

STABLE ISOTOPE EVIDENCE FOR DIAGENESIS OF THE ORDOVICIAN COURTTOWN AND TRAMORE LIMESTONES, SOUTH-EASTERN IRELAND

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Abstract

Use of Lower Palaeozoic carbonate fossils for palaeothermometry as derived from stable isotope geochemistry is increasing. With all these studies, there is the concern of how pristine the skeletal carbonate is in relation to diagenesis. In this study, we compared the stable isotopes of calcitic brachiopod and bryozoan allochems with secondary cements to determine if the skeletal isotopes were reset during diagenesis. The study was conducted on the Courtown and Tramore Limestone Formations of the Ordovician (Llanvirn–Caradoc) Duncannon Group, which outcrops in south-eastern Ireland. These formations consist of calcareous mudrocks and argillaceous limestones. Bryozoans and brachiopods are common allochems in both formations. The Duncannon sediments were cleaved, folded and faulted by compression associated with the Caledonian and Hercynian orogenies. Bulk rock samples were slabbed and thick-sectioned. Fifty three $\geq 20\mu\text{g}$ samples of carbonate from bryozoans, brachiopods and matrix (cements and veins) were collected with $1\mu\text{m}$ spatial precision using a computer-driven micromilling device to minimise mixing of allochems and matrix. Results indicate $\delta^{13}\text{C}$ values of -8.8‰ to $+0.3\text{‰}$ VPDB and $\delta^{18}\text{C}$ values of -17.8‰ to -11.5‰ VPDB. In the Courtown samples, the brachiopod and bryozoan $\delta^{18}\text{C}$ values were consistently more similar to each other than either was to the matrix, but this was not true for the Tramore samples. This suggests different alteration histories (more likely) or a different source of carbonate for the Courtown matrix (i.e. sparry cement) as opposed to that of the Tramore matrix (i.e. abraded skeletal material) (the less likely explanation). Palaeotemperature calculations from the oxygen isotopes (78°C to 128°C) indicate exposure to isotopically light groundwater or meteoric fluids following the previous and hotter Caledonian and Hercynian orogenies. All three phases of alteration would have overprinted any original palaeoenvironmental signal that might once have existed.

Introduction

The use of carbonate fossils for palaeothermometry as derived from stable isotope geochemistry

is a well-established approach for geoscientists. Originally this work was done on relatively young fossils (such as those from the Cenozoic era) with obviously unaltered original skeletal

mineralogy (e.g. aragonite). Because of the effectiveness of this tool, its use has been expanded (e.g. Stanton *et al.* 2002) to include older fossils in which diagenetic alteration of the skeletal mineralogies is more difficult to determine (for example, those with low-to-high Mg calcite). With all these studies, there is the concern about (1) how pristine the skeletal carbonate is in relation to diagenesis and (2) whether or not diagenetic cements were included in the sample of skeletal carbonate.

In this study, we compare the light-stable isotopes of low-Mg calcite brachiopod and bryozoan allochems from the Ordovician Duncannon Group with their surrounding matrix to determine if the skeletal isotopes were reset during diagenesis. Our first hypothesis was that if the brachiopod and bryozoan isotope values were consistently more similar to each other than either was to the matrix and/or cements, then there was minimal diagenetic alteration of the geochemistry of the allochems, and thus their skeletal carbonate would be amenable for use in palaeothermometry. Our second hypothesis was that if all the $\delta^{18}\text{O}$ values were isotopically light, then there had been some post-depositional alteration confounding any original palaeoenvironmental signal in the allochems that might once have existed.

Stratigraphy of the Duncannon Group

This study was conducted on bryozoans and brachiopods collected from the Ordovician Courtown and Tramore Limestone Formations of the Duncannon Group, which crop out in south-eastern Ireland (Fig. 1). The Duncannon Group (Gardiner 1974), which occurs in a band trending north-east to south-west from its southern extremity near Dungarvan, Co. Waterford, and north-eastwards to south County Wicklow, is part of the Leinster Terrane. It comprises a Middle to Upper Ordovician suite (Upper Llanvirn to Caradoc) of limestones, black shales and basaltic, andesitic and rhyolitic arc volcanics (Owen and Parkes 2000), of which the laterally equivalent Courtown Limestone Formation and the Tramore Limestone Formation locally form basal units. These both consist of gray calcareous mudstones, siltstones and sandstones with

interbedded blue-gray argillaceous nodular limestone beds and contain a rich shelly fauna. Bryozoans and brachiopods are common allochems in both formations. The two units sit unconformably on sediments of the Lower Ordovician Ribband Group (Brück *et al.* 1979; Carlisle 1979; Tietzsch-Tyler and Sleeman 1994b; 1995b; Sleeman and McConnell 1995b; Harper and Parkes 2000), which has been shown to be Arenig in age on the basis of graptolites (Skevington 1970; Rushton 1996) and does not extend into the Llanvirn as once thought (Brenchley *et al.* 1977). The age of various formations in the Duncannon Group have been constrained using trilobites, brachiopods, graptolites and microfossils (Harper and Parkes 2000), and here we follow the recent revised correlation for the Ordovician (Fortey *et al.* 1995; 2000).

