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Stable isotope values in modern bryozoan carbonate from New Zealand and implications for paleoenvironmental interpretation

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Abstract Bryozoan carbonate contains useful geochemical evidence of temperate shelf paleoenvironments. Stable isotope values were determined for 103 modern marine bryozoan skeletons representing 30 species from New Zealand. $\delta^{18}O$ values range from –1.4 to 2.8‰ VPDB, while $\delta^{13}C$ range from –4.5 to 2.8‰ VPDB (values uncorrected for mineralogical variation). These values are distinct from those of both tropical marine skeletons and New Zealand Tertiary fossils. Most bryozoans secrete carbonate in or near isotopic equilibrium with sea water, except for *Celleporina* and *Steginoporella*. The complex and variable mineralogies of the bryozoans reported here make correction for mineralogical effects problematic. Nevertheless, mainly aragonitic forms display higher isotope values, as anticipated. Both temperature and salinity constrain $\delta^{18}O$ and $\delta^{13}C$ values, and vary with latitude and water depth. Ten samples from a single branch of *Cinctipora elegans* from the Otago shelf cover a narrow range, although the striking difference in carbon isotope values between the endozone and exozone probably reflects different mineralisation histories. Our stable isotope results from three different laboratories on a single population from a single location are encouragingly consistent. Monomineralic bryozoans, when carefully chosen to avoid species suspected of vital fractionation, have considerable potential as geochemical paleoenvironmental indicators, particularly in temperate marine environments where bryozoans are dominant sediment producers.

Keywords bryozoans; carbonate; oxygen isotopes; carbon isotopes; New Zealand shelf

INTRODUCTION

Marine organisms precipitate carbonate skeletons by extracting ions from sea water. The resulting skeletal material records geochemical information that can be related to the environment of precipitation. Stable oxygen and carbon isotope values have proved particularly useful for paleothermometry and paleoenvironmental reconstruction (e.g., Anderson 1990; Corfield 1995). Stable isotope studies have generally focused on foraminifera and invertebrates such as brachiopods which have been shown to precipitate skeletal carbonate in isotopic equilibrium with ambient sea water. Stable isotope paleothermometry has been used in both modern and ancient tropical settings (e.g., Corfield 1995) and, to a lesser extent, in temperate carbonates (e.g., Rao & Nelson 1992; Bone & James 1997; Goodwin et al. 2001).

Carbonate sediments on austral temperate shelves are dominated by skeletal remains of bryozoans and molluscs (Rao 1996). These "bryomol" skeletal carbonates stretch for >4000 km along the southern Australian shelf (James 1997), and the New Zealand shelf is blanketed with some 56 000 km^2 of carbonate deposits that consist of 30–90% bryozoan material (Nelson et al. 1988a). Cenozoic analogues crop out onshore, with particularly extensive cool-water bryozoan limestones in the mid-Tertiary of both Australia (e.g., James & Bone 1989, 1991, 1994) and New Zealand (Nelson 1978; Nelson et al. 1988b). There are nearly 1000 bryozoan species in New Zealand (Nelson & Gordon 1997), but only a few large erect shelf species (e.g., *Cinctipora elegans*, *Celleporaria agglutinans*, *Hippomenella vellicata*, *Adeonellopsis* spp., and *Hornera* spp.) are responsible for most carbonate sediment formation. Large colonies may produce up to 200 g carbonate over the course of a colonial lifespan of some 20 yr (Smith et al. 2001).

Stable isotope values in bryozoan carbonate are proving to be useful in a variety of applications as it seems that most bryozoans precipitate carbonate in isotopic equilibrium with sea water (Forester et al. 1973; Bone & James 1997; Rahimpour-Bonab et al. 1997a; Crowley & Taylor 2000), apparently free of the vital effects which render, for example, echinoderms unreliable for paleoenvironmental analysis (Weber & Raup 1966). Stable isotope profiles within single colonies have been used to determine age and growth rate in several species (Pätzold et al. 1987; Brey et al. 1999; Bader 2000). Paleoenvironmental studies also have used

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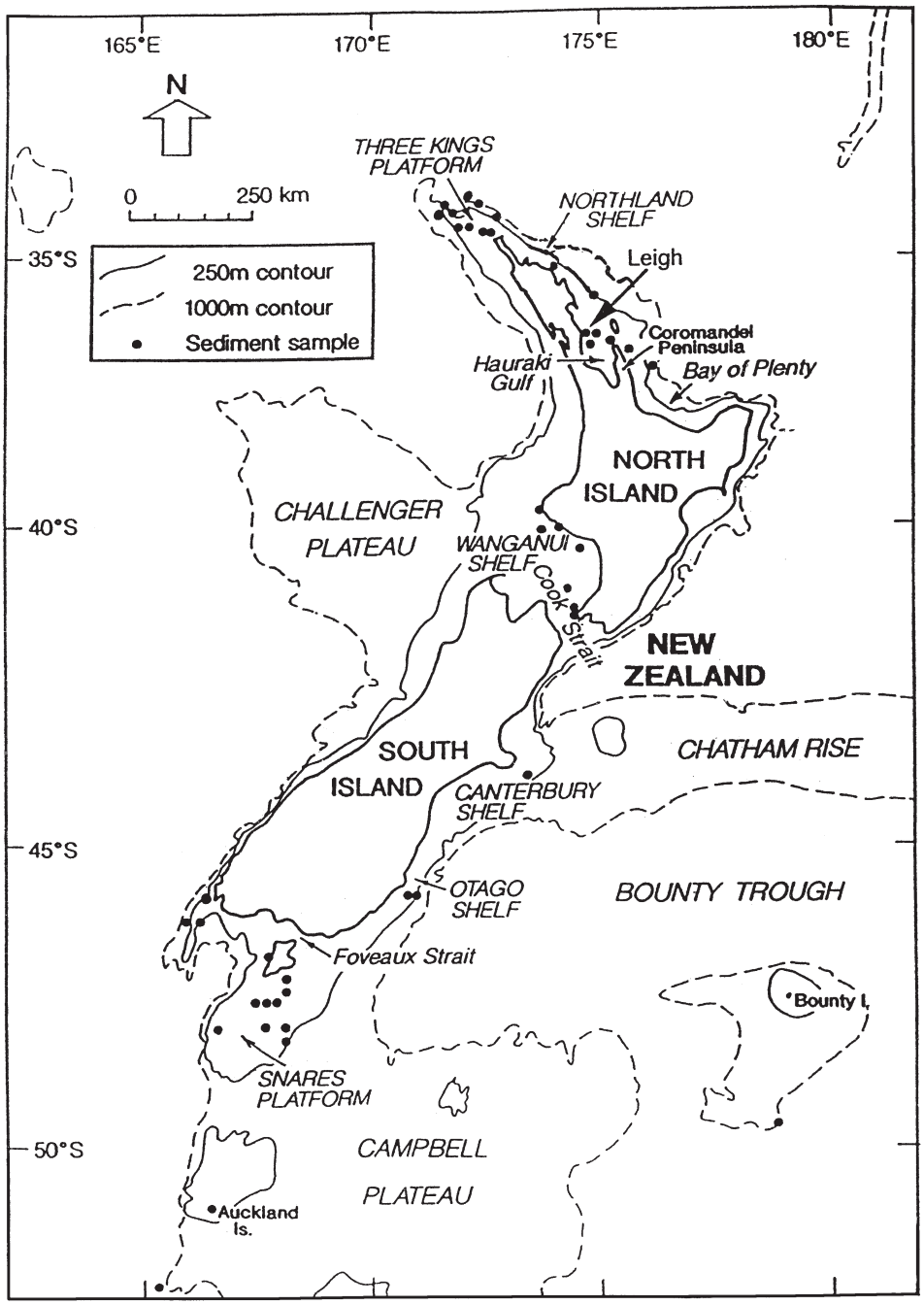

Fig. 1 Sample locations for 103 specimens of extant bryozoans from New Zealand (see Table 1).

stable isotope values of bryozoans for paleoecological and paleoclimatic reconstructions (e.g., Taviani et al. 1993; Nelson & Smith 1996; Rao 1996; Rahimpour-Bonab et al. 1997b; Smith & Key 2004).

