

# MINERALOGY AND GEOCHEMISTRY OF MODERN TEMPERATE CARBONATES FROM KING ISLAND, TASMANIA, AUSTRALIA

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**ABSTRACT:** Shelf sediments around King Island range from siliciclastics to mixed carbonates and to pure carbonates. Carbonates consist mainly reworked calcitic fauna, such as bryozoans, foraminifera, echinoderms and red algae with minor intragranular  $\text{CaCO}_3$  cements. Gastropods are the main aragonitic fauna and these are rare. Bulk sediments are analyzed by both X-ray diffraction, atomic absorption spectrophotometry, X-ray fluorescence and mass spectrometry. Minerals detected by XRD are mainly high-Mg calcite, quartz and aragonite with minor low-Mg calcite. The Ca, Mg and  $\text{SiO}_2$  contents confirm the occurrence of siliciclastics to mixed carbonates and to pure carbonates. The concentrations of Sr and Na vary with carbonate mineralogy and skeletal content. The high Fe and Mn contents in calcite are due to sedimentation in reducing marine environments.

The  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  field of bulk sediments overlaps isotope fields of bryozoans, foraminifera and brachiopods. All these isotope fields are dissected by both trendlines of seafloor diagenesis and upwelling water because sediments and fauna are in equilibrium with marine waters. The ambient water temperatures determined from  $\delta^{18}\text{O}$  values range from about 10 to 15°C, which are about 3°C lower than measured surface water temperatures.

Originally calcitic ancient carbonates are abundant in stratigraphic sequences and their geochemistry can be better understood by comparison with baseline geochemical data of modern temperate calcitic carbonates rather than with modern tropical aragonitic carbonates. Many of these ancient originally calcitic bryozoan, foraminifera and echinoderm carbonates are of nontropical origin as coeval tropical aragonitic carbonates occur elsewhere.

## INTRODUCTION

Recognition of ancient non-tropical carbonates is a problem, because modern nontropical carbonates occur on many temperate (Lees, 1975; Nelson, 1988) and polar (Domack, 1988) shelves and yet, only a few ancient non-tropical carbonates have been recognized (e.g. Nelson, 1978; Rao, 1981a, 1988a, b; Brookfield, 1988; Draper, 1988; James and Bone, 1989, 1992). This paucity exists because we need to know more on modern non-tropical carbonates that aid in the interpretation of temperatures of formation of ancient carbonates. The present study deals with mineralogy and elemental and isotopic composition of modern temperate carbonates and associated siliciclastics from King Island, Tasmania, Australia (Fig. 1).

Modern temperate carbonates differ from tropical ones in types of skeletal (mainly bryozoans, foraminifera, echinoderms and molluscs) and non-skeletal grains (mainly intraclasts; Lees, 1975), mineralogy and diagenesis (Alexandersson, 1978; Rao, 1981 b; Reeckmann, 1988; Rao and Adabi, 1992; James and Bone, 1992), oxygen and carbon isotopes (Rao and Green, 1983; Rao and Nelson, 1992), and in major and minor elements (Rao, 1986, 1990a). These data with those from western Tasmania (Rao, 1990a; Rao and Adabi, 1992; Rao and Nelson, 1992), eastern Tasmania (Rao, 1993; Rao and Stait, 1993) and from the present study of samples from King Island should help in the recognition of ancient temperate carbonates and also serve as

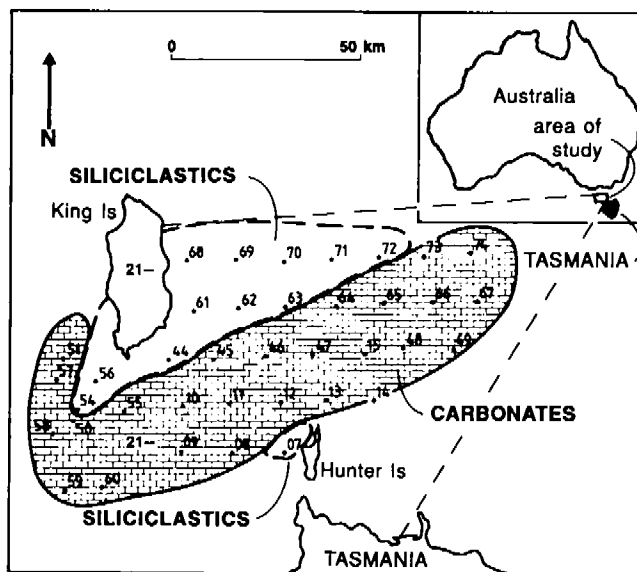


Fig. 1. Location of samples from King Island, Tasmania, Australia. Note that siliciclastics occur close to King Island and Hunter Island, whereas carbonates occur away from coastal areas.

