

TEMPERATE SHELF CARBONATES REFLECT MIXING OF DISTINCT WATER MASSES, EASTERN TASMANIA, AUSTRALIA

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ABSTRACT: In cold shallow seas undersaturated with CaCO_3 , carbonates disintegrate and dissolve away within a short period of time. Understanding the mixing of water masses from oceanographic and isotope point of view is important because these water masses provide nutrients and maintain CaCO_3 in cold shallow seawater.

Temperature and salinity variations in surface seawater off the coast of eastern Tasmania are caused by influxes of different waters. Water from Coral Sea water provided by the East Australian Current prevails in the summer, whereas Subantarctic water dominates during the winter. Throughout the year the Tasman Sea water is mixed with low salinity and low temperature deep Antarctic Intermediate water. The Antarctic Intermediate water and Subantarctic water contain an admixture of about 4% glacial melt water, resulting in $\delta^{18}\text{O}$ values that range from -0.8 to -1.7‰ SMOW. The $\delta^{13}\text{C}$ values are -0‰ in Antarctic Intermediate water and they are -1‰ in Subantarctic water.

The Tasmanian carbonates consist mainly of reworked calcitic fauna, such as bryozoans, foraminifera, echinoderms and red algae with variable intragranular CaCO_3 cements. The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ isotope fields of eastern Tasmanian bulk carbonates, bryozoans, benthic foraminifera and brachiopods overlap and all grade into the field typical of deep-sea carbonates. The trend lines of seafloor diagenesis and upwelling water pass through fields of temperate skeletons and bulk carbonates because they are in equilibrium with mixed seawaters having $\delta^{18}\text{O}$ values of -1 to 0‰ and $\delta^{13}\text{C}$ values of 0 to 1‰. They are forming at a slower rate than tropical water carbonates. Temperate carbonates form in zones of mixing of nutrient rich cold waters saturated with CaCO_3 and warmer shelf waters.

INTRODUCTION

Modern temperate carbonates are widespread on many mid- to high-latitude shelves (Lees 1975; Nelson 1988), including those around southern Australia (James et al. 1992, 1994). In Tasmanian waters, temperate shelf carbonates predominate over terrigenous clastics (Fig. 1; Davies and Marshall 1973; Rao 1981a). Accepting the concept of uniformitarianism, widespread temperate carbonates should be present in the rock record, but only a few have been documented (eg.; Nelson 1978; Brookfield 1988; Draper 1988; Rao 1988a; James and Bone 1989, 1992). This anomaly results from a lack of data on modern temperate carbonates and from inadequate temperature data for ancient carbonates. Available data on original carbonate mineralogy and elemental and O and C isotopic composition of ancient carbonates indicate the possibility of occurrence of extensive non-tropical carbonates in the rock record (Rao and Jayawardane 1994; Rao and Adabi 1994).

Earlier workers (Conolly and Von der Borch 1967; Wass et al., 1970) postulated that upwelling of nutrient-rich cold Antarctic waters over the shelf-slope break provided favorable conditions that allowed temperate carbonates to form. Oxygen and carbon isotope (Rao and Green 1983; Rao and Nelson 1992; Rao and Adabi 1992) studies support the role of mixing of water masses in the formation of temperate carbonates. In cold seas undersaturated with CaCO_3 , carbonates disintegrate and dissolve away within a short period of time (Alexandersson 1978). Understanding the mixing of water

masses from oceanographic and isotope point of view is important since these water masses provide nutrients and maintain saturation of CaCO_3 in seawater (Rao 1993b). Ancient nontropical carbonates should have been formed in the zones of mixing, where cold nutrient rich waters saturated with CaCO_3 encounter warmer shelf waters (Rao 1981b). The present study assesses temperature and salinity data around eastern Tasmania, as related to local water masses, freshwater input, variations in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in seawater, skeletal components and to the bulk carbonate.

SEDIMENTOLOGY

Tasmanian shelf carbonates, which occur at depth of 30 to 200 m, are composed mainly of bryozoans, foraminifera, molluscs, echinoderms and calcareous red algae (Rao and Jayawardane, 1993). Bryozoa, foraminifera and echinoderms range from 60 to 96% and thus they are the dominant faunal elements. Gastropods and bivalves (molluscs) are next in abundance (0 to 92%). Brachiopods are <1% in each sample. Skeletal grains range from fresh to etched, bored and encrusted by epibiota. Skeletons contain up to 90% intragranular cements (Rao 1981a, 1990a, 1993a). Bulk sediments contain mainly high-Mg and low-Mg calcite with minor amounts of aragonite (Rao and Adabi 1992). Geochemical trends involving Ca, Mg, Sr, Na, Mn, and Fe and their relation to $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ are indicative of marine diagenesis in cold waters (Rao 1986, 1990a, 1991; Rao and Adabi 1992) and do not show meteoric diagenetic trends.