We present oxygen and carbon stable isotopic data from modern New Zealand bryozoans, taking a species approach in order to evaluate their utility for paleoenvironmental analysis. We compare our data with other published work on New Zealand and Australian bryozoans, most of which group species together in taxa or growth form categories, and we discuss correlation of bryozoan stable isotopic geochemistry with environment.

METHODS

Ninety-three specimens comprising 30 species of sediment-forming bryozoans from 33 different sample locations were selected for analysis, with a further 10 samples from a single specimen (see below). Sediment samples were collected by grab sampler or dredge from areas of carbonate accumulation on the New Zealand shelf and adjacent subantarctic islands. They ranged in latitude from 34 to 52°S, and water depths ranged from 8 to 292 m (Table 1; Fig. 1; see also Smith & Nelson 1993). Clean, unaltered specimens were selected under a binocular microscope, washed in distilled water,

Table 1 Stable isotopes in skeletons of New Zealand bryozoans. Sample locations from Smith & Nelson (1993) (Waikato data), with the exception of samples QQ from the Otago shelf which comprise a series of measurements along a single branch of *Cinctipora elegans* (Syracuse data).

Sample locations				Bryozoan species					Stable isotopes	
Sample location	Latitude (°S)	Longitude (°E)	Water depth (m)	Genus	Species	Taxon*	Growth form†	Carbonate mineralogy‡	(mg/g) $\delta^{18}O$	VPDB $\delta^{13}C$
D114	44.20	173.30	84	*Adeonellopsis*	sp.	CH as	ERro	A/(IMC)	1.82	2.19
D38	51.97	165.47	252	*Adeonellopsis*	sp.				2.72	2.49
D44	47.50	168.01	120	*Adeonellopsis*	sp.				2.26	2.73
E26	47.68	167.40	144	*Adeonellopsis*	sp.				2.35	2.68
E820	46.58	165.97	220	*Adeonellopsis*	sp.				1.97	2.18
P609	40.01	174.08	75	*Adeonellopsis*	sp.				0.89	2.45
P448	34.39	172.47	101	*Annectocyma*	sp.	CY tu	ERro	LMC	0.89	0.96
P614	40.17	174.58	90	*Annectocyma*	sp.				0.06	0.89
C12	36.49	175.38	53	*Arachnopusia*	*unicornis*	CH as	ENul	IMC/(A)	0.48	0.34
L21	36.08	175.04	71	*Arachnopusia*	*unicornis*				1.19	0.83
L33	36.17	174.83	58	*Arachnopusia*	*unicornis*				0.92	0.58
P609	40.01	174.08	75	*Arachnopusia*	*unicornis*				–0.47	0.77
C12	36.49	175.38	53	*Cellaria*	*immersa*	CH an	EFbr	LMC/IMC	0.66	1.04
E26	47.68	167.40	144	*Cellaria*	*immersa*				1.58	1.58
E27	47.67	167.65	131	*Cellaria*	*immersa*				1.84	1.66
E820	46.58	165.97	220	*Cellaria*	*immersa*				1.84	1.56
P448	34.39	172.47	101	*Cellaria*	*immersa*				1.24	1.35
P454	34.25	172.16	292	*Cellaria*	*immersa*				2.37	1.57
P614	40.17	174.58	90	*Cellaria*	*immersa*				0.40	1.23
B488	46.50	166.24	164	*Celleporaria*	*agglutinans*	CH as	ENml	IMC	1.30	0.83
C12	36.49	175.38	53	*Celleporaria*	*agglutinans*				0.74	0.67
LF	36.27	174.80	8	*Celleporaria*	*agglutinans*				0.25	0.00
P609	40.01	174.08	75	*Celleporaria*	*agglutinans*				0.04	1.00
P454	34.25	172.16	292	*Celleporina*	*costazii*	CH as	ENnd	IMC/(A)	2.26	1.68
P558	33.98	171.72	178	*Celleporina*	*costazii*				1.68	1.74
P609	40.01	174.08	75	*Celleporina*	*costazii*				0.29	1.55
P614	40.17	174.58	90	*Celleporina*	*grandis*	CH as	ERro	LMC	–0.06	1.29
D114	44.20	173.30	84	*Cinctipora*	*elegans*	CY ci	ERro	LMC/(A)	1.93	1.22
D38	51.97	165.47	252	*Cinctipora*	*elegans*				1.79	1.40
G9	48.00	166.59	170	*Cinctipora*	*elegans*				1.50	1.26
P609	40.01	174.08	75	*Cinctipora*	*elegans*				0.16	1.10
QQ	45.56	170.47	80	*Cinctipora*	*elegans*				0.85	0.94
QQ	45.56	170.47	80	*Cinctipora*	*elegans*				1.01	0.86
QQ	45.56	170.47	80	*Cinctipora*	*elegans*				1.00	0.90
QQ	45.56	170.47	80	*Cinctipora*	*elegans*				0.94	0.83
QQ	45.56	170.47	80	*Cinctipora*	*elegans*				0.28	1.04
QQ	45.56	170.47	80	*Cinctipora*	*elegans*				0.59	–0.74
QQ	45.56	170.47	80	*Cinctipora*	*elegans*				0.85	0.42
QQ	45.56	170.47	80	*Cinctipora*	*elegans*				1.21	0.31
QQ	45.56	170.47	80	*Cinctipora*	*elegans*				1.11	0.33
QQ	45.56	170.47	80	*Cinctipora*	*elegans*				0.57	0.94
DPG3	41.13	174.50	30	*Cornuticella*	*taurina*	CH as	EFlt	IMC	0.57	–0.55
D44	47.50	168.01	120	*Escharina*	*waiparensis*	CH as	ENul	IMC	1.26	1.58
DPG2	41.17	174.67	20	*Euthyroides*	*episcopalis*	CH as	EFlt	IMC	0.65	–0.91
DPG4	40.80	174.17	40	*Euthyroides*	*jellyae*	CH as	EFlt	IMC/A	1.48	0.95
B488	46.50	166.24	164	*Foveolaria*	*cyclops*	CH an	ENul	IMC/A	0.55	1.68
D38	51.97	165.47	252	*Foveolaria*	*cyclops*				2.16	1.52
P507	34.15	172.75	100	*Foveolaria*	*cyclops*				0.37	1.59
D38	51.97	165.47	252	*Galeopsis*	*polyporus*	CH as	ERde	IMC	1.94	0.94
L17	36.17	174.92	52	*Galeopsis*	*polyporus*				0.84	0.10
P448	34.39	172.47	101	*Galeopsis*	*polyporus*				0.96	0.89
P454	34.25	172.16	292	*Galeopsis*	*polyporus*				1.56	1.03
P609	40.01	174.08	75	*Galeopsis*	*polyporus*				–0.33	0.38
C10	36.38	175.38	50	*Galeopsis*	*porcellanicus*	CH as	ERde	IMC	0.99	1.52
DPG5	49.75	179.00		*Galeopsis*	*porcellanicus*				1.87	1.69
L13	36.20	175.04	30	*Galeopsis*	*porcellanicus*				–0.67	1.56
LF	36.27	174.80	8	*Galeopsis*	*porcellanicus*				0.88	0.97
P448	34.39	172.47	101	*Galeopsis*	*porcellanicus*				1.27	1.58
C10	36.38	175.38	50	*Hippellozoon*	*novaezelandiae*	CH as	ERfe	IMC	0.88	2.15
P454	34.25	172.16	292	*Hippellozoon*	*novaezelandiae*				1.76	1.83
P507	34.15	172.75	100	*Hippellozoon*	*novaezelandiae*				–0.28	1.80
P609	40.01	174.08	75	*Hippellozoon*	*novaezelandiae*				0.44	2.13
E842	33.90	172.28	187	*Hippomenella*	*vellicata*	CH as	ERfo	IMC/A	0.24	1.65
P614	40.17	174.58	90	*Hippomenella*	*vellicata*				0.43	0.94
D38	51.97	165.47	252	*Hornera*	spp.	CY ho	ERro	LMC	1.97	1.56

