

THE CARBON ISOTOPE ORGANIC GEOCHEMISTRY OF EARLY ORDOVICIAN ROCKS FROM THE ANNASCAUL FORMATION, COUNTY KERRY

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Abstract

Ireland is well known to geologists as containing some of the thickest successions of Early Ordovician (485–470 Ma; Walker *et al.* 2012) sedimentary rocks in the world. The carbon stable isotope compositions ($\delta^{13}\text{C}$ value) of similarly aged rocks have been reported for only very few places in the world (i.e., Argentina, southern China, and southern France), and no such analyses have been performed on the Early Ordovician, organic-rich rocks of Ireland. Here we report the $\delta^{13}\text{C}$ values of bulk organic material and organic isolates recovered from the Annascaul Formation of Southwestern Ireland. Members of the Annascaul Formation spanning the Early Ordovician were sampled at multiple sites within five localities on the Dingle Peninsula, County Kerry. Mean bulk organic $\delta^{13}\text{C}$ values for the organic matter within rocks of the Farranacarriga, Tinal, Illaunglass, Bealacoon, and Killelton Members ranged from -28.7‰ (Farranacarriga) to -22.1‰ (Illaunglass); the average $\delta^{13}\text{C}$ values of organics isolated from the Farranacarriga and Bealacoon Members were -29.0 and -28.4‰ , respectively. No statistical difference was observed between the $\delta^{13}\text{C}$ value of isolates and the $\delta^{13}\text{C}$ value of bulk sediment from which organics had been isolated ($P = 0.85$, Farranacarriga, $n = 6$; $P = 0.81$, Bealacoon, $n = 5$; paired t -test). The $\delta^{13}\text{C}$ values we present here agree well with the previously published $\delta^{13}\text{C}$ values for Early Ordovician organic carbon (average = -28.4 , -25.4 , -25.5‰) from Argentina, southern China, and southern France (respectively). Our new data from the Annascaul Formation are $\sim 3.3\text{‰}$ higher than the average value reported for $\delta^{13}\text{C}$ values of organic matter of marine origin for the same period, raising the possibility that terrestrial bryophytes (or other terrestrial photosynthesizers) contributed to these Early Ordovician sediments. Further equivocal evidence is provided by the abundant organic macerals found within the Farranacarriga Member with possible vitrinite origin. The $\delta^{13}\text{C}$ values of palynomorph-sized organic isolates from the Annascaul Formation reflect a marine origin for these organisms, consistent with their previous identification as acritarchs. Given the recognition of the earliest thalloid macrofossils and land-plant cryptospores in the Middle Ordovician sediments of the Appalachian basin (USA) and Argentina, respectively, our results highlight the Early–Middle Ordovician boundary as a potentially crucial time of terrestrial ecosystem expansion and development.

Introduction

The Earth's sediments contain relatively few organic-rich deposits of Ordovician age (485–444 Ma; Walker *et al.* 2012) (e.g., Illinois Basin, USA, Guthrie, 1996; Iowa, USA, Pancost *et al.* 1999; South China, Zhang *et al.* 2010); however, the geology of Ireland is particularly rich in Cambrian (541–485 Ma), Ordovician (485–444 Ma) and Silurian (444–419 Ma) sequences (McConnell and Gatley 2006). These geologic periods are of particular interest because they bracket the colonization of land from the ocean, resulting in densely vegetated terrestrial ecosystems by the Middle Devonian (393–383 Ma; Kenrick *et al.* 2012). There is ample reason to believe that terrestrial ecosystems existed long before the Silurian Period (444–419 Ma) (Gensel 2008; Wellman and Gray 2000), which marks the first known morphologically complex plant macrofossils (e.g., Kotyk *et al.* 2002) and the oldest fertile erect land plant fossils in the form of *Cooksonia* from the Wenlock strata of Ireland (Edwards and Feehan 1980; Edwards *et al.* 1983). Fossil terrestrial prokaryotes have been reported within the Proterozoic (Horodyski and Knauth 1994), and the oldest complete fungal microfossils are Middle Ordovician (470–458 Ma) in age (Redecker *et al.* 2000). Although molecular data initially indicated a Precambrian origin for land plants (Heckman *et al.* 2001), additional molecular data suggest that land plants originated between 490 and 425 Ma (Sanderson 2003). More provocatively, it has recently been suggested that the iconic Ediacaran (635–541 Ma) fossil *Dickinsonia* must be a terrestrial lichenized fungus (Retallack 2007) based on the description of its contextual sediments as paleosols (Retallack 2013). This theory has been widely condemned as unfounded (Switek 2012) but it comprises the oldest of many studies that would place the development of terrestrial ecosystems back millions of years before the Silurian (e.g., Rubinstein *et al.* 2010).

If terrestrial ecosystems existed just prior to the Silurian, during the Ordovician, sediments of the time might contain carbon contributed by terrestrial photosynthesizers. One method that has been used extensively in order to study the carbon cycle of the past (Hayes *et al.* 1999), as well as to evaluate the possibility of terrestrial input into marine environments (Meyers 1997), is the characterization of the carbon stable isotope composition within the reduced organic fraction of sedimentary rocks. Although this technique has been extensively

applied to Ordovician-age rocks in other parts of the world (e.g., Appalachian basin, USA; Tomescu *et al.* 2009), the rocks of Ireland have never been analysed in this way. In order to address this, we sampled organic-rich rocks with abundant and well-characterized organic carbon content of Early Ordovician age from southwestern Ireland for stable isotope analysis. Focus was placed on the Annascaul Formation as exposed on the Dingle Peninsula; the age of these rocks has been constrained to the Tremadocian and Arenigian (Floian) Stages (485–470 Ma) using extensive palynological and graptolitic biostratigraphy (Higgs and Callaghan 1996; Todd *et al.* 2000). We also provide ancillary organic geochemical observations, in order to characterize these ancient sedimentary deposits thoroughly.

