COMPARISON BETWEEN MODERN POLAR AND TEMPERATE SKELETAL CARBONATE MINERALOGY AND OXYGEN AND CARBON ISOTOPES, ANTARCTIC AND TASMANIAN SHELVES

by C. Prasada Rao, Zahra Z. Amini and Dennis C. Franklin

(with one table and eight text-figures)

C.P. RAO, AMINI, Z.Z. & FRANKLIN, D.C., 1996 (xi): Comparison between modern polar and temperate skeletal carbonate mineralogy and oxygen and carbon isotopes, Antarctic and Tasmanian shelves. *In* Banks, M.R. & Brown, M.J. (Eds): *CLIMATIC SUCCESSION AND GLACIAL HISTORY OF THE SOUTHERN HEMISPHERE OVER THE LAST FIVE MILLION YEARS. Pap. Proc. R. Soc. Tasm.* 130 (2): 87-93. https://doi.org/10.26749/rstpp.130.2.87 ISSN 0080-4703. Department of Geology (CPR, ZZA) and Antarctic CRC (DCF), University of Tasmania, GPO Box 252-80, Hobart, Tasmania, Australia 7001.

Modern bryozoan skeletal mineralogy varies with seawater temperature: polar Antarctic bryozoans are mainly low-Mg calcite, whereas temperate Tasmanian bryozoans are predominantly high-Mg calcite with variable amounts of aragonite. Bivalve molluscs from both polar and temperate regions are mainly aragonite with variable amounts of low-Mg calcite. The $\delta^{18}O$ and $\delta^{13}C$ isotope fields of polar skeletons are clearly separated from the temperate fields, due to differences in seawater temperatures, levels of $\delta^{13}C$ in seawater and the circulation of seawater masses. $\delta^{18}O$ values of bryozoa, benthic foraminifera and bivalve molluscs give near-equilibrium seawater temperatures. Small differences in $\delta^{18}O$ and $\delta^{13}C$ values between skeletons are due to their variable growth rates. Meltwater effects are small (<7%) in the polar Antarctic Sea and high (<25%) in the shallow Arctic Sea because ice sheets do not melt in the Antarctic region, whereas significant melting of ice sheets occurs in summer in the Arctic regions. Skeletal carbonate mineralogy and $\delta^{18}O$ and $\delta^{13}C$ variations can be used in the recognition of ancient, non-tropical carbonate skeletons and carbonate rocks.

Key Words: Recent cold-water carbonates, carbonate mineralogy, oxygen and carbon isotopes, Antarctica, Tasmania.

INTRODUCTION

Carbonate skeletons are abundant in modern shallow seas from tropical, temperate to polar regions. Accumulation of carbonate skeletons forms carbonates in all climatic regions. Temperate and polar carbonates are mainly biogenic sediments (e.g. Domack 1988, Nelson 1988, Taviani & Aharon 1989, Anderson *et al.* 1992). The carbonate mineralogy of many skeletons varies with seawater temperatures (e.g. Morse & McKenzie 1990, Rao 1993). Comparison of carbonate skeletal mineralogy from temperate and polar sediments is presented here to illustrate temperature control on carbonate skeletal mineralogy.

The ^{18}O fractionation related to water temperature is well established (e.g. Friedman & O'Neil 1977). The ^{13}C in surface seawater varies from temperate to polar regions, due to atmospheric CO_2, oxidation of organic matter and mixing of water masses (Kroopnick 1985). Rate of skeletal precipitation affects the $\delta^{18}O$ and $\delta^{13}C$ composition of skeletons (e.g. McConnaughey 1989). This study presents $\delta^{18}O$ and $\delta^{13}C$ fields for polar Antarctic bryozoans, benthic foraminifera and bivalve molluscs, compares these fields with those of similar fauna previously established for the subpolar Greenland Shelf and for the temperate Tasmanian Shelf (fig. 1; Rao 1994) and discusses relative rates of skeletal precipitation of polar Antarctic bryozoans, benthic foraminifera and bivalve molluscs. The implications of our findings in understanding the origin of modern and ancient temperate to polar skeletal accumulations are presented.

METHODS OF STUDY

Tasmanian samples studied are grab samples from eastern Tasmania (fig. 1; Rao 1993) and range from about 30 to 200 m water depths. Antarctic samples from the Prydz Bay Shelf (fig. 1) are grab samples at water depths from 0 to 121 m and from a 0.6 m long, deep core (with samples at about 25 mm intervals) at 134 m water depth. Both Tasmanian and Antarctic samples range from siliciclastics to carbonates. However, Tasmanian samples are mainly carbonates, whereas Antarctic ones are predominantly siliciclastics. After washing the samples, bryozoans, benthic foraminifera and bivalves were hand-picked using a binocular microscope. Bryozoans and bivalves were subjected to X-ray

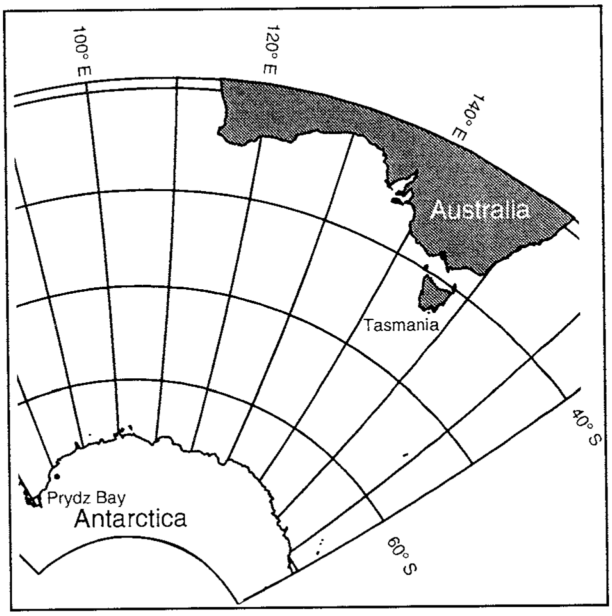

FIG. 1 — Location of Tasmania, Australia, and Prydz Bay, Antarctica. Note – Tasmania is in the cool temperate region and Prydz Bay is in the polar region.