(continued)

Table 1 *(continued)*

Sample locations				Bryozoan species					Stable isotopes	
Sample location	Latitude (°S)	Longitude (°E)	Water depth (m)	Genus	Species	Taxon*	Growth form†	Carbonate mineralogy‡	(mg/g) $\delta^{18}O$	VPDB $\delta^{13}C$
E27	47.67	167.65	131	*Hornera*	spp.				1.47	1.60
G9	48.00	166.59	170	*Hornera*	spp.				1.80	1.61
P448	34.39	172.47	101	*Hornera*	spp.				0.94	1.38
P454	34.25	172.16	292	*Hornera*	spp.				1.58	1.62
P614	40.17	174.58	90	*Hornera*	spp.				0.60	1.57
L13	36.20	175.04	30	Idmidroneiforms	spp.	CY tu	ERde	LMC	–0.73	0.40
P454	34.25	172.16	292	*Iodictyum*	*yaldwini*	CH as	ERfe	IMC	1.97	1.72
C12	36.49	175.38	53	*Macropora*	*grandis*	CH an	ENul	LMC/IMC	1.00	–0.08
C10	36.38	175.38	50	*Mecynoecia*	*purpurascens*	CY tu	ERde	LMC	0.56	0.28
C11	36.40	175.40	47	*Mecynoecia*	*purpurascens*				–0.80	–4.50
C12	36.49	175.38	53	*Mecynoecia*	*purpurascens*				1.02	0.00
LS	36.27	174.80	8	*Mecynoecia*	*purpurascens*				0.36	–0.64
P507	34.15	172.75	100	*Mecynoecia*	*purpurascens*				0.12	0.62
P609	40.01	174.08	75	*Mecynoecia*	*purpurascens*				0.53	–0.51
P614	40.17	174.58	90	*Mecynoecia*	*purpurascens*				0.15	–0.02
P507	34.15	172.75	100	*Menipea*	*zelandica*	CH an	EFbr	LMC	0.07	1.00
P558	33.98	171.72	178	*Menipea*	*zelandica*				1.56	1.37
P454	34.25	172.16	292	*Metroperiella*	*mucronifera*	CH as	ERro	IMC/(A)	1.59	2.01
C10	36.38	175.38	50	*Otionella*	*squamosa*	CH an	FLvg	A/(IMC)	1.37	2.58
L17	36.17	174.92	52	*Otionella*	*squamosa*				1.41	2.70
L33	36.17	174.83	58	*Otionella*	*squamosa*				1.67	2.49
P454	34.25	172.16	292	*Otionella*	*squamosa*				2.75	2.65
P492	34.36	172.61	85	*Otionella*	*squamosa*				1.57	2.81
C12	36.49	175.38	53	*Patsyella*	*flemingi*	CH an	ENul	IMC/A	1.44	0.91
L13	36.20	175.04	30	*Patsyella*	*flemingi*				–0.46	0.66
C10	36.38	175.38	50	*Steginoporella*	*magnifica*	CH an	ENul	IMC/(A)	0.58	0.63
P448	34.39	172.47	101	*Steginoporella*	*magnifica*				0.73	–0.09
P454	34.25	172.16	292	*Steginoporella*	*magnifica*				1.64	–0.03
L13	36.20	175.04	30	*Steginoporella*	*neozelanica*	CH an	EFrt	IMC	–1.35	–3.08
OF	36.72	175.83	20	*Steginoporella*	*neozelanica*				0.30	–1.81
P448	34.39	172.47	101	*Steginoporella*	*neozelanica*				0.39	–1.48
P489	34.30	172.68	88	*Steginoporella*	*perplexa*	CH an	ENul	IMC/(A)	0.72	–1.06
P507	34.15	172.75	100	*Steginoporella*	*perplexa*				–0.13	–1.08
C12	36.49	175.38	53	*Telopora*	*buski*	CY fa	ERra	LMC	0.55	0.78
L10	36.20	174.92	53	*Telopora*	*buski*				0.94	1.02
L21	36.08	175.04	71	*Telopora*	*buski*				0.92	0.89
P507	34.15	172.75	100	*Telopora*	*buski*				0.49	1.39
P609	40.01	174.08	75	*Telopora*	*buski*				–0.57	1.06
n				25	30	4	12	7	103	103
Min.	33.90	165.47	8						–1.35	–4.50
Max.	51.97	179.00	292						2.75	2.81
Mean	39.68	172.41	111						0.93	0.96

*Taxonomic abbreviations: CH Cheilostomata: an anascan, as ascophoran. CY Cyclostomata: ci cinctiporid, fa fasciculate, ho horneroid, tu tubuliporine.
†Growth form abbreviations (adapted from Nelson et al. 1988; Smith 1992; Hageman 1998): EN encrusting: ml multilaminar, ul unilaminar, nd nodular. ER erect rigid: de delicate branching, fe fenestrate, fo foliose, ra radiate, ro robust branching. EF erect flexible: br branching, lt lightly calcified, rt rooted. FL free-living: vg vagrant.
‡Mineralogical abbreviations (data from Smith et al. 1998): A Aragonite; LMC low Mg calcite (<5 wt%); IMC intermediate Mg calcite (5–10 wt%). Where two minerals are listed, the first is dominant, the second subdominant. Where a mineral is in parentheses, it is found in trace amounts only in a few specimens.

dried, and ground to powder. Small samples were roasted at 200°C to remove organic contaminants, crushed, and reacted completely with 100% orthophosphoric acid at 50°C. Stable isotope ratios of the resulting CO_2 gas were determined using a VG Micromass 602E mass spectrometer at the University of Waikato, after the method of Shackleton (1965). Values are given in delta notation as per mil deviation of the $^{18}O/^{16}O$ and $^{13}C/^{12}C$ in the sample relative to the VPDB standard (i.e., $\delta^{18}O$ and $\delta^{13}C$, respectively) by repeated analyses of the international standard NBS-19. Analytical precision for isotopic analyses is ±0.05 to 0.1‰.

A single colony of *Cinctipora elegans* from the Otago shelf (QQ in Table 1) was thin-sectioned and polished on the exposed upper surface. Micromilling of skeletal carbonate was performed (sensu Wurster et al. 1999) on a computer controlled, 3D positioning stage set under a fixed high-precision dental drill with 1 µm spatial sampling resolution, resulting in powdered samples of 20–40 µg for carbon and oxygen isotopic analysis. The 10 carbonate samples (five from the interior, thin-walled zooecia (endozone) and five from the exterior, thick-walled zooecia (exozone)) were roasted *in vacuo* at 200°C to remove water and volatile organic

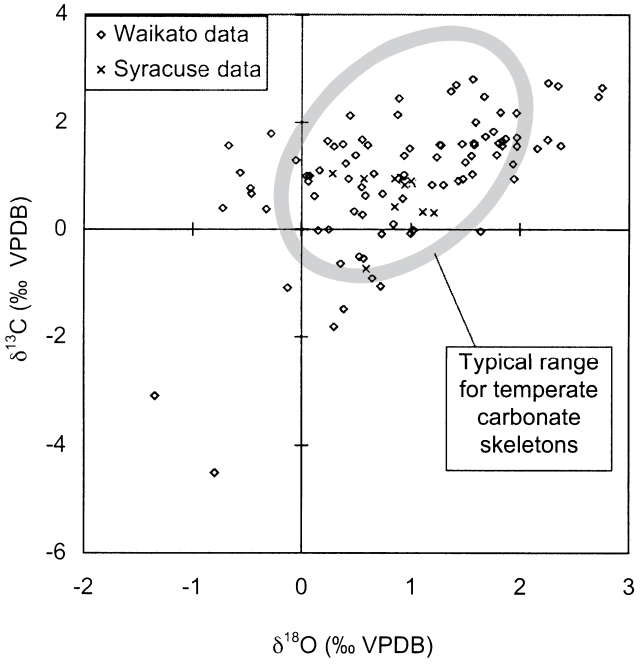

Fig. 2 Oxygen and carbon stable isotopes for 103 specimens of 30 species of extant bryozoans from New Zealand with the typical range for temperate carbonate skeletons circled (from Rao & Nelson 1992).