Regional geological context

Immediately south of the Iapetus suture trace in southwest Ireland lies the Dingle Peninsula of County Kerry (Todd 1991), once part of Avalonia (e.g., Todd *et al.* 1991 and references therein). The geology of the Dingle Peninsula, described comprehensively by Pracht (1996), is dominated by Paleozoic sedimentary rocks (Fig. 1). The Annascaul Formation, a clastic mudrock-dominated unit that outcrops in a narrow strip running SW–NE across the peninsula, has recently been placed within the Early Ordovician based on palynomorphic and graptolitic biostratigraphy, field relationships, tectonic and metamorphic histories, and regional correlations (Todd *et al.* 2000). The Annascaul, along with the Ballynane, Caherconree, and Derrymore Glen Formations of the Dunquin Group, had previously been placed within the Silurian (Parkin 1976). The age re-evaluation described by Todd *et al.* (2000) established the Annascaul Formation as the oldest sediments in southwestern Ireland associated with the paleoenvironment of the Iapetus ocean.

The Annascaul Formation contains five members (Table 1); the stratigraphy, petrology, and palynomorphs of these members have been extensively described elsewhere (Higgs and Callaghan 1996; Todd *et al.* 2000 and references therein). Lithologies in the Annascaul Formation range from claystones to conglomerates and exhibit a range of bed thickness. Three members of the Annascaul Formation were determined to be of Early Ordovician age by Todd *et al.* (2000): the Farranacarriga Member contains *S. stelligerum*, which indicates Tremadocian-aged deposits based on its range of occurrence in Algeria

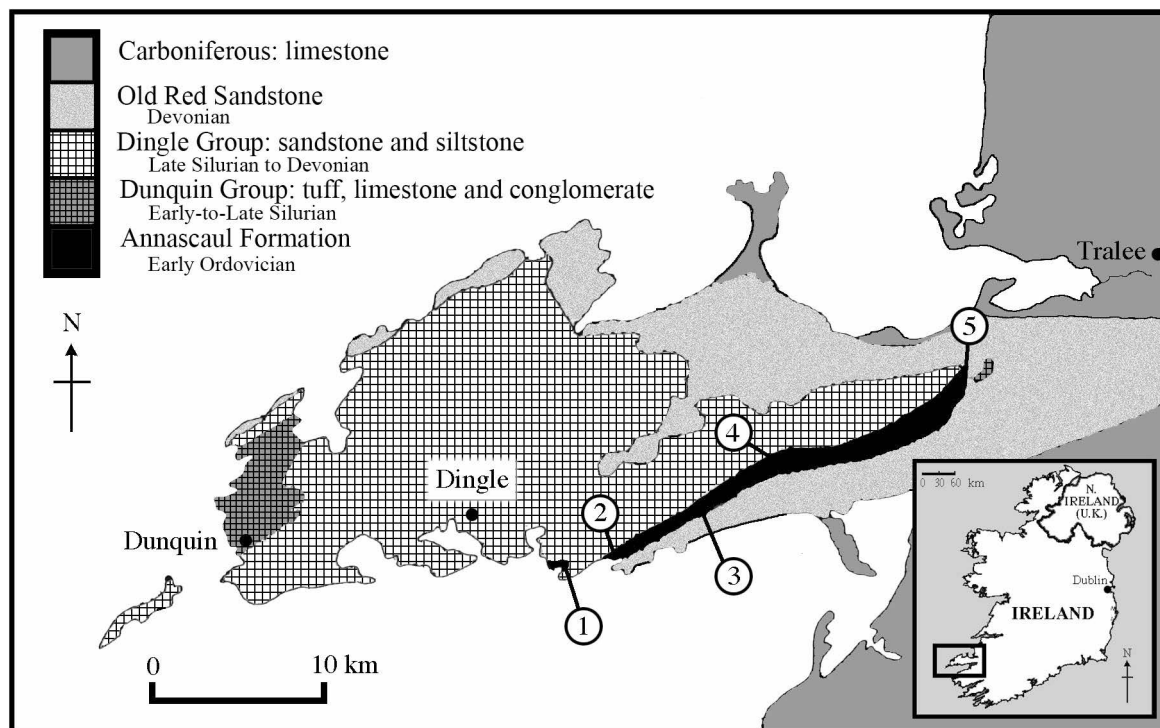


Fig. 1—Map of the Dingle Peninsula showing the Lower Paleozoic rocks of the area and highlighting the Early Ordovician Annascaul Formation and the five sampling localities of this study: (1) Bull's Head; (2) Minard Bay; (3) Farranacarriga Township; (4) Annascaul Township; (5) Killelton Township.

Table 1—Age and rock descriptions of the members of the Annascaul Formation^a

Period	(495 Ma) Early Ordovician (470 Ma)				
Epoch	Tremadocian			Arenigian	
	Early	Late		Early	Middle
Members of Annascaul Fm.	Farranacarriga	Tinal	Illauglass	Bealacoon	Killelton
Rock description	Dark, fine-grained claystones and siltstones; black slates	Grey phyllitic claystones; thin sandstone beds	Purplish phyllitic claystones; some siltstones	Mud-matrix supported chaotic melange and shales	Massively bedded sandstone; micro-conglomerate
Dated using ^b	<i>Stelliferidium stelligerum</i>	Field relationships	<i>Cymatiogalea messauoudensis</i> , <i>Stelliferidium trifidum</i> , <i>Coryphidium spp.</i>	<i>Coryphidium bohemicum</i>	Field relationships

^aDouble lines indicate unconformities between members

^bAcrutarchs used to date members as described in Higgs and Callaghan (1996) and Todd *et al.* (2000); other members were placed within the Early Ordovician using observed field relationships and discussions in Parkin (1976)

(Todd *et al.* 2000). The rocks of the Tinal Member bear a strong resemblance to those of the Illaunglass Member, which contains a *C. messaoudensis*–*S. trifidum* assemblage, and is dated by graptolites from the Skiddaw Slate Group of NW England. The Bealacoon Member contains *Coryphidium bohemicum*, which first appears in the *D. varicosus* graptolite biozone in NW England; the Killelton Member's massive purple sandstones and microconglomerate layers are distinct from the other members. Parkin (1976) placed the Tinal Member stratigraphically beneath the Illaunglass Member, and placed the Killelton Member at the top of the Annascaul Formation due to its proximity to the Ballynane and Derrymore Glen Formations; these placements agree with the field observations of this study (Table 1).