a data base for contrasting marine diagenesis with meteoric and burial diagenesis of originally predominantly calcitic limestones, which are abundant in ancient sequences

METHODS OF STUDY

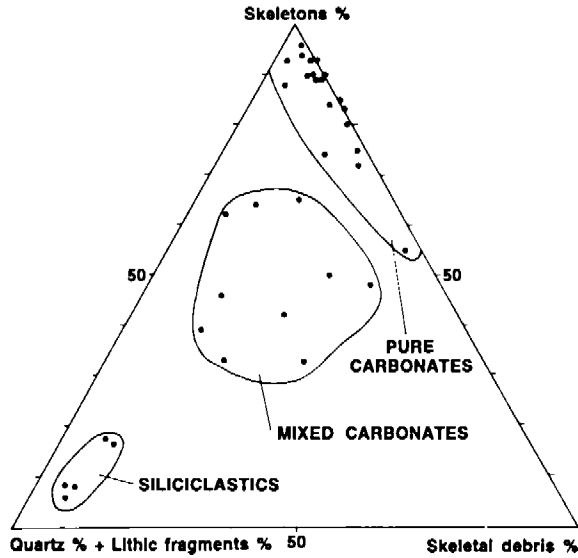


Fig. 2. Petrographic estimates of relative percentages of skeletons, skeletal debris and quartz and lithic fragments. Note occurrence of pure carbonates to mixed carbonates (impure carbonates) to siliciclastics from King Island.

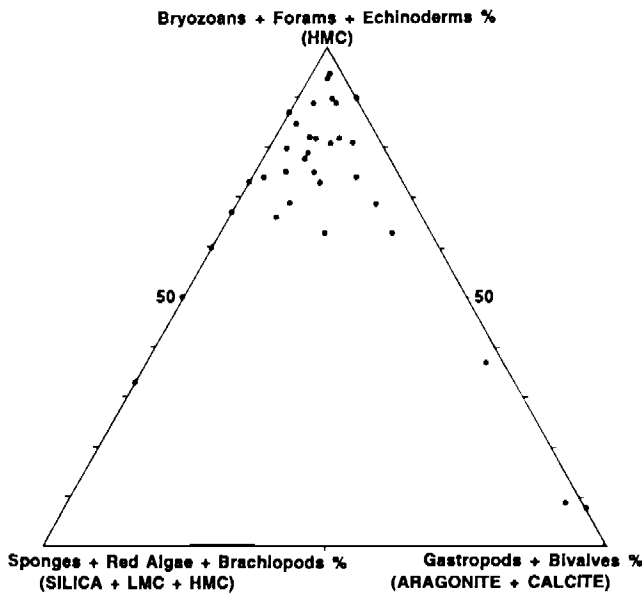


Fig. 3. Petrographic estimates of relative percentages of major groups of biota in King Island sediments. Note bryozoans, foraminifera and echinoderms are the dominant faunal elements and these are mainly high-Mg calcite skeletons. HMC=High-Mg calcite; LMC=Low-Mg calcite.

(James and Bone, 1989, 1992). King Island is situated (Fig. 1) northwest of Tasmania (39°5 to 40°3S) in Tasmania and thus occurs between cool temperate to warm temperate regions. King Island samples are composed of both siliciclastics and carbonates, unlike pure carbonates (<10% insoluble residue) studied earlier from western Tasmania from about 30 to 200m water depth range (Rao, 1990a; Rao and Adabi, 1992).