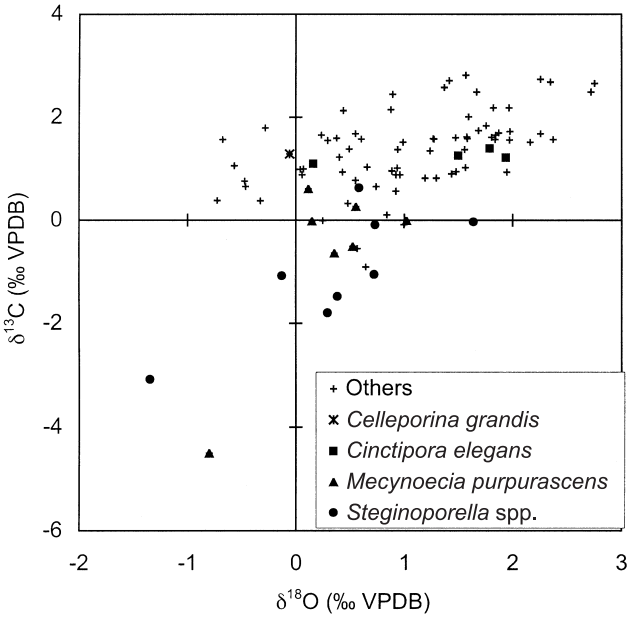

Fig. 3 Oxygen and carbon stable isotopes for species in which one or more specimens lie well outside the typical range for temperate marine carbonate.

contaminants. Stable isotope values were obtained using a Finnigan Kiel-III automated carbonate preparation system directly coupled to the inlet of a Finnigan MAT 252 gas ratio mass spectrometer in the stable isotope laboratory at Syracuse University. Carbonate was reacted at 70°C with two drops of anhydrous phosphoric acid for 90 s. Isotopic ratios were corrected for acid fractionation and ^{17}O contribution, and reported in per mil notation relative to the VPDB standard (i.e., $\delta^{18}O$ and $\delta^{13}C$). Precision and calibration of data were monitored through daily analysis of NBS-18 and NBS-19 carbonate standards, which bracketed the $\delta^{18}O$ values of the samples. Precision for these samples is better than ±0.1‰ for both carbon and oxygen isotope values.

RESULTS

Stable isotope results are given in Table 1. The 103 bryozoan samples have $\delta^{18}O$ values ranging from –1.4 to 2.8‰, with a mean of 0.9‰ and $\delta^{13}C$ values from –4.5 to 2.8‰, with a mean of 1.0‰.

The 30 bryozoan species selected came from 25 genera, 2 orders, and 2 classes. The 30 species comprised 12 different growth forms (sensu Nelson et al. 1988b; Smith 1992; Hageman 1998): 3 encrusting forms, 5 erect rigid forms, 3 erect flexible forms, and 1 free-living form (Table 1). Carbonate mineralogy among the species studied also covered a wide range, from mainly aragonite to entirely calcite, including low-Mg and intermediate-Mg calcite (Smith et al. 1998), as well as two species that precipitate both forms of calcite (Table 1). There were seven combinations of carbonate minerals among the New Zealand specimens.

Replicate stable isotope values from a single branch of *Cinctipora elegans* from the Otago shelf (QQ in Table 1) cover a narrower range than the other New Zealand shelf specimens. $\delta^{18}O$ values varied from 0.3 to 1.2‰, with a mean of 0.8‰, while $\delta^{13}C$ ranged from –0.7 to 1.0‰, with a mean of 0.6‰ (Table 1, Fig. 2).

DISCUSSION

Isotopic equilibrium in bryozoans

Many marine invertebrates secrete a skeleton in which the carbonate is close to isotopic equilibrium with the CO_2 of ambient sea water (Corfield 1995). Likewise, most bryozoans have been shown to precipitate carbonate near isotopic equilibrium with sea water (Forester et al. 1973; Rao & Nelson 1992; Bone & James 1996; Crowley & Taylor 2000). But bryozoans such as *Celleporina grandis* with internal symbiotic hydroids may not (Crowley & Taylor 2000), possibly due to the effects of respiration. Indeed, our single specimen of *C. grandis* shows an unusually low oxygen isotope value (Fig. 3), consistent with vital fractionation.

The relatively wide spread of the bryozoan stable isotope data (Fig. 2) reflects the wide range of shelf environments sampled, from warm to cold temperate (i.e., 34–54°S latitude) and from coastal to deep shelf waters (i.e., 8–292 m). Most of the data fall well within the normal field for cool-water carbonates (Fig. 2), but there are a few outliers exhibiting unusually low stable isotope values (Fig. 3).

The lowest carbon isotope value (–4.5‰) coincides with a low oxygen value (–0.8‰) in a specimen of *Mecynoecia purpurascens* from outer Hauraki Gulf. The other six specimens of *M. purpurascens* in the dataset, two of which come from adjacent samples in Hauraki Gulf, show normal values (Fig. 3). *Cinctipora elegans*, too, has only one sample with an unusually low oxygen value. In these cases it may be