Methods

The Annascaul Formation was sampled at five localities on the Dingle Peninsula (Fig. 1); at each of the localities one or two members were sampled (Table 1). Within each member, between two and ten sampling sites separated by at least 10 m (stratigraphically and laterally) were identified for specimen collection. At each sampling site, a fresh face was exposed using a hammer and chisel, and approximately 2 kg of rock was collected from the outcrop. Freshly polished rock fragments were used for reflected light microscopic observations and reflectance analysis. Random reflectance was measured using an AXIOPLAN II microscope with 156 nm light with the application of immersion oil, and under a total magnification of 500. A reflectance value of $R_r = 3.2\%$ was used as reference.

In the laboratory, ~300 g portions of all samples were homogenized to mm-scale particles using a mortar and pestle, and placed in 50 ml plastic centrifuge tubes. One-half of the homogenized sample was designated for bulk organic carbon analysis and was soaked in 1M HCl for 72 h, and then rinsed five times in distilled deionized water. No reaction was observed between the specimens and the HCl, suggesting that none of the samples contained carbonate. After being lyophilized, samples were again homogenized with a mortar and pestle, and weighed into tin capsules for isotopic analysis.

The other half of the homogenized sample was designated for organic isolate analysis and was soaked in 49% HF for 96 h in order to remove silicate minerals. Afterwards, the acid was decanted, and the remaining material was soaked in 1M HCl

for 48 h. Samples were then rinsed ten times with distilled and deionized water; between rinses, samples were allowed to settle for 24 h in order to avoid centrifugation, which might damage palynomorphs, a desired isolate. The remaining material was suspended in distilled and deionized water and subjected to a multiple-sieve technique that employed stackable micro-mini-sieves with eight different-sized mesh inserts (25, 35, 45, 68, 80, 120, 170, and 230 mesh per linear inch; Fisher Catalog # 37846-0000). This method has recently been shown to separate polymorphs from solution effectively across hundreds of palynomorphologies (Jahren 2004). The sieves were stacked with the coarsest mesh at the top, grading to finer mesh towards the bottom, all set within a large petri dish that served as a catch-pan. Liquid from the catch-pan was allowed to settle for 24 h, partially decanted, resuspended, and split into two portions. One portion was prepared for light microscopy *via* exposure to Schulze's solution (composed of equal parts of 70% HNO₃ and a saturated solution of KClO₃) for 24 h. Samples were then rinsed three times with distilled deionized water, mounted on microscope slides, and the palynomorph content of samples was verified at high (500×) magnification (Fig. 2). The other portion of sieved fluid was allowed to settle for 24 h. After being decanted, these organic isolates were lyophilized and weighed into tin capsules for isotopic analysis (Jahren 2004; Loader and Hemming 2000). Because no palynomorphs have been described within the Killelton and Tinal Members (Todd *et al.* 2000), no attempt was made to isolate organic fractions from these low-organic facies; we were not able to isolate consistently an amount of organic fraction from the Illaunglass Member sufficient for isotopic analysis.

Bulk organic and isolate samples were analysed in triplicate using a Eurovector automated combustion system. This combustion also resulted in a quantification of percent carbon (‰C) in each sample, and resultant values of TOC were confirmed *via* combustion of larger samples under vacuum and manometric measurement of the resultant CO₂ gas. Purified CO₂ gas was analysed for ¹³C/¹²C using an Isoprime Isotope Ratio Mass Spectrometer (IRMS). Precision associated with measurements was within ±0.05‰ in all samples. All results are reported in standard isotopic δ-notation (‰) relative to the Vienna Pee Dee belemnite standard (VPDB).

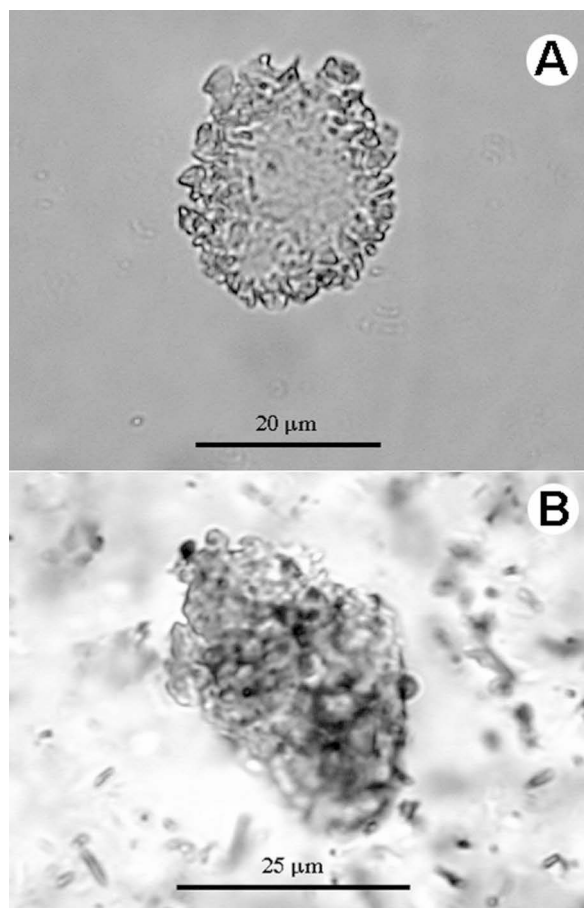


Fig. 2—Light microscope photographs of palynomorph-sized isolate (possibly *Lophodiastrodium* sp.) from the Farranacarriga Member of the Annascaul Formation. (A) Treatment with Schulze's-solution rendered isolates more translucent than (B) those that were isolated using only HF, HCl, and microsieves but did not change the overall composition of the specimens. Full descriptions of palynomorph assemblages seen in these rocks can be found elsewhere (Higgs and Callaghan 1996; Todd *et al.* 2000 and references therein).

