

# Controls, variation, and a record of climate change in detailed stable isotope record in a single bryozoan skeleton<sup>☆</sup>

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## Abstract

The long-lived (about 20 yr) bryozoan *Adeonellopsis* sp. from Doubtful Sound, New Zealand, precipitates aragonite in isotopic equilibrium with seawater, exerting no metabolic or kinetic effects. Oxygen isotope ratios ( $\delta^{18}\text{O}$ ) in 61 subsamples (along three branches of a single unaltered colony) range from  $-0.09$  to  $+0.68\text{‰PDB}$  (mean =  $+0.36\text{‰PDB}$ ). Carbon isotope ratios ( $\delta^{13}\text{C}$ ) range from  $+0.84$  to  $+2.18\text{‰PDB}$  (mean =  $+1.69\text{‰PDB}$ ). Typical of cool-water carbonates,  $\delta^{18}\text{O}$ -derived water temperatures range from  $14.2$  to  $17.5$  °C. *Adeonellopsis* has a minimum temperature growth threshold of  $14$  °C, recording only a partial record of environmental variation. By correlating seawater temperatures derived from  $\delta^{18}\text{O}$  with the Southern Oscillation Index, however, we were able to detect major events such as the 1983 El Niño. Interannual climatic variation can be recorded in skeletal carbonate isotopes. The range of within-colony isotopic variability found in this study ( $0.77\text{‰}$  in  $\delta^{18}\text{O}$  and  $1.34$  in  $\delta^{13}\text{C}$ ) means that among-colony variation must be treated cautiously. Temperate bryozoan isotopes have been tested in less than 2% of described extant species — this highly variable phylum is not yet fully understood.

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**Keywords:** Bryozoa; Stable isotopes;  $\delta^{18}\text{O}$ ;  $\delta^{13}\text{C}$ ; Climate; ENSO; New Zealand

## Introduction

Carbonate skeletons of marine invertebrates often contain a geochemical record of seawater conditions (e.g., temperature) throughout their lives. Stable isotope paleothermometry has been used in both modern and ancient tropical settings (see, e.g., Corfield, 1995), but to a large extent temperate shelf environments have been ignored (one rare exception is Goodwin et al., 2001).

Carbonate sediments on Southern Hemisphere temperate shelves are dominated by skeletal remains of bryozoans and molluscs (James, 1997; Nelson et al., 1988). Bryozoans are more significant contributors to cool-water carbonates than their tropical counterparts, so much so that several of the cool-water, shallow marine carbonate facies (e.g., bryomol, bryoderms) are named after this abundant component (Nel-

son et al., 1988; Rao, 1996; James, 1997). In some areas of the New Zealand shelf, the ‘bryomol’ province may be up to 80 wt% bryozoans (Nelson et al., 1988). Large erect shelf species may weigh up to 200 g and live some 20 years (Smith et al., 2001).

It was Forester et al. (1973) who first suggested that bryozoans precipitate  $\text{CaCO}_3$  skeletons in equilibrium with surrounding seawater. They studied mainly cheilostome bryozoans, making no corrections for mineralogy, nor did they correlate the isotopic composition of seawater with skeletal carbonate. Pätzold et al. (1987) used fine-scale variations in oxygen isotopes in the bryozoan *Pentapora foliacea* to elucidate seasons and therefore growth rate, as did others later (e.g., Brey et al., 1999, Bader, 2000). Rao and Nelson (1992) concluded that modern temperate bryozoan skeletons were reliable indicators of seawater chemistry, being little affected by kinetic and metabolic considerations. Surveys of Australian living and Recent bryozoans of various mineralogies agreed (Rahimpour-Bonab et al., 1997a; Bone and James, 1997). By the end of the last century it appeared that cool-water bryozoans (as represented by 180 specimens from 49 genera and 65

<sup>☆</sup> Supplementary data for this article (Appendix) are available on Science Direct (<http://www.sciencedirect.com>).

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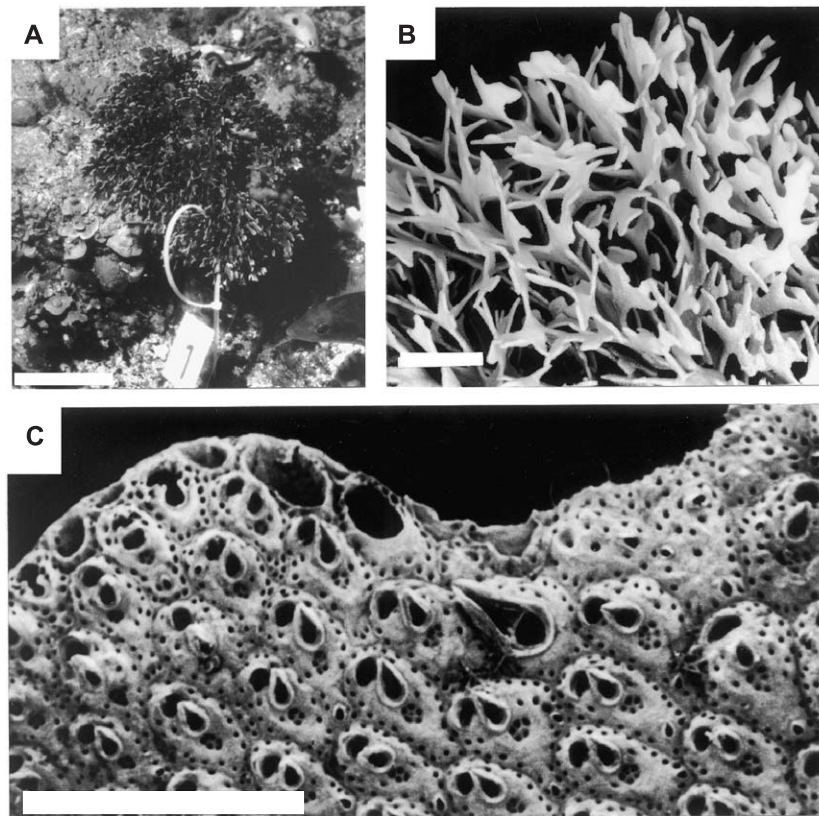