Surface sediment samples studied (Fig. 1) are grab samples, which were collected several years ago on a 10 nautical-mile grid (Davies and Marshall, 1973). Bulk sediment powders were analyzed by X-ray diffraction (XRD) for quartz, calcite and aragonite. The peak area ratios of quartz, calcite and aragonite were used in the calculation of percentages of these minerals. The same powders used for XRD analyses were dissolved in IN HCl and analyzed by Atomic Absorption Spectrophotometry (AAS) for Ca, Mg, Sr, Na, Fe and Mn concentrations. The detection limits are +1% for Ca and Mg and +5% for Sr, Na, Mn and Fe (Robinson, 1980). Residues left after this acid dissolution of carbonate were used in the calculation of insoluble residue contents. These elements are reported here as raw values because numbers are found to be statistically simpler. Selected samples are analyzed for SiO<sub>2</sub> by X-ray fluorescence. D-spacings of calcites from XRD are compared with Mg contents from AAS to determine the spectrum of low- to high-Ma calcites. Portions of the same carbonate powders used for XRD and AAS were allowed to react with 100° C phosphoric acid in reaction tubes and vacuum at 25° C for 24 hours. The CO<sub>2</sub> extracted from each sample was analysed for δ<sup>18</sup>O and δ<sup>13</sup>C by mass spectrometry (Micromass, 602D). Precision of data is +0.1% for both δ<sup>18</sup>O and δ<sup>13</sup>C and all data are reported as 1% values vs the PDB standard using conventional delta (δ) notation (Craig, 1957). The King Island insoluble residue%, carbonate%, aragonite%, calcite% and quartz% and δ<sup>18</sup>O and δ<sup>13</sup>C values and Ca, Mg, Sr, Na, Mn and Fe values are analyzed by correlation and factor analysis using Statview programme on MacIntosh computer.

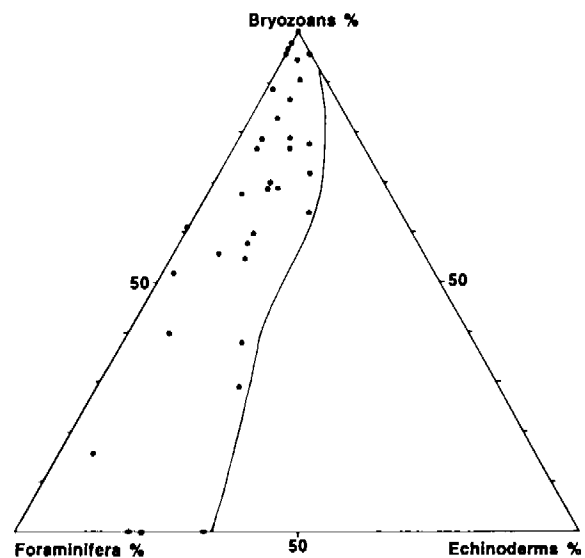


Fig. 4. Petrographic estimates of relative percentages of bryozoans, foraminifera and echinoderms. Note King Island fauna varies mainly between bryozoans and foraminifera.

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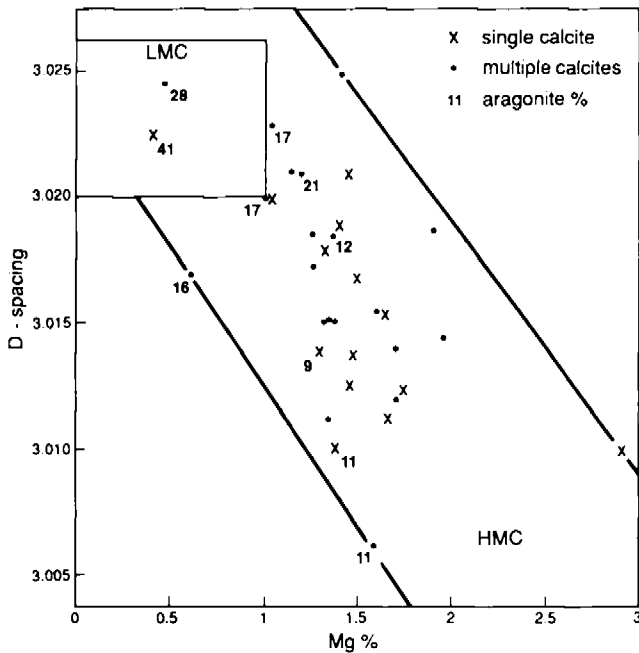


Fig. 5. Plot of calcite D-spacing from X-ray diffraction (XRD) and Mg% from AAS analysis. Note high-Mg calcites (HMC) predominate over low-Mg calcites (LMC) and many samples contain a spectrum of more than one calcite peak due to occurrence of multiple calcites.