TEMPERATE SHELF CARBONATES, EASTERN TASMANIA, AUSTRALIA

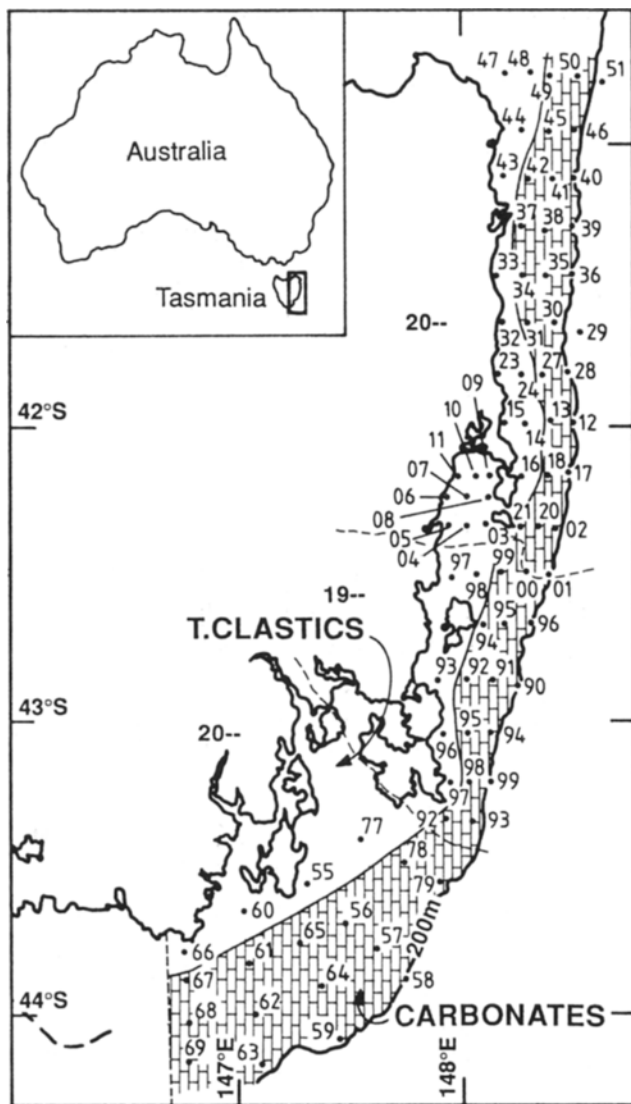


Figure 1. Location of samples on eastern Tasmanian shelf seawater. Numbers refer to samples studied. Note coastal sediments are terrigenous clastics (T. Clastics) and these grade into carbonate sediments with increasing water depth (>30 m).

METHODS OF STUDY

Samples (Fig. 1) were collected in 1973 on a 10 nautical mile grid (Davies and Marshall 1973). Dried, salt-free bulk sediment samples were crushed and reacted with 100% anhydrous H_3PO_4 at 25°C. The evolved CO_2 gas was analyzed on a Micromass 602D at the University of Tasmania for $\delta^{18}O$ and $\delta^{13}C$. The precision of data is $\pm 0.1\%$ for both O and C. Table 1 lists bulk sediment isotope data. Temperature and salinity measurements and satellite images are made by CSIRO, Marine Sciences, Hobart.

ISOTOPIC VARIATIONS IN TASMANIAN SHELF CARBONATES

The $\delta^{18}O$ and $\delta^{13}C$ isotope fields of eastern Tasmanian bulk sediments (this study), bryozoans (Rao 1993a), benthic foraminifera and brachiopods overlap the fields of temperate brachiopods from North Atlantic and South Pacific shallow seas (Fig. 2). All these isotope fields grade into the field typical of deep-sea carbonates (Fig. 2). Isotope fields for temperate water carbonates differ from those typical of tropical skeletons and bulk carbonates in having higher $\delta^{18}O$ values and a wider range of $\delta^{13}C$ values. Temperate carbonate isotopes do not fall on tropical aragonite-calcite mixture line (Fig. 2; Rao 1993a, b). They are therefore not in equilibrium with atmospheric CO_2 . The temperate carbonates are now forming in water depths from 30 to 200 m and their