Fig. 1. *Aeonellopsis* sp. from Doubtful Sound, New Zealand: (A) living colony in situ on the wall of Bauza Island in 12 m water depth (scale = 5 cm); (B) bleached and dried colony (scale = 1 cm); (C) scanning electron micrograph of growing tip showing zooid characteristics (scale = 1 mm).

species) lay in the typical range for temperate carbonates and that seawater temperatures could be reliably predicted using  $\delta^{18}\text{O}$ , though interpretation of  $\delta^{13}\text{C}$  was sometimes more problematic due to the competing kinetic and metabolic effects on fractionation (*sensu* Crowley and Taylor, 2000). These conclusions were rigorously tested in a detailed study of New Zealand's Otago shelf bryozoans, which included measurements of  $\delta^{18}\text{O}_{\text{sw}}$  and  $\delta^{13}\text{C}_{\text{DIC}}$  and corrected values for temperature and salinity (Crowley and Taylor, 2000). At least 2 of the species examined did not precipitate oxygen in isotopic equilibrium, and nine of the ten species examined precipitated carbon in isotopic disequilibrium (Crowley and Taylor, 2000), calling into question the assumptions of previous studies.

Almost all isotopic measurements reported in the literature are either whole-colony or one-sample-per-colony. There is very little within-colony replication, and few studies examine systematic variation within colonies, allowing reliable understanding of variation among colonies. Some studies (e.g., Rao and Nelson, 1992) test bulk samples identified only as “bryozoans” without giving particulars of species or mineralogy. Others have grouped bryozoans by colonial growth form (Bone and James, 1993), including different mineralogies in a single group. The degree of geochemical and mineralogical complexity within this phy-

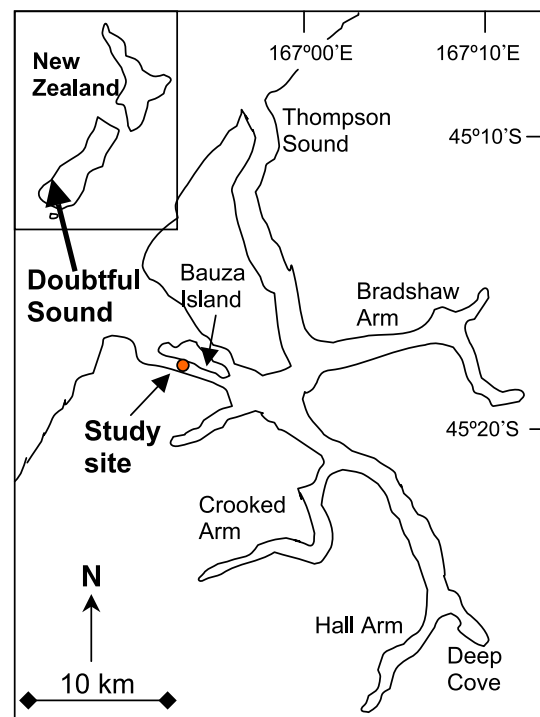


Fig. 2. Location map of study site near Bauza Island, Doubtful Sound, southwest South Island, New Zealand.

lum (Smith et al., 1998) and probable interspecific variability requires at least genus- and probably species-level identification.

In this paper we present stable isotope profiles along three branches of a single colony of *Adeonellopsis* sp., a long-lived, cool-water shelf bryozoan. We describe within-colony variation and potential controls on stable isotopes within a single colony.

The erect, robust-branching bryozoan *Adeonellopsis* is a large, conspicuous subtidal genus found throughout New Zealand (Nelson et al., 1988). Initially, all New Zealand members of the Adeonidae (Gymnolaemata: Cheilostomata: Ascophorina) were classified as *A. yarraensis*, but it is now clear that at least five morphologically similar *Adeonellopsis* species occur in New Zealand and Australian waters (Lidgard and Buckley, 1994). The erect rigid robust-branching species of *Adeonellopsis* used in this study (Fig. 1) is probably morphospecies B of Lidgard and Buckley (1994).

*Adeonellopsis* skeletons are formed mainly of aragonite, with 0 to 11 (mean 3.1) wt% calcite (Smith et al., 1998). The small amount of calcite found in this species is intermediate Mg calcite (IMC of Bone and James, 1997) with on average about 6 wt% MgCO<sub>3</sub> (Smith et al., 1998). Average annual growth rate along a branch is 7 mm/yr, as determined by mark-and-recapture of *Adeonellopsis* from the same study site (Smith et al., 2001). Large colonies, 20–30 cm high, may be some 20 years old (Smith et al., 2001).

In Doubtful Sound, a temperate fiord on the west coast of South Island, New Zealand (Fig. 2), conspicuous purplish-black colonies of *Adeonellopsis* grow in exposed areas on the near-vertical rock walls close to the entrance of the fiord. In some areas, such as around Bauza Island, colonies may be found in water depths of 10 to 25 m at densities up to 1 colony/m<sup>2</sup>. Estimated carbonate production by these bryozoans is 24 g CaCO<sub>3</sub>/m<sup>2</sup>/yr (Smith et al., 2001). Longevity, size, and SCUBA accessibility mean that *Adeonellopsis* sp. in Doubtful Sound is an excellent candidate for elucidation of a record of climate (on the order of tens of years) from its skeleton.

## Methods

A large colony of *Adeonellopsis* sp. was collected in 12 m water depth just off Bauza Island (45° 18'S, 166° 55'E) in Doubtful Sound in January 1998. The colony was killed in ethanol, rinsed, and picked clean of sediment and epifauna. Ten long branches, each with a definite growing tip, were separated out. Three branches were randomly chosen for this study, three were used in a morphometric study (Smith et al., 2001), and three more were reserved for elemental analysis yet to be reported, with the final branch archived at University of Otago. The three branches for isotopic profiling were stripped of side-branches, bleached in 5% NaOH, rinsed in de-ionized water, and dried for 24 h at 90 °C. They were then sectioned into 5-mm intervals and powdered.

Branch A was 115 mm long and yielded 23 subsamples, Branch B was 100 mm long and yielded 20 subsamples, and Branch C was 90 mm long and yielded 18 subsamples, for a total of 61 subsamples.