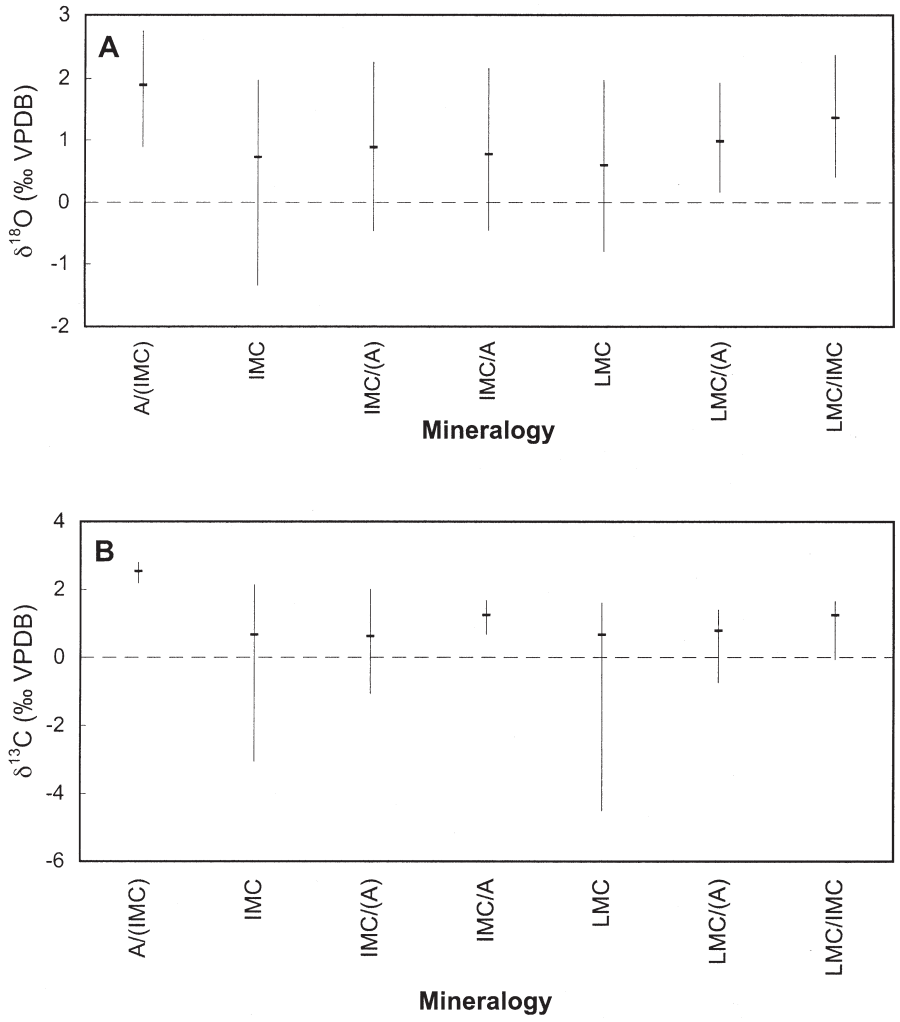

Fig. 4 Range and mean of oxygen (**A**) and carbon (**B**) stable isotopes in bryozoan carbonate of different mineralogies (A = aragonite, LMC = low Mg calcite with <5 wt% $MgCO_3$, IMC = intermediate Mg calcite with 5–10 wt% $MgCO_3$). Where two minerals are listed, the first is dominant and the second subdominant. Where a mineral is in parentheses, it is found in trace amounts in only a few specimens.

that single relict specimens showing some degree of diagenetic alteration, perhaps in meteoric water, have been inadvertently included. Sample contamination by epibiotic organisms could result in such a distribution, although care was taken to avoid such contamination in sample preparation.

The samples of genus *Steginoporella*, however, show a different range of isotope values. One specimen of *Steginoporella neozelanica* yields the lowest oxygen value in the dataset (–1.4‰), along with a low carbon value (–3.1‰). In this case, other specimens of *Steginoporella* (including the species *S. perplexa* and *S. magnifica*) also show low carbon values. This pattern suggests that at least some species within the genus probably do not precipitate carbonate in isotopic equilibrium with sea water, exerting some kinetic effect.

Temperate regime

In general, tropical marine carbonates have $\delta^{18}O$ values ranging from c. –4 to 1‰, and higher $\delta^{13}C$ values (–2 to 5‰) (see, e.g., Nelson & Smith 1996). Low oxygen values reflect high sea-water temperatures, and high carbon values may be due, at least in part, to algal metabolic activity (Nelson & Smith 1996). The few modern temperate carbonates studied previously, principally from off southern Australia and Tasmania, have shown a different relationship (Rao & Green 1983; Rao & Nelson 1992). There, $\delta^{13}C$ values are intermediate, with a narrower range (–0.2 to 2‰), and $\delta^{18}O$ are higher (–2 to 2‰), reflecting cool temperate conditions. The New Zealand bryozoans reported here fall in the temperate carbonate field, but with a slightly wider range of $\delta^{13}C$ values (–2 to 3‰) and higher $\delta^{18}O$ values (0 to 3‰) (Fig. 2).

New Zealand bryozoans cover a wider isotope range than New Zealand carbonate sediments, reflecting the averaging effect of bulk sediment sampling. The positive diagenetic co-variation identified by Rao & Nelson (1992) in Tasmanian carbonates is less obvious in the New Zealand specimens ($\delta^{13}C = 0.8\ \delta^{18}O + 0.2$; $R^2 = 0.32$), but may still appear within some species. Despite their regional differences, both sets of temperate data clearly occupy a different range of values from their tropical counterparts.

Mineralogy and stable isotope values

In aragonite, vaterite, and high-Mg calcite, $\delta^{18}O$ and $\delta^{13}C$ are enriched relative to low-Mg calcite (Tarutani et al. 1969). New Zealand bryozoans show isotope enrichment in aragonite, but less in intermediate-Mg calcites (Fig. 4). A similar observation

was made in Tasmanian bryozoans (Rao & Green 1983), and in some bryozoans from the Lacepede Shelf, South Australia (Bone & James 1997).

While most bryozoan species from this study are low or intermediate Mg calcite, many (47%) are bimineralic. For example, not one species listed here is entirely aragonitic—in each one at least some specimens contain at least some calcite, usually intermediate-Mg calcite (5–10 wt% $MgCO_3$) rather than low-Mg calcite (0–4 wt% $MgCO_3$). Some calcitic species contain the occasional specimen with some aragonite (20%), and there are also species which combine dominant low-Mg calcite with some intermediate-Mg calcite (20%). There are no known species of bryozoan which consistently precipitate high-Mg calcite, with >10 wt% $MgCO_3$ (Smith et al. 1998). Seven different mineralogical combinations are found among the 30 species listed here (Appendix 1).

The relationship of mineralogy to stable isotopes is well documented, as high-Mg calcite and aragonite both concentrate heavier oxygen isotopes (c. 0.6‰ higher) and carbon isotopes (c. 1.5‰ higher) than calcite precipitated under the same conditions (see, e.g., Bone & James 1997; Rahimpour-Bonab et al. 1997b; Crowley & Taylor 2000). Such mineralogical effects can be removed by calculating the calcite-equivalent isotope values (e.g., Tarutani et al. 1969; Romanek et al. 1992). In the case of our bryozoans, however, mixed mineralogies and variable proportions of different minerals among specimens make such calculations problematic. We have elected not to transform our data because of this complexity. Regardless, most bryozoans are monomineralic or contain only trace amounts of a secondary mineral, and they are the ones which should be used for paleoenvironmental reconstruction.

As expected, aragonite-dominated specimens (comprising two species) show the highest mean oxygen isotope values, with low-Mg calcite (seven species) giving the lowest mean (Fig. 4A). Aragonite-dominated specimens (n = 11, mean = 1.9‰ VPDB) have significantly higher $\delta^{18}O$ compared to the other mineralogies (n = 92, mean = 0.8‰) (t-test, $P < 0.001$). Low-Mg calcite specimens have significantly lower $\delta^{18}O$ (n = 24, mean = 0.6‰ VPDB) compared to the other mineralogies (n = 79, mean = 1.0‰ VPDB) (t-test, $P < 0.001$). There is no significant difference among the other mainly calcite mineralogies.

The aragonite-dominated specimens also show high carbon isotope values, and in a narrow range (Fig. 4B). Aragonite-dominated specimens have significantly higher $\delta^{13}C$ (n = 11, mean = 2.5‰ VPDB) compared to the other mineralogies (n = 92, mean = 0.8‰ VPDB) (t-test, $P < 0.001$). The four species (eight specimens) consisting of intermediate-Mg calcite with subdominant aragonite also cover a more narrow range of carbon isotopes than all the other calcite combinations (Fig. 4B). It has been suggested elsewhere that low-Mg calcite-precipitating bryozoans exert vital fractionation effects more often than do aragonitic or intermediate-Mg calcitic bryozoans (Bone & James 1997), perhaps due to variations in growth rate, which could explain the much greater variability within the low-Mg calcite bryozoans.

The mineralogical complexity inherent in bryozoan skeletons must be acknowledged in all geochemical work with this phylum. In particular, paleoenvironmental reconstruction using geochemical proxies such as $\delta^{18}O$ can only be reliable in species whose mineralogy is well constrained.

Taxonomic position

The 30 species studied here fall into two different orders in two different classes. The Order Cyclostomata in the Class Stenolaemata is an ancient marine clade, persisting since the Ordovician Period and particularly dominant during the Mesozoic Era. Of the six sub-groups in the Cyclostomata (after Boardman 1998), four are represented in our dataset (Table 1): the horneroids (6 specimens, 1 genus with undescribed species), tubuliporines, (10 specimens, 3 species), fasciculates (5 specimens, 1 species), and Cinctiporids (14 specimens, 1 species).

Cheilostomate bryozoans (Class Gymnolaemata, Order Cheilostomata) became dominant in the Cretaceous Period. They are thus younger evolutionarily but morphologically more complex and taxonomically more diverse than cyclostomes. Cheilostomates are divided into the super-families Anasca (28 specimens, 9 species in this study) and Ascophora (30 specimens, 13 species).