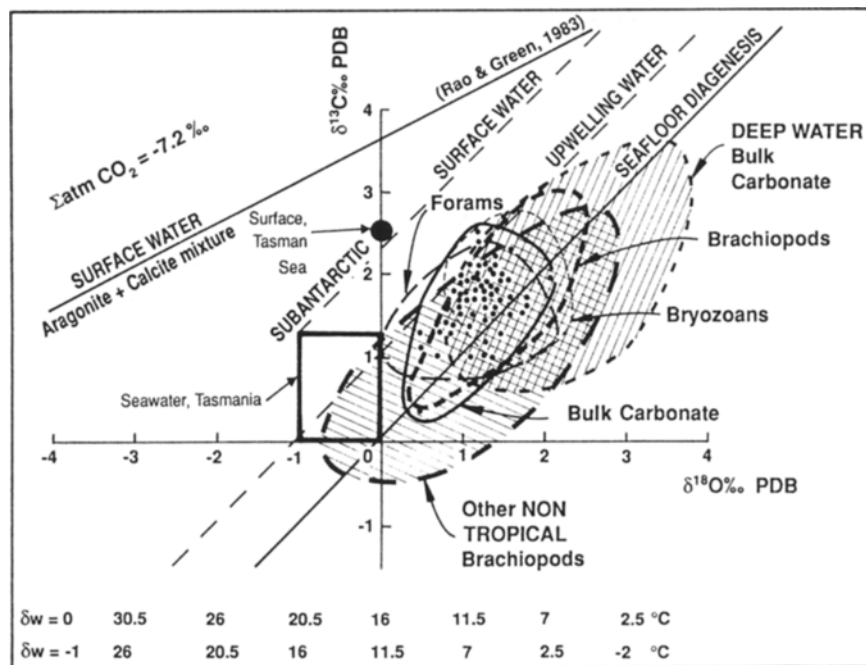


Figure 2. Variations of $\delta^{18}O$ and $\delta^{13}C$ isotopes of bulk sediments. Note bulk sediment isotope field overlaps eastern Tasmanian isotope fields of bryozoans (Rao 1993a), benthic foraminifera and brachiopods as well as brachiopods from other temperate regions. Note also that all these isotope fields grade into the deep-sea carbonate isotope field of Milliman (1974). Equilibrium line with atmospheric CO_2 for aragonite and calcite mixture (Rao and Green 1983) is separated from the temperate isotope fields because temperate skeletons and bulk carbonates are not in equilibrium with atmospheric CO_2 . The labels tropical surface water (Rao and Green 1983), Subantarctic surface water, surface Tasman Sea, Seawater Tasmania and upwelling water are $CaCO_3$ in equilibrium with such waters.

Table 1. O and C isotopes in (PDB) of bulk sediments, eastern Tasmania.

Sample No.	Bulk sediment		Sample No.	Bulk sediment	
	$\delta^{13}\text{C}\text{‰}$	$\delta^{18}\text{O}\text{‰}$		$\delta^{13}\text{C}\text{‰}$	$\delta^{18}\text{O}\text{‰}$
1902	1.6	1.0	2026	1.7	1.6
1903	1.7	1.0	2027	1.7	1.0
1904	1.9	1.0	2028	2.1	1.4
1905	2.0	1.4	2030	1.7	1.2
1906	1.7	1.0	2031	1.7	1.3
1907	2.0	1.4	2032	1.0	1.3
1908	2.1	1.1	2033	1.1	0.5
1909	1.9	1.2	2034	1.4	0.8
1990	1.9	1.1	2035	1.6	1.3
1991	1.3	0.5	2037	1.4	1.1
1992	1.3	1.3	2038	1.4	1.4
1993	1.2	1.2	2039	1.8	1.2
1994	1.9	1.5	2040	1.7	1.3
1995	1.4	1.4	2041	1.7	1.5
1996	1.5	1.2	2042	1.3	1.3
1998	1.3	1.3	2043	2.4	1.2
1999	1.4	1.0	2044	1.8	0.8
2000	1.6	1.2	2045	1.6	1.4
2001	2.2	1.4	2046	1.8	1.4
2002	1.9	1.5	2047	1.4	1.2
2003	1.0	1.1	2048	1.5	1.0
2004	1.5	1.4	2049	2.1	1.2
2005	0.4	0.5	2050	1.8	1.3
2006	1.8	1.4	2051	1.7	1.8
2007	1.5	1.1	2052	2.0	1.2
2011	1.3	0.7	2054	1.9	2.1
2012	1.6	1.8	2055	1.5	1.6
2013	1.4	0.9	2056	1.9	1.5
2014	1.4	1.1	2057	1.5	1.9
2015	1.3	1.1	2058	1.8	1.3
2016	1.3	0.9	2059	1.8	1.3
2017	1.7	1.0	2063	1.9	1.2
2018	1.9	1.3	2064	1.4	1.2
2020	1.8	1.3	2065	1.8	0.9
2021	2.1	1.3	2067	2.3	1.6
2024	1.3	1.5	2068	1.4	1.1
2025	1.0	0.7	2069	1.9	1.0
			2076	2.5	1.2

isotopic composition falls on trend lines of seafloor diagenesis and upwelling water pass through temperate skeletons and whole carbonates (Fig. 2). They are therefore in equilibrium with waters having $\delta^{18}\text{O}$ values of -1 to 0‰ (SMOW) and $\delta^{13}\text{C}$ values of 0 to 1‰ (Rao 1993b). The observed variation of $\delta^{18}\text{O}$ in Tasmanian shallow marine brachiopods and bulk carbonates (Fig. 3) results from strong seasonal effect caused by mixing with Subantarctic water masses in winter (Rao and Adabi 1992; Rao 1993b).

FLUID MIXING AND VARIATIONS IN SEAWATER TEMPERATURE, SALINITY, $\delta^{18}\text{O}$ AND $\delta^{13}\text{C}$

Satellite false color images around Tasmania in

summer (Fig. 4) and winter (Fig. 5) differ markedly due to mixing of water masses. In summer, seawater temperatures are warmer than winter ones due to influx of eastern Australian current. In winter, seawater temperatures decrease by the introduction of Subantarctic cold water.