Courtown Limestone Formation

The Courtown Limestone Formation, which crops out at various localities close to the town of Courtown, Co. Wexford (Fig. 1D), comprises a 50m-thick sequence of white to blue fossiliferous limestones, calcareous sandstones and siltstones, with a basal conglomerate developed in places (Gardiner 1974). Biogenic reworking in the limestones has resulted in some fragmentation of the allochems, particularly the crinoids (Crimes and Crossley 1968). A moderately rich brachiopod–trilobite fauna has been described from the Courtown Limestone Formation (Brenchley and Treagus 1970; Mitchell *et al.* 1972; Parkes 1994). It has been deformed, which has produced a well-developed cleavage in the formation.

The age of the Courtown Limestone Formation has been debated by various authors. On palaeontological and stratigraphical evidence, Carlisle (1979) argues that the formation ranged from Middle Llandeilo (a stage name that is now not in use) to the Costonian Stage of the Caradoc, whereas Brück *et al.* (1979) give a Llandeilo age. The brachiopods (Mitchell *et al.* 1972) suggest a Caradoc age, possibly extending down into the Llandeilian age. However, in a review of the geology of the region, Tietzsch-Tyler and Sleeman (1995a; 1995b) give an older age range of Late Llanvirn to Middle Llandeilo

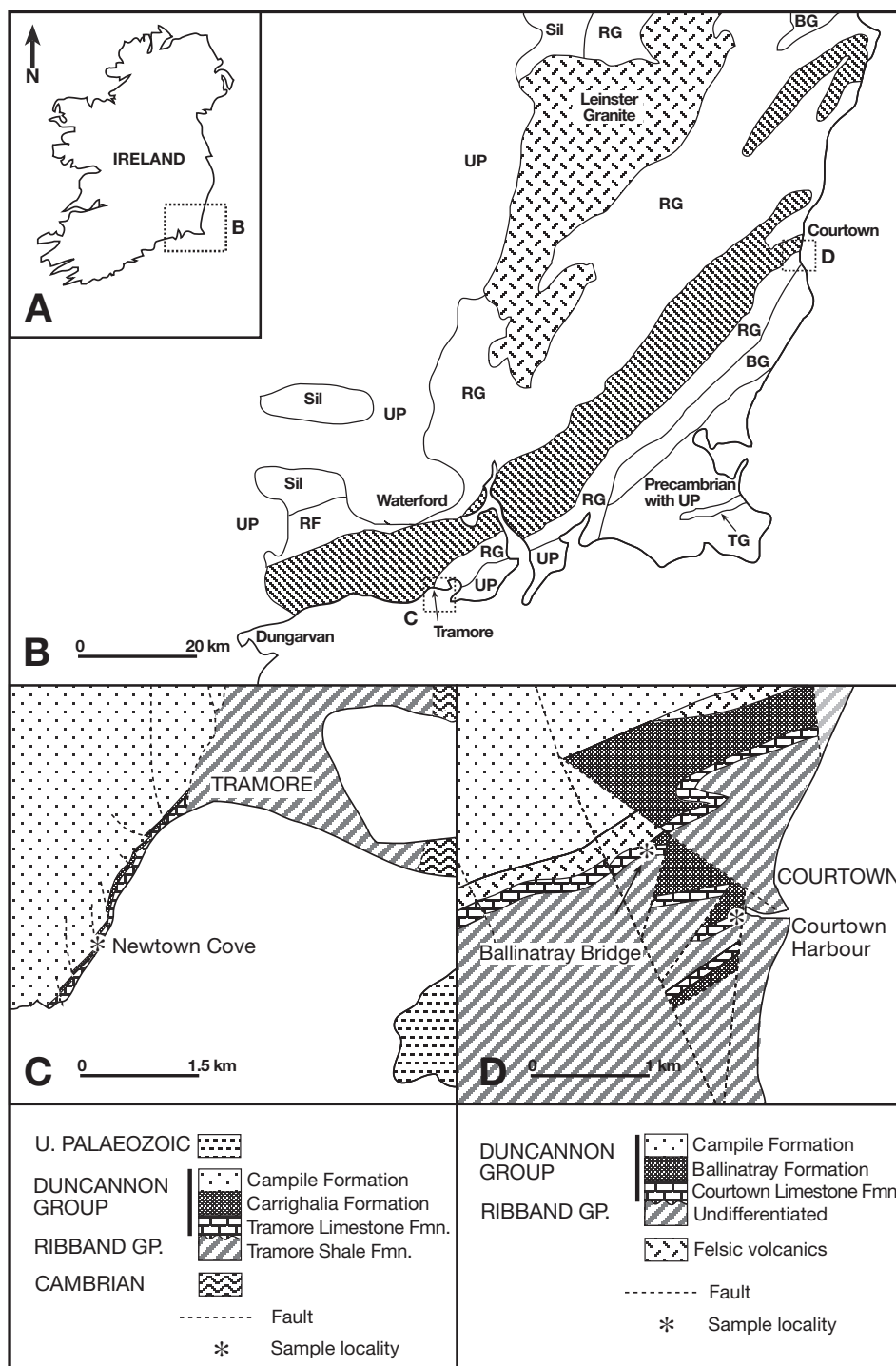


Fig. 1—Geological map of southeastern Ireland indicating position of the Duncannon Group (diagonally shaded) as well as Courttown and Tramore sampling localities.