Results

Examination of several bulk-rock specimens in thin section under the petrographic microscope revealed a fine-grained quartz matrix with abundant and uniformly distributed organic material (Fig. 3). The organic carbon content (by mass) determined *via* combustion varied between 0.02 and 0.28% in bulk-rock samples (Table 2). Further inspection of the organic geochemistry of the stratigraphically oldest samples, the Farranacarriga Member, revealed average vitrinite reflectance (R_o) of $2.86 \pm 0.78\%$ ($n = 100$), a value characteristic for low-grade metamorphism. This same Member yielded abundant organic macerals (Fig. 4) probably composed of

highly matured hydrocarbons (pirobitumens); however, a vitrinite origin cannot be ruled out. Pyrolysis of rock samples revealed that organic matter consisted of unstructured lipids with a thermal alteration index of 4, which agrees with Todd *et al.*'s (2000) previous estimate of thermal alteration in excess of 250 °C. The small amount of organic material present in the Tinal and Killelton Members was dominated by undifferentiated lipids with very high maturity ($R_o > 1.3\%$) and no distinct texture.

Stable isotope analyses of bulk organic carbon yielded a wide range of carbon isotope values ($\delta^{13}\text{C} = -30.7$ to -17.0‰ , average $\pm 1\sigma = -25.3 \pm 3.3\text{‰}$, $n = 43$) (Table 3). Total variability in the $\delta^{13}\text{C}$ value of bulk organic samples from all samples at the same locality ranged from 1.9 to 8.8‰. Bulk organic $\delta^{13}\text{C}$ values of the Illaunglass, Tinal, and Killelton Members were notably higher than values measured for the Bealacoon and Farranacarriga Members. Average bulk organic $\delta^{13}\text{C}$ value was -22.1‰ in the Illaunglass Member, -23.4‰ in the Tinal Member, and -24.1‰ in the Killelton Member; average bulk organic $\delta^{13}\text{C}$ value was -26.4 and -28.7‰ for the Bealacoon and Farranacarriga Members, respectively. We note that the average %C measured in the Tinal and Killelton Members ($\%C = 0.02 \pm 0.03$) (Table 2) approaches the limits for which accurate $\delta^{13}\text{C}$ values can be measured; all %C values determined for the Annascaul Formation, however, are consistent with values reported in other Ordovician rocks previously used for bulk organic carbon isotope determination (e.g., 0.02 to 0.31%C measured in carbonates and mudstones of southern China, $n = 100$; Zhang *et al.* 2010). The member with the highest $\delta^{13}\text{C}$ value (Illauglass) also had the highest average %C ($0.28 \pm 0.34\%$), indicating that high $\delta^{13}\text{C}$ values did not result from low amounts of carbon in our samples. We also note that the Tinal and Killelton Members are predominantly sandstone, and within large grain-sized substrates, organic matter may not be preserved without diagenesis (Briggs *et al.* 2000). Diagenesis, however, causes an isotope change commonly less than 1‰ (Peters-Kottig *et al.* 2006) and grain-size (or lithology) does not systematically affect the $\delta^{13}\text{C}$ value of bulk organic material (Strauss and Peters-Kottig 2003). Our data support this observation as the claystone-rich Illauglass Member had similar $\delta^{13}\text{C}$ values to the sandstone-rich Tinal and Killelton Members (Table 2), which further suggests that the samples with low %C produced reliable $\delta^{13}\text{C}$ values. Lastly, large variability has also been measured across other Early

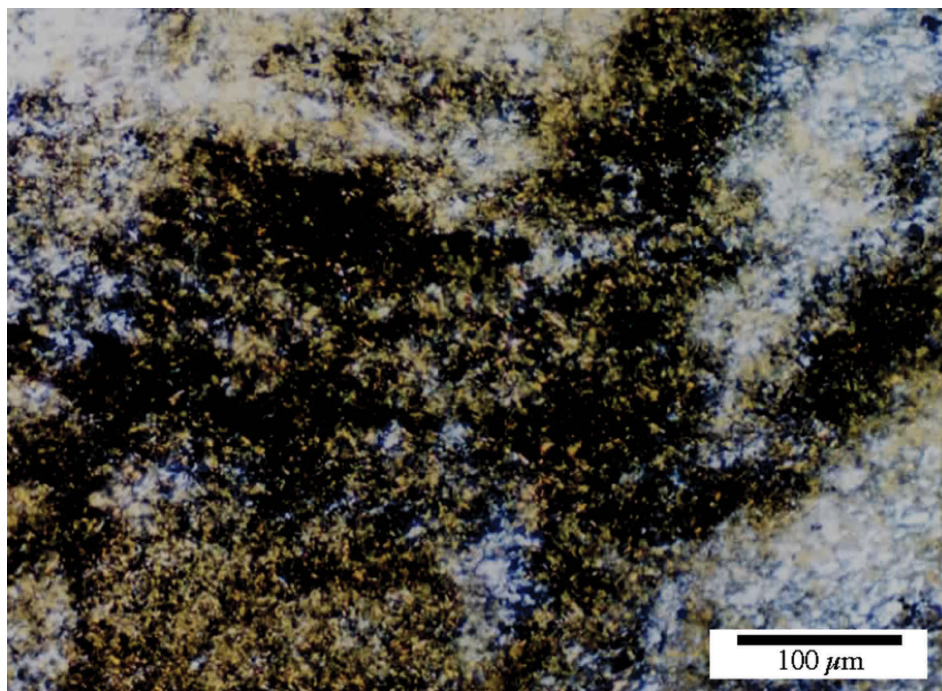


Fig. 3—Petrographic thin-section of the Farranacarriga Member claystone that was analysed for bulk organic stable isotope composition; photograph was taken with crossed polars. Other thin sections of the Illaunglass and Bealacoon Members revealed similarly abundant organic matter within a fine-grained quartz matrix, occasionally with small amounts of chlorite and illite.

