of ~1‰ occurs across the E–G boundary. However, the reverse broad trends are recorded in $\delta^{13}C_{org}$, with the Arkona Shale Formation exhibiting less depleted values (~–26.5‰) than the Widder Formation (~–28.5‰). Both the partial pressure in CO_2 (pCO_2) and isotopic composition of the CO_2 will cause a greater carbon isotopic excursion in organic matter than carbonate (Hayes et al. 1989); a difference of twice the magnitude has been recorded in Cretaceous isotopic records (see Gröcke et al. 1999), which is concordant with the Hungry Hollow data.

Explaining the global environmental triggers of the Kačák–*otomari* Event is problematic. The presence of black shales high in TOC are reported in Sageman et al. (2003) and this study would support evidence for global anoxia during the Kačák–*otomari* Event. Several mechanisms have been invoked as the driving force behind negative $\delta^{13}C$ excursions in the geological record: oceanic upwelling of organic-rich oxidized (^{12}C-enriched) organic matter (Küspert 1982); global wildfires of terrestrial organic matter (Finkelstein et al. 2006); volcanic-derived CO_2 (Kump and Arthur 1999); and the massive release of continental margin methane clathrate reservoirs (Hesselbo et al. 2000). Speculating on the bolide triggering mechanism at the E–G boundary (Ellwood et al. 2003) is not within the focus of our study.

The Kačák–*otomari* negative $\delta^{13}C$ excursion at Hungry Hollow

At Hungry Hollow, the negative $\delta^{13}C$ excursion in the stratigraphic section is initiated at the top of the Arkona Shale concurrent with regionally variable, thin, blackish lenticular shales, which suggests a period of increased biologic productivity and organic carbon burial. However, complete oceanic anoxia is not immediately achieved as $\delta^{13}C_{carb}$ values trend to pre-excursion values and limestone deposition occurs. This would suggest that the ocean, at least regionally, experienced oxygenation and possibly sea-level shallowing for the carbonate factory to form, which may have been due to regional tectonic fluctuations. It is interesting to note that the $\delta^{13}C_{org}$ curve does not return to less negative values after the initial negative $\delta^{13}C_{carb}$ excursion. This would suggest a complex interplay between productivity and carbonate platform formation, possibly from upwelling events or complex oceanic communication between surface waters of the Michigan Basin and Appalachian Foreland Basin. The depositional hiatus between the Arkona Shale and Hungry Hollow formations is an interval of minimal missing time, as suggested by the lack of any major shifts in $\delta^{13}C_{carb}$, $\delta^{13}C_{org}$, and TOC.

Continued burial of organic matter, as evidenced from increasing TOC concentrations, resulted in ^{13}C enrichment of dissolved inorganic carbon in surface waters and subsequently elevated $\delta^{13}C_{carb}$ values (Fig. 6). The maximum geochemical expression of the Kačák–*otomari* Event in $\delta^{13}C_{carb}$ is recorded during a second, larger magnitude negative excursion (~2‰) occurring near the top of U1–U4, in which there is a subsequent lithologic transition to black shale deposition (U5 in the Hungry Hollow Formation).

TOC levels within the initiation of black shale deposition (U1–U4) gradually climb up to 12%, after which they gradually decline to values of ~4%. During deposition of the black shale (U5) TOC values show a sudden increase to reach 12.45%, with a sudden drop off to ~0.7% (Fig. 6). Over the E–G boundary, eustatic sea level rise coupled with increased surface productivity created continued anoxic benthic conditions from continual respiration of organic matter (Werne et al. 2002). Increased organic matter deposition (as indicated by TOC enrichment) from the top of the Arkona Shale Formation into the Hungry Hollow Formation without continued accumulation is possibly the result of complex linkages between large-scale tectonic activity and the resulting accommodation space within the Appalachian Basin (see Werne et al. 2002 and references therein for more discussion). A re-establishment of oxygenated, circulated oceanic conditions is corroborated by the return to limestone deposition, lower organic matter accumulation (decreased TOC), and the formation of a well-developed coral biostrome in the Hungry Hollow Formation.