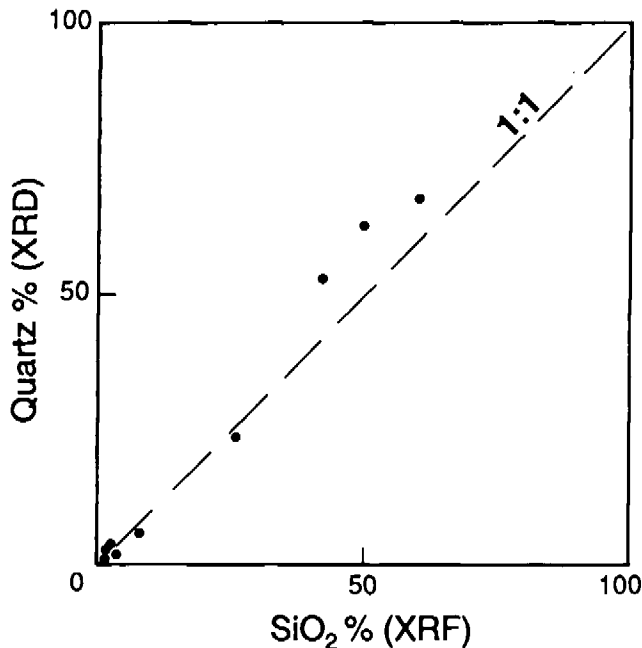


Fig. 6. Plot of quartz % from XRD and  $\text{SiO}_2$  % from XRF. Note samples fall close to 1:1 slope of Quartz % and  $\text{SiO}_2$  %.

### KING ISLAND SEDIMENTS

King Island shelf sediments range from pure terrigenous clastics, to mixed clastics and carbonates, to pure carbonates (Davies and Marshall, 1973). Their distribution based on 50% quartz content, determined by XRD, shows

that terrigenous clastics occur in shallow settings around King Island and these grade to carbonates further offshore (Fig. 1). Volumetric petrographic estimates (Figs. 2, 3 and 4) indicate King Island sediments are composed mainly of skeletons, skeletal debris and quartz and lithic fragments (Fig. 2) and range from siliciclastics, to mixed clastics and carbonates to pure carbonates. The amount of quartz ranges from 0 to 88 % and it occurs in much higher concentrations than lithic fragments (<10%). Skeletal debris ranges up to 40% and consists of unrecognizable skeletons. Skeletons range from about 10 to 96% and they are abundant in pure carbonates (Fig. 2). These skeletons are reworked and are moderate to well sorted. Some fauna are encrusted by new bryozoans and worm tubes due to slow rate of sedimentation.  $\text{CaCO}_3$  cementation within chambers of fauna is minor relative to the large amount (up to 90%) of cements in western Tasmanian carbonates (Rao, 1981b, 1990a; Rao and Adabi, 1992).

The biota in King Island sediments can be divided into three major groups based on relative abundance and mineralogy of biota (Fig. 3). Bryozoa, foraminifera and echinoderms range from 60 to 96% in most samples and this they are the dominant faunal elements. These fauna are predominantly high-Mg calcites (Milliman, 1974; Rao, 1981b; Morse and MacKenzie, 1990). Gastropods and bivalves (molluscs) are next in abundance (0-92%). They comprise of either aragonite (gastropods) or calcite to aragonite mixed mineralogies (bivalves). The third group comprises of 0-67% of fauna and it is dominated by siliceous sponge spicules, moderate high-Mg calcite red algae and minor low-Mg calcite brachiopods. Thus, King Island biota is characterised by high-Mg calcite mineralogy with minor amounts of low-Mg calcite and quartz.

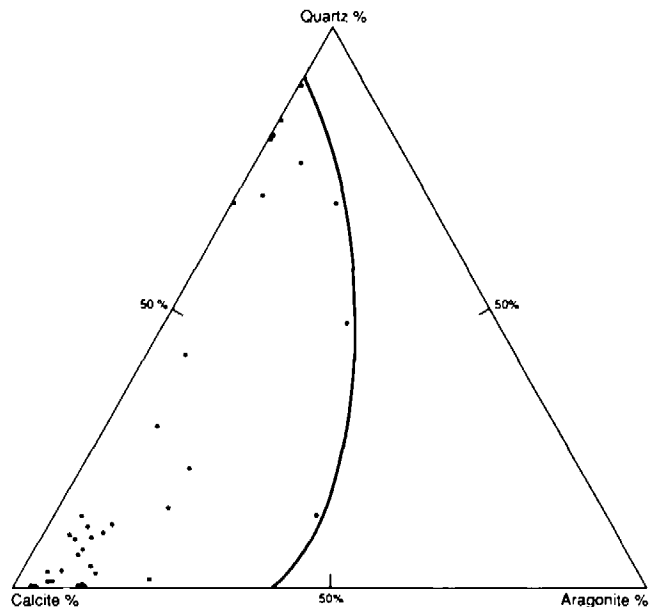


Fig. 7. Variation of contents of calcite, aragonite and quartz. Note that the King Island samples vary mainly between contents of calcite and quartz and carbonate minerals are mainly mixtures of calcite (high-Mg calcite) and aragonite.