The salinity and temperature of seawater off eastern Tasmania (Fig. 6) are influenced by water masses of four different origins (Newell 196; Harris et al. 1987): (1) Coral Sea water introduced by the East Australian current (CSW), (2) upwelling Antarctic Intermediate water (AIW), (3) Subantarctic water (SAW), and (4) Tasman Sea water (TSW). The salinity and $\delta^{18}\text{O}$ of seawater off eastern Tasmania (ETS) is governed by the following mixing equation:

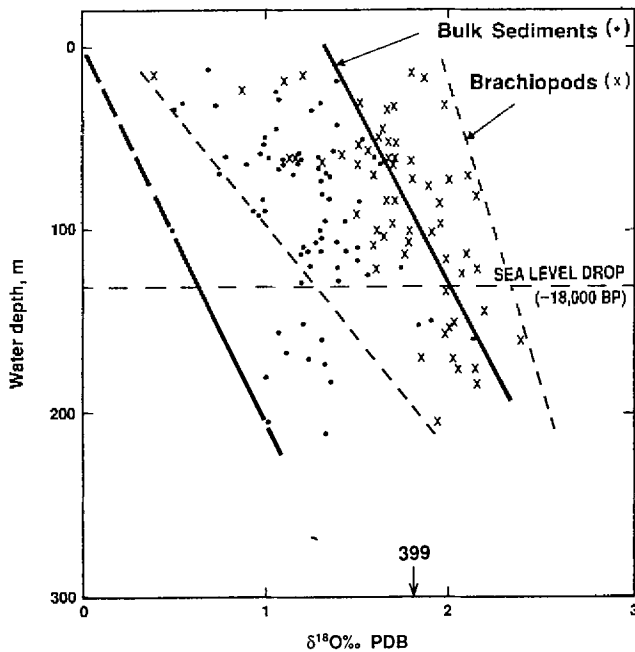


Figure 3. Variation of $\delta^{18}\text{O}$ values of bulk sediments and brachiopods from eastern Tasmania with water depth. $\delta^{18}\text{O}$ values become heavier with water depth due to decreasing water temperatures. Note that the $\delta^{18}\text{O}$ values in shallow waters (~30 m) vary considerably due to seasonal variations in surface water temperatures.

$$C_{i,EIS} = X_{CSW} C_{i,CSW} + X_{AIW} C_{i,AIW} + X_{SAW} C_{i,SAW} + X_{TSW} C_{i,TSW} \quad (1)$$

where C_{ij} = value of parameter i (eg. salinity or $\delta^{18}\text{O}$) in water mass j , and X_j = mass fraction of water mass j . Along with the effects of seasonal warming and cooling, equation (1) governs the temperature of seawater off the eastern Tasmanian coast. As surface Tasman Sea water masses are mixtures of Coral Sea and Subantarctic water (Fig. 7; Newell 1961; Harris et al. 1987), equation (1) reduces to:

$$C_{i,EIS} = X_{CSW} C_{i,CSW} + X_{AIW} C_{i,AIW} + X_{SAW} C_{i,SAW} \quad (2)$$

Temperature and salinity changes of eastern Tasmanian surface seawater (Fig. 7) are caused by changes in influx of different water masses with the changing seasons. The increases in temperature and salinity in summer (Fig. 7B and 7D) relate to the influx of Coral Sea water from the East Australian Current, whereas the decreases in temperature and salinity during winter result from a greater influx of Subantarctic or Antarctic Intermediate water (Fig. 7A and 7C). Throughout the year, the Tasman Sea water is mixed with low salinity and temperature deep Antarctic Intermediate water (Fig. 6). In summer, the subtropical convergence moves just south of Tasmania with the influx of Coral Sea water. In winter, the subtropical convergence moves northwards with the wind system, bringing cold, low-salinity Subantarctic water from the Circumpolar West Wind Drift around Tasmania. The decrease in both salinity and temperature is also due to convective overturn and mixing with deeper cooler and lower salinity waters (Rochford 1977).

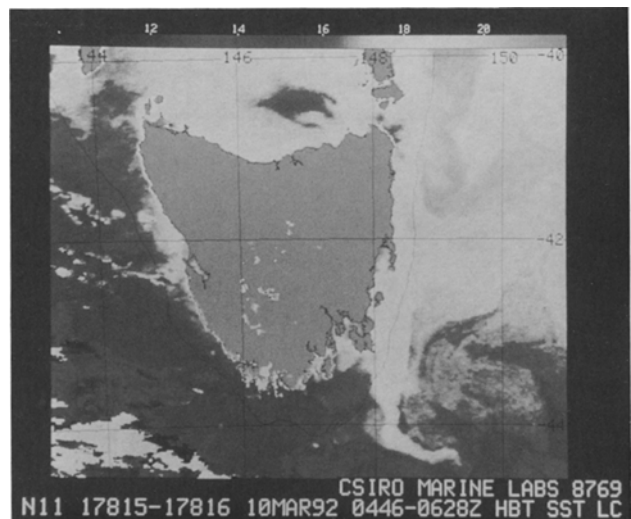


Figure 4. Satellite false color image in summer. Colors refer to summer surface seawater temperatures as indicated by the color bar, at top of the figure. Note introduction of eastern Australian current along eastern Tasmania.

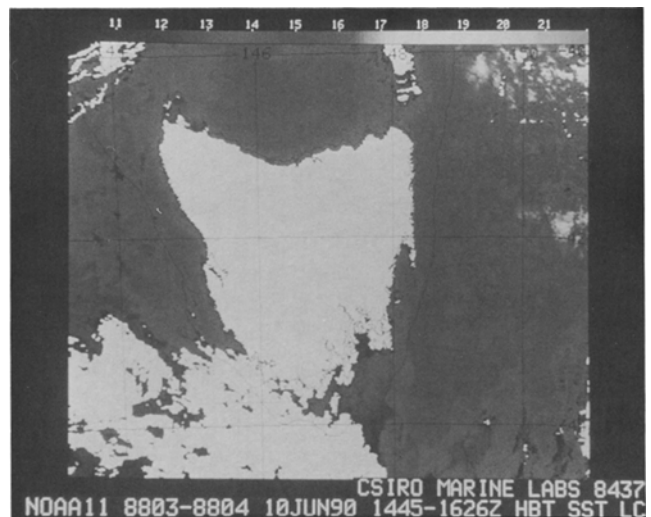


Figure 5. Satellite false color image in winter. Colors refer to winter surface seawater temperatures as indicated by the color bar, at the top of the figure. Cold water temperatures prevail in winter due to introduction of Subantarctic water around Tasmania.