Global anoxia and $\delta^{13}C$ at the Eifelian–Givetian boundary

Although the global perturbation at the Kačák–*otomari* Event does not mirror the magnitude of other Paleozoic isotopic events (i.e., Silurian–Devonian boundary: e.g., Saltzman 2005) or biologic extinctions (i.e., Frasnian–Famennian boundary: e.g., Buggisch 1991), a significant global event occurred at the E–G boundary causing the extinction of 15% of marine genera (Sepkoski 1996) and an isotopic perturbation that has been found in other marine basins around the Devonian globe (e.g., Hladíková et al. 1997; Ellwood et al. 2003; Sageman et al. 2003; Buggisch and Joachimski 2006). The Kačák–*otomari* Event is associated with widespread black shale deposition (Budil 1995; House 2002); and the thin black shale facies in the Hungry Hollow Formation is interpreted as additional supporting evidence for this event.

Geochemical evidence for significant organic carbon burial at Hungry Hollow is recorded in TOC, where values rise from a background near 1% in the Arkona Shale Formation to 12.45% in the Hungry Hollow Formation (Fig. 5). The onset of the TOC spike occurs in the upper Arkona Shale

Formation, and corresponds to a rapid negative $\delta^{13}C$ shift in both the carbonate and organic phases. A second broad TOC enrichment up to 3.1% occurs in the coral biostrome of the Hungry Hollow Formation, which is concordant with a decrease in $\delta^{13}C_{carb}$ to pre-excursion values ($\sim 0.5‰$), a shift from background to excursion values in the organic carbon record ($\delta^{13}C_{org}$ from $\sim -27‰$ to $\sim -29‰$) (Fig. 5), and evidence of massive activity in the biologic system with significant coralline development.

Shifts in the $\delta^{13}C$ value of marine sediments and fossils in the Devonian have recently received more attention (Ellwood et al. 2003; Sageman et al. 2003; Buggisch and Mann 2004; Joachimski et al. 2004; Saltzman 2005). Of particular reference to this study, a carbon isotope stratigraphic approach on the E–G boundary began with the efforts of Hladíková et al. (1997) on the Barrandian Basin in the Czech Republic. Hladíková et al. (1997) reported a positive $\delta^{13}C_{carb}$ excursion ($\sim 1.8‰$) at the top of the Kačák interval from Volf Gorge (see their fig. 7), which shifted back to pre-excursion values marking the E–G boundary. The $\delta^{13}C_{org}$ produced in that same section was obtained from a much lower sampling resolution, although there is a negative shift of $\sim 2‰$ from the pre-Kačák interval to the Kačák interval. A similar $\delta^{13}C$ pattern was observed in a lower resolution stable isotope investigation from the "U dubu sedmi brat" outcrop (Hladíková et al. 1997), suggesting that isotope stratigraphy has the potential to constrain the position of the Kačák–*otomari* Event and E–G boundary. Redrafting of the Hladíková et al. (1997) data from Jirásek in Buggisch and Mann (2004) reveals considerable variability and no obvious isotopic excursion. However, the Jirásek section is a shallow-marine carbonate sequence, and the $\delta^{13}C_{carb}$ curve generated may be strongly influenced by shallow-water diagenesis (Marshall 1992), thus producing the homogenous curve at Jirásek. Another $\delta^{13}C_{carb}$ curve was generated by Ellwood et al. (2003), which identified a major negative $\delta^{13}C_{carb}$ excursion in the latest Eifelian of $\sim 7‰$, followed by a slight positive $\delta^{13}C_{carb}$ excursion compared to pre-excursion values of $\sim 1‰$. The cause of this negative $\delta^{13}C$ excursion was proposed by Ellwood et al. (2003) to be a massive bolide impact, ecosystem collapse, and subsequent release of methane gas hydrates.

As noted earlier, the definition of the E–G boundary in North America (ancient Laurasia) is typically associated with a question mark. It has been shown in the Mesozoic that global $\delta^{13}C$ isotopic excursions can be used to assign stratigraphic correlations in the oceanic carbon reservoir (Jenkyns et al. 2002). Thus, the identification of the negative $\delta^{13}C$ excursion across the Kačák–*otomari* Event (Figs. 5, 6) could be used to test the global extent of this event and constrain the position of the E–G boundary. Sageman et al. (2003) produced a very detailed $\delta^{13}C_{org}$ curve through the Middle–Upper Devonian of the Appalachian Basin (see their fig. 4). Within this high-resolution curve, there are many isotopic shifts between more negative and less negative $\delta^{13}C_{org}$ values, which Sageman et al. (2003) interpret as potential cyclic changes in sea level and thus shifts from anoxic to suboxic oceanic conditions. On closer inspection of this $\delta^{13}C_{org}$ curve (see their fig. 5), there is a major negative $\delta^{13}C_{org}$ excursion on the order of 2‰ that corresponds to TOC enrichment up to 18% across the Union Springs and Oatka Creek formations, equivalent to the E–G boundary. Virtually no discussion of this negative excursion was presented by Sageman et al. (2003), but in light of the data generated from Hungry Hollow, we suggest that this negative $\delta^{13}C_{org}$ excursion and high TOC values are likely expressions of the Kačák–*otomari* Event.