(A) Map of Ireland showing general area of interest; (B) modified from Owen and Parkes (2000, Fig. 1). (C) modified from Tietzsch-Tyler and Sleeman (1994a); (D) modified from Tietzsch-Tyler and Sleeman (1995a). Abbreviations: BG = Bray Group; RF = Ross Formation (probably part of the Duncannon Group and late Caradoc in age); RG = Ribband Group; Sil = Silurian; TG = Taggart Group; UP = Upper Palaeozoic.

for the formation. Here we are following the findings of Williams (1972), Carlisle (1979) and Parkes (1994) and the recent correlation chart (Harper and Parkes 2000) that shows the formation to be exclusively Caradoc in age (base: Aurelucian stage, Velfreyan substage, *gracilis* biozone; top: Aurelucian stage, Costonian substage, *gracilis* biozone). It lies unconformably on the Riverchapel Formation, the youngest part of the Ribband Group, which has been dated as Lower Arenig on the basis of graptolites (Crimes and Crossley 1968; Skevington 1970; Harper and Parkes 2000). Succeeding the Courtown Limestone Formation is the Ballinatray Formation; shales at the base of this formation have yielded graptolites of the *gracilis* biozone and a deep-water brachiopod fauna (Parkes 1994) that indicate a Caradoc age.

Tramore Limestone Formation

The Tramore Limestone Formation crops out between Tramore Bay in the east and Ballydowane Bay in the west (Carlisle 1979; Tietzsch-Tyler and Sleeman 1994a; Sleeman and McConnell 1995a). Exposures are excellent along the 30–60m high coastal sea cliffs but are only accessible by the occasional entrenched gully. The formation consists of grey calcareous mudstones, siltstones and sandstones and is interbedded with blue-grey argillaceous nodular limestone beds that contain a rich shelly fauna (Murphy 1958; Mitchell *et al.* 1972; Carlisle 1979; Donovan 1985; Tietzsch-Tyler and Sleeman 1994b; Sleeman and McConnell 1995b; Owen and Parkes 2000; Wyse Jackson *et al.* 2002). The more carbonate-rich beds represent buildups of shelly faunas in shallow waters adjacent to the volcanic island arc to the south-east (Tietzsch-Tyler and Sleeman 1994b). In response to contemporaneous faults downthrown to the north-west, the Tramore Limestone Formation grades from a shallower shelf facies some 65m thick in the east to a deeper basal facies (referred to by some authors as the Dunabrattin Limestone Formation) with a maximum thickness of 450m in the west (Phillips *et al.* 1976; Carlisle 1979; Boland 1983; Harper and Parkes 2000). The transition from shelf to basal facies occurs between Black Rock and

Dunabrattin Head (Sleeman and McConnell 1995b).

The Tramore Limestone Formation has been assigned an age range from the Middle Llandeilo to the Costonian stage of the Caradoc on the basis of shelly faunas (Williams *et al.* 1972a; Brenchley *et al.* 1977; Carlisle 1979; Parkes 1994; Sleeman and McConnell 1995b). Conodonts suggest the *E. lindstroemi* subzone of the *P. serra* biozone (Bergström and Orchard 1985). In a recent revision of Ordovician chronostratigraphy, the age of the Tramore Limestone Formation was given as ranging from the Llandeilian stage of the Llanvirn series to the Costonian substage of the Aurelucian stage of the Caradoc series (Fortey *et al.* 1995). Further recent refinements tabulated in Harper and Parkes (2000) show that the formation ranges in age from the Llanvirn series (Abereddian stage, *murchisoni* biozone) to the Caradoc series (Aurelucian stage, Costonian substage, *gracilis* biozone). The Tramore Limestone Formation is overlain by the thin Carrighalia Formation and succeeding Campile Formation (Stillman 1978; Carlisle 1979; Sleeman and McConnell 1995a; 1995b; Tietzsch-Tyler and Sleeman 1994a; 1994b; 1995a; 1995b; Harper and Parkes 2000). The former extends from the Aurelucian to the Burrelian stage.

Correlation of the Courtown and Tramore Limestone Formations

The Courtown Limestone Formation and the Tramore Limestone Formation crop out some 75km apart (Fig. 1B). Nevertheless, on the basis of their faunal similarities and stratigraphic position they have been closely correlated. Both contain some taxa typical of the Scoto-Appalachian fauna (Harper and Parkes 1989). Correlation was initially made on the basis of the common occurrence of the rare trinucleid trilobite *Eirelithus* (Lamont 1941; Crimes and Crossley 1968) and on the fact that the overlying shales in both localities have yielded the graptolite *Nemagraptus gracilis* (Crimes and Crossley 1968), and was subsequently supported on the basis of additional faunal elements (Mitchell *et al.* 1972; Carlisle 1979). Twelve brachiopod genera and four trilobite genera are common to both

formations, with the presence of the stratigraphically restricted brachiopod *Glyptorthis crispa* (M'Coy) and the trilobite *Eirelithus* being particularly important for their correlation (Mitchell *et al.* 1972). Gardiner (1974) suggested a similar correlation based on the volcanic successions of the Campile Formation found in both areas above the fossiliferous horizons.