diffractometry for carbonate minerals. Skeletons from Tasmania and Antarctica were reacted with 100% anhydrous H_3PO_4 at 25°C. The evolved CO_2 gas was analysed on a VG SIRA series II mass-spectrometer at the University of Tasmania for $\delta^{18}O$ and $\delta^{13}C$, the values being expressed in conventional per mil notation relative to the PDB standard. The precision of data, established from duplicate analysis, is ±0.1‰ for both O and C. Data used in this study are from shallow seawater depths (<399 m): bryozoan and bivalve molluscan mineralogy and $\delta^{18}O$ and $\delta^{13}C$ values of bryozoans, benthic foraminifera and bivalve molluscs from Antarctica and bivalve molluscs from Tasmania (table 1); ^{14}C dates obtained from hand-picked fauna and sediments from Prydz Bay (Harris *et al.* 1996); $\delta^{18}O$ and $\delta^{13}C$ values of aragonite bivalves from Greenland (Israelson *et al.* 1994).

RADIOCARBON AGES OF ANTARCTIC SEDIMENTS

The ^{14}C dates of 17 grab samples from Prydz Bay range from 2470 to 140 yr BP. Two dates are from cores (GCO3) are 4314 ± 96 yr BP at 0.15 cm and 8030 ± 100 yr BP at 0.55 to 0.57 m. In Antarctica, many living marine organisms yield older ^{14}C ages — up to 1770 yr BP (Stuiver *et al.* 1981) — because the ^{14}C reservoir effect is pronounced around Antarctica (Harris *et al.* 1996). All these ages firmly establish that the Antarctic sediments studied here were deposited during the Late Holocene.

CARBONATE MINERALOGY

X-ray diffractometric analyses indicate that Antarctic bryozoans are calcites with a predominance of low-Mg calcite (<5% mole % $MgCO_3$) relative to high-Mg calcite (>5 mole % $MgCO_3$; fig. 2), whereas temperate Tasmanian bryozoans (Rao 1993) are mainly high-Mg calcite with variable amounts of aragonite up to 90% (fig. 2). Bivalve molluscs from Antarctica and Tasmania are mainly aragonite with variable amounts of calcite up to 90% (fig. 3). The type of calcite in bivalve molluscs is low-Mg calcite. X-ray d-spacings of Antarctic bryozoan calcite reveal that mole% Mg in this calcite ranges from about 1 to 8% with most being less than 5% (fig. 2). Experimental studies on abiotic calcite demonstrate that mole% $MgCO_3$ decreases with decreasing seawater temperatures (fig. 4; Kinsman & Holland 1969, Fuchtbauer & Hardie 1976, Mucci 1987, Burton & Walter 1991). Comparison of bryozoan mole% $MgCO_3$, obtained from X-ray d-spacings, and temperatures, calculated from $\delta^{18}O$ values of bryozoans, shows that the calcite mineralogy and mole% $MgCO_3$ of bryozoans vary with seawater temperatures, as do those of abiotic calcites. The low-Mg calcite bryozoans mainly grow in cold (–2°C) Antarctic seawater and predominantly high-Mg calcite bryozoans grow in cool (7°–13°C) temperate Tasmanian shelf water (fig. 4).

OXYGEN AND CARBON ISOTOPES

The $\delta^{18}O$ values of polar Antarctic bryozoans (2.89–4.17), benthic foraminifera (2.89–4.20) and bivalve molluscs (3.41–5.01) are more positive than those of similar fauna from the temperate Tasmanian Shelf (fig.5). In contrast to $\delta^{18}O$ values, $\delta^{13}C$ values of polar Antarctic bryozoans (–0.15 to 1.93), benthic foraminifera (–0.71 to 1.30) and bivalve molluscs (–1.07 to 1.72) overlap and extend to lower values compared with similar skeletons from the temperate Tasmanian Shelf (fig. 5). Both Tasmanian and Antarctic isotope fields are below the temperature equilibrium lines of calcite and aragonite equilibrium with surface seawater (Rao 1993), because these non-tropical carbonates are in equilibrium with bottom seawater. High positive $\delta^{18}O$ values and lack of negative $\delta^{18}O$ values on Antarctic skeletons indicate that melt-water dilution is minimal in the samples studied, as expected (Taviani & Aharon 1989, Taviani *et al.* 1993).