Of specific interest to this study is the identification of the negative $\delta^{13}C$ prior to black shale formation and TOC enrichment. We identify this perturbation in the carbon cycle with the global Kačák–*otomari* Event located at the E–G boundary using the available conodont biostratigraphy (Fig. 7). It is proposed that this negative $\delta^{13}C$ signature at the Kačák–*otomari* Event is global in extent based on corroboration from previous research generated from ancient Laurasia, Gondwana, and this study (Fig. 7). Further high-resolution stable isotope investigations across the E–G boundary will enable us to assess the true nature of the carbon cycle perturbation associated with the Kačák–*otomari* Event.

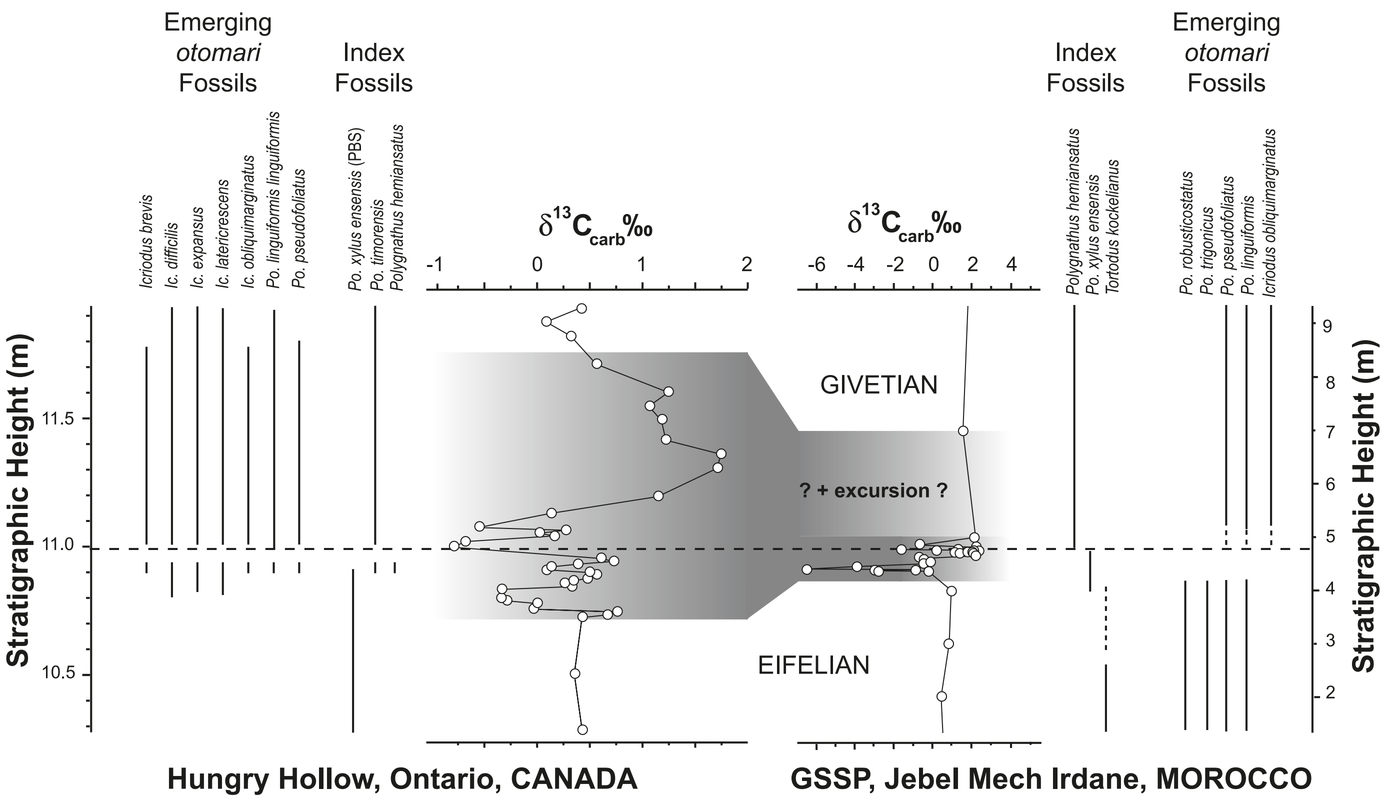
The duration of the Kačák–*otomari* Event has yet to be constrained through detailed study. However, duration can be quasi-extrapolated from a cyclostratigraphic study by House (1995) on the duration of the Givetian and uppermost Eifelian. This study included the Bou Tchrafine section from Morocco, which is close (~ 25 km) to the GSSP of the E–G boundary. Assuming that the Ellwood et al. (2003) negative $\delta^{13}C_{org}$ and iridium anomaly are concordant with the Kačák–*otomari* Event, this would indicate that it occurred in a stratigraphic interval of ~ 34 cm (between the base of Bed 117 and Bed 122). Using the description that 5.6 cm represents a 19.9 ka couplet in House (1995), this would indicate a duration of ~ 121 ka. This estimate is much less than that reported by Racki and Koeberl (2004: "perhaps 1 million years in duration", p. 471b), although based on the updated time scale for the Devonian by Kaufmann (2006), the estimate of ~ 121 ka is in agreement.