Samples were reacted with 3 drops of H<sub>3</sub>PO<sub>4</sub> at 75 °C in an automated individual carbonate reaction (Kiel) device connected to a Finnegan MAT252 mass spectrometer at the National Institute of Water and Atmosphere, Wellington, New Zealand. Both δ<sup>18</sup>O (internal precision 0.04–0.08‰ external precision 0.07‰) and δ<sup>13</sup>C (internal precision 0.01–0.04‰ external precision 0.04‰) were measured using the NBS-19 calcite standard. Results were corrected for <sup>17</sup>O and are reported in ‰ with respect to the PDB (Pee Dee Belemnite) standard.

Oxygen isotopic ratios from biogenic carbonate can serve as a thermometer, indicating water temperature at the time of carbonate precipitation (Corfield, 1995), as long as δ<sup>18</sup>O seawater is known. Macrellis (2001) measured δ<sup>18</sup>O<sub>seawater</sub> in intertidal bottom water in Doubtful Sound at Corset Cove (45° 17.1'S, 166° 53.9'E, about 2 km from Bauza Island) to be –0.79‰ SMOW. Equilibrium water temperature for each sample was calculated using this figure and Grossman and Ku's (1986) equation for aragonitic carbonate:

$$T = -20.6 - 4.34(\delta^{18}\text{O}_{\text{carbonate(PDB)}} - \delta^{18}\text{O}_{\text{seawater(SMOW)}}).$$

## Results

Oxygen isotope ratios (δ<sup>18</sup>O) in *Adeonellopsis* carbonate were mainly small and positive, ranging from –0.09 to +0.68‰ PDB (mean = +0.36‰) (Table 1). Only two specimens gave low negative values. Carbon isotope ratios (δ<sup>13</sup>C) were also small and positive, ranging from +0.84 to +2.18‰ PDB (mean = +1.69‰) (Table 1). These values occupy the slightly positive area (Fig. 3) typical of cool-water carbonate skeletons (see Nelson and Smith, 1996; Rao, 1996; Bone and James, 1997). Calculated equilibrium water temperatures range from 14.2 to 17.5 °C (mean = 15.6 °C) (Table 1). Individual branch profiles (Fig. 4) show that δ<sup>18</sup>O varies within the same range along each branch, but that δ<sup>13</sup>C generally decreases closer to the branch tips.

Two-sample *t* tests show no significant differences among the branches in carbon isotopes (*P* > 0.05). Oxygen isotopes in branches B and C are not significantly different (*P* > 0.05), but branch A is significantly different from both B and C (*P* = 0.0026 and 0.00019, respectively), at least partly because it is longer and presumably represents a longer period of time.

## Discussion

### Controls on oxygen isotopes

Oxygen isotopic ratios measured in biogenic carbonate represent a theoretical equilibrium with oxygen isotopic

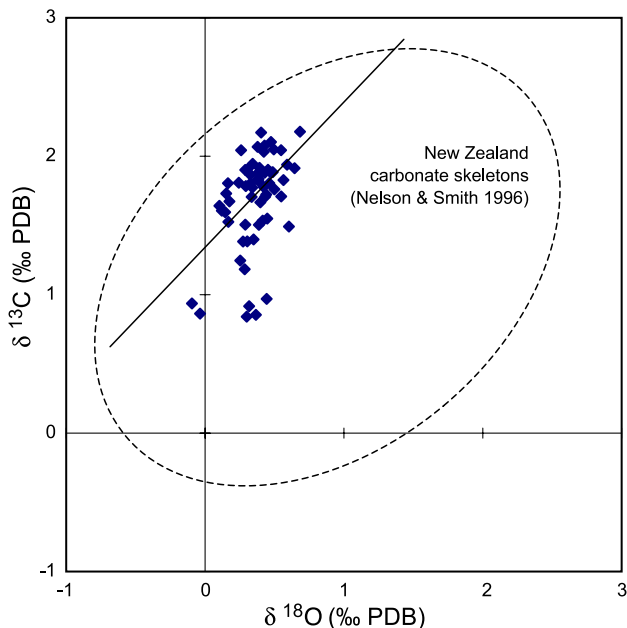


Fig. 3. Oxygen and carbon stable isotope results for 61 samples of *Adeonellopsis* sp. from Doubtful Sound, New Zealand, with comparison to normal range for New Zealand carbonate skeletons (dotted circle) (Nelson and Smith, 1996).

composition of seawater at the time of precipitation. Theoretical isotopic composition may be modified in carbonate skeletons by one or more variables, including (1) vital/metabolic effects, (2) kinetic/mineralogical effects, (3) post-precipitation alteration, and (4) environmental effects (e.g., water temperature). It has been suggested that the extent of

metabolic and kinetic effects may be less in temperate settings than in the tropical realm (Rao, 1996), possibly due to reduced metabolic rates in cooler water or the temperate carbonate-producing assemblage. Oxygen isotopes in temperate carbonate may thus serve as paleoenvironmental indicators. Although many environmental factors could affect shell chemistry and growth, temperature is the dominant factor (Goodwin et al., 2001), and oxygen isotopic ratios from biogenic carbonate are often used in paleothermometry (Corfield, 1995).

At least two bryozoans may exert vital effects on stable isotope composition (Crowley and Taylor, 2000). In contrast, various genera in family Adeonidae from southern Australia, including *Adeona* and *Adeonellopsis*, have been shown to exert no vital effects on isotopic composition (Bone and James, 1996, 1997; Rahimpour-Bonab et al., 1997b; Machiyama et al., 2003). Based on these studies, *Adeonellopsis* in New Zealand most likely exerts little vital effect, at least on oxygen isotopes.

Aragonite is preferentially enriched in the heavy isotope of oxygen relative to calcite precipitated in the same environment (Tarutani et al., 1969) due to kinetic constraints on the lattice structure. There is therefore a mineralogical effect on stable isotopes to be taken into account. *Adeonellopsis* is dominantly aragonite (89 to 100% aragonite (mean = 97%) according to Smith et al., 1998).