The $\delta^{18}O$ values of Antarctic and Tasmanian fauna are related to seawater temperatures, which can be calculated with ^{18}O thermometry. These calculated temperature ranges (fig. 5) are similar for bryozoa (–3° to 3°C), benthic foraminifera (–3° to 3°C) and bivalve molluscs (–3° to 5°C). Since the average Antarctic seawater temperature is approximately –2°C (actually –1.98° to –1.87°C), equilibrium $\delta^{18}O$ lines are drawn for calcite and aragonite at –2°C, using $\delta^{18}O$ equations of calcite and aragonite mollusca (Grossman & Ku 1986). Eighty percent of bryozoan $\delta^{18}O$ values fall on the low-Mg calcite equilibrium line at –2°C (fig. 5A), confirming that bryozoan $\delta^{18}O$ values are reliable indicators of seawater temperatures. Bryozoans that indicate warmer temperatures than –2° are high-Mg calcite. Benthic foraminifera $\delta^{18}O$ values fall on the low-Mg calcite equilibrium line at –2°C and deviate to lower $\delta^{18}O$ values (fig. 5B), thus indicating relatively warmer seawater temperatures. Bivalve mollusca $\delta^{18}O$ values fall at the edge of the aragonite equilibrium line at –2°C and deviate to lower values (fig. 5C), thus indicating relatively warmer seawater temperatures. The low-Mg calcite equilibrium line at –2°C dissects the bivalve mollusca isotope field, due to the occurrence of variable amounts of low-Mg calcite in bivalve molluscs (fig. 5C). Antarctic bivalve molluscs (*Adamussium colbecki* and *Laternula elliptica)*were demonstrated to show different $\delta^{18}O$ values in various parts of the skeletons (Barrera *et al.* 1994), which should be the case for crushed bulk bivalves analysed in this study. Despite this apparent variation in $\delta^{18}O$ values in different parts of the shell, the Antarctic bulk bivalve molluscs provide near equilibrium isotopic estimates of seawater temperatures (Barrera *et al.* 1994).

$\delta^{18}O$ values of Antarctic bivalves are much higher than those of bivalves from shallow (<30 m) depths in the Arctic Sea around Greenland (fig. 6). Though measured seawater temperatures around Greenland are very cold and range from –1.8° to 1°C, the temperatures calculated from $\delta^{18}O$ values of bivalves give anomalously warm temperatures ranging from 9° to 21° C. These high temperatures are due to strong meltwater dilution of up to 25% (fig. 6) that reduces the $\delta^{18}O$ of seawater from 0 to –9‰ SMOW (fig. 7), because measured meltwater $\delta^{18}O$ values around Greenland are around –38‰ SMOW. The temperatures warmer than –1.8°C, obtained from some bryozoans, benthic foraminifera and bivalves from Antarctica, are possibly due to small amounts (<7%) of meltwater. This amount of meltwater around Antarctica is calculated from the most negative $\delta^{18}O$ value of 2.9‰ and a carbonate–water fractionation factor ($\Delta^{18}O$) of 35‰ at –2°C (Rao & Green 1982).

$\delta^{18}O$ values lower than equilibtium lines of low-Mg calcite and aragonite at –2°C in all fauna are probably due

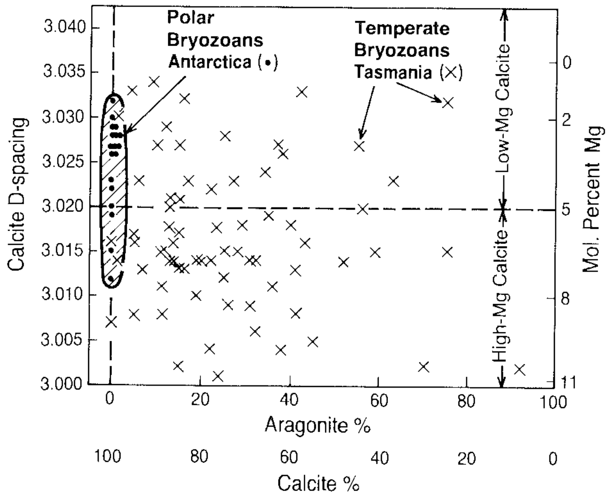

FIG. 2 — Calcite d-spacing versus relative percentages of calcite and aragonite. Note – polar bryozoans from Antarctica are mainly low-Mg calcite with minor high-Mg calcite without aragonite, whereas Tasmanian bryozoans are mainly high-Mg calcite with minor low-Mg calcite and variable amounts of aragonite. Mole % $MgCO_3$ shown is based on calcite d-spacings.

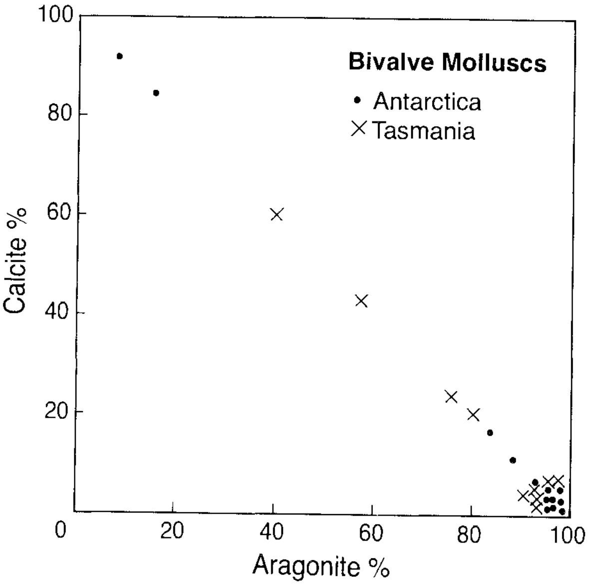

FIG. 3 — Relative percentages of calcite and aragonite in bivalve molluscs from Antarctica and Tasmania. Note – bivalve molluscs from both Antarctica and Tasmania are predominantly aragonite with variable amounts of calcite, which is low-Mg calcite.