Because of the variable sample numbers among the sub-groups, comparisons can only be suggestive. There is, however, no apparent phylogenetic effect on either oxygen or carbon isotopes in bryozoans (Fig. 5). There are no significant differences between cheilostomes and cyclostomes in either their $\delta^{18}O$ or $\delta^{13}C$ values (t tests, $P > 0.05$). Not surprisingly, the variability in groups where we have only one species represented is much less than those covering a wider taxonomic range.

Growth form

Bryozoans are exceptionally variable in terms of their colonial growth forms (e.g., Nelson et al. 1988b; Hageman 1998). Our group of 30 species consists of 12 different growth forms. Figure 6 shows there are some differences in isotopic composition among these colonial growth forms.

The New Zealand dataset contains three encrusting forms: thick multilaminar encrusters (1 species), nodule-formers (1 species), and thin unilaminar encrusters (8 species) (Appendix 1). All three groups generally show a wide range of oxygen isotope values and a narrow range of carbon isotope values (Fig. 6).

Erect flexible branching (2 species), lightly calcified (3 species), and rooted (1 species) forms show a similar degree of variability. The extremely low isotopic values for the erect flexible rooted category results from the possible disequilibrium fractionation by *Steginoporella neozelanica*, the species that makes up this category.

Erect rigid forms vary from the delicate branching (4 species), radiate (1 species), fenestrate (2 species), foliose (1 species), and robust branching (6 species) forms. The extremely low variability among some of these categories is partially the result of single-species categories, but may also indicate environmental preferences among some growth forms (e.g., Smith 1995). The free-living vagrant (1 species) is the most heavily aragonitic of the species in the study. Its high isotope values are thus explained by carbonate mineralogy.

A growth form classification of bryozoans was suggested by Nelson et al. (1988b) as a way to simplify identification. Mineralogical groupings among growth forms have been elucidated by Bone & James (1993), and ecological preferences have also been suggested for particular growth forms (e.g., Smith 1995). There is also probably some phylogenetic overprint for growth form. There is no way to decouple growth form from these confounding factors, and

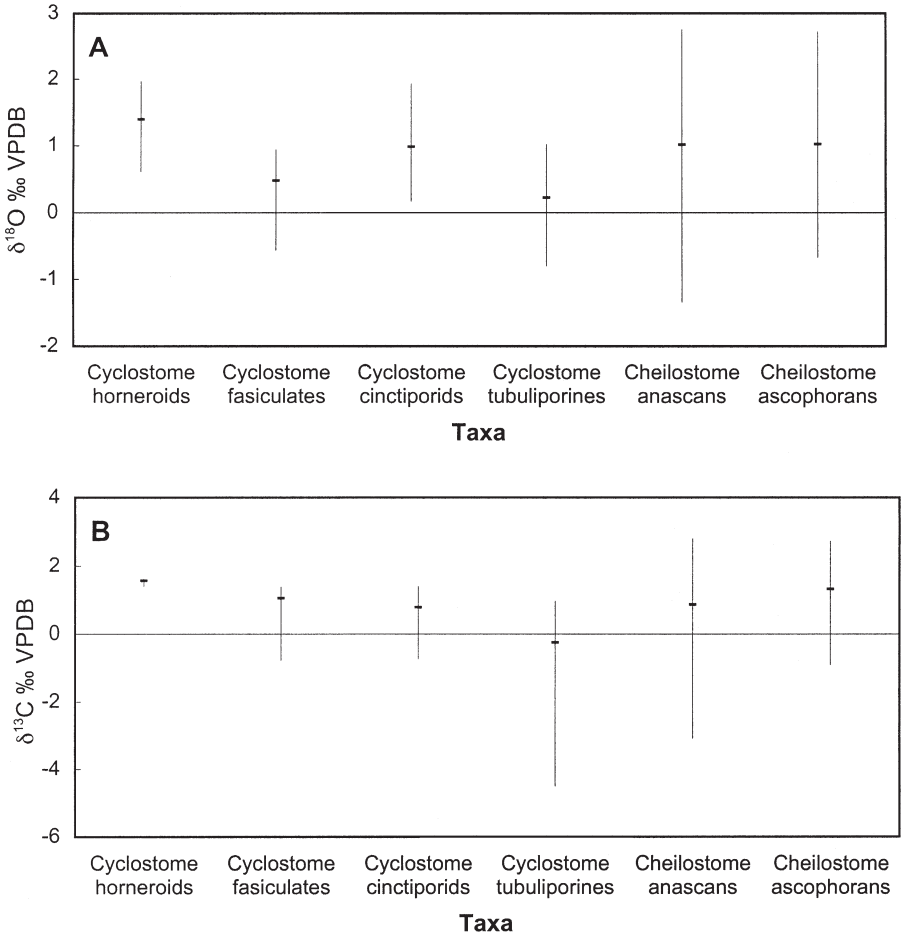

Fig. 5 Range and mean of oxygen (**A**) and carbon (**B**) stable isotopes in bryozoan carbonate of different phylogenetic positions.

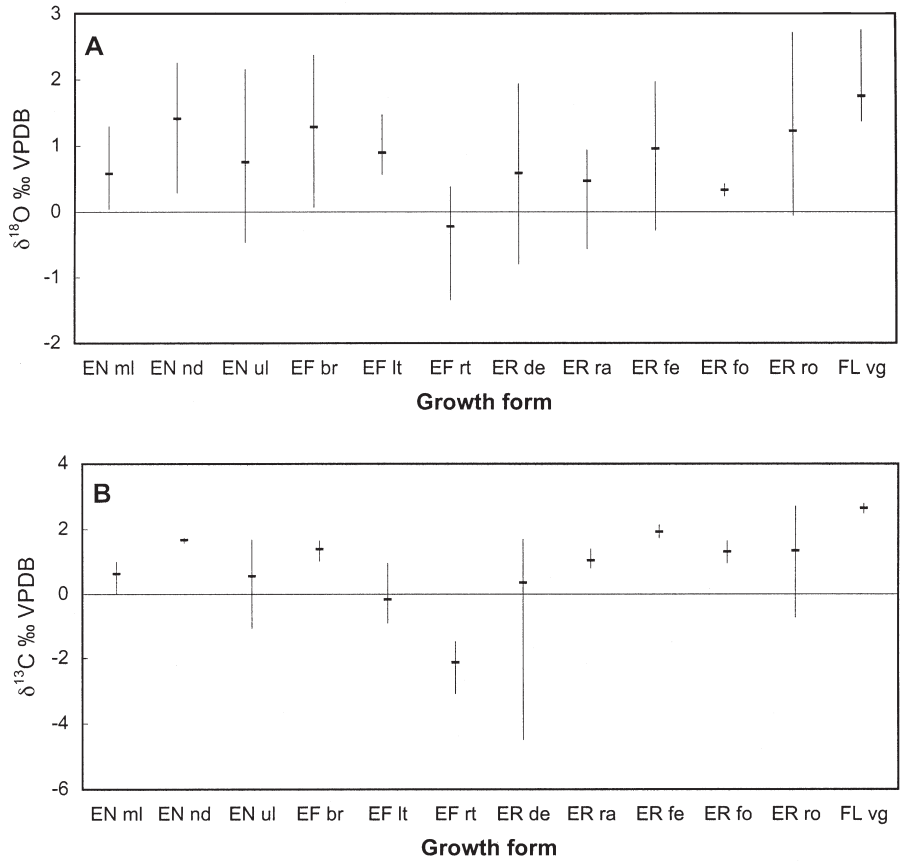

Fig. 6 Range and mean of oxygen (**A**) and carbon (**B**) stable isotopes in bryozoan carbonate of different colony growth forms (EN = encrusting: ml, multilaminar; ul, unilaminar; nd, nodular. ER = erect rigid: de, delicate branching; fe, fenestrate; fo, foliose; ra, radiate; ro, robust branching. EF = erect flexible: br, branching; lt, lightly calcified; rt, rooted. FL = free living: vg, vagrant).