Comparing the Kačák–*otomari* Event and Toarcian (Jurassic) Ocean Anoxic Event

Oceanic anoxic events (OAEs) in the Mesozoic have principally recorded two generic isotope curves: (1) a negative $\delta^{13}C$ excursion (>3‰ in $\delta^{13}C_{org}$) followed by a positive $\delta^{13}C$ excursion, with the latter occurring after maximum organic burial (e.g., Posidonienschiefer event (Early Toarcian): Hesselbo et al. 2000; Selli event (earliest Aptian): Gröcke et al. 1999); and (2) a broad positive $\delta^{13}C$ (>2‰ in $\delta^{13}C_{carb}$) excursion with no negative $\delta^{13}C$ excursion (e.g., Weissert event (Valanginian–Hauterivian boundary): Gröcke et al. 2005; Bonarelli event (Cenomanian–Turonian boundary): Sageman et al. 2006). However, of all the Mesozoic OAEs, the Toarcian OAE is enigmatic in that several sections show a positive $\delta^{13}C_{carb}$ excursion, but this excursion has yet to be shown in the organic reservoir (Hesselbo et al. 2000, 2007). Although Devonian black shales and Mesozoic black shales have never been compared from an OAE perspective, the isotopic signature of the Kačák–*otomari* Event from Hungry Hollow compares closely with the Toarcian OAE, and thus warrants discussion.

The E–G boundary $\delta^{13}C_{carb}$ curve from Hungry Hollow records a significant negative excursion ($\sim 1‰$) immediately followed by a positive excursion ($\sim 2‰$; Fig. 6). This excursion is equally more impressive in the $\delta^{13}C_{org}$ record,

Fig. 7. A comparison of the Kačák–*otomari* Event at Hungry Hollow, Canada, to the Global Stratotype Section and Point (GSSP) in Jebel Mech Irdane, Morocco. The GSSP conodont biostratigraphy is after Walliser et al. (1995) and Walliser (2000), whereas the $\delta^{13}C_{carb}$ data are after Ellwood et al. (2003). The lower sampling resolution before and after the Eifelian–Givetian boundary may have missed important features of the $\delta^{13}C_{carb}$ curve for this interval. As shown through this comparison, the 2 m gap above the E–G boundary at the GSSP may contain the positive $\delta^{13}C_{carb}$ excursion that is recorded from Hungry Hollow; the entire positive $\delta^{13}C_{carb}$ excursion at Hungry Hollow is within 1 m. PBS, Plub Brook Shale.



except that the positive excursion is lacking (Fig. 6). The Toarcian OAE isotopic record from Europe shows a similar relationship, albeit a larger magnitude excursion, where the subsequent positive excursion is recorded in $\delta^{13}C_{carb}$ and not in $\delta^{13}C_{org}$ (Hesselbo et al. 2000, 2007). Secular explanations accounting for an absence of a positive $\delta^{13}C_{org}$ excursion have only been speculative, but they have consisted of a shift in CO_2 concentrations, a change in dissolved inorganic carbon, and a shift in flora or fauna of the upper ocean leading to a bias in the carbonate isotopic record (see Jenkyns 2003 and Hesselbo et al. 2007). However, there are other features of the Toarcian OAE isotopic record that are similar to the Kačák–*otomari* Event, which we present here briefly:

(1) **Seawater strontium isotopes**: Both initiate during a strontium isotope ($^{87}Sr/^{86}Sr$) minimum followed subsequently by a rapid increase (van Geldern et al. 2006; Waltham and Gröcke 2006). The rise after the Toarcian OAE has been interpreted as a large increase in continental weathering due to an intensified hydrological cycle (Waltham and Gröcke 2006).

(2) **Biological carbonate**: Mid-Devonian brachiopods (van Geldern et al. 2006) and Toarcian belemnites (van de Schootbrugge et al. 2005) show extremely positive $\delta^{13}C_{carb}$ values after the maximum deposition of black shale. It is still uncertain why this is the case although a shift in habitat from deeper water to shallower settings may be an explanation.

(3) **Atmospheric setting**: pCO_2 records are sparse for both events, although they tend to indicate high pCO_2 concentrations followed by rapid drawdown (Rothman 2002; McElwain et al. 2005; Royer 2006). The construction of a $\Delta^{13}C$ curve ($\Delta^{13}C = \delta^{13}C_{carb} - \delta^{13}C_{org}$; Fig. 6), which is a function of biological fractionation and pCO_2, suggests that surface water pCO_2 increased rapidly during the Kačák–*otomari* Event and remained high thereafter, a similar result to that reported in Rothman (2002).

(4) **Algae record**: An increase in prasinophytes (algae) is associated with the Toarcian OAE (Prauss et al. 1991; Bucefalo Palliani et al. 2002), and the Kačák–*otomari* Event has been shown to have elevated C_{28}/C_{29} sterane ratios (>1) indicating a shift from primitive to more opportunistic algal communities (such as prasinophytes: Schwark and Empt 2006, see their fig. 4). In the Toarcian, this has been explained through decreased surface water salinity (freshwater cap) from increased activity in the hydrological cycle as a consequence of global warming.

(5) **Chronological duration**: Both the Toarcian OAE and Kačák–*otomari* Event have similar short durations, ~120–150 ka (Hesselbo et al. 2000; Kemp et al. 2005) and ~121 ka (see estimate in earlier section), respec-

Table 1. Geochemical data from the Hungry Hollow section, Ontario.

Height (m)	$\delta^{13}C_{carb}$ ‰	$\delta^{18}O_{carb}$ ‰	$\delta^{13}C_{org}$ ‰	TOC (wt.%)
21.75	0.84	–5.72	–29.03	0.72
21.35	0.80	–5.79	–28.95	0.81
21.15	0.79	–5.75	–29.08	0.65
20.95	0.57	–5.93	–28.81	0.56
20.75	0.61	–5.92	–28.39	0.48
20.35	0.41	–5.76	–28.31	0.69
20.15	0.41	–5.87	–28.57	0.57
19.95	0.60	–5.78	–28.14	0.58
19.35	0.54	–5.74	–28.19	0.55
19.15	0.49	–6.11	–27.86	0.61
18.95	0.33	–5.79	–28.05	0.48
18.55	0.58	–5.93	–27.63	0.51
18.15	0.49	–5.90	–28.34	0.54
17.95	1.03	–5.67	–28.65	0.49
17.55	0.74	–5.79	–28.38	0.53
17.35	0.61	–6.02	–28.19	0.55
17.15	1.25	–5.65	–28.86	0.84
16.95	0.69	–5.73	–28.45	0.64
16.75	0.55	–5.82	–28.36	0.61
16.55	0.62	–5.82	–28.31	0.62
16.35	0.62	–5.80	–28.51	0.71
15.95	0.67	–5.69	–28.57	0.57
15.75	0.86	–5.87	–28.52	0.62
15.55	0.80	–5.91	–28.27	0.57
15.35	0.78	–5.87	–29.14	0.79
15.15	0.68	–5.91	–28.52	0.68
14.95	0.79	–5.90	–28.41	0.66
14.75	0.63	–5.78	–27.97	0.62
14.55	0.56	–5.77	–28.37	0.60
14.35	0.74	–5.90	–28.49	0.61
14.15	0.62	–6.03	–28.47	0.62
13.95	0.71	–5.89	–28.20	0.75
13.75	0.81	–5.70	–28.74	0.96
13.55	1.00	–5.68	–29.47	1.20
13.35	1.19	–5.69	–28.83	0.90
13.15	1.13	–5.57	–28.70	0.87
12.95	0.88	–5.71	–28.51	0.92
12.85	1.01	–5.42	–28.36	1.35
12.80	1.21	–5.41	–28.33	1.33
12.75	0.60	–5.98	–28.53	1.29
12.70	0.48	–5.99	–28.38	1.24
12.65	0.40	–6.05	–28.48	1.80
12.60	0.87	–5.47	–28.53	1.79
12.55	0.71	–5.70	–28.21	1.60
12.50	0.74	–5.84	–28.29	1.64
12.45	0.25	–6.25	–28.43	1.57
12.40	0.66	–5.91	–28.74	1.75
12.35	1.05	–5.63	–28.70	2.06
12.30	0.39	–6.29	–28.52	1.78
12.25	0.73	–5.92	–29.39	2.10
12.20	0.57	–6.04	–28.53	1.46
12.15	0.61	–5.83	–28.46	1.38
12.05	0.68	–5.82	–28.01	3.17
12.00	0.13	–6.36	–27.90	1.56
11.95	0.80	–5.65	–28.13	1.43
11.90	0.42	–5.98	–28.21	1.72
11.85	0.09	–6.36	–28.48	1.88