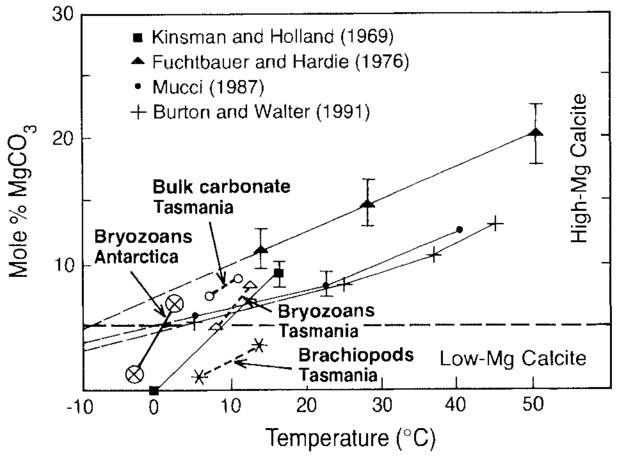

FIG. 4 — Mole % $MgCO_3$ in calcite and seawater temperatures. Note – mole% $MgCO_3$ in calcite decreases with decreasing seawater temperatures both in experimental studies on abiotic calcite (Kinsman & Holland 1969, Fuchtbauer & Hardie 1976, Mucci 1987, Burton & Walter 1991) and in bryozoans from Antarctica and Tasmania.

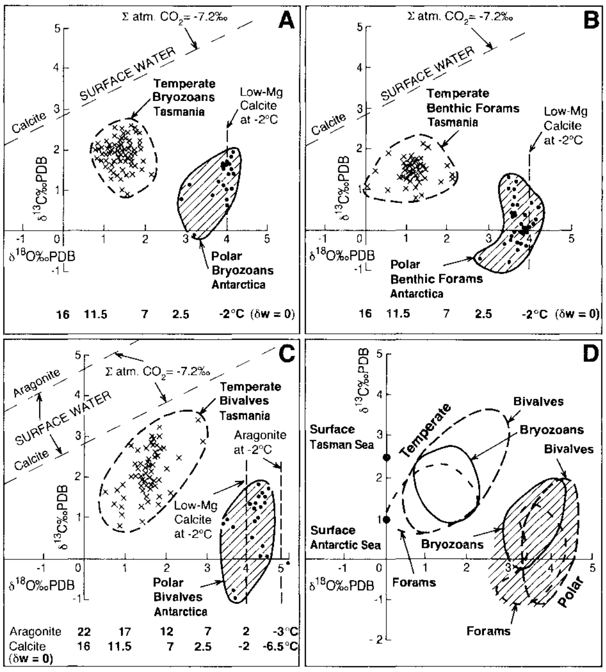

FIG. 5 — $\delta^{18}O$ and $\delta^{13}C$ fields of bryozoa (A), benthic foraminifera (B), bivalve molluscs (C), and composite fields of skeletons (D) from Tasmania and Antarctica. Surface equilibrium calcite and aragonite lines (Rao 1993) and seawater temperatures obtained from $\delta^{18}O$ values of calcite and aragonite and $\delta^{13}C$ in atmosphere. $\delta^{13}C$ values in surface seawater off Tasmania (2.5‰) and Antarctica (1‰) vary (Kroopnick et al. *1977, Kroopnick 1985). Note – the isotope fields of polar skeletons are clearly separated from temperate ones, due to differences in seawater temperatures, $\delta^{13}C$ in seawater and the circulation of seawater masses. See text for details.*

TABLE 1

δ^{18}O and δ^{13}C values* of bivalves, bryozoans and foraminifera from Prydz Bay, Antarctica and δ^{18}O and δ^{13}C values of bivalves from eastern Tasmania

		Antarctica										
		Bivalves		Bryozoans		Foraminifera		Bryozoans			Bivalves	
Sample No	Depth, m	∂^{13}C	∂^{18}O	∂^{13}C	∂^{18}O	∂^{13}C	∂^{18}O	Calcite d-Spacing	Calcite %	Aragonite %	Calcite %	Aragonite %
93009	Grab 98					0.303	3.897					
93031C	Grab 101					0.142	3.933					
93035	Grab 88					0.133	4.122					
93036 A	Grab 69			-0.152	3.202	0.236	4.132	3.019	100	0		
93037	Grab 95					-0.082	3.958					
93038C	Grab 110	0.764	3.67	1.135	3.036	-0.336	3.865	3.012	100	0	90	10
93040	Grab 85	0.841	3.407	0.757	2.89	0.028	3.945	3.015	100	0	84	16
93058	Grab 38	0.936	3.502			-0.273	3.72					
93099	Grab 26					-0.169	3.56					
93102	Grab 21	-0.8	3.75									
93103	Grab 21					-0.715	2.858					
93104	Grab 33	0.307	4.361			0.338	3.965				7	93
93108	Grab 30					1.304	3.529					
93132	Grab 76					-0.693	3.34					
JMW3	Grab 5	0.909	4.179			0.67	4.022					
JMW6	Grab 5	0.974	4.264			-0.03	3.991				16	84
Bivalve 1	Grab 0	1.528	4.227								0	100
Bivalve 2	Grab 0	1.255	4.303								0	100
Bivalve 3	Grab 0	1.659	4.268									
Bivalve 4	Grab 0	1.802	4.222								0	100
Bivalve 5	Grab 0	1.29	4.176								0	100
Bivalve 6	Grab 0	1.319	4.092								0	100
Bivalve Lat 1	Grab 0	1.349	4.398									
Bivalve Lat 2	Grab 0	1.719	4.452									
Bivalve Lat 3	Grab 0	1.351	4.193									
Bivalve Lat 4	Grab 0	1.497	4.409									
Gco3-12.5cm	Core 134			1.216	3.793	1.072	3.462					
Gco3-15cm	Core 134	0.576	4.065	1.934	4.166	1.183	3.682					
Gco3-17.5cm	Core 134			1.686	4.073	1.038	3.676	3.028	100	0		
Gco3-20cm	Core 134	-1.07	3.744	1.676	4.055	0.353	3.644	3.032	100	0		
Gco3-22.5cm	Core 134			1.826	4.17	0.559	3.613					
Gco3-25cm	Core 134			1.646	3.914	-0.795	3.572					
Gco3-27.5cm	Core 134			1.584	4.048	0.366	3.562	3.029	100	0		
Gco3-30cm	Core 134			1.665	3.904	0.82	3.614	3.03	100	0		
Gco3-32.5cm	Core 134	-0.07	5.011	1.155	3.902	0.604	3.717	3.03	100	0		
Gco3-35cm	Core 134			1.264	4.105	0.393	3.636	3.026	100	0		
Gco3-37.5cm	Core 134	0.038	4.432	1.536	4.107	0.435	3.651	3.023	100	0		
Gco3-40cm	Core 134			0.623	4.033	-0.039	3.696	3.029	100	0		
Gco3-42.5cm	Core 134			1.382	4.129	-0.033	3.846	3.029	100	0		
Gco3-45cm	Core 134			0.774	4.085	0.087	3.959	3.026	100	0		
Gco3-47.5cm	Core 134			1.082	4.11	0.122	3.799	3.027	100	0		
Gco3-50cm	Core 134			1.025	4.075	0.07	3.777	3.02	100	0		
Gco3-52.5cm	Core 134			0.863	3.657	0.548	4.198	3.022	100	0		
Gco3-55cm	Core 134	0.052	4.318	1.401	4.089	-0.514	3.731	3.027	100	0		
Gco3-57.5cm	Core 134			1.567	3.987	0.007	3.825	3.028	100	0		