Table 2—Average $\delta^{13}\text{C}$ and %C values of samples from the Annascaul Formation^a

Locality ^b	Members sampled ^b	$\delta^{13}\text{C}$ of bulk organics (‰)	%C of bulk organics	$\delta^{13}\text{C}$ of organic isolates (‰)	%C of organic isolates
1	Bealacoon	-26.4 ± 3.0 (15)	0.16 ± 0.12 (15)	-28.4 ± 1.3 (5)	4.06 ± 1.75 (5)
2	Illauglass	-22.1 ± 3.1 (7)	0.28 ± 0.34 (7)	—	—
	Tinal	-23.4 ± 2.0 (9)	0.02 ± 0.03 (9)	—	—
3, 4	Farranacarriga	-28.7 ± 1.3 (8)	0.21 ± 0.13 (8)	-29.0 ± 1.4 (6)	2.54 ± 1.54 (6)
5	Killelton	-24.1 ± 0.8 (4)	0.02 ± 0.03 (4)	—	—

^a Values reported as the average $\pm 1\sigma$. Values in parentheses represent number of samples.

^b As indicated on Fig. 1

Ordovician formations, and the average $\delta^{13}\text{C}$ values determined in each of the Early Ordovician members reported here overlapped with the average $\delta^{13}\text{C}$ values reported across other Early Ordovician formations from geographically diverse sites (Fig. 5).

Stable carbon isotope analyses of organic isolates yielded a range of $\delta^{13}\text{C}$ values between -30.5 and -26.7‰ (average = $-28.7 \pm 1.3\text{‰}$, $n = 11$) for the two members analyzed (Bealacoon and Farranacarriga). The variability in $\delta^{13}\text{C}$ values of organic isolates from sampling sites at a single locality was similar to the variability seen for bulk organic samples: the range was 3.1‰ in the Bealacoon

($n = 5$) and 3.6‰ ($n = 6$) in the Farranacarriga (Table 3). Mean $\delta^{13}\text{C}$ values of palynomorph isolate samples were statistically the same between the two members analysed ($P = 0.49$); this value was $-28.4 \pm 1.3\text{‰}$ in the Bealacoon and $-29.0 \pm 1.4\text{‰}$ in the Farranacarriga ($\pm 1\sigma$). A comparison of palynomorph isolate $\delta^{13}\text{C}$ value to bulk organic $\delta^{13}\text{C}$ value at each site revealed that organic isolate $\delta^{13}\text{C}$ value \approx bulk organic $\delta^{13}\text{C}$ value (\pm less than 2‰ in all cases), consistent with previous work (Peters-Kottig *et al.* 2006; Tomescu *et al.* 2009); the average value of $\delta^{13}\text{C}_{\text{bulk}} - \delta^{13}\text{C}_{\text{isolate}}$ was 0.09‰ ($n = 11$). Organic isolate $\delta^{13}\text{C}$ value and bulk

Table 3—Carbon isotope values of all samples analysed

<i>Sample name</i>	<i>Member</i>	<i>Stage</i>	$\delta^{13}\text{C}$ of bulk organics (‰)	$\delta^{13}\text{C}$ of organic isolates (‰)
F-1	Farranacarriga	Tremadocian	−27.70	
F-2	Farranacarriga	Tremadocian	−28.46	
F-3	Farranacarriga	Tremadocian	−30.72	−30.52
F-4	Farranacarriga	Tremadocian	−30.32	−30.24
F-5	Farranacarriga	Tremadocian	−27.43	−26.90
F-6	Farranacarriga	Tremadocian	−27.19	−28.99
F-7	Farranacarriga	Tremadocian	−28.77	−28.01
F-8	Farranacarriga	Tremadocian	−28.84	−29.05
T-1	Tinal	Tremadocian	−23.39	
T-2	Tinal	Tremadocian	−20.54	
T-3	Tinal	Tremadocian	−22.62	
T-4	Tinal	Tremadocian	−24.85	
T-5	Tinal	Tremadocian	−25.75	
T-6	Tinal	Tremadocian	−21.04	
T-7	Tinal	Tremadocian	−26.56	
T-8	Tinal	Tremadocian	−22.61	
T-9	Tinal	Tremadocian	−23.45	
I-1	Illaunglass	Tremadocian–Arenigian	−16.97	
I-2	Illaunglass	Tremadocian–Arenigian	−23.46	
I-3	Illaunglass	Tremadocian–Arenigian	−24.31	
I-4	Illaunglass	Tremadocian–Arenigian	−23.43	
I-5	Illaunglass	Tremadocian–Arenigian	−24.09	
I-6	Illaunglass	Tremadocian–Arenigian	−24.51	
I-7	Illaunglass	Tremadocian–Arenigian	−18.24	
B-1	Bealacoon	Arenigian	−25.27	
B-2	Bealacoon	Arenigian	−29.15	
B-3	Bealacoon	Arenigian	−20.87	
B-4	Bealacoon	Arenigian	−26.49	
B-5	Bealacoon	Arenigian	−26.33	
B-6	Bealacoon	Arenigian	−28.22	
B-7	Bealacoon	Arenigian	−25.86	
B-8	Bealacoon	Arenigian	−26.13	−27.37
B-9	Bealacoon	Arenigian	−27.71	−26.66
B-10	Bealacoon	Arenigian	−29.63	
B-11	Bealacoon	Arenigian	−29.39	−28.67
B-12	Bealacoon	Arenigian	−21.02	
B-13	Bealacoon	Arenigian	−29.61	−29.74
B-14	Bealacoon	Arenigian	−28.44	−29.42
B-15	Bealacoon	Arenigian	−22.47	
K-1	Killelton	Arenigian	−24.00	
K-2	Killelton	Arenigian	−24.33	
K-3	Killelton	Arenigian	−25.05	
K-4	Killelton	Arenigian	−23.17	