Calcite precipitated under the same conditions as aragonite will be lower by 0.6 to 0.8‰ (Tarutani et al., 1969). The addition of up to 11% calcite would thus lower the assumed isotope composition of pure aragonite by no more than about 0.08‰, the same level as the analytical precision of the

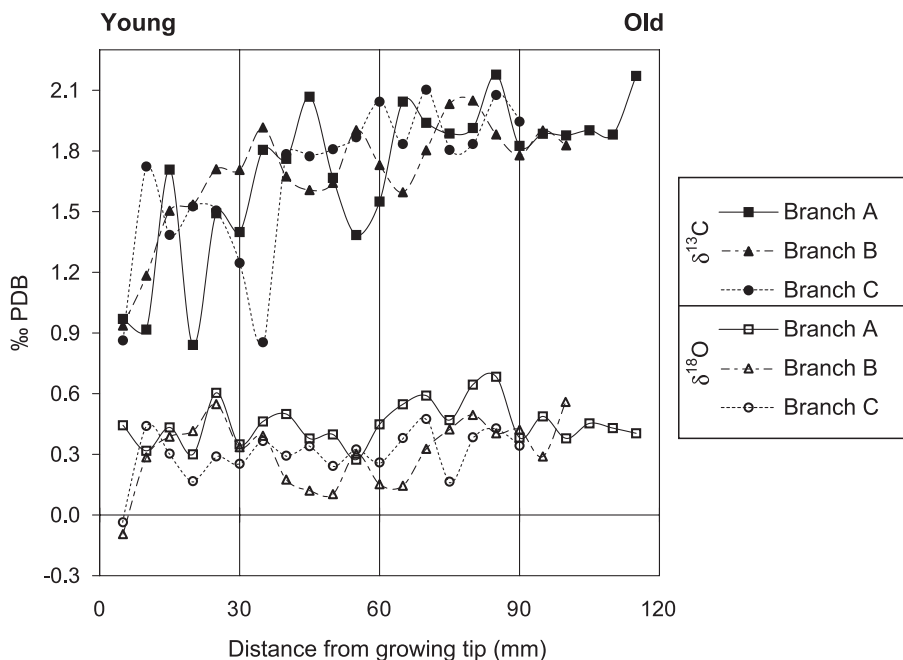


Fig. 4. Oxygen and carbon stable isotope profiles along three branches from one colony of *Adeonellopsis* sp. from Doubtful Sound, New Zealand. Each measurement is obtained from the carbonate of the entire preceding section (e.g., the data presented as 5 mm are the figure for carbonate from the tip to 5 mm).

Table 1

Oxygen and carbon stable isotope data for three branches of *Adeonellopsis* sp. from Doubtful Sound, New Zealand

Branch	Distance from growth tip (mm)	$\delta^{18}\text{O}$ (‰PDB)	$\delta^{13}\text{C}$ (‰PDB)	Balance <sup>a</sup>	T(°C) <sup>b</sup> from $\delta^{18}\text{O}$
A	5	0.44	0.97	0.88	15.25
A	10	0.32	0.92	0.86	15.79
A	15	0.43	1.71	0.87	15.29
A	20	0.30	0.84	0.90	15.87
A	25	0.60	1.49	0.89	14.55
A	30	0.35	1.40	0.89	15.66
A	35	0.46	1.81	0.89	15.17
A	40	0.50	1.76	0.91	15.00
A	45	0.38	2.07	0.89	15.53
A	50	0.40	1.67	0.90	15.44
A	55	0.27	1.38	0.91	15.98
A	60	0.45	1.55	0.92	15.23
A	65	0.55	2.04	0.92	14.80
A	70	0.59	1.94	0.89	14.61
A	75	0.47	1.89	0.90	15.13
A	80	0.64	1.91	0.86	14.37
A	85	0.68	2.18	0.88	14.21
A	90	0.38	1.83	0.92	15.51
A	95	0.49	1.89	0.91	15.06
A	100	0.38	1.88	0.92	15.53
A	105	0.45	1.90	0.90	15.20
A	110	0.43	1.88	0.87	15.31
A	115	0.40	2.17	0.90	15.42
<b>Branch A means (N = 23)</b>		<b>0.45</b>	<b>1.70</b>	<b>0.89</b>	<b>15.21</b>
B	5	-0.09	0.94	0.91	17.58
B	10	0.29	1.18	0.89	15.93
B	15	0.39	1.50	0.90	15.49
B	20	0.42	1.53	0.86	15.37
B	25	0.55	1.71	0.87	14.79
B	30	0.34	1.71	0.89	15.72
B	35	0.39	1.92	0.87	15.47
B	40	0.18	1.67	0.92	16.41
B	45	0.12	1.61	0.88	16.65
B	50	0.10	1.64	0.92	16.72
B	55	0.30	1.90	0.88	15.86
B	60	0.15	1.73	0.92	16.51
B	65	0.14	1.60	0.92	16.54
B	70	0.33	1.80	0.91	15.75
B	75	0.42	2.03	0.86	15.34
B	80	0.49	2.05	0.88	15.02
B	85	0.40	1.88	0.91	15.42
B	90	0.42	1.78	0.89	15.34
B	95	0.29	1.90	0.90	15.92
B	100	0.56	1.83	0.89	14.72
<b>Branch B means (N = 20)</b>		<b>0.31</b>	<b>1.70</b>	<b>0.89</b>	<b>15.83</b>
C	5	-0.04	0.86	0.89	17.33
C	10	0.44	1.72	0.86	15.26
C	15	0.30	1.38	0.91	15.85
C	20	0.17	1.53	0.89	16.44
C	25	0.29	1.51	0.92	15.91
C	30	0.25	1.25	0.88	16.07
C	35	0.37	0.85	0.90	15.58
C	40	0.29	1.78	0.92	15.90
C	45	0.34	1.77	0.90	15.70
C	50	0.24	1.81	0.90	16.12
C	55	0.32	1.87	0.86	15.76
C	60	0.26	2.04	0.92	16.04
C	65	0.38	1.83	0.90	15.52
C	70	0.47	2.10	0.91	15.11

Table 1 (continued)