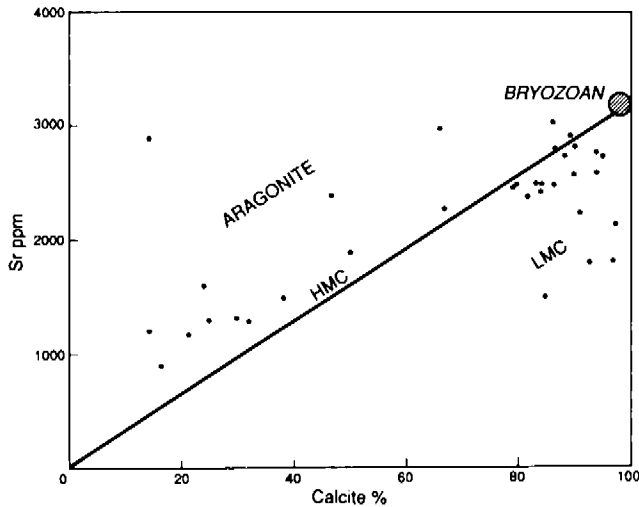


Fig. 8. Plot of calcite% against Sr ppm; solid line is the regression line. Note Sr content increases with increasing bryozoan and aragonite content.

Relative per cent estimates of bryozoans, foraminifera and echinoderms in King Island sediments (Fig. 4) reveal that bryozoans are the dominant fauna (~50-100%) in most samples with variable amounts of foraminifera (0-80%) and minor amounts of echinoderms (0-33%). Modern temperate carbonate fauna are considered to be either *foramol assemblages* (foraminifera and mollusca; Lees, 1977) or *bryomol assemblages* (bryozoans and mollusca; Nelson, 1988). In contrast to these, King Island fauna are mainly composed of bryozoan and foraminifera assemblages (Fig. 4) probably due to carbonate sedimentation in off-shore regions (Fig. 1).

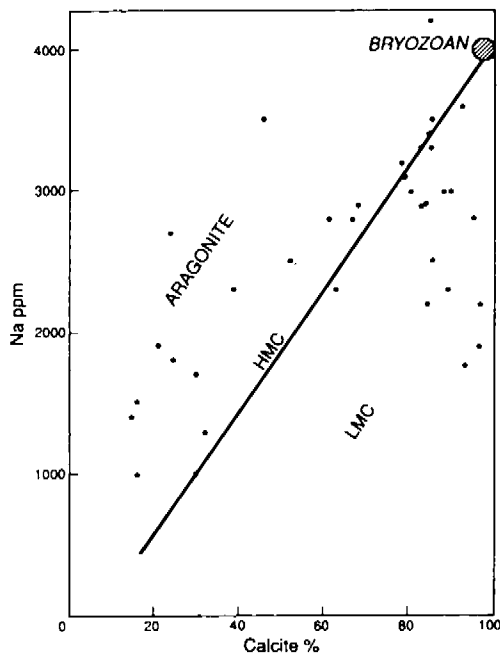


Fig. 9. Plot of calcite% against Na ppm; note Na content increases with increasing bryozoan content and aragonite content.

The King Island bulk sediments data on mineralogy, major and minor elements and oxygen and carbon isotopes are listed in Table 1. Data on individual fauna are not yet made for lack of funds.

MINERALOGY

The plot of values of D-spacing of major calcite peaks obtained from XRD analysis against Mg% determined from AAS analysis (Fig.5) shows that the major carbonate minerals in the King Island bulk samples are mainly a spectrum of high-Mg calcites (38-98%) and aragonite (0-41%) with minor amounts of low-Mg calcite (0-84%; mostly <10%). This carbonate mineralogy is different from western Tasmanian one, which is mainly a mixture of high- to low-Mg calcites and minor aragonite (Rao and Adabi, 1992). Lack of appreciable amounts of low-Mg calcite in the King Island samples is due to warmer water temperatures >5°C because experimental studies (Kinsman and Holland, 1969; Burton and Walter, 1987) indicate that low-Mg calcite predominates at water temperatures <5°C. Mg content in calcitic fauna, such as bryozoa, foraminifera, echinoderms and red algae, also decreases with decreasing water temperatures (Morse and McKenzie, 1990; Rao and Adabi, 1992).