* X-ray diffraction data pertaining to calcite d-spacing and relative per cent of calcite and aragonite of bryozoans and bivalves from Prydz Bay, Antarctica, and bivalves from eastern Tasmania.

to variable rates of skeletal precipitation. Equilibrium δ^{18}O values occur at slow rates of skeletal precipitation, and disequilibrium δ^{18}O values at faster rates (McConnaughey 1989, Rao 1994). Since δ^{18}O values of most Antarctic bryozoans are in equilibrium with seawater temperatures of around −2°C, and δ^{18}O values of most Antarctic benthic foraminifera and bivalve molluscs are in slight disequilibrium with an average temperature of −2°C, it appears that Antarctic bryozoan skeletons formed at a slow rate. In contrast, δ^{18}O values of benthic foraminifera and bivalve mollucs suggests that they formed at a faster rate than bryozoans. In Tasmania, temperate benthic foraminifera δ^{18}O values are lower than those of bryozoans in the same samples, due to benthic foraminifera forming at a faster rate than bryozoans (Rao 1994).

Experimental studies indicate abiotic calcite δ^{13}C values are inversely related to the rate of calcite formation (Turner 1982). The δ^{13}C values of Antarctic bryozoans are higher than those of benthic foraminifera and bivalve molluscs (fig. 8), due to the slower rate of bryozoan skeletal precipitation than of benthic foraminifera and bivalve molluscs. Since the percentile distribution curves of δ^{13}C of benthic

Table 1 cont.

		Tasmania			
		Bivalves			
Samples	Depth, m	$\partial^{13}C$	$\partial^{18}O$	Calcite %	Aragonite %
2000	106	2.315	1.655		
2001	184	2.887	1.66		
2003	45	1.236	1.429		
2004	42	0.817	0.796		
2006	18	1.05	0.8	0	100
2007	24	1.361	0.729	0	100
2010	16	1.613	2.123		
2011	14	1.482	0.973		
2013	88	2.325	1.565		
2014	70	1.8	1.475		
2015	28	2.747	1.149		
2016	64	2.684	1.295		
2017	205	2.863	2.284		
2018	104	2.103	1.616		
2020	100	2.436	1.716		
2021	73	2.417	1.522	43	57
2024	53	1.423	1.548		
2025	33	2.376	1.625	0	100
2026	60	1.514	1.506	0	100
2027	84	2.797	1.751	24	76
2028	128	3.008	1.603		
2033	31	2.297	1.377	0	100
2034	71	1.723	1.396	19	81
2043	60	2.184	1.297		
2044	60	2.099	1.168		
2047	33	1.277	1.821		
2049	62	2.097	1.379		
2050	82	1.858	1.605		
2051	399	2.497	2.308		
2052	113	3.244	1.809	60	40
2054	161	3.415	2.771		
2055	62	2.2	1.994		
2056	121	2.622	1.744		
2057	146	2.713	1.824		
2059	175	2.575	1.736		
2060	84	1.971	1.418		
2061	128	2.168	1.574		
2062	148	2.281	1.541		
2064	154	2.741	1.857		
2065	95	3.021	1.811		
2066	104	2.75	1.535		
2067	124	2.854	1.62		
2068	168	3.574	1.932		
2076	108	2.834	1.678	0	100
2077	97	2.244	1.493		

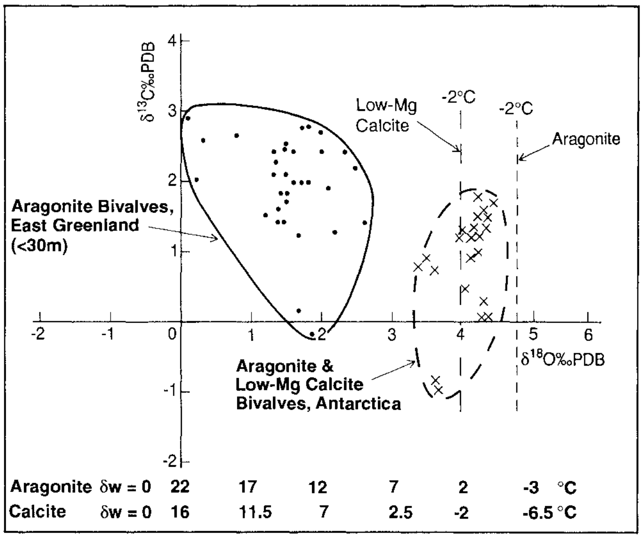

FIG. 6 — Comparison of $\delta^{18}O$ and $\delta^{13}C$ values of bivalves from Antarctic and Greenland waters (Israelson et al. *1994). Note – though seawater temperatures in both regions are cold (around 1° to –1.5°C off Greenland and –1.8°C off Antarctica), the temperatures determined from $\delta^{18}O$ values of bivalves are warmer than those measured, due to meltwater effect during the growth of bivalves. See text for details.*