Branch	Distance from growth tip (mm)	$\delta^{18}\text{O}$ (‰PDB)	$\delta^{13}\text{C}$ (‰PDB)	Balance <sup>a</sup>	T(°C) <sup>b</sup> from $\delta^{18}\text{O}$
C	75	0.17	1.81	0.85	16.46
C	80	0.38	1.83	0.91	15.50
C	85	0.43	2.08	0.90	15.31
C	90	0.34	1.95	0.88	15.68
<b>Branch C means (N = 18)</b>		<b>0.30</b>	<b>1.67</b>	<b>0.89</b>	<b>15.86</b>
Mean		0.36	1.69	0.89	15.60
Minimum		-0.09	0.84	0.85	14.21
Maximum		0.68	2.18	0.92	17.58
Standard Dev		0.15	0.33	0.02	0.63

<sup>a</sup> Balance greater than 0.80 indicates reliable results.<sup>b</sup> Temperature calculated from  $\delta^{18}\text{O}$  using equation of Grossman and Ku (1986).

measurement technique. Thus the inclusion of up to 11% calcite exerts a barely measurable effect on oxygen isotopes in *Adeonellopsis*.

A series of eight mineralogical determinations using X-ray diffraction on a branch from this same colony showed all were less than 6.5 wt% calcite (Table 2). With such small calcite amounts, we can treat the specimens as if they were 100% aragonite (see, e.g., Pätzold et al., 1987).

As the bryozoan colonies were alive (at least at the growing tips) when collected, we can assume no significant diagenetic alteration has occurred. There is no apparent diagenetic offset in the data; recrystallisation and cementation are unlikely in a modern cool-water shallow marine setting (Nelson and Smith, 1996). While the effects of cementation by marine carbonate would be not obvious if carbonate cements precipitated under the same conditions as the skeletal carbonate, bryozoans, like all organisms, present difficulties for ancient isotopic records if porous skeletons are cemented by meteoric carbonate.

Table 2

Carbonate mineralogy of subsamples collected from a single branch of *Adeonellopsis* sp. from Doubtful Sound, New Zealand

Sample	Distance from growth tips (mm)	Wt% calcite <sup>a</sup>	Wt% aragonite	Wt % MgCO <sub>3</sub> in calcite <sup>b</sup>
AD0a	0	5.2	94.8	6
AD0b	0	3.7	96.3	6
AD0c	0	4.6	95.4	6
AD2	2	2.1	97.9	6
AD5	5	2.7	97.3	6
AD15	15	6.3	93.7	6
AD20	20	3.4	96.6	6
AD25	25	2.3	97.7	4
Mean of branch (N = 8)		3.8	96.2	5.75

<sup>a</sup> Calcite/aragonite ratio calculated from XRD peak intensities.<sup>b</sup> Wt% MgCO<sub>3</sub> calculated from position of calcite peak (Smith et al., 1998).

Peake et al. (2001) measured salinity and temperature in 1994 at a site within 1 km of our study site at Bauza Island. At 12 m water depth, salinity was 32 psu in both winter and summer, and temperature at that depth ranged from 10.5 to 17.5 °C. Moored continuous CTD data from four sites nearby (ranging from 1 to 15 km away) in Doubtful Sound from 1992 to 1999 are also available (Gibbs et al., 2000; Lamare et al., 2002). For example, water temperatures at 12 m water depth ranged from 12.2 °C to 17.3 °C in 1998, with an average of 14.3 °C (SD = 1.1). Salinity in the same period was measured at 33 to 34 psu (SD = 1.1). While salinity varies along the fiord and with water depth, in a single location and depth, as in this study, it remains very consistent (Gibbs et al., 2000).

The difference between measured temperatures (10.5 to 17.5 °C) and the range given by the oxygen isotope data (14.2 to 17.5 °C) indicates that significant growth (and calcification) occurs only in warmer water temperatures. *Adeonellopsis* may have a minimum “shutdown” temperature, or a critical threshold of growth, at about 14 °C. Interpretation of paleoenvironments through geochemistry thus becomes more difficult, as one can only infer the environment when growth occurred, not the total history of the environment where the colony lived (e.g., Goodwin et al., 2001). While morphological evidence for winter growth checks has not been found in *Adeonellopsis*, some temperate bryozoans do have “growth bands” which indicate slowing or cessation of growth in winter (Stebbing, 1971; Ryland, 1976; Pätzold et al., 1987; Barnes, 1995; Bader, 2000), whereas others do not (Brey et al., 1999; Cocito and Ferdeghini, 2001).

#### *Stable isotopic composition of bryozoans as a record of climate*

Mark-and-harvest data from the same location (Smith et al., 2001) show that growth in *Adeonellopsis* in Doubtful Sound slows considerably in the colder months (5 mm over 6 months in summer/autumn, but only 2 mm over 6 months in winter/spring). If their mean annual growth rate of 7 mm/y is correct, the branches measured here are 12 to 16 years old, but they do not represent a continuous record of temperature. They probably represent growth only in late spring, summer, and early autumn (i.e., October to April).

Each of the subsamples containing 5 mm of branch length thus represents 6 to 9 months of environmental data time-averaged into a single value. Different samples contain different amounts of data, too, reflecting winter/summer growth variation and hiatuses in growth (if any) as well as among-branch variation (i.e., branch A is significantly different from branches B and C). These variations and time averaging restrict the utility of isotope paleothermometry in skeletal organisms (e.g., Goodwin et al., 2001). Our coarse sampling averages out seasonal water temperature cycles, a standard method of determining growth rate (e.g., Pätzold et al., 1987). But significant interannual variations

such as El Niño–Southern Oscillation (ENSO) events could be recorded, especially in large colonies that may be more than a decade old.

Because the study colony was collected and killed in January 1998, the Southern Hemisphere summer, and each branch had living growing tips at that time, we can anchor the temperature calculated from the branch tips to January 1998. Early 1998 was marked by a rapid increase in the Southern Oscillation Index (SOI, calculated from the time-averaged differences in pressure anomalies between Tahiti and Darwin Islands in the Pacific) (Queensland Department of Natural Resources and Mines, 2003) associated with the transition from a severe El Niño to a large La Niña. The SOI went from –25 to +18 in 4 months. The temperatures recorded in the growth tips of this colony are highly variable, which may reflect the speed of that change.