^aEach value is reported as the mean of three replicate analyses. Standard deviation was <0.05‰ for all samples.

organic $\delta^{13}\text{C}$ value showed a positive correlation ($R^2 = 0.60$) whereby samples with higher bulk organic $\delta^{13}\text{C}$ values also had higher organic isolate $\delta^{13}\text{C}$ values. The chemical preparation methods used in this study did not alter the carbon isotope composition of either the bulk organics or the organic isolates: previous studies have shown that

both HCl and HF treatments result in little or no alteration of organic substrate $\delta^{13}\text{C}$ value (Jahren 2004; Midwood and Boutton 1998). Other very oxidative agents such as Schulze's reagent (65% nitric acid containing potassium chlorate) have also been shown not to alter the $\delta^{13}\text{C}$ value of organic matter even when heated (Peters-Kottig *et al.* 2006).

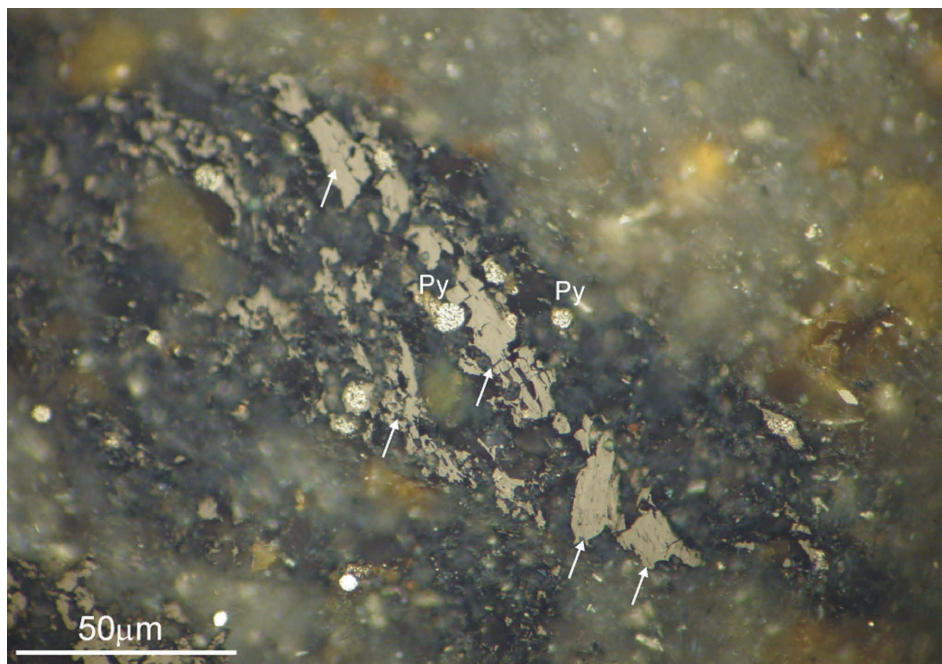


Fig. 4—Light microscope photograph of organic macerals from the Farranacarriga Member of the Annascaul Formation. It is probable that these organic particles (highlighted by arrows) represent either (pseudo)vitrinite grains or solid bitumens but a precise identification is precluded by high thermal maturation. The symbol Py denotes the presence of pyrite grains.

Organic isolates contained ~4 to ~25 times more carbon (by mass) than the bulk organic material from which they were isolated; sampled sites varied between 2.54 and 4.06% C in the average organic carbon content of palynomorph isolates (Table 2).

No clear temporal trends in isotopic value were apparent in samples from the Annascaul Formation throughout the Early Ordovician. The average bulk organic $\delta^{13}\text{C}$ values ($\pm 1\sigma$) of Annascaul Formation samples representing the Tremadocian (488–479 Ma; Farranacarriga and Tinal Members) and the Arenigian (479–472 Ma; Bealacoon and Killelton Members) were equal to $-25.9 \pm 3.2\text{‰}$ ($n = 17$) and $-25.6 \pm 2.8\text{‰}$ ($n = 18$), respectively, and not statistically different from each other ($P = 0.95$). However, the average bulk organic $\delta^{13}\text{C}$ value of the Illaunglass Member ($-22.1 \pm 3.1\text{‰}$, $n = 7$), which falls between the ages of the Farranacarriga/Tinal and Bealacoon/Killelton, was significantly higher than with the Tremadocian ($P = 0.02$) or Arenigian ($P = 0.007$) aged members of the Annascaul Formation. The average $\delta^{13}\text{C}$ value of the Illaunglass Member, however, was not significantly different from the Tinal ($P = 0.37$) or Killelton ($P = 0.15$) Members separately. Thus, the Illaunglass Member, although containing the highest average $\delta^{13}\text{C}$ value of all the members within the Annascaul Formation, does not represent anomalously high $\delta^{13}\text{C}$ values

relative to other members, and simply reflects the large range and high variability in organic $\delta^{13}\text{C}$ values observed in Early Ordovician rocks (Fig. 5).