Table 1 (*continued*).

Height (m)	$\delta^{13}C_{carb}$ ‰	$\delta^{18}O_{carb}$ ‰	$\delta^{13}C_{org}$ ‰	TOC (wt.%)
11.80	0.32	–5.97	–27.99	2.12
11.70	0.57	–6.00	–28.08	1.01
11.60	1.25	–5.36	–27.68	1.19
11.55	1.07	–5.58	–26.81	1.28
11.50	1.19	–5.39	–27.36	0.58
11.43	1.23	–5.27	–27.33	0.61
11.38	1.76	–5.25	–27.19	0.63
11.33	1.72	–5.04	–27.29	0.66
11.23	1.15	–5.67	–27.32	0.66
11.12	–0.56	–6.29	–28.93	0.75
11.11	0.27	–5.42	–29.31	9.29
11.10	0.02	–5.67	–29.28	12.45
11.09	0.16	–5.25	–28.63	3.41
11.07	–0.69	–6.53	–28.70	2.90
11.05	–0.80	–6.76	–29.52	5.43
11.01	0.61	–5.21	–29.22	6.94
11.00	0.73	–4.96	–28.85	7.84
10.99	0.39	–5.57	–28.96	8.28
10.98	0.14	–5.76	–29.08	9.19
10.97	0.09	–5.85	–28.68	9.04
10.96	0.49	–5.38	–29.21	10.26
10.95	0.56	–5.44	–29.16	5.52
10.94	0.48	–5.51	–29.43	5.54
10.93	0.34	–5.58	–28.97	5.24
10.91	0.32	–5.39	–29.49	5.33
10.90	–0.34	–6.23	–28.67	5.04
10.87	–0.34	–6.75	–28.35	5.60
10.86	–0.30	–6.58	–28.74	1.82
10.85	0.00	–6.31	–27.75	2.62
10.82	0.76	–5.80	–26.81	3.81
10.81	0.67	–5.40	–27.37	0.94
10.80	0.43	–5.99	–26.60	0.48
10.60	0.36	–6.15	–27.06	1.41
10.40	0.43	–5.93	–26.54	0.80
10.00	0.48	–6.13	–26.20	0.64
9.80	0.40	–5.85	–26.31	0.47
9.60	0.47	–5.96	–26.79	0.68
9.40	0.15	–5.82	–26.23	0.70
9.20	0.14	–5.68	–26.45	0.73
9.00	0.11	–5.91	–26.57	0.45
8.80	0.06	–6.35	–26.44	0.64
8.60	–0.01	–6.12	–26.83	0.61
8.40	–0.08	–6.28	–26.80	0.69
8.20	0.14	–6.14	–26.32	0.50
8.00	0.11	–6.14	–26.64	0.49
7.80	0.24	–6.28	–26.46	0.51
7.60	–0.62	–6.47	–26.41	0.49
7.40	–0.29	–6.24	–26.37	0.53
7.20	–0.80	–6.56	–26.47	0.67
7.00	–0.65	–6.22	–26.59	0.61
6.80	–0.38	–6.56	–26.68	0.63
6.40	0.17	–6.17	–26.88	0.51
6.20	–0.05	–6.37	–26.58	0.75
6.00	–0.13	–6.47	–26.64	0.60
5.80	–1.35	–6.49	–26.22	0.68
5.60	0.03	–6.39	–26.59	0.42
5.40	–0.39	–6.34	–26.37	0.60

Table 1 (*concluded*).