There were four El Niños during the estimated time of this colony’s life: one in 1998, two weaker ones in 1991 and 1987, and a massive one in 1983. There was one particularly large La Niña in 1989 (Fig. 5). Each branch has a more-or-less obvious high-temperature peak which we correlate with the 1989 La Niña event. The two longer branches also show a deep low which could be associated with the 1983 El Niño. If we stretch each branch’s profile (assuming a constant growth rate) to align these large features (Fig. 5), we can estimate an average growth rate.

Branch A, which is 120 cm long, appears to be the slowest growing. It grew about 84 mm between the 1983 El Niño event and 1998 — an average growth rate of 5.6 mm/yr, equivalent to 0.35 g CaCO<sub>3</sub>/yr, assuming 0.058 g/mm branch length (Jamet, 1999). It may be that this branch is significantly different from the other two (see Results) because it is the longest and therefore includes more of the harsh 1983 El Niño event. Branch B has a less obvious correlation, but if it began growing in 1983 (100 cm), it was growing 6.6 mm/yr and calcifying at 0.38 g CaCO<sub>3</sub>/yr. Branch C appears to have a high point for the La Niña of 1989, which would put its rate of growth at 8.3 mm/yr (0.48 g CaCO<sub>3</sub>/yr). An independent mark-and-harvest study on this colony, among others (Smith et al., 2001), suggested a growth rate of about 7 mm/yr, close to the above values (mean of 6.8 mm/yr).

If the correlation is reasonable, we would expect our interpolated temperatures to be consistent with Peake et al.’s (2001) reported measurements from 1994. In branches A and C, at least, the temperature in summer 1994 is 15–16 °C, a reasonable approximation (given time-averaging effects) of the measured summer temperature of 17.5 °C. Of course, there will be no isotopic record of the low winter temperatures due to cessation of growth.

Correlation between the SOI and calculated time-averaged water temperatures in Doubtful Sound is far from perfect. Local variations in water temperature and among-branch differences in growth rate mean that the medium-term climate signal (on the order of tens of years) is weak. Only the strongest SOI events can be detected. Finer-

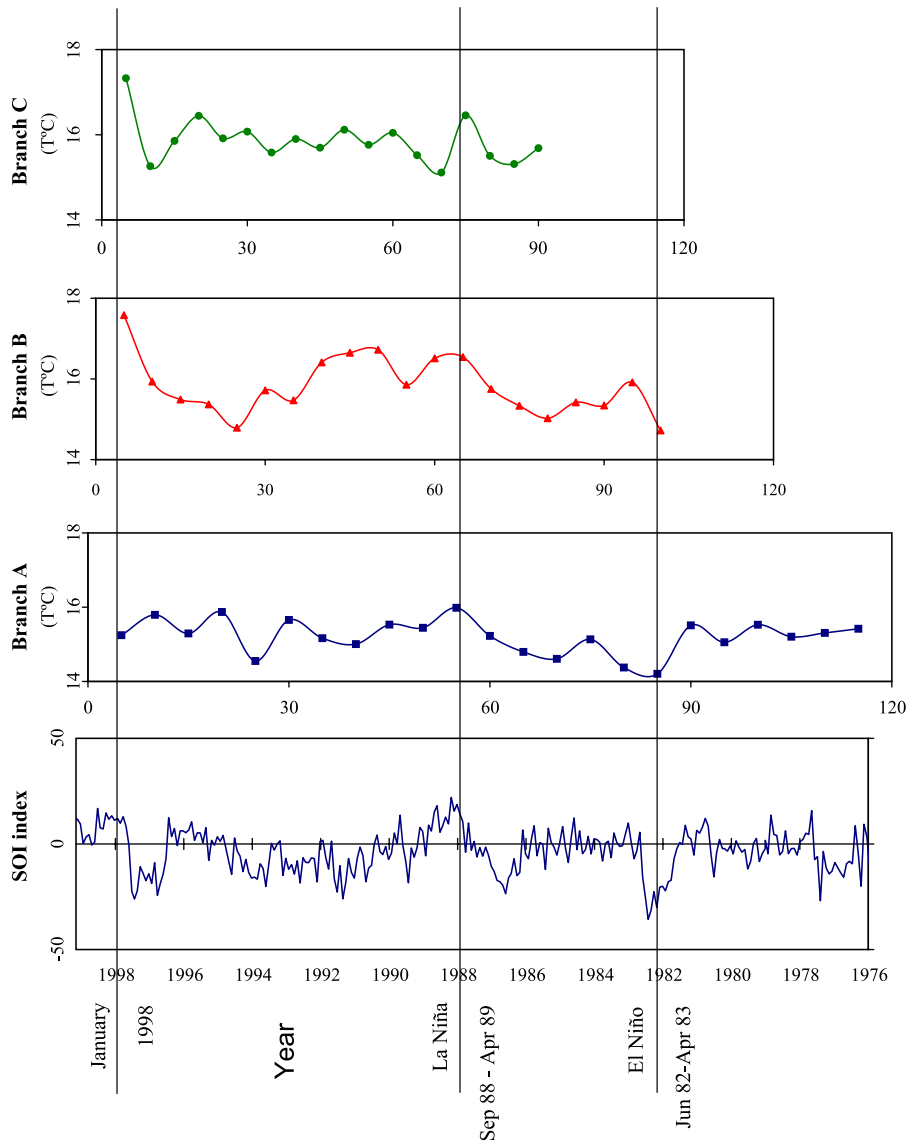


Fig. 5. Correlations between the Southern Oscillation Index (SOI) as recorded by the Queensland Department of Natural Resources and Mines (2003) and stable isotope profiles in *Aeonellopsis* sp. from Doubtful Sound, New Zealand.

scaled sampling along branches would allow elucidation of seasonal variation and perhaps allow better discrimination of climatic signals.

It is, however, noteworthy that some of the variation in stable isotopes in bryozoan carbonate may be due to interannual climatic variations. There is potential for bryozoan colonies to act as recorders of interannual temperature, perhaps even in the distant past. Bryozoans are abundant and large, often long-lived, at least in temperate carbonates, and therefore a rich source of potential information about environmental change. In addition, unaltered or proxy data from fossil bryozoans can be used in the same way, although aragonite bryozoans are the most likely to be diagenetically neomorphosed to low-magnesium calcite (e.g., Kyser et al., 1998).