Biogeography and palaeogeography of the Duncannon Group

The various shelly faunas in south-eastern Ireland south of the Iapetus suture zone have been variously attributed to the Avalonian, Baltic, Scoto-Appalachian, and Celtic faunal provinces (Williams 1969a; 1969b; Williams *et al.* 1972a; Harper *et al.* 1996; Parkes and Harper 1996). The Tramore Limestone Formation fauna (especially the brachiopods) has mixed affinities to the Scoto-Appalachian and Anglo-Welsh faunas (Neuman 1984; Harper and Parkes 1989; Murphy *et al.* 1991; Parkes 1992). This is in contrast to the Laurentian affinities of the faunas in north-western Ireland on the north side of the Iapetus suture zone, which are palaeobiogeographically and tectonically allochthonous (Harper and Parkes 1989; Murphy *et al.* 1991; Harper *et al.* 1996; Williams *et al.* 1996).

During the initial stages of the Caledonian Orogeny, from the upper Llanvirn to the lower Caradoc of the Ordovician, there was a volcanic island arc-trench system extending from the Lake District in England to south-eastern Ireland (Phillips *et al.* 1976; Stillman 1986; Sleeman and McConnell 1995b). The island arc, referred to as the Irish Sea Horst by Williams (1969b) and the Irish Sea Landmass by Fitton and Hughes (1970) and Phillips *et al.* (1976), was created as Iapetus oceanic crust was subducted to the south-east along the margin of the Eastern Avalonia microcontinental plate (Phillips *et al.* 1976; Stillman 1978; 1986; Stillman and Williams 1978; Max *et al.* 1990; Parkes 1992; Sleeman and McConnell 1995b). This places the island arc at ~45°S latitude (Torsvik and Trench 1991; Torsvik *et al.* 1992; Dalziel 1997). During this episode of subduction, oceanic islands were accreted onto Eastern Avalonia as a series of discrete crustal terranes (Neuman 1984; Max *et al.* 1990; Murphy *et al.* 1991). To the north-west of

the island arc was the south-eastern Iapetus Ocean and to the south-east was the shallow Welsh Back-Arc basin (Phillips *et al.* 1976; Stillman 1986; Parkes 1992). The shallow marine environments along the north-west coast of the island arc deepened to the north-west into a basin of the Iapetus Ocean locally referred to as the Leinster Basin (Phillips *et al.* 1976). Turbidites carried shallow marine sediments north-westwards into deeper waters of the basin (Phillips *et al.* 1976; Penney 1980; Boland 1983). It was in these shallow coastal and deeper basinal environments that sediments of the Duncannon Group accumulated. Due to the subduction, the Leinster Basin was tectonically active during this time, so the sedimentary accumulations of the Duncannon Group represent a period of relative geologic quiescence before the extensive volcanism that dominates the overlying Campile Formation (Brück *et al.* 1979; Carlisle 1979). The basin floor adjacent to the volcanic island arc eventually collapsed, presumably after volcanic evacuation of the magma chamber underneath it, and this is represented by the mudstones of the overlying Carrighalia Formation (Tietzsch-Tyler and Sleeman 1994b).

Material

This paper uses thick sections contained in the Geological Museum, Trinity College, Dublin [prefix TCD] and the Geological Survey of Ireland, Dublin [GSI].

- GSI:F08024a, b; Ballintra Bridge, Ballintra Lower, Co. Wexford; Courtown Limestone Formation, Caradoc, Ordovician. GSI 19th century collection (Hardman 1887); see Crimes and Crossley (1968) and Parkes (1994) for details of this locality.
- GSI:F11391b, GSI:F11397b; Courtown Harbour, Courtown, Co. Wexford; Courtown Limestone Formation, Caradoc, Ordovician. GSI 19th century collection (Hardman 1887).
- GSI:F14407a, b; Newtown Cove, Tramore, Co. Waterford; Tramore Limestone Formation, Llanvirn to Caradoc, Ordovician; GSI 19th century collection (Baily 1865).
- TCD.35827a, TCD.35827b, TCD.35827c; Protruding point, south of Newtown Cove,

Tramore, Co. Waterford; Tramore Limestone Formation, Llanvirn to Caradoc, Ordovician. Karen and Nils Spjeldnaes Collection 1952.

Methods

The bulk rock samples were slabbed. Slabs were chosen that had both brachiopod and bryozoan allochems as well as the ubiquitous matrix. Nine selected slabs were thick-sectioned (100 μ m) onto 2" \times 3" or 1" \times 3" glass slides and polished on the exposed upper surface. Brachiopod and bryozoan allochems were sampled separately from the surrounding finer grained matrix and cements. When sampling the brachiopods' carbonate, the hinge, brachidium, foramen, and muscle scars were avoided because their calcite can be abnormally depleted in both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ (Carpenter and Lohmann 1995). When sampling the bryozoans' carbonate, the thinner endozonal skeletal walls were avoided because their samples could have been more contaminated by adjacent cements than the thicker exozonal skeletal walls (Key *et al.* 2005). When sampling the matrix's carbonate, fine-grained allochems, micrite and cements were not distinguished, but veins cements were. Since only five veins were sampled, their values are included with the matrix.