Quartz is a major non-carbonate mineral detected in X-ray diffractograms. Other non-carbonate minerals are minor and they are mostly feldspars and clays. The quartz% determined by XRD is plotted against SiO<sub>2</sub> (Fig.6) obtained from X-ray Fluorescence (XRF). As most samples plot near 1:1 slope between quartz% and SiO<sub>2</sub>, the percentage determinations of quartz from XRD are reasonable ones. Many samples contain >50% quartz (Fig. 1) as there is appreciable amounts of terrigenous clastics in samples shoreward from King Island.

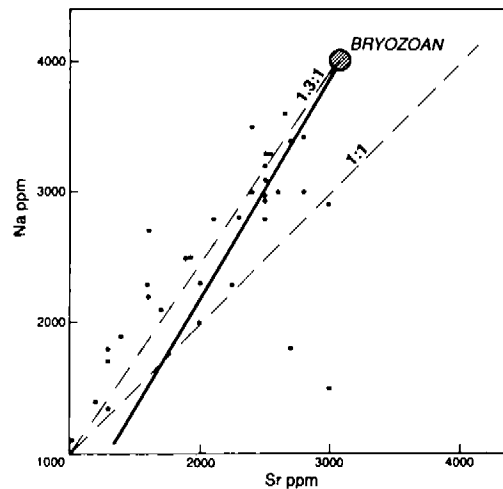


Fig. 10. Plot of Sr ppm versus Na ppm; solid line is the regression line. Note the ratio of Na:Sr range mostly from 1.3:1 to 1:1.

The triangular diagram (Fig. 7) depicting mineralogical variations indicates that King Island bulk samples

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are mainly a mixture of calcite (16-97%) and quartz (0-72%) with variable amounts of aragonite (0-41%). The aragonite% observed in King Island samples is higher than that found in western Tasmanian bulk samples (Rao and Adabi, 1992), which is due to minor molluscs content and some cementation in bryozoans (Rao, 1993). Aragonite content increases with increasing water temperature because it is low in temperate carbonates but it is high in tropical carbonates (Milliman, 1974; Morse and MacKenzie, 1990).

CORRELATION AND FACTOR ANALYSIS

To understand the statistical relationship between major minerals with major (Ca, Mg) and minor (Sr, Na, Mn and Fe) elements and  $\delta^{18}O$  and  $\delta^{13}C$  values, correlation and factor analysis of King Island data are made. The correlation matrix of King Island data (Table 2) indicates strong positive correlation (0.96) between quartz% and insoluble residue% (IR%) because the dominant non-carbonate mineral is quartz. The soluble fraction from the carbonate content in the sample is indicated by strong positive correlation (0.96) between soluble fraction (carbonate%) and Ca% and with that of calcite% (0.91). Positive correlations between carbonate% and contents of Mg, Sr and Na also confirm the presence of these elements in the carbonate and these are not leached from siliciclastics. Strong positive correlation (0.84) between Mg% and calcite% indicates that Mg is in high-Mg calcite, which is the dominant mineral in the King Island samples. The contents of Na and Sr are strongly correlated (0.71). The contents of Mn and Fe are strongly positively correlated (0.83) and both these elements are related to Mg indicating that Fe and Mn concentrations are in high Mg-calcite and that they have not been appreciably leached from terrigenous clastics.

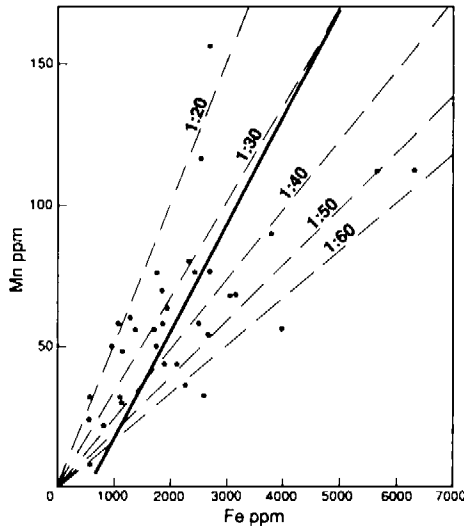


Fig. 11. Plot of Mn against Fe concentrations; solid line is the regression line. Note Fe concentrations are mainly 20 to 60 times the Mn concentrations.