$\delta^{18}\text{O}$ AND $\delta^{13}\text{C}$ VALUES OF THE WATER MASSES

Table 2 summarizes the temperature, salinity, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of each water mass present off eastern Tasmania. Although the temperature and salinity of each mass are well established, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of several water masses are poorly known and have to be estimated. Temperatures and salinities are high in the Coral Sea water because of warm atmospheric temperatures and high evaporation in low latitudes. Conversely, in the Tasman Sea and Subantarctic water salinities are lower because of cooler climate and lower evaporation (Rochford 1977; Edwards 1979). As few major rivers contribute freshwater runoff to Tasman Sea, the salinity de-

Table 2. Water masses and their temperatures and salinities (after Newell, 1961 and Harris et al., 1987), $\delta^{13}\text{C}$ (after Kroopnick et al., 1977) and estimated $\delta^{18}\text{O}$ values, eastern Tasmania, Australia.

Water mass	Temperature °C	Salinity ‰	$\delta^{18}\text{O}$ ‰SMOW	$\delta^{13}\text{C}$ ‰PDB
Surface Tasman Sea	<13 to 17°C	<35.0 to 35.6	0	2.5
Subantarctic water	0 to <12°C	34.1 to <35.0	-6 to -1.7	1.3
Coral Sea water	>21°C	35.7 to 35.8	>0 to 0.5	2
Antarctic intermediate water	3-5°C	34.4 to 34.6	-0.8 to -1.7	0

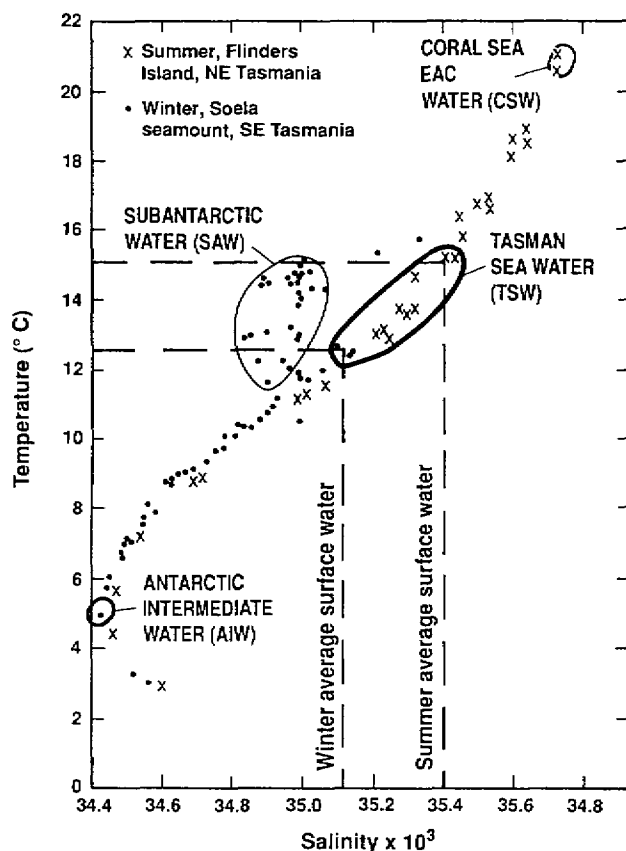


Figure 6. Variation of seawater temperatures and salinity at two stations from northeastern Tasmania (Flinders Island) and southeastern Tasmania (Soela seamount). Note the occurrence of four water masses, namely, Coral Sea water (CSW), Tasman Sea water (TSW), Subantarctic water (SAW) and Antarctic Intermediate water (AIW). Seawater in eastern Tasmania is a mixture of all these four types. See the text for further explanations.

crease from 35.7 to 34.2‰ is due to mixing with low salinity Subantarctic Sea water and upwelling deep water, complemented perhaps somewhat by local precipitation.

Antarctic Intermediate water can be regarded as the result of the mixing of small quantities of glacial melt water (GMW) into an average oceanic water (AOW). The portion of melt water can be estimated by solving the following for X_{GMW} :

$$S_{\text{IAW}} = X_{\text{GMW}} S_{\text{GMW}} + (1 - X_{\text{GMW}}) S_{\text{AOW}} \quad (3)$$

where S_i = salinity of water mass i . Using the Antarctic Intermediate water salinity of 34.4‰, the salinity of Coral Sea water of 35.7‰, and the salinity of glacial melt water of 0.0‰, the mass fraction of glacial melt water in the Antarctic Intermediate water is 4%. This mass fraction, together with the $\delta^{18}\text{O}$ values for average oceanic water (0‰ SMOW; Craig and Gordon 1965) and Antarctic Glacial meltwater (-30‰ SMOW; Rao and Green 1982), gives $\delta^{18}\text{O}$ value of Antarctic Intermediate water:

$$\delta^{18}\text{O}_{\text{AIW}} = X_{\text{GMW}} \delta^{18}\text{O}_{\text{GMW}} + (1 - X_{\text{GMW}}) \delta^{18}\text{O}_{\text{AOW}} \quad (4)$$

This estimate is -1.2‰. As melt waters from different parts of Antarctica vary from -20 to -43‰ SMOW (Hendy et al. 1979; Matsubaya et al. 1979), the $\delta^{18}\text{O}$ values of Antarctic Intermediate water can range from -0.8 to -1.7‰ SMOW, respectively.