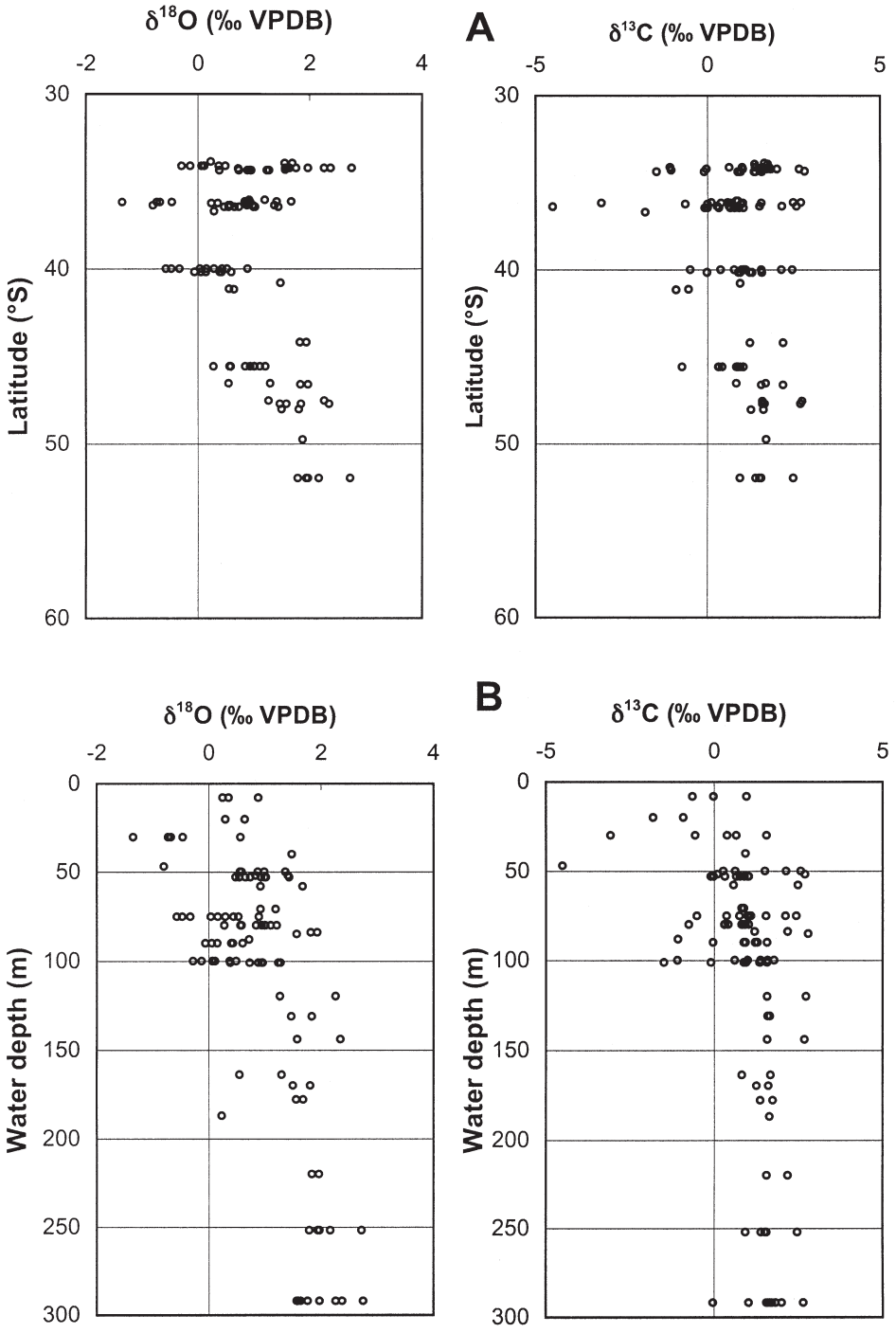

Fig. 7 Oxygen and carbon stable isotopes in bryozoan skeletons across latitudes (**A**) and water depths (**B**).

indeed there seems to be no mechanism by which bryozoans of a particular morphology would necessarily have a particular isotopic signature.

Environment

The most important geological application for oxygen isotopes has been in calculating paleotemperature. A simple binomial relationship between $\delta^{18}O$ and temperature of formation (e.g, Kim & O'Neil 1997) appears to give consistent results in modern carbonates. Applied only to the calcitic New Zealand bryozoans considered here, the formula gives temperatures of 7–15°C (Smith & Nelson 1993; Smith & Key 2004), similar to New Zealand shelf bottom temperatures which typically range from 9 to 15°C (Rao & Nelson 1992). There is significant scatter in Fig. 7A, but nevertheless cold high-latitude samples have both high $\delta^{18}O$ values, as expected, and a narrower range of temperatures than the samples from warmer temperate regions.

In general, one expects water depth to have an effect on isotope composition since temperature of bottom water decreases as depth increases (Rao & Nelson 1992; Amini & Rao 1998). Superimposed on this is a water mass signature—deep waters often have lower DIC $\delta^{13}C$ values (e.g., Kroopnick 1974, Rao & Green 1983). Within each of the shelf, slope,

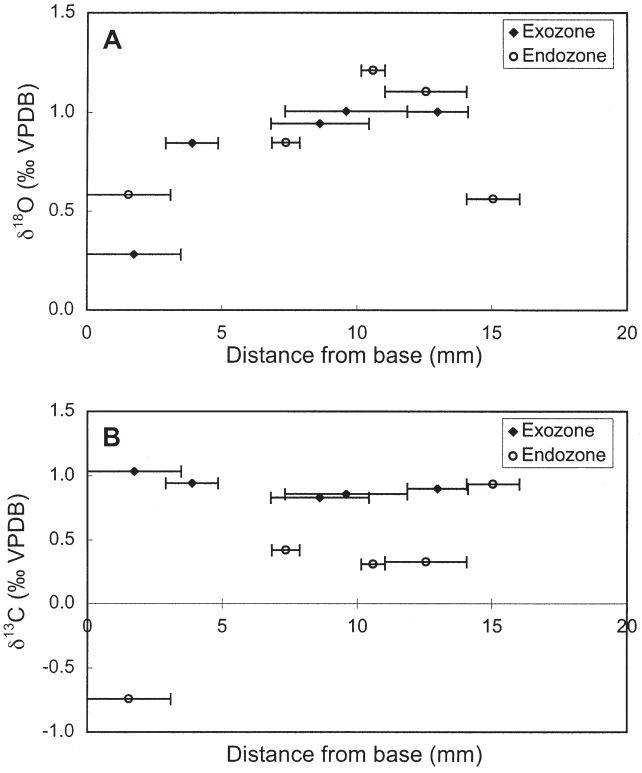

Fig. 8 Variation in oxygen (**A**) and carbon (**B**) stable isotopes along a single branch of *Cinctipora elegans* from the Otago shelf.

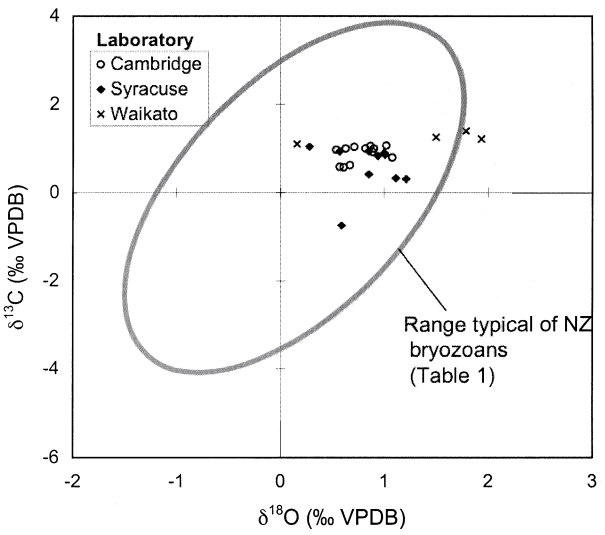

Fig. 9 Comparison of oxygen and carbon stable isotopes derived from similar skeletal material of *Cinctipora elegans* from the Otago shelf, measured at three different laboratories.

and deep-sea settings, in general, $\delta^{18}O$ and $\delta^{13}C$ values in carbonate increase with depth (and decreasing temperature), but there are considerable differences among the settings, particularly as DIC $\delta^{13}C$ values decrease with water depth.