Height (m)	$\delta^{13}C_{carb}$ ‰	$\delta^{18}O_{carb}$ ‰	$\delta^{13}C_{org}$ ‰	TOC (wt.%)
5.20	–0.71	–6.25	–26.55	0.47
5.00	–0.83	–6.53	–26.52	0.43
4.80	–0.65	–5.73	–26.46	0.57
4.60	–0.71	–6.25	–26.74	0.48
4.40	–0.29	–6.29	–26.69	0.88
4.20	–0.79	–6.64	–26.55	0.55
4.00	–0.50	–6.62	–26.17	0.55
3.80	–0.80	–6.31	–26.47	0.44
3.60	–0.83	–7.07	–26.66	0.57
3.40	–0.21	–6.19	–26.55	0.68
3.20	0.19	–6.42	–26.51	0.74
3.00	–0.57	–4.85	–26.91	0.44
2.80	–1.01	–6.16	–26.63	0.84
2.60	–0.96	–6.22	–26.98	0.63
2.40	–0.64	–6.26	–26.55	0.70
2.20	–0.89	–6.15	–26.46	0.76
2.00	–1.17	–6.43	–26.79	0.42
1.80	–1.11	–6.57	–26.79	0.61
1.60	–0.95	–5.80	–26.56	0.58
1.40	–0.84	–6.07	–26.79	0.66
1.20	–0.99	–6.48	–26.68	0.51
1.00	–0.95	–6.15	–26.51	0.49
0.80	–0.84	–5.93	–26.62	0.66
0.60	–0.02	–5.86	–26.86	0.66
0.40	–0.89	–6.12	–26.78	0.58
0.00	–0.83	–6.16	–26.74	0.65

Note: All isotopic ratios are expressed against VPDB. Weight percent (wt.%) total organic carbon (TOC) was obtained from the isotopic analysis.

tively. More research is required on this to make direct comparisons with the well-studied Paleocene–Eocene Thermal Maximum (PETM, Cohen et al. 2007).

(6) Other similarities: High concentrations of TOC (up to 12.45% and 18% for the Kačák–*otomari* Event and Toarcian OAE, respectively), sea-level transgressions, finely laminated sediments, and marine extinctions (see Hesselbo et al. 2000; House 2002; Sageman et al. 2003; Kaufmann 2006).

Although the temptation to postulate a similar causal mechanism (such as the massive release of methane gas hydrates) for both the Kačák–*otomari* Event and the Toarcian OAE (see Hesselbo et al. 2000, 2007) is appealing, at present there is limited data to directly suggest this mechanism (albeit the negative $\delta^{13}C$ excursion and that discussed previously). A key factor required is to obtain greater cyclostratigraphic control on the Kačák–*otomari* $\delta^{13}C$ excursion and the generation of more geochemical data sets; such a comparison has been achieved between the PETM and Toarcian OAE with success (Cohen et al. 2007).

Conclusions

A high-resolution stable isotope study on bulk sediments has been conducted across the E–G boundary from the Hamilton Group in Ontario, Canada. Based on conodont assemblages throughout this stratigraphic section, the "*otomari* Event" can be recognized. The Kačák–*otomari* Event is associated with a negative $\delta^{13}C$ excursion that occurs prior to the deposition of organic-rich black shales with TOC values up to 12.45%. In corroboration with other isotopic studies across the Eifelian–Givetian boundary, it is suggested that the Kačák–*otomari* Event may best be represented by major negative $\delta^{13}C_{org}$ excursions. Preliminary comparisons with other Middle Devonian records show considerable similarities between the Kačák–*otomari* Event and the Toarcian OAE, implying a common causal mechanism. Continued high-resolution investigations of Devonian black shale intervals may reveal more similarities with Mesozoic OAEs than previously considered and possibly more broadly applicable causative mechanisms.

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