Discussion

Todd *et al.* (2000) assigned a deep-water origin to the Annascaul Formation, due to the fine grain size, the presence of turbiditic sandstones, and the few crinoid columnals previously reported by Parkin (1976). The limestones, tuffs, and shelly fauna of the overlying Ballynane unit were assigned a shallow-water origin when they were upgraded to formational status (Todd *et al.* 2000). Additionally, trace fossils from the Ballynane Formation resemble those of modern intertidal worms (G.J. Retallack, pers. comm.). Note that, assuming the boundaries are all conformable between the members of the Annascaul Formation, there is a broad coarsening-upwards trend through the formation, from the black shales and claystones of the Farranacarriga Member, through the mudstones and siltstones of the Illaunglass Member, to the massive sandstones of the Killelton Member. Numerous studies have demonstrated the effective transport of terrestrial organic matter to modern (Gordon and Goni 2003), recent (Weijers *et al.* 2009) and ancient (Schoon *et al.* 2011) marine sediments. Although the sediments of the

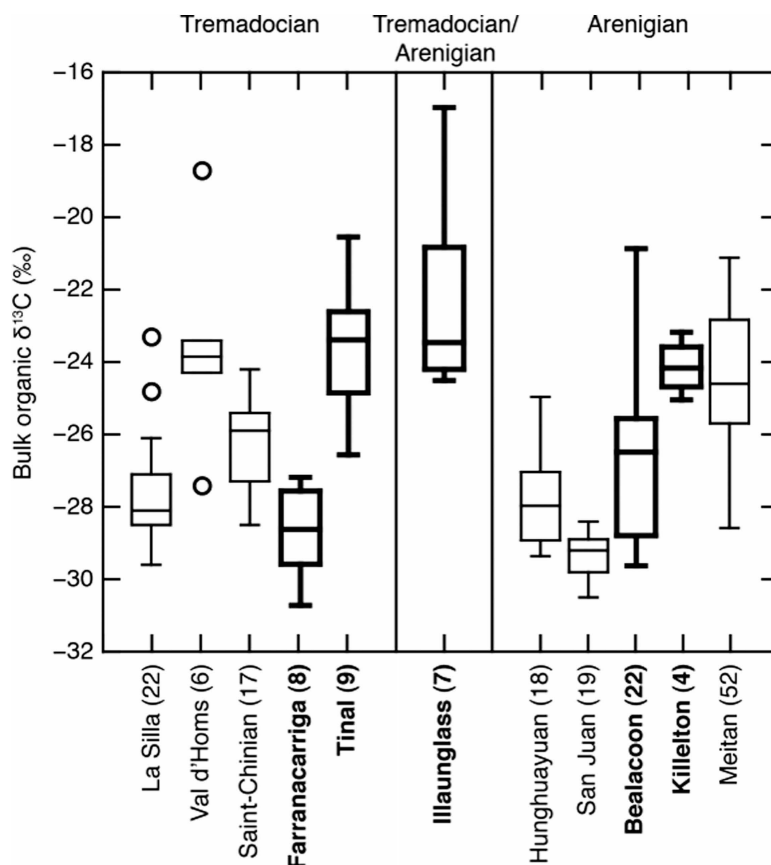


Fig. 5—Box plots of Early Ordovician carbon isotope data of bulk organic matter of marine origin compiled from Argentina (La Silla and San Juan Formations, Buggisch *et al.* 2003), southern China (Hunghuayuan and Meitan Formations, Zhang *et al.* 2010), and southern France (Val d'Homs and Saint-Chinian Formations, Alvaro *et al.* 2008) compared to our new bulk organic $\delta^{13}\text{C}$ data for the Farranacarriga, Tinal, Illaunglass, Bealacoon, and Killelton Members of the Annascaul Formation, Ireland (**bold**). The Illaunglass Member spans the Tremadocian–Arenigian boundary (478 Ma). The number of measurements is indicated in parentheses. Data for Ireland can be found in Table 3.

Annascaul Formation were formed at a variety of depths within marine environments, if terrestrial ecosystems existed in the area, carbon from these systems could have been incorporated into adjacent marine sediments. If extensive terrestrial communities existed in the field area during the Early Ordovician, one might expect carbon from these communities to have contributed to the local sediments in the form of palynomorphs or other organic matter.

The average $\delta^{13}\text{C}$ values ($\pm 1\sigma$) of Early Ordovician bulk organic carbon from published Tremadocian ($\delta^{13}\text{C} = -26.5 \pm 2.1\text{‰}$, $n = 45$) and Arenigian ($\delta^{13}\text{C} = -26.3 \pm 2.6\text{‰}$, $n = 89$) sites in Argentina, China, and France are indistinguishable from the values presented here for the Ireland sites of Tremadocian ($\delta^{13}\text{C} = -25.9 \pm 3.2\text{‰}$, $n = 17$, $P = 0.44$) and Arenigian ($\delta^{13}\text{C} = -26.0 \pm 2.8\text{‰}$, $n = 19$, $P = 0.64$) ages. Fig. 5 presents the results

of all bulk carbon isotopic analyses for each member of the Annascaul Formation sampled within the Early Ordovician together with published data (Alvaro *et al.* 2008; Buggisch *et al.* 2003; Zhang *et al.* 2010). Because of the rarity of body fossils representing the earliest land plants, several Paleozoic researchers have turned to geochemical techniques (e.g., Kenrick *et al.* 2012), including stable isotope measurements (Tomescu *et al.* 2009), to better constrain the origin of bryophytes and to differentiate bryophyte from lichen metabolism (Jahren *et al.* 2003). Based on the findings of Tomescu *et al.* (2009), one would expect that any significant input of carbon from terrestrial bryophytes (or other terrestrial photosynthesizers) to Early Ordovician sediments would result in $\delta^{13}\text{C}$ values that are higher than the global $\delta^{13}\text{C}$ value of sedimentary carbon of marine origin. Fig. 5 shows that the average $\delta^{13}\text{C}$ value ($\pm 1\sigma$) of the previously