The New Zealand bryozoans used in this study were collected no deeper than 300 m. Within the shelf setting, the trend in New Zealand bryozoans is for $\delta^{18}O$ and $\delta^{13}C$ values to increase with depth (Fig. 7B), consistent with observations from elsewhere (e.g., Rao & Nelson 1992). There is a significant ($P < 0.001$) positive linear correlation between water depth and $\delta^{18}O$ ($R^2 = 0.414$), and a significant ($P < 0.001$) but weak ($R^2 = 0.141$) positive linear correlation between water depth and $\delta^{13}C$.

Within-colony variation

Oxygen isotope values along a single branch of *Cinctipora elegans* show little variation along the branch. In contrast, carbonate at the colony surface (exozone) shows higher carbon isotope values than the corresponding endozone (carbonate material closer to the centre of the branch), although it is not statistically significant (*t*-test, $P > 0.05$). Exozone carbon isotope values are fairly consistent along the branch, whereas the endozone material became significantly ($R^2 = 0.83$, $P = 0.03$) higher with distance from the base in the colony sampled (Fig. 8).

We have no explanation for this hitherto unknown observation. There may be some mechanism whereby the source of carbon is different for endozone and exozone carbonate. Perhaps growth rate, and hence precipitation rate, is different. Or maybe metabolic factors influence the endozone but not the more distal exozone. This should be a fruitful area for further investigation.

Cross-correlation of results

Interpretation of stable isotope data can be problematic, and additionally confounded by inconsistencies of sample preparation, collection times, and measurements. We have here an opportunity to compare similar datasets analysed in three different laboratories with different protocols. Stable isotopes in the low-Mg calcite cyclostomate bryozoan *Cinctipora elegans* from the Otago shelf were analysed in two of the laboratories (Cambridge and Syracuse), and another four samples of the same species from the open shelf around New Zealand's South Island were analysed at Waikato.

The *C. elegans* data cover a small range of carbon isotope values compared to the total range in both this study and that of Crowley & Taylor (2000). Oxygen isotope values are more variable, especially in the Waikato data, no doubt due to the wider geographic spread and corresponding wider range in water temperatures. There are no significant differences between the Waikato and Syracuse samples in either their $\delta^{18}O$ or $\delta^{13}C$ values (*t*-tests, $P > 0.05$). The agreement between the Waikato and Syracuse data and Crowley & Taylor's (2000) Otago study is encouraging and indicates the reliable nature of the data (Fig. 9).

CONCLUSIONS

Many bryozoans appear to precipitate carbonate (both calcite and aragonite) in isotopic equilibrium with ambient sea water. Exceptions may, however, occur, particularly in the case of *Celleporina grandis*, which harbours a symbiotic hydroid, and *Steginoporella neozelanica*. Any further isotopic study must ascertain the degree of vital fractionation before assuming bryozoan stable isotopes in a particular species to be reliable (paleo)environmental indicators.

Stable isotope values of New Zealand bryozoans fall, as expected, in a range typical of temperate carbonates, with $\delta^{18}O$ from –1.4 to 2.8‰ VPDB, and $\delta^{13}C$ from –4.5 to 2.8‰ VPDB. There is a distinctive temperate isotope signature with higher $\delta^{18}O$ values relative to tropical carbonates,

which reflects the considerable differences between the two environments of deposition.

Both oxygen and carbon isotope values are naturally higher in aragonite than in calcite. In aragonite, $\delta^{18}O$ is elevated by 1–2‰ PDB, and $\delta^{13}C$ by c. 1‰ VPDB. The complex and variable mineralogies of bryozoans make simple isotopic corrections difficult.

Whereas phylogenetic position and colony growth form are not obviously linked to stable isotope signatures, environment of deposition can be. There is a strong trend in bryozoans from the New Zealand shelf to have higher isotope values with higher latitudes and deeper waters, both related to temperature.

While there is variability among bryozoan specimens and species, it is less within a single colony. Nevertheless, an intriguing trend in carbon isotope values along a branch of *Cinctipora elegans* suggests that, at least in this species, endozone and exozone carbonate may be recording seawater carbon isotopes differently, perhaps due to different calcification histories. Our results from three different laboratories on a single population from a single location are encouragingly consistent.

Bryozoan isotope studies have been used to infer age of colonies (Pätzold et al. 1987; Brey et al. 1999; Bader 2000), to describe modern climate variation (Smith & Key 2004), to determine paleotemperatures (Rao & Jayawardane 1994), and to describe past environments in deep-sea sediments (Machiyama et al. 2003). We suspect that geochemical application of bryozoans for helping characterise the environmental conditions accompanying modern and ancient sediment facies has been underutilised in favour of other taxa such as brachiopods. Given the importance of bryozoans as biotic contributors throughout much of the Phanerozoic record, their chemical utility is likely to increase in future studies.

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Appendix 1 Stable isotope data from Table 1 organised according to sub-categories. Abbreviations as for Table 1.

	Number of		$\delta^{18}O$			$\delta^{13}C$		
	specimens	species	Min.	Max.	Mean	Min.	Max.	Mean
Mineralogy								
A/(IMC)	11	2	0.89	2.75	1.89	2.18	2.81	2.54
IMC	25	9	–1.35	1.97	0.73	–3.08	2.15	0.66
IMC/(A)	13	5	–0.47	2.26	0.88	–1.08	2.01	0.61
IMC/A	8	4	–0.46	2.16	0.77	0.66	1.68	1.24
LMC	24	7	–0.80	1.97	0.60	–4.50	1.62	0.65
LMC/(A)	14	1	0.16	1.93	0.98	–0.74	1.40	0.77
LMC/IMC	8	2	0.40	2.37	1.37	–0.08	1.66	1.24
Taxon								
CY ho	6	1	0.60	1.97	1.39	1.38	1.62	1.56
CY fa	5	1	–0.57	0.94	0.47	–0.78	1.39	1.03
CY ci	14	1	0.16	1.93	0.98	–0.74	1.40	0.77
CY tu	10	3	–0.80	1.02	0.21	–4.50	0.96	–0.25
CH an	28	9	–1.35	2.75	1.01	–3.08	2.81	0.85
CH as	40	13	–0.67	2.72	1.02	–0.91	2.73	1.30
Growth form								
EN ml	4	1	0.04	1.30	0.58	0.00	1.00	0.62
EN nd	3	1	0.29	2.26	1.41	1.55	1.74	1.66
EN ul	16	8	–0.47	2.16	0.75	–1.08	1.68	0.55
EF br	9	2	0.07	2.37	1.28	1.00	1.66	1.37
EF lt	3	3	0.57	1.48	0.90	–0.91	0.95	–0.17
EF rt	3	1	–1.35	0.39	–0.22	–3.08	–1.48	–2.12
ER de	18	4	–0.80	1.94	0.58	–4.50	1.69	0.35
ER ra	5	1	–0.57	0.94	0.47	0.78	1.39	1.03
ER fe	5	2	–0.28	1.97	0.95	1.72	2.15	1.93
ER fo	2	1	0.24	0.43	0.33	0.94	1.65	1.30
ER ro	30	6	–0.06	2.72	1.22	–0.74	2.73	1.33
FL vg	5	1	1.37	2.75	1.75	2.49	2.81	2.65