Sampling of the carbonate was performed on the thick sections via micromilling on a computer-controlled three-dimensional positioning stage set under a fixed high-precision dental drill that offered a 1 μ m spatial sampling resolution (Wurster *et al.* 1999). Enough carbonate was milled to create samples of >20 μ g of powder for carbon and oxygen isotopic analysis. The carbonate samples were heated *in vacuo* at 200°C to remove water and volatile organic contaminants. Stable isotope values were obtained using a Kiel-III automated carbonate preparation system coupled to the inlet of a Finnigan MAT 252 gas-ratio mass spectrometer in the stable isotope laboratory at Syracuse University. The carbonate was reacted at 70°C with two drops of anhydrous phosphoric acid for 90 seconds. Isotope ratios were corrected for acid fractionation and ^{17}O contribution and reported in per mil notation relative to the VPDB standard. Precision ($\pm 0.1\%$) and calibration of data were monitored through daily analysis of NBS-18 and NBS-19

carbonate standards. $\delta^{18}\text{O}$ values of the samples were bracketed by those of the standards.

Of the original data set of 62 samples, four were eliminated due to machine error, and a further five samples were eliminated due to insufficient carbonate mass (i.e. < 20 μ g), as shown by low gas pressure and/or voltage in the mass spectrometer. Thus, the final culled data set contained 53 samples.

Stable isotope results

Of the 53 total samples, 30 were from the Courtown Limestone Formation and 23 were from the Tramore Limestone Formation. Fifteen of the samples were brachiopods, nineteen bryozoans and nineteen matrix. Summary statistics for the carbon isotope data are found in Table 1 and those for the oxygen isotope data are found in Table 2.

Brachiopod vs. bryozoan allochems

Courtown. The isotopic signature of the Courtown brachiopods is different from that of its bryozoans (Fig. 2). For $\delta^{13}\text{C}$ ($\%$ VPDB), the brachiopods (mean = -1.4) are significantly isotopically heavier than the bryozoans (mean = -2.6; *t*-test, *p* = 0.005). For $\delta^{18}\text{O}$ ($\%$ VPDB), the brachiopods (mean = -16.0) are significantly isotopically lighter than the bryozoans (mean = -15.2; *t*-test, *p* = 0.003).

Tramore. The isotopic signature of the Tramore brachiopods is different from that of its bryozoans based on the carbon isotopes but indistinguishable based on the oxygen isotopes (Fig. 2). For $\delta^{13}\text{C}$ ($\%$ VPDB), the brachiopods (mean = -0.3) are significantly isotopically heavier than the bryozoans (mean = -0.9; *t*-test, *p* = 0.007). For $\delta^{18}\text{O}$ ($\%$ VPDB), the brachiopods (mean = -14.4) are not significantly different from the bryozoans (mean = -13.5; *t*-test, *p* = 0.170).

Matrix vs. Allochems

Courtown. The isotopic signature of the Courtown matrix is different from that of its brachiopod and bryozoan allochems (Fig. 2). For $\delta^{13}\text{C}$ ($\%$ VPDB), the matrix (mean = -6.2) is significantly isotopically lighter than both the brachiopods (mean = -1.4; *t*-test, *p* < 0.001) and bryozoans (mean = -2.6; *t*-test, *p* < 0.001).

Table 1—Summary data table for carbon isotope values of brachiopods, bryozoans and matrix from the Courtown and Tramore Limestone Formations.

<i>Formation</i>	<i>Material analysed</i>	<i>Number</i>	<i>Range $\delta^{13}\text{C}$ ‰ (VPDB)</i>	<i>Mean $\delta^{13}\text{C}$ ‰ (VPDB)</i>	<i>Standard deviation $\delta^{13}\text{C}$ ‰ (VPDB)</i>
CLF	Brachiopods	9	−2.3 to −0.6	−1.4	0.7
CLF	Bryozoans	10	−4.5 to −1.1	−2.6	1.1
CLF	Matrix	11	−8.8 to −2.2	−6.2	1.7
CLF	Brachiopods, bryozoans and matrix combined	30	−8.8 to −0.6	−3.6	2.4
TLF	Brachiopods	6	−0.9 to 0.3	−0.3	0.4
TLF	Bryozoans	9	−1.2 to −0.6	−0.9	0.2
TLF	Matrix	8	−2.5 to −1.0	−1.4	0.5
TLF	Brachiopods, bryozoans and matrix combined	23	−2.5 to 0.3	−0.9	0.6

CLF = Courtown Limestone Formation

TLF = Tramore Limestone Formation

For $\delta^{18}\text{O}$ (‰ VPDB), the matrix (mean = −13.6) is significantly isotopically heavier than both the brachiopods (mean = −16.0; *t*-test, *p* < 0.001) and bryozoans (mean = −15.2; *t*-test, *p* = 0.006).