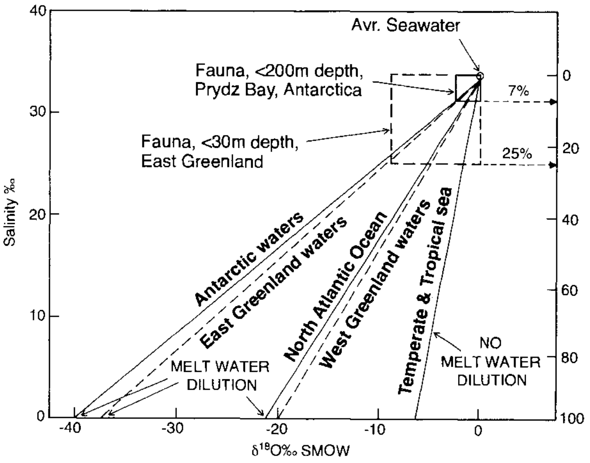

FIG. 7 — Salinity versus ^{18}O composition of seawater with meltwater dilution around Antarctica, off Greenland and in the North Atlantic Ocean, and in temperate to tropical seas with no meltwater dilution. See text for details.

foraminifera and bivalve molluscs overlap (fig. 8), both these faunal elements probably formed at almost equal growth rates. In Tasmania, $\delta^{13}C$ values of temperate benthic foraminifera are lower than those of bryozoans in the same samples, due to benthic foraminifera forming at a faster rate (Rao 1994).

The $\delta^{13}C$ values in skeletons depend on $\delta^{13}C$ in seawater, which ranges up to about 2.5‰ in shallow seas and to about 0‰ in well-mixed deep seawater (Kroopnick *et al.* 1977, Kroopnick 1985). The difference in $\delta^{13}C$ values in polar Antarctic skeletons and temperate Tasmanian skeletons (fig. 5D) is due to lower $\delta^{13}C$ values in polar Antarctic surface seawater (1‰) than in cool temperate Tasmanian surface seawater (2.5‰; Kroopnick *et al.* 1977). The $\delta^{13}C$ values in tropical surface seawater are around 2‰ and change laterally, depending on depositional environments, to lower values by as much as 4‰, due to evaporation, freshwater discharge and $CaCO_3$ withdrawal (Patterson & Walter 1994). In non-tropical shallow seas, evaporation of seawater is too low to cause significant shifts in $\delta^{13}C$ values. Freshwater input from rivers is minimal in the Tasman Sea (e.g. Rao & Huston 1995). Only small amounts of meltwater are added to the Antarctic waters, because Antarctica is the driest continent and the atmospheric temperatures are not warm enough to melt ice appreciably. As for $\delta^{18}O$, $\delta^{13}C$ values of these marine

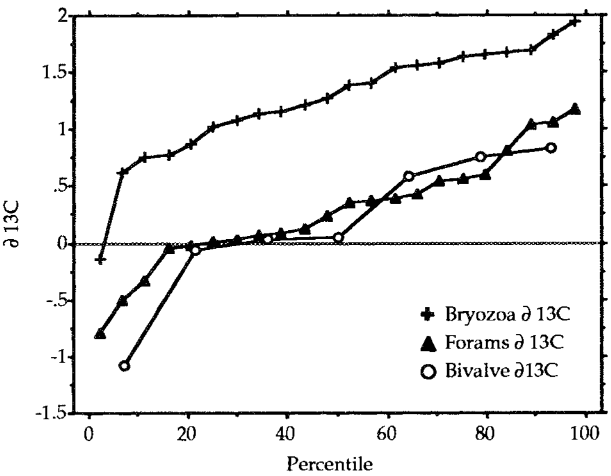

FIG. 8 — Percentile distribution of $\delta^{13}C$ values in bryozoans, benthic foraminifera and bivalve molluscs from samples that contain all these three skeletons. Note – the $\delta^{13}C$ distribution curve of bryozoans is above those of benthic foraminifera and bivalve molluscs, due to higher $\delta^{13}C$ values in bryozoans than in other skeletons.

waters are not significantly affected by freshwater input. The rate of $CaCO_3$ production in non-tropical seas is lower than in tropical seas (Rao 1994) and, thus, the withdrawal of $\delta^{13}C$ from non-tropical seas is too low to significantly decrease $\delta^{13}C$ values in those seas. Kinetic effects are minimal in non-tropical skeletons (Rao 1993), so the variation in $\delta^{13}C$ values in skeletons is due to mixing of seawater masses. Lower $\delta^{13}C$ values in some Antarctic skeletons compared with Tasmanian ones, therefore, are due to strong mixing of seawater and oxidation of organic matter. In Prydz Bay, physical oceanographic evidence indicates the operation of a large cyclonic effect (Smith *et al.* 1984), and this affects the distribution of fauna and sediment types (Franklin 1993). Carbonates around Antarctica are observed to be preserved in areas of strong upwelling (Domack 1988, Taviani *et al.* 1993). Off Tasmania, $\delta^{18}O$ and $\delta^{13}C$ values of skeletons indicate mixing of shelf waters with warm, Coral Sea water in summer, with cold subantarctic water in winter, and with upwelled cold, deep water all year round (Rao & Huston 1995).