published data ($-26.35 \pm 2.42\text{‰}$, $n = 134$) is within $\sim 1\text{‰}$ of the average value we calculate here for the Annascaul Formation ($\delta^{13}\text{C} = -25.31 \pm 3.26\text{‰}$, $n = 43$). The average isotopic composition of the entire Early Ordovician dataset, including our new data from the Annascaul Formation is $-26.10 \pm 2.67\text{‰}$ ($\pm 1\sigma$; $n = 177$; Fig. 5), which is $\sim 3.3\text{‰}$ higher than the average value reported for $\delta^{13}\text{C}$ values of organic matter of marine origin for the same period. Average global $\delta^{13}\text{C}$ value of sedimentary carbon of marine origin was -29.43‰ during the Early Ordovician (480 Ma), according to the compilation of Hayes *et al.* (1999), which summarized in 10 Ma increments available Paleozoic and Early Mesozoic (Cambrian through Jurassic) records of $\delta^{13}\text{C}$ values of separated kerogen and other organics of marine origin. Based on this dissimilarity, we might conclude that the bulk organic material of the Annascaul Formation could be isotopically enriched relative to the global average due to a terrestrial input of carbon, with the most enriched sites originating within the sediments of the Annascaul Formation.

Because sporulation can be thought of as a terrestrial strategy for reproduction, numerous workers have investigated the fossil record for evidence of Lower Paleozoic terrestrial ecosystems by describing palynomorph assemblages. Palynomorphs that are widely accepted to be spores have not been reported before the Middle Ordovician (Steemans 2000), although Middle Cambrian cryptospores have been described from Grand Canyon shales (Strother and Beck 2000). Geographically widespread cryptospore-generating organisms existed by the Middle Ordovician (470–474 Ma) according to the microfossil record of both Laurentia (Wellman and Gray 2000; Wellman *et al.* 2000) and Saudi Arabia (Strother *et al.* 1996). For the sediments of the Annascaul Formation, we note that the average $\delta^{13}\text{C}$ value of palynomorph-sized organic isolates ($\delta^{13}\text{C} = -28.7\text{‰}$) is significantly depleted compared to the average isotopic value of the bulk organics within the same formation ($\delta^{13}\text{C} = -25.3\text{‰}$), and instead very similar to the average global $\delta^{13}\text{C}$ value of sedimentary carbon of marine origin ($\delta^{13}\text{C} = -29.43\text{‰}$ during the Early Ordovician (480 Ma; Hayes *et al.* 1999); this is perhaps not surprising given the description of the palynomorph assemblages from the Annascaul Formation. In particular, the assemblage contained abundant acritarchs, which are commonly thought to be derived from unicellular marine algae. Two of the acritarch genera present in the Annascaul

Formation belong to the galeate acritarchs, a group of morphologically complex genera widely documented throughout the Ordovician (Stricanne and Servais 2002). Four other acritarch genera isolated from the Annascaul Formation, specifically *Caldariola*, *Coryphidium*, *Cymatiogalea*, and *Stelliferidium*, have been found in North African Ordovician sediments (Stricanne and Servais 2002; Todd *et al.* 2000). One notes that, while this study revealed a marine origin for the palynomorph isolates of the Annascaul Formation, the technique employed here could be used to look for the first chemical evidence of terrestrial spores within palynomorph assemblages, possibly within the Middle or Late Ordovician sediments that are also abundant within Ireland (e.g., Bruck and Vanguetstaine 2005).

Nevertheless, our study did reveal multiple lines of equivocal evidence for a terrestrial influence within the sediments of the Annascaul Formation. In addition to the relatively enriched carbon isotope composition of bulk organic matter, the abundant organic macerals (Fig. 4) found within the Farranacarriga Member have a possible vitrinite origin. The organic content of the rocks studied may be sufficiently high to support future analysis for primary or secondary terrestrial biomarkers such as *n*-alkanes and triterpenoids, which have been successfully identified in ancient sediments (e.g., van Dongen *et al.* 2006; Romero-Sarmiento *et al.* 2011). In closing, we note that the absence of unequivocal terrestrial influence in these Early Ordovician sediments and organic isolates, taken in conjunction with the recognition of thalloid macrofossils (Tomescu *et al.* 2009) and land-plant cryptospores (Rubinstein *et al.* 2010) in the Middle Ordovician sediments of the Appalachian basin (USA) and Argentina, respectively, highlights the Early–Middle Ordovician boundary as a potentially crucial time of terrestrial ecosystem expansion and development.

Conclusions

The average $\delta^{13}\text{C}$ values ($\pm 1\sigma$) of Early Ordovician bulk organic carbon are presented here for the Ireland sites of Tremadocian ($\delta^{13}\text{C} = -25.9 \pm 3.2\text{‰}$) and Arenigian ($\delta^{13}\text{C} = -26.0 \pm 2.8\text{‰}$) ages. These values are indistinguishable from the values previously published for Tremadocian and Arenigian sites in Argentina, China, and France.

The average isotopic composition of the entire Early Ordovician dataset, including our new data from the Annascaul Formation, was $\sim 3.3\text{‰}$ higher than the average value reported for $\delta^{13}\text{C}$ values of

organic matter of marine origin for the same period, constituting equivocal evidence for remote terrestrial inputs to the Early Ordovician sediments of Southwestern Ireland.

The average $\delta^{13}\text{C}$ value of palynomorph-sized organic isolates ($\delta^{13}\text{C} = -28.7\text{‰}$) from the sediments of the Annascaul Formation was significantly depleted compared to the average isotopic value of the bulk organics within the same formation ($\delta^{13}\text{C} = -25.3\text{‰}$), confirming previous identification of these as acritarchs derived from unicellular marine algae.

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