Tramore. The isotopic signature of the Tramore matrix is different from that of its brachiopod and bryozoan allochems based on the carbon isotopes but indistinguishable based on the oxygen isotopes (Fig. 2). For $\delta^{13}\text{C}$ (‰ VPDB), the matrix (mean = −1.4) is significantly isotopically lighter than both the brachiopods (mean = −0.3; *t*-test, *p* < 0.001) and bryozoans (mean = −0.9; *t*-test, *p* = 0.005). For $\delta^{18}\text{O}$ (‰ VPDB), the matrix (mean = −13.9) is not significantly different from both the brachiopods (mean = −14.4; *t*-test, *p* = 0.297) and bryozoans (mean = −13.5; *t*-test, *p* = 0.203).

Courtown vs. Tramore

All data

The isotopic signature of the Courtown samples taken as a whole is different from that of the Tramore samples (Fig. 2). For $\delta^{13}\text{C}$ (‰ VPDB), the Courtown samples (mean = −3.6) are significantly isotopically lighter than the Tramore samples (mean = −0.9; *t*-test, *p* < 0.001). For $\delta^{18}\text{O}$ (‰ VPDB), the Courtown samples (mean = −14.8) are significantly isotopically lighter than the Tramore samples (mean = −13.9; *t*-test, *p* = 0.009).

Brachiopods. The isotopic signature of the Courtown brachiopods is different from that of the Tramore brachiopods (Fig. 2). For $\delta^{13}\text{C}$ (‰ VPDB), the Courtown samples (mean = −1.4) are significantly isotopically lighter than the Tramore samples (mean = −0.3; *t*-test, *p* < 0.001). For $\delta^{18}\text{O}$ (‰ VPDB), the Courtown samples (mean = −16.0) are significantly isotopically lighter than the Tramore samples (mean = −14.4; *t*-test, *p* = 0.048).

Table 2—Summary data table for oxygen isotope values of brachiopods, bryozoans and matrix from the Courtown and Tramore Limestone Formations.

<i>Formation</i>	<i>Material analysed</i>	<i>Number</i>	<i>Range $\delta^{18}\text{O}$ ‰ (VPDB)</i>	<i>Mean $\delta^{18}\text{O}$ ‰ (VPDB)</i>	<i>Standard deviation $\delta^{18}\text{O}$ ‰ (VPDB)</i>
CLF	Brachiopods	9	−16.8 to −15.1	−16.0	0.5
CLF	Bryozoans	10	−15.7 to −14.0	−15.2	0.7
CLF	Matrix	11	−15.8 to −11.5	−13.6	1.7
CLF	Brachiopods, bryozoans and matrix combined	30	−16.8 to −11.5	−14.8	1.5
TLF	Brachiopods	6	−17.8 to −12.4	−14.4	2.0
TLF	Bryozoans	9	−14.9 to −12.2	−13.5	1.0
TLF	Matrix	8	−15.5 to −12.8	−13.9	0.9
TLF	Brachiopods, bryozoans and matrix combined	23	−17.8 to −12.2	−13.9	1.3

CLF = Courtown Limestone Formation

TLF = Tramore Limestone Formation

Bryozoans. The isotopic signature of the Courtown bryozoans is different from that of the Tramore bryozoans (Fig. 2). For $\delta^{13}\text{C}$ (‰ VPDB), the Courtown samples (mean = −2.6) are significantly isotopically lighter than the Tramore samples (mean = −0.9; *t*-test, $p < 0.001$). For $\delta^{18}\text{O}$ (‰ VPDB), the Courtown samples (mean = −15.2) are significantly isotopically lighter than the Tramore samples (mean = −13.5; *t*-test, $p < 0.001$).

Matrix. The isotopic signature of the Courtown matrix is different from that of the Tramore matrix based on the carbon isotopes but indistinguishable based on the oxygen isotopes (Fig. 2). For $\delta^{13}\text{C}$ (‰ VPDB), the Courtown samples (mean = −6.2) are significantly isotopically lighter than the Tramore samples (mean = −1.4; *t*-test, $p < 0.001$). For $\delta^{18}\text{O}$ (‰ VPDB), the Courtown samples (mean = −13.6) are not significantly different from the Tramore samples (mean = −13.9; *t*-test, $p = 0.278$).

Palaeotemperature results

The $\delta^{18}\text{O}$ values were used to calculate palaeotemperatures using Kim and O'Neil's (1997) equation for calcite and assuming a $\delta^{18}\text{O}$ value for seawater of 0.0‰ VPDB. The absolute values of these results would be slightly different if the $\delta^{18}\text{O}$ value for Ordovician seawater was different or the salinity of Ordovician seawater was different (e.g. Veizer *et al.* (1999) suggested an $\delta^{18}\text{O}$ value of −5 (‰ PDB) and Hay (2000) suggested a salinity of 50 ppm). Despite these potential changes in absolute palaeotemperature values, the relative differences between the allochems and matrix would not change. The mean calculated palaeotemperatures (range: 78–128°C, mean = 100°C) were well above the limits tolerated by brachiopods and bryozoans, indicating some form of post-depositional alteration. The mean palaeotemperatures calculated for the Courtown Limestone Formation (range:

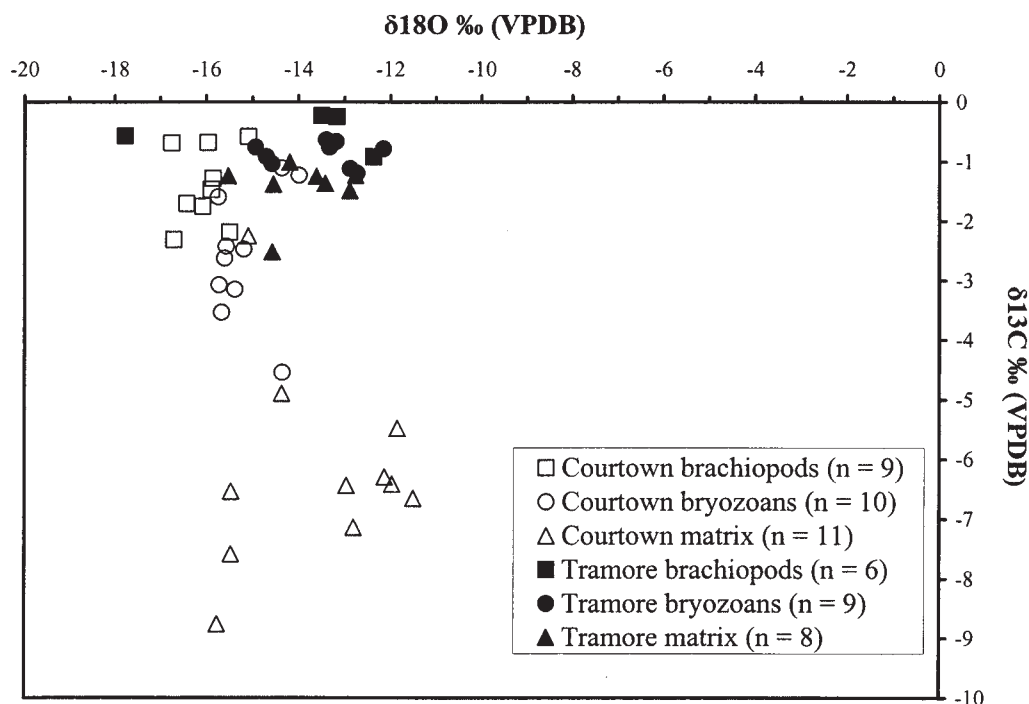


Fig. 2—Plot of $\delta^{18}\text{O}$ vs $\delta^{13}\text{C}$ for the brachiopod and bryozoan allochems and the matrix from the Courtown and Tramore Limestone Formations.

78–119°C, mean = 104°C) were significantly higher than those for the Tramore Limestone Formation (range: 83–128°C, mean = 96°C; t -test, $p = 0.009$).

Discussion

$\delta^{13}\text{C}$

Globally, $\delta^{13}\text{C}$ values in biogenic and abiogenic carbonates range from -50‰ to $+20\text{‰}$ PDB, but most marine sediments and limestones are in the range of -3‰ to $+5\text{‰}$ PDB (Nelson and Smith 1996). The values from this study, which range from -8.8‰ to $+0.3\text{‰}$, generally overlap but are also slightly lighter. Carbon isotopes are less susceptible to alteration than oxygen isotopes, but they can be affected by different sources (Marshall 1992). Alteration and mixing of carbon sources aside, the heavier values would indicate a normal marine organic carbon source, whereas the lighter values indicate alteration and/or a more terrestrial source, perhaps via runoff (Nelson and Smith 1996). The Courtown samples exhibit a greater range in $\delta^{13}\text{C}$ values (8.2‰ PDB vs. 2.8‰ for Tramore) (Fig.

2), suggesting they may have been exposed to a greater range of carbon sources (e.g. marine, terrestrial, upwelling, etc.).

$\delta^{18}\text{O}$

Globally, $\delta^{18}\text{O}$ values in carbonates range from -10‰ to $+5\text{‰}$ PDB, but most marine carbonate sediments and limestones are in the range of -10‰ to $+2\text{‰}$ PDB (Nelson and Smith 1996). The values from this study, which range from -17.8‰ to -11.5‰ (mean = -14.4‰ VPDB), fall outside this range, indicating either contamination by isotopically light groundwater or meteoric water ($\sim -15\text{‰}$) and/or exposure to hot fluids from deep diagenetic burial (Nelson and Smith 1996). Diagenetic alteration of carbonate commonly results in depletion of $\delta^{18}\text{O}$ values (Hudson 1977). Thus, the light $\delta^{18}\text{O}$ values suggest a thermal history for these sediments involving temperatures at the high end of sedimentary diagenesis. This heating probably resulted in the alteration of the original oxygen isotopic signature *sensu* Pichler *et al.* (2000).