Subantarctic water can also be regarded as the result of mixing of small quantities of high latitude precipitation and glacial melt water into surface sea water. As the minimum salinities of Subantarctic water of 34.2‰ are similar to those of Antarctic Intermediate water, its $\delta^{18}\text{O}$ values will also range from -0.8 to -1.7‰ SMOW. On the other hand, the Subantarctic water that mixes with the Tasman Sea surface water has an average salinity of ~34.9‰ (Fig. 6). The $\delta^{18}\text{O}$ values of such Subantarctic water will be therefore constrained to -0.5 to -0.7‰. Noteworthy is also the high nutrient content of these low salinity waters (Harris et al. 1987).

The distribution of $\delta^{13}\text{C}$ in world oceans (Kroopnick 1985) is controlled by equilibration with atmospheric CO_2 , replenishment in bottom water, and addition of CO_2 from organic matter decomposition and CaCO_3 dissolution. The $\delta^{13}\text{C}$ values in surface seawater are latitude dependent (Kroopnick et al. 1977) and vary from tropical (~2‰), through mid latitudes (~-2.5‰) to high latitudes (~-1.3‰) due to addition of $\delta^{13}\text{C}$ depleted water along the equator and at high latitudes. $\delta^{13}\text{C}$ values decrease from 2.5 to 1.3‰ in surface seawater between about 40° and 60°S, as water temperature decreases from 12° to 0°C. Bottom water $\delta^{13}\text{C}$ values decrease due to the addition of ^{12}C ($\delta^{13}\text{C} < -20$ ‰) from oxidizing organic matter (Kroopnick 1985). In most deep seawaters $\delta^{13}\text{C}$ is 0‰—except for the oldest deepwater, such as in the North Pacific where it is -0.5‰. Where deep seawater rises and mixes with

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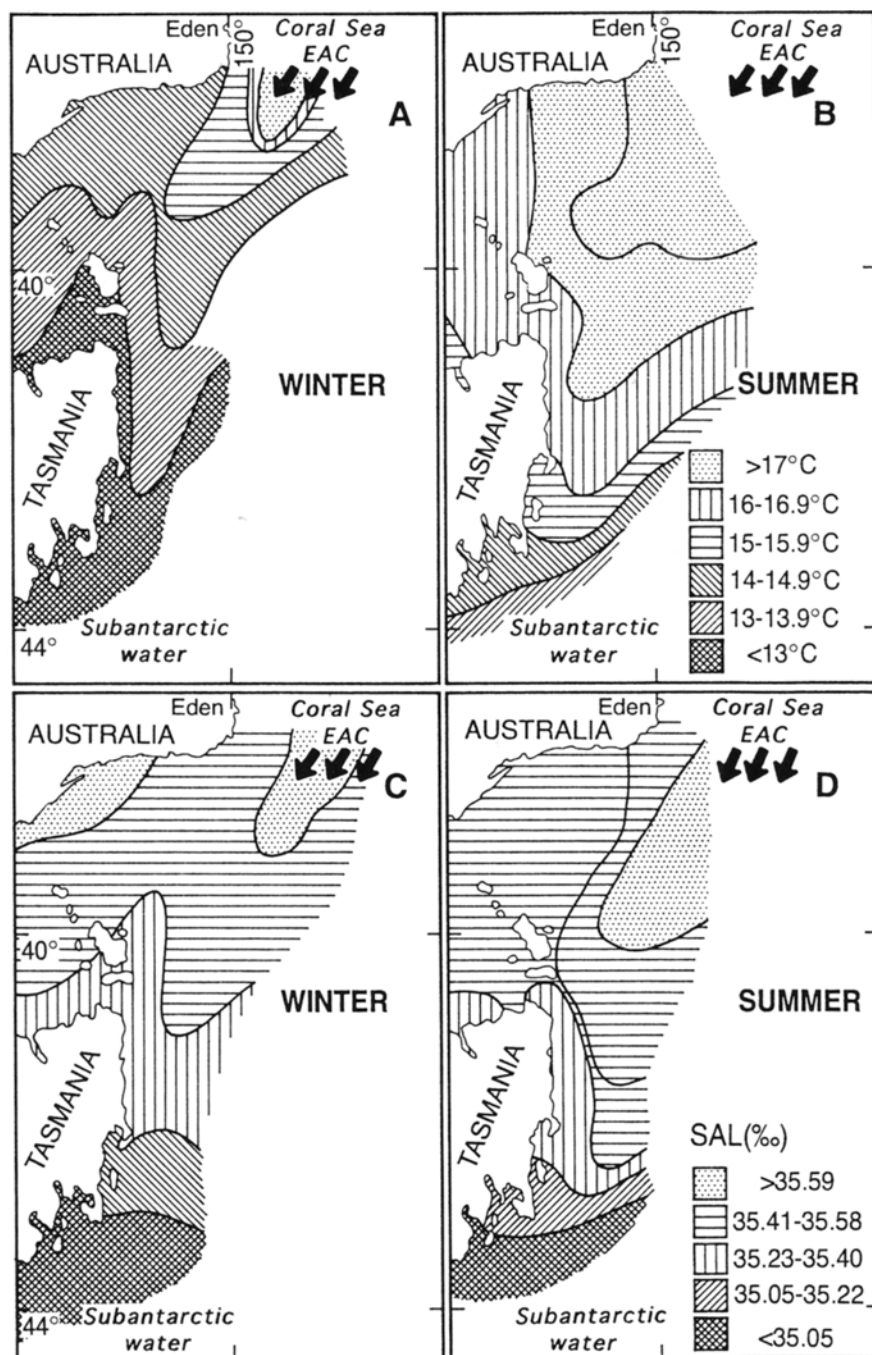