GEOLOGIC IMPLICATIONS

A significant problem in sedimentary geology is the recognition of ancient non-tropical carbonates. Modern temperate and polar shelf carbonates extend over large areas (e.g. Domack 1988, Nelson 1988), yet anomalously few ancient polar carbonates have been recognised (Rao 1981, Rao & Green 1982). Modern temperate and polar carbonates are mainly biogenic. Bryozoa, foraminifera and mollusca are the major fauna in non-tropical carbonates (e.g. Nelson 1988). Importantly, many ancient limestones contain abundant bryozoans, foraminifera and molluscs (Wilson 1975). Carbonate mineralogy and elemental and isotopic composition of ancient carbonates suggest extensive non-tropical carbonates worldwide (e.g. Rao & Jayawardane 1994). Since bryozoa skeletal mineralogy is dependent on seawater temperature in modern temperate Tasmanian and polar Antarctic shelves, the original skeletal calcitic mineralogy is important in the recognition of ancient non-tropical carbonates and terrigenous clastic sediments that contain skeletons. Heavy $\delta^{18}O$ values indicate non-tropical or hypersaline environments (Taviani 1991). $\delta^{18}O$ values of bryozoa, benthic foraminifera and mollusca in non-tropical shallow seas, unaffected by meltwater dilution, give near-equilibrium seawater temperatures (Rao 1994); thus, these skeletal values can be used in the determination of palaeotemperatures (Taviani & Aharon 1989). Bryozoan $\delta^{18}O$ values are excellent palaeoclimatic indicators (Rao 1993, Bone & James 1995) because their skeletons form at a slower rate than benthic foraminifera and bivalve molluscs. The differences in $\delta^{18}O$ and $\delta^{13}C$ between bryozoans, benthic foraminifera and bivalve mollusca are due to variable growth rates, which determine the relative frequency abundances of skeletons in modern environments (Rao 1994). Similar relationships can occur in the geologic record. In contrast to tropical shallow seas, evaporation rates, freshwater discharge and $CaCO_3$ rate of formation are low in temperate and polar shallow seas with minor meltwater dilution. Thus non-tropical skeletal $\delta^{13}C$ values are due to mixing of seawater masses, oxidation of organic matter and cooler temperatures. Last Glacial carbonates formed around Antarctica have similar $\delta^{18}O$ and $\delta^{13}C$ values to modern Antarctic skeletons, because the Pleistocene glacial bank carbonates (>200 m) have not been affected by meltwater dilution (Taviani *et al.* 1993). In regions of strong meltwater dilution, both $\delta^{18}O$ and $\delta^{13}C$ values of skeletons will appreciably decrease from original marine values, as in the modern sea off Greenland (Israelson *et al.* 1994), the Canadian Arctic (Hillaire-Marcel 1981) and the polar Permian sea of Tasmania (Rao & Green 1982).

ACKNOWLEDGEMENTS

This project is funded by the Australian Antarctic Science Advisory Committee. We thank the Antarctic CRC and AGSO for providing samples, Mike Power and Christine Cook for isotope analysis, Debbie Harding for drafting illustrations and Mohammad Adabi, Peter Harris and Andrew McMinn for reading earlier versions of the manuscript. We also thank M. Taviani and an anonymous reviewer for valuable comments.

REFERENCES

Anderson, J.B., Reid, D.E. & Taviani, M., 1992: Compositional and geochemical characteristics of Recent biogenic carbonates from the Ross Sea (Antarctica). *Mem. Soc. Geol. Italy* 46: 561–562.

Barrerra, E., Tevesz, M.J.S., Carter, J.G. & McCall, P.L., 1994: Oxygen and carbon isotopic composition of shell microstructure of the bivalve *Laternula elliptica* from Antarctica. *Palaios* 9: 275–287.

Bone, Y. & James, N.P., 1995: Cool-water bryozoa and stable isotopes. *COOL AND COLD-WATER CARBONATE CONFERENCE ABSTRACTS, VICTORIA, AUSTRALIA*. Geological Society of Australia Specialist Group in Sedimentology: 9–10.

Burton, E.A. & Walter, L.K., 1991: The effects of pCO_2 and temperature on magnesium incorporation in calcite in seawater and $MgCl_2$–$CaCl_2$ solutions. *Geochim. Cosmochim. Acta* 55: 777–785.

DOMACK, E.W., 1988: Biogenic facies in the Antarctic glacimarine environment: Basis for a polar glacimarine summary. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 63: 357–372.

FRANKLIN, D.C., 1993: Recent diatom and foraminiferal assemblages in surficial sediments of Prydz Bay, Antarctica. *ANARE Res. Notes* 90: 27 pp.

FRIEDMAN, I. & O'NEIL, J.R., 1977: Compilation of stable isotope fractionation factors of geochemical interest. *In* Fleischer, M. (Ed.): *DATA OF GEOCHEMISTRY.* 6th edn. *US Geol. Surv. Prof. Pap.* 440-KK: 1–12.

FUCHTBAUER, H. & HARDIE, L.A., 1976: Experimentally determined homogeneous distribution co-efficients for precipitated magnesian calcites. *ABSTRACTS ANNUAL PROGRAM MEETING GEOLOGICAL SOCIETY OF AMERICA*: 877.

GROSSMAN, E.L. & KU, T.L., 1986: Oxygen and carbon isotope fractionation in biogenic aragonite: Temperature effects. *Chem. Geol.* 59: 59–74.