Palaeozoic brachiopods are commonly used in oxygen isotope palaeotemperature studies

(e.g. Popp *et al.* 1986; Qing and Veizer 1994), but bryozoans are underutilised as sources of palaeotemperature information. If the brachiopods and bryozoans were growing in the same environment and they did not fractionate oxygen differently (i.e. they did not exert vital effects), then they should have similar isotopic signatures. This was true for the Tramore Limestone Formation but not for the Courtown Limestone Formation, where the brachiopods were slightly isotopically lighter than the bryozoans ($\delta^{18}\text{O}$: -0.8% VPDB). This could indicate a vital effect in one or both groups (not substantiated in the literature), mineralogical differences in Mg content between the groups (not substantiated in the literature) or, most likely, differential alteration in response to different porosities and permeabilities between brachiopod and bryozoan skeletons.

Thermal history of the Duncannon Group

The Duncannon Group was affected by a variety of heating events during the Caledonian and Hercynian orogenies. During the Late Silurian – Early Devonian Caledonian Orogeny, the Ordovician rocks in North America and Scandinavia were pushed down to greater depths and subjected to extreme temperatures and pressures, unlike those in Britain and Ireland, which escaped such extremes (Williams *et al.* 1972b; Phillips *et al.* 1976; Tietzsch-Tyler and Sleeman 1994b). The regional deformation from the orogeny resulted in the rocks of south-eastern Ireland being exposed to at least some degree of degradational metamorphism (Stillman and Williams 1978; Tietzsch-Tyler and Sleeman 1994b; Diskin 1996), and the maximum limit was probably greenschist facies (Stillman and Williams 1978). The greenschist facies represents a temperature range of 300–500°C (Bucher and Frey 1994).

Caledonian metamorphism of the Duncannon Group was probably initially caused by the emplacement of the overlying Campile Formation volcanics. The orogeny continued resulting in tectonic downwarping, which led to further burial of the Duncannon Group. This can be seen from the results of the palaeotemperature determinations on the Tramore Limestone For-

mation carried out using the conodont Color Alteration Index (CAI). Bergström (1980) analysed two samples from Newtown Head and Dunabrattin Head and determined a CAI of 5, which translates to an estimated heating temperature of 300–400°C. These temperatures in the Tramore Limestone Formation were attributed to burial due to overburden as well as localised igneous intrusions (Bergström 1980).

During the Late Carboniferous – Early Permian Hercynian Orogeny, the Tramore Limestone Formation was further cleaved, folded and faulted, but it only reached subgreenschist facies (Penney 1980; Tietzsch-Tyler and Sleeman 1994b; Diskin 1996). Accepted temperatures for the subgreenschist facies are 100–300°C (Bucher and Frey 1994). The subgreenschist level of metamorphism for the Tramore Limestone Formation was further refined by Diskin (1996) as diagenetic to anchizone in degree, with a mean estimated heating temperature of 175°C for outcrops at Dunabrattin Head and westwards. Anchizone alteration, which begins at 200°C (Kisch 1987), marks the transition between normal diagenetic burial temperatures and true metamorphism, the lowest grade of which is greenschist facies.

This alteration may have been associated with the Hercynian Orogeny. Hercynian hydrothermal fluid flow related to the Carboniferous Irish Zn–Pb orefields to the north of our study area (Johnston 1999) may have affected the Duncannon Group if the fluids were cycled through the Silurian–Ordovician basement in large-scale convection cells. Hydrothermal fluid temperatures in the south-eastern Irish Zn–Pb deposits have been estimated at 100°C (Hitzman *et al.* 1998) to 200°C (Wilkinson and Earls 2000). Less is known about the alteration history of the Courtown Limestone Formation, but it too has a well-developed cleavage (Crimes and Crossley 1968), suggesting a similar deformation and hydrothermal alteration.

Subsequent to these orogenic thermal events, the Duncannon Group probably experienced minimal heat flow (Diskin 1996). The Duncannon Groups rocks would still have been susceptible to alteration from groundwater and meteoric water during its post-Hercynian history. The oxygen isotope values found in this study

probably represent this final phase of history. The isotope values were probably repeatedly reset during the previous thermal events, but these were all overprinted by subsequent recrystallisation. This is shown by the lower palaeotemperatures derived from the oxygen isotopes (range: 78–128°C, mean = 100°C). The Duncannon Group carbonates sampled in this study were probably recrystallised by a younger diagenetic event involving isotopically light groundwater or meteoric water ($\delta^{18}\text{O} \sim -15\text{‰}$). This can be seen north of our study area, where Becker *et al.* (2002) reported $\delta^{18}\text{O}$ values of -12‰ to -17‰ in diagenetic cements of the Lower Carboniferous Zn–Pb district of Ireland and attributed these light isotopes to the incursion of meteoric fluids.

Conclusions

$\delta^{13}\text{C}$ values (-8.8‰ to $+0.3\text{‰}$ VPDB) are indicative of a normal marine carbon source in both the Courtown and Tramore Limestone Formations with some mixing of terrestrial carbon in the Courtown. This suggests minimal alteration of the carbon isotopes. $\delta^{18}\text{O}$ values (-17.8‰ to -11.5‰ VPDB) indicate recrystallisation by isotopically light groundwater or meteoric water. Palaeotemperature calculations from the oxygen isotopes (78°C to 128°C) do not record the thermal histories from the presumably hotter Caledonian and Hercynian orogenies, only the younger diagenetic event. The Courtown Group has experienced a multi-phase thermal history.

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Palaeoenvironmental interpretation of the Tramore

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