Figure 7. Salinity and temperature variations in surface seawaters from eastern Tasmania (after Newell 1961). Temperatures and salinity off the coast of eastern Tasmania are caused by changes in the fluxes of Coral Sea water from the East Australian Current in summer and from Subantarctic water in winter.

shallow waters, the $\delta^{13}\text{C}$ in shallow waters decreases to values of 0.5‰ or less.

OXYGEN AND CARBON VARIATIONS IN CARBONATES: RELATION TO MIXING OF WATER MASSES

Temperature dependent fractionation of $\delta^{18}\text{O}$ in calcite is well established (Friedman and O'Neil 1977), so calcite formation temperatures can be calculated using the equation of Shackleton and Kennett (1974):

$$T^{\circ}\text{C} = 16.9 - 4.38 (\delta\text{c} - \delta\text{w}) + 0.10 (\delta\text{c} - \delta\text{w})^2 \quad (5)$$

(δc being the $\delta^{18}\text{O}$ of calcite and δw being $\delta^{18}\text{O}$ of formation

water). Using seawater $\delta^{18}\text{O}$ values of -1 to 0‰, the temperatures of seawater in equilibrium with Tasmanian bulk carbonates ranges from $\sim 2^{\circ}$ to $\sim 15^{\circ}\text{C}$ (Fig. 2), similar to the range obtained from $\delta^{18}\text{O}$ values of Tasmanian brachiopods as well as to measured temperatures of ~ 2 to 17°C off the east coast of Tasmania (Fig. 7). Thus, the variations in $\delta^{18}\text{O}$ values in Tasmanian carbonates are due to temperature changes associated with the mixing of water masses.

The cause of $\delta^{13}\text{C}$ variations in marine carbonate includes: (1) equilibrium with atmospheric CO_2 (Romanek et al. 1992), (2) kinetic fractionation during CO_2 hydration and hydroxylation, (3) variations in $\delta^{13}\text{C}$ of seawater with depth, (4) equilibrium with bicarbonate in seawater (Rubinson

and Clayton 1969; Emrich et al. 1970), (5) fractionation during precipitation, and (6) mixing water masses and equilibrium formation of calcite.

Although at equilibrium with atmospheric CO₂ would result in a positive trend between δ¹⁸O and δ¹³C in carbonate minerals (Fig. 2; Rao and Green 1983; Rao 1993a, b), the temperate carbonates are not in equilibrium with atmospheric CO₂. This is because: (1) they were deposited at 30 to 200 m water depth (2) temperature variations from 0 to 15°C alone would produce a total δ¹³C range from ~-3.5 to 5‰, significantly greater than the observed variations, and (3) the atmospheric δ¹³C would have to be about -10‰, at odds with the known values of around -7‰ (Francis 1980).

Kinetic fractionation during CO₂ hydration and hydroxylation common to many tropical biological carbonates (McConnaughey 1989) causes simultaneous depletions of both δ¹⁸O and δ¹³C in such carbonates. Kinetic fractionation for δ¹⁸O-bearing molecules is twice that of δ¹³C-bearing molecules (Grossman 1984), resulting in a slope of 0.5. As the slopes of Tasmanian carbonate isotope fields are roughly one (Fig. 2), kinetic effects do not dominate in Tasmanian carbonates.

δ¹³C values in seawater vary from about 2.5‰ at the surface to about 0‰ in the oxygen minimum zone (~500m) and bottom waters are generally between -0.2 to 0.2‰ in a 'typical' mid-latitude Pacific Ocean (Kroopnick et al. 1977). This decrease in δ¹³C of aqueous CO₂ with increasing water depth results from variable productivity and mixing of water masses, particularly where upwelling cold, deep polar waters add isotopically light δ¹³C from oxidation of organic matter at depth. Calcite formed from seawater will have δ¹³C values between ~-3.3‰ at the surface to ~-1‰ at the oxygen minimum and below (using Romanek et al. 1992 fractionation factors). As bottom waters tend to be colder than surface waters, δ¹⁸O of calcite would increase with decreasing temperature and have a negative correlation with δ¹³C, as opposed to the observed positive correlation.