#### Controls on carbon isotopes

While diagenetic effects may reset oxygen isotopic values, it has been noted that original carbon isotopic values may be retained (Bone and James, 1997).  $\delta^{13}\text{C}$ , if precipitated in isotopic equilibrium, reflects source(s) of bicarbonate to seawater, that is, the  $\delta^{13}\text{C}$  of dissolved inorganic carbon (DIC) in seawater.  $\delta^{13}\text{C}$  in seawater is often very near 0‰ with lighter values reflecting carbon sources subject to dissolution, soil weathering, photosynthesis, and respiration (Nelson and Smith, 1996). Bryozoan carbonate from the Antarctic has been shown to record changes in local productivity in the  $\delta^{13}\text{C}$  signal (Brey et al., 1999). There is, however, no obvious seasonal signal in the *Aeonellopsis* carbon isotopic data.

Another possible influence on  $\delta^{13}\text{C}_{\text{DIC}}$  is freshwater incursion, which may contribute DIC with an isotopic composition significantly lower than normal seawater. Ordinarily, surface freshwater draining out of Doubtful Sound would be less than 6 m thick at Bauza Island and much less than that before the 1969 construction of a tailrace that drains Lake Manapouri through a hydroelectrical power generation plant which discharges freshwater into the inner fiord (Lamare, 1997; Gibbs et al., 2000). After a storm or flood, freshwater could affect *Adeonellopsis* located at 12 m water depth, but it would be a very short-term signal (on the order of days) and not discernable at the sampling resolution we use here.

Typically,  $\delta^{18}\text{O}$  values in biogenic carbonate fluctuate over time while the  $\delta^{13}\text{C}$  profile stays relatively flat (e.g., Goodwin et al., 2001). But when upwelling or other water-mass changes are influencing temperature, there may be at least some correlation between the two isotopic ratios (Bemis and Geary, 1996). A regression between  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  lies at  $yr = 1.0562x + 1.307$  with an  $R^2$  of 0.22, suggesting that freshwater incursions are not significantly affecting water temperature,  $\delta^{18}\text{O}$ , or  $\delta^{13}\text{C}$  in seawater, as can happen in shallow marine environments (e.g., Swart et al., 1996). Crowley and Taylor's (2000) estimate  $\delta^{13}\text{C}_{\text{DIC}}$  in shallow seawater near New Zealand to be about  $+1.5\text{‰}$  ( $\pm 0.3$ ); the mean of our  $\delta^{13}\text{C}$  data is close at  $+1.7\text{‰}$ . There may be minor continuous mixing with the overlying freshwater layer, but episodic incursions are not indicated.

The  $\delta^{13}\text{C}$  values recorded in an *Adeonellopsis* skeleton from Doubtful Sound do not appear to contain information about temperature or other water mass characteristics. While the values fluctuate, they do not appear to correlate across branches the way the oxygen isotopes do (Fig. 4). There is an overall decrease in  $\delta^{13}\text{C}$  over the almost 20-yr record, however, which may be related to a global trend of decreasing  $\delta^{13}\text{C}$  in seawater since at least the 1930s (Swart et al., 1996). It may be that changes in land use, with increasing runoff and sewage disposal in the sea, increase the proportion of  $^{12}\text{C}$  in coastal seawater, though Doubtful Sound itself is relatively unaffected by these anthropogenic changes. It is more likely that carbon isotopes in the global ocean are decreasing due to increasing amounts of atmospheric fossil-fuel-derived  $\text{CO}_2$  (Keeling, 1979).

Alternatively, lighter carbon isotopes in younger carbonate may be related to mineralogy. Some bryozoans with mixed mineralogies have higher calcite content in early ontology, precipitating aragonite afterward as a secondary thickening (Ryland, 1976). We have no evidence to suggest that *Adeonellopsis* does this in sufficiently large amounts (see Table 2), but in bryozoans that do, isotopic composition could be affected.

#### The wider context and other studies

There is now published a large collection of information on stable isotopes in modern bryozoan carbonate represented

by 230 specimens from 55 genera and 70 species (Appendix, available from ScienceDirect on <http://www.sciencedirect.com>). The *Adeonellopsis* data from Doubtful Sound reported in this study can be compared to these published data by correcting it to theoretical syndepositional calcite values using Tarutani et al.'s (1969) correction of  $-0.6\text{‰}$  for  $\delta^{18}\text{O}$  and Romanek et al.'s (1992) correction of  $-1.7\text{‰}$  for  $\delta^{13}\text{C}$ . The *Adeonellopsis* data lie in a loose cluster at the light end of the spectrum (because we assumed they were all aragonite and some may be up to 10% calcite, leading to overcorrection) (Fig. 6) in the overall mixture. This distribution is far wider than might be expected for one colony of one species. If one colony of *Adeonellopsis* alone covers such a range, can we make deductions based on differences among species?

While the collated data in the Appendix are substantial, they remain insufficient to draw hard-and-fast conclusions about the utility of bryozoan stable isotopes in general. Most of the species studied are cheilostomes (42 genera studied out of some 900 extant genera, about 5%); very few are cyclostome bryozoans (11 genera of some 250 extant, 4%). In all, 71 species have been tested (some only once) out of about 4000 bryozoan species known (Ryland, 1976), a total of 2%.

#### Recommendations for future studies

Stable isotopes measured in a single colony of *Adeonellopsis* sp. cover a range of  $0.77\text{‰}$  in  $\delta^{18}\text{O}$  and  $1.34\text{‰}$  in  $\delta^{13}\text{C}$ . Bader (2000) found a range of  $1.14\text{‰}$  in  $\delta^{18}\text{O}$  in two colonies of *Cellaria sinuosa*, and Pätzold et al. (1987) found a seasonal range of  $0.8\text{‰}$  in  $\delta^{18}\text{O}$  within one colony of *Pentapora foliacea* (both fairly short-lived bryozoans with life-spans of 1–3 yr). In two colonies of *Cellaria incula* from Antarctica,  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  both varied by  $1.0\text{‰}$  (Brey et al., 1999). With within-colony variation of this magnitude, among-colony variation must be treated with considerable caution.