The factor analysis of King Island data (Table 3) indicates that 3 factors account for 95% of total variance. Factor 1 is a carbonate factor in that it is positively correlated with contents of carbonate, calcite, Ca, Mg, Na and Sr and inversely with IR and quartz. Factor 2 is a Mn-Fe

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q
1	Sample no.	Latitude	Longitude	Depth,m	% Quartz	% Calcite	% Aragonite	18 O	13 C	%Residue	%Carbonate	%Ca	%Mg	Nappm	Fe ppm	Mn ppm	Sr ppm
2	2107	40°30.5	144°37.5	44	54.82	38.4	6.79	0.8	1.6	39.1	60.89	22.60	2.296	2296	2326	80	1596
3	2108	40°30	144°23.4	50	4.2	85.8	10	0.4	1.2	24.7	75.26	20.32	2.2	3516	7592	200	2574
4	2109	40°29.8	144°09.7	71	2.69	90.98	6.33	1.2	1.7	2.37	97.63	30.72	1.32	2296	1862	70	2242
5	2110	40°20	144°10	58	7.24	85.33	7.43	0.9	1.6	9.14	90.86	30.36	1.28	2198	6298	112	1492
6	2111	40°20	144°22.9	55	2.42	93.61	3.96	1	2.4	6.76	93.24	31.32	1.64	3588	4000	56	2650
7	2112	40°20	144°36.4	55	9.53	86.72	3.75	0.6	1.4	17.8	82.18	25.8	1	2510	5644	112	1880
8	2113	40°19.8	144°48.5	49	14.69	68.53	16.78	1.4	1.4	9.27	90.73	32.64	0.96	2814	2682	156	2284
9	2114	40°20.2	145°02.5	49	28.98	62.74	8.28	1.2	1.3	15.1	84.94	30.16	1.08	2320	2550	116	1980
10	2115	40°10.2	145°00.7	53	9.69	81.36	8.95	1.2	1.3	5.51	94.49	29.96	1.12	2988	1768	76	2378
11	2144	40°10.2	144°06.5	49	83.91	16.09	0	1.4	1.5	47.2	52.78	19.16	0.88	1072	1880	44	968
12	2145	40°10.5	144°18.6	51	2.63	85.91	11.46	0.5	1.7	3.54	96.46	31.12	1.32	4238	3040	68	3142
13	2146	40°10	144°32.6	59	11.41	79.23	9.36	0.7	1.4	8.12	91.88	30.72	1.28	3134	1842	58	2494
14	2147	40°10	144°45.8	59	1.59	78	20.41	0.7	1.7	4.46	95.54	35.92	1.12	3212	2438	76	2454
15	2148	40°09.2	145°11.6	51	9.03	83.65	7.32	0.6	1.1	7.1	92.9	35.6	1.52	2936	3794	90	2436
16	2149	40°09.5	145°25.5	64	11.07	83	5.93	0.8	1.1	9.75	90.25	33.2	1.52	2936	2662	54	2474
17	2150	40°22.5	143°39	128	0	96.7	3.3	1.4	1.6	3.58	96.42	34.4	1.88	1874	2700	76	1892
18	2153	40°20	143°27.5	106	0.17	88.65	11.18	1	2	2.19	97.81	34.56	1.56	2862	1768	50	2982
19	2154	40°20.5	143°41	86	69.05	30.95	0	1.2	2	43.2	56.76	18.4	0.92	1348	2250	36	1316
20	2155	40°21.2	143°53.6	59	69.8	13.81	16.4	0.4	2	59.6	40.37	14.2	0.52	1368	570	8	1176
21	2157	40°13.8	143°35.7	95	0.84	94.54	4.62	0.4	1.3	3.1	96.9	34.0	1.32	2784	3098	68	2454
22	2158	40°24.8	143°34.3	110	0.17	96.72	3.12	1.3	1.7	2.01	97.99	36	1.60	2132	1972	64	1692
23	2159	40°36.5	143°37	108	0.5	89.69	9.81	1	1.9	2.85	97.15	36.72	1.56	2950	1166	30	2590
24	2160	40°36.4	143°47	90	0	89.04	10.96	0.8	1.9	1.71	98.29	34.64	1.32	3000	1380	56	2804
25	2161	40°00.1	144°13.7	33	69.25	14.51	16.24	0.3	0.7	51.9	48.14	16.32	0.28	1498	948	50	2934
26	2163	40°00	144°38.5	46	47.41	24.24	28.35	1	1.3	24.8	75.23	25.8	0.36	2706	580	32	1638
27	2164	40°00	144°52.6	53	21.72	61.55	16.73	1	1.4	13.4	86.61	30.64	0.88	2764	1078	58	2054
28	2166	40°00	145°19	55	8.78	86.22	5.01	1.1	1.1	8.09	91.91	29.88	1.32	3306	2498	58	2502
29	2167	40°00	145°32.5	6	6.12	86.76	7.11	1	1.5	10.4	89.56	31.24	1.12	3378	2596	32	2684
30	2168	39°49.6	144°11.9	27	72.02	20.98	7.01	0.6	0.8	49.8	50.25	18.6	0.52	1872	1130	32	1216
31	2169	39°49.9	144°25.3	37	68.1	24.77	7.13	1.4	1.3	46.2	53.84	18.76	0.72	1814	836	22	1266
32	2170	39°50	144°38.7	46	65.56	29.63	4.81	0.8	1.3	46	53.97	18.56	0.68	1670	1124	48	1316
33	2171	39°50	144°51.3	49	41.95	51.8	6.25	1.2	1.4	24.7	75.26	25.28	0.96	2506	1228	60	1862
34	2172	39°50	145°04.6	51	12.75	46.04	41.2	1	1.4	4.88	95.12	36.6	0.4	3520	556	24	2358
35	2173	39°50	145°18.0	59	12.35	82.59	5.06	1.1	1.2	10.9	89.09	30.72	1.32	3334	2076	44	2502
36	2174	39°50	145°31.0	68	0.72	94.29	4.99	0.7	1.7	4.01	95.99	35.52	1.4	1770	1702	56	2722