HARRIS, P.T., O'BRIEN, P.E., SEDWICK, P. & TRUSWELL, E.M., 1996: Late Quaternary History of sedimentation on the MacRobertson Shelf, East Antarctica: problems with ^{14}C-dating of marine sediment cores. *Pap. Proc. R. Soc. Tasm.* 130(2): 00–00.

HILLAIRE-MARCEL, C., 1981: Paleo-oceanographic isotopique des mers post-glaciares du Quebec. *Paleogeogr. Paleoclimatol. Paleoecol.* 35: 63–119.

KINSMAN, D.J.J. & HOLLAND, H.D., 1969: The co-precipitation of cations with $CaCO_3$-IV. The co-precipitation of Sr^{+2} with aragonite between 16° and 96°C. *Geochim. Cosmochim. Acta* 33: 1–17.

KROOPNICK, P.M., 1985: The distribution of ^{13}C of CO_2 in the world oceans. *Deep Sea Res.* 32: 57–84.

KROOPNICK, P.M., MARGOLIS, S.V. & WONG, C.S., 1977: ^{13}C variations in marine carbonate sediments as indicators of the CO_2 balance between the atmosphere and the oceans. *In* Anderson, N.R. & Malahoff, A.(Eds): *THE FATE OF FOSSIL FUEL CO_2 IN THE OCEANS.* Plenum Press, New York, NY: 305–321.

ISRAELSON, C., BUCHARDT, B., FUNDER, S. & HUBBERTEN, H.W., 1994: Oxygen and carbon isotope composition of Quaternary bivalve shells as a water mass indicator: Last interglacial and Holocene, East Greenland. *Paleogeogr. Paleoclimatol. Paleoecol.* 111: 119–134.

MCCONNAUGHEY, T., 1989: ^{13}C and ^{18}O isotopic disequilibrium in biological carbonates. I. Patterns. *Geochim. Cosmochim. Acta* 53: 151–162.

MORSE, J.W. & MACKENZIE, F.T., 1990: *GEOCHEMISTRY OF SEDIMENTARY CARBONATES.* Elsevier, Amsterdam: 707 pp.

MUCCI, A., 1987: Influence of temperature on the composition of magnesian calcite overgrowths precipitated from seawater. *Geochem. Cosmochim. Acta* 5: 1977–1984.

NELSON, C.S., 1988: An introductory perspective on non-tropical shelf carbonates. *Sediment. Geol.* 60: 3–12.

PATTERSON, W.P. & WALTER, L.M., 1994: Depletion of ^{13}C in seawater $\sum CO_2$ in modern carbonate platforms: Significance for the carbon isotopic record of carbonates. *Geology* 22: 885–888.

RAO, C.P., 1981: Criteria for recognition of cold-water carbonate sedimentation: Berriedale Limestone (Lower Permian), Tasmania, Australia. *J. Sediment. Petrol.* 53: 117–129.

RAO, C.P., 1993: Carbonate minerals, oxygen and carbon isotopes in modern temperate bryozoa, eastern Tasmania, Australia. *Sediment. Geol.* 88: 123–135.

RAO, C.P., 1994: Implications of isotopic fractionation and temperature on rate of formation of temperate shelf carbonates, eastern Tasmania, Australia. *Carbonates Evaporites* 9: 33–41.

RAO, C.P. & GREEN, D., 1982: Oxygen and carbon isotopes of Early Permian cold-water carbonates of Tasmania, Australia. *J. Sediment. Petrol.* 52: 1111–1125.

RAO, C.P. & HUSTON, D., 1995: Temperate shelf carbonates reflect mixing of distinct water masses, eastern Tasmania, Australia. *Carbonates Evaporites* 1: 105–113.

RAO, C.P. & JAYAWARDANE, M.P.J., 1994: Major minerals, elemental and isotopic composition in modern temperate shelf carbonates, eastern Tasmania, Australia: Implications for the occurrence of extensive ancient non-tropical carbonates: *Paleogeogr. Paleoclimatol. Paleoecol.* 107: 49–63.

SMITH, N.R., DONG, Z., KERRY, K.R. & WRIGHT, S., 1984: Water masses and circulation in the region of Prydz Bay, Antarctica. *Deep Sea Res.* 31: 1121–1147.

STUIVER, M., DENTON, G.H., HUGHES, T.J. & FASTOOK, J.L., 1981: History of marine ice sheet in West Antarctica during last glaciation: a working hypothesis. *In* Denton, G.H. & Hughes, T.J. (Eds): *THE LAST GREAT ICE SHEETS.* Wiley Interscience, New York: 319–436.

TAVIANI, M., 1991: Stable isotope composition of Recent Antarctic biogenic carbonates and its bearing to the problem of ancient cold water limestones. *6TH INTERNATIONAL SYMPOSIUM, ANTARCTIC EARTH SCIENCES TOKYO, ABSTRACTS.* National Institute of Polar Research: 577.

TAVIANI, M. & AHARON, 1989: An assessment of stable isotope composition of calcareous modern benthic fauna from the Ross Sea (Antarctica). *Antarct. J. US* 24: 131–132.

TAVIANI, M., REID, D.E. & ANDERSON, J.B., 1993: Skeletal and isotopic composition and paleoclimatic significance of Late Pleistocene carbonates, Ross Sea, Antarctica. *J. Sediment. Petrol.* 63: 84–90.

TURNER, J.V., 1982: Kinetic fractionation of carbon-13 during calcium carbonate precipitation: *Geochim. Cosmochim. Acta* 46: 1183–1191.

WILSON, J.L., 1975: *CARBONATE FACIES IN GEOLOGIC TIME.* Springer-Verlag, New York: 471 pp.

(accepted 13 August 1996)