This degree of within-colony variation has implications for routine isotopic data collection in bryozoans. Sampling procedures will need to be developed that account for this by collecting multiple systematic subsamples within a colony. This labour-intensive sampling is standard practice in other organisms, e.g., Foraminifera (Purton and Brasier, 1999) and bivalves (Goodwin et al., 2001, 2003).

Even though the vast majority of bryozoans analysed have no vital effects, at least two species have demonstrated vital disequilibrium precipitation of carbonate (Crowley and Taylor, 2000). Thus the species to which a sample colony belongs must be identified prior to isotopic analysis. Isotopes fractionate differently depending on carbonate mineralogy (kinetic effect). Bryozoan mineralogy can vary within a colony and within a species (Smith et al., 1998); thus, the mineralogy of the colony or at least the species must also be determined.



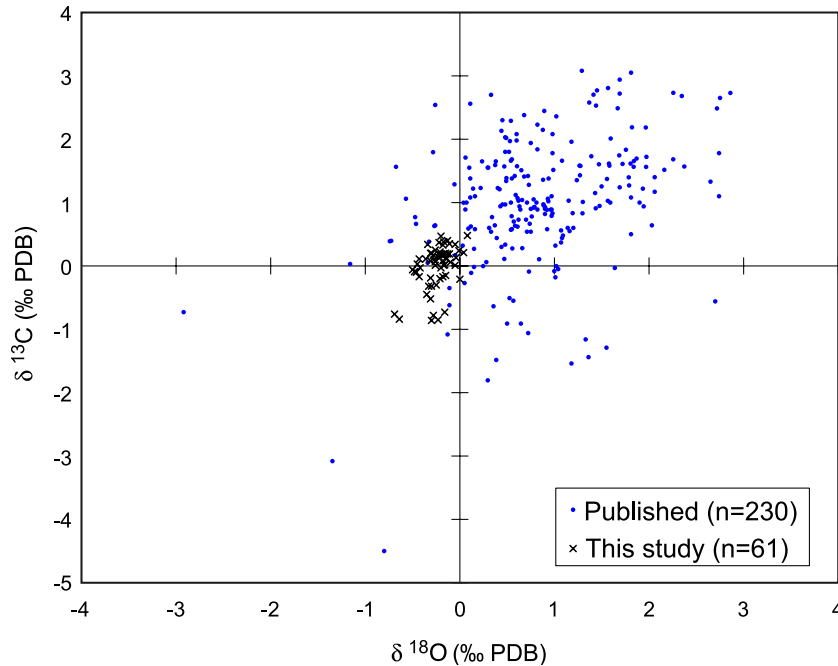


Fig. 6. Published oxygen and carbon stable isotope values from 230 bryozoan specimens, compared with 61 samples from one colony of *Adeonellopsis* from Doubtful Sound, New Zealand. Doubtful Sound data are corrected to syndepositional calcite values using equations of Tarutani et al. (1969) and Romanek et al. (1992). These data are presented in the Appendix, which is available on ScienceDirect (<http://www.sciencedirect.com>).

Growth rates and calcification rates can vary seasonally (Smith et al., 2001). Therefore elucidation of environmental signals requires closely spaced within-colony sampling. Homogenization of a colony may seem to be a labour-saving approach, but the resulting weighted average may not be useful, as it does not indicate the degree of within-colony variation, and of course useful seasonal or climatic information, for example, is lost.

We join our colleagues in agreeing that bryozoan skeletons are useful recorders of environmental information. These records can be used in short-term seasonal studies (e.g., Pätzold et al., 1987, Bader, 2000) and in wider ecological/environmental explanations (e.g., Bone and James, 1997; Amini and Rao, 1998), and even in the distant past (as Jones and Quitmyer, 1996, did with Jurassic bivalves). With careful subsampling design, the potential of bryozoans as paleoenvironmental tools can be realised.

## Conclusions

Oxygen isotopic ratios ( $\delta^{18}\text{O}$ ) in 61 subsamples (taken along three branches of a single unaltered colony of *Adeonellopsis* sp. from New Zealand) range from  $-0.09$  to  $+0.68\text{‰PDB}$  (mean =  $+0.36\text{‰}$ ). Carbon isotopic ratios ( $\delta^{13}\text{C}$ ) range from  $+0.84$  to  $+2.18\text{‰PDB}$  (mean =  $+1.69\text{‰}$ ). This wide range of variation ( $0.77\text{‰}$  in  $\delta^{18}\text{O}$  and  $1.34\text{‰}$  in  $\delta^{13}\text{C}$ ) within a single colony is surprising and suggests that fine-scale environmental information may be recorded with-

in bryozoan skeletal carbonate. Among-colony variation smaller than this within-colony variation cannot be considered significant.

*Adeonellopsis* appears to have a minimum temperature growth threshold of  $14\text{ }^{\circ}\text{C}$ , and no upper limit to growth in Doubtful Sound (where temperatures range from  $10.5$  to  $17.5\text{ }^{\circ}\text{C}$ ). Annual growth of about  $7\text{ mm/yr}$  therefore probably occurs in spring, summer, and early autumn.

A long-lived bryozoan like *Adeonellopsis* may also contain a record of climate variations on the order of 10–20 years. Large climatic events as the 1983 El Niño may be discerned in the record of seawater temperatures derived from  $\delta^{18}\text{O}$ . Comparison with the SOI allows the determination of growth rates for individual branches based on the location of such events. The three branches studied here grew, on average,  $6.8\text{ mm/yr}$  ( $0.4\text{ g CaCO}_3/\text{yr}$ ). Not only can we use the SOI to determine growth rates, but we also note that bryozoan carbonate is a potential source of information about medium-term climatic variation in the past.

Although large and significant studies of temperate bryozoan isotopes have been undertaken, only 2% of known species have actually been measured. We cannot assume that stable isotope chemistry of this highly variable phylum is completely known. In a mineralogically variable taxon like bryozoans, with highly variable growth rates, a careful subsampling design, while labour-intensive, can result in detailed and useful information about growth and mineralogy of the species under study, its environment, and possibly larger-scale climatic trends.

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