Using experimental data on calcite-bicarbonate and aragonite-bicarbonate temperature dependence (Emrich et al. 1970; Morse and MacKenzie 1990) and δ¹³C_{HCO₃} of 0‰, Tasmanian carbonates formed over the range of 0 to 15°C should have values of -0.5 to 0.2‰ in calcite and 1.4 to 2.1‰ in aragonite. As the mineralogy of Tasmanian carbonate is mainly calcite with minor aragonite (Rao and Adabi 1992), the range of δ¹³C values in Tasmanian carbonates should be 0‰ ±0.5 in contrast to the observed (0.4 to 2.9‰).

Experimental study (Turner 1982) indicates that calcite-bicarbonate fractionation increases with decreasing rate of precipitation from 0.4 to 2.3‰ ±0.3. At faster precipitation rates non-equilibrium conditions exist due to strong kinetic fractionation. At slower precipitation rates, on the other hand, thermodynamic equilibrium favors precipitation of the

heavier ¹³C-bearing ions (Turner 1982). Slower precipitation from colder water would facilitate a near equilibrium calcite-bicarbonate fractionation and higher δ¹³C, whereas rapid precipitation from warmer waters would result in lower calcite-bicarbonate fractionation and lower calcite δ¹³C values by up to 2‰. Application of experimental inverse relationship of δ¹³C values and rate of precipitation in temperate skeletons and whole carbonate indicates slow rate of formation with brachiopods forming at the slowest rate, bryozoa at moderate rate and forams at fastest rate (Rao 1994).

Slower rate of skeletal formation in Tasmanian temperate carbonates, relative to warm water carbonates, is indicated by extensive borings, encrustations on fauna and cementation (Rao 1981a, 1990; Rao and Adabi 1992; Rao 1994). As both δ¹⁸O and δ¹³C are positively correlated with a slope of 1 (Fig. 2), temperature controls on calcite deposition rates could effect the calcite-bicarbonate fractionation significantly and cause the observed variation in δ¹³C and the correlation between δ¹⁸O and δ¹³C in eastern Tasmanian carbonates. The scatter about the observed correlation trend, which is bracketed by the seafloor diagenesis and upwelling trend of Rao (1993a), could be caused by small variations (~1‰) in δ¹⁸O and δ¹³C in eastern Tasmanian water from the mixing of water masses. As both trend lines of seafloor diagenesis and upwelling water pass through the origin at 0‰, the δ¹³C values of Tasman Sea are 0‰ due to strong mixing with upwelling of deep water.

As δ¹⁸O and δ¹³C values are positively correlated in temperate carbonates, the δ¹³C values of brachiopods and even bulk carbonates can be used to determine equilibrium temperatures in the empirical equation:

$$T^{\circ}\text{C} = -4.5 (\delta^{13}\text{C}_{\text{calcite}}) + 16$$

In ancient carbonates, the δ¹³C values tend to be near marine values, despite pronounced phreatic meteoric diagenesis (Lohmann 1988). Therefore, the marine δ¹³C values can be used to estimate temperatures in ancient carbonates considered to be cold water in origin on geological and geochemical evidence. Application of this δ¹³C approach in paleo-temperature measurements for cold-water Permian (Rao and Green 1982) and Ordovician (Brookfield 1988) have given reasonable ambient water temperatures.

CONCLUSIONS

The salinity and temperature of seawater off eastern Tasmania are influenced by four different water masses, namely, Coral Sea water, Subantarctic water, Tasman Sea water and upwelling Antarctic Intermediate water. In summer, the subtropical convergence moves just south of Tasmania with the introduction of the Coral Sea water from the East Australian Current. In winter, the subtropical convergence moves northwards with the introduction of cold, low-salinity Suban-

tartic water around Tasmania. Throughout the year the local Tasman Sea water is mixed with low salinity and cold deep Antarctic intermediate water.

Subantarctic water and Antarctic Intermediate water contain 4% of glacial melt water and thus their $\delta^{18}\text{O}$ values range from -0.8 to -1.7‰ considering -20 to -43‰ SMOW melt waters around Antarctica. The well mixed Subantarctic water with Tasman Sea water may have $\delta^{18}\text{O}$ values of around -0.5‰. The $\delta^{13}\text{C}$ values are -1‰ in Subantarctic waters and 0‰ in Antarctic Intermediate waters.

The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ isotope fields of eastern Tasmanian bulk sediments, bryozoans, benthic foraminifera and brachiopods overlap other brachiopods from North Atlantic and South Pacific shallow seas and deep-sea bulk carbonates. Positive correlation exists between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values with a slope of 1 in temperate carbonates because of thermodynamic equilibrium at slower rates of skeletal growth than tropical counterparts. The trend line of seafloor diagenesis passes through temperate skeletons and bulk carbonates and deep-sea bulk carbonates because these carbonates are in equilibrium with waters with both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of 0‰. The upwelling water trend line also passes through some skeletons and bulk carbonates of Tasmania. This is because Tasmanian carbonates are in equilibrium with mixed seawater with $\delta^{18}\text{O}$ values of -1 to 0‰ and $\delta^{13}\text{C}$ values of 0 to 1‰.

Temperate shelf carbonates form in areas of mixing of water masses. Mixing and upwelling of cold waters provides nutrients and maintains saturation of CaCO_3 in cold, undersaturated shallow seas.

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