Table 1. King Island sample localities, mineralogy, isotopes and major and minor elements of bulk samples.

factor because of positive correlation with Mn and Fe; and inversely with  $\delta^{18}\text{O}$  and water depth. Factor 3 is an aragonite factor as it is strongly positively related to aragonite content, and inversely to Mg%.

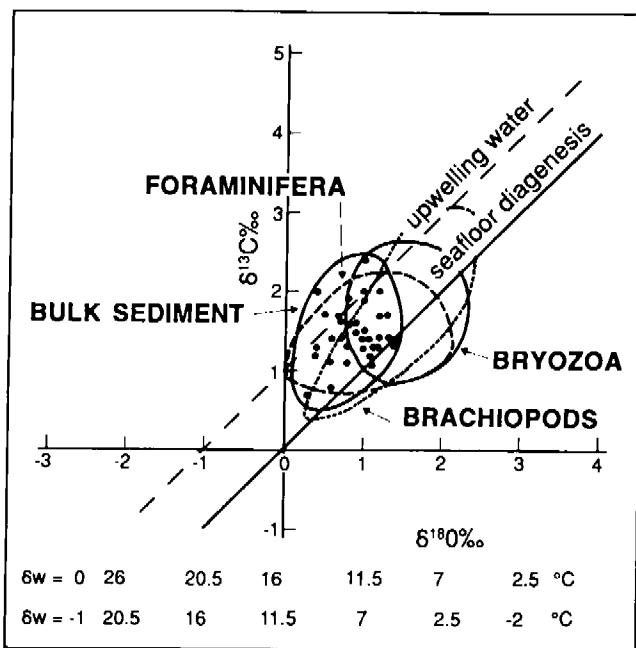


Fig. 12. Plot of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values of bulk sediments from King Island. Note the isotopic field of King Island bulk sediments overlaps isotope fields of bryozoa, benthic foraminifera and brachiopods from eastern Tasmania (Rao, 1993; Rao and Stait, 1993). All these isotope fields are dissected by trendlines of both upwelling water and seafloor diagenesis.

## MAJOR AND MINOR ELEMENTS

### Calcium and Magnesium

The Ca content varies from 14.2% to 36.6% (Table 2) due to about 35 to 97% carbonate content in the King Island sediments chemically analyzed. Carbonate in relatively pure siliciclastics is not chemically analyzed. The Mg content strongly correlates with contents of calcite, carbonate, Ca, Fe and water depth (Table 2) because these elements are in calcite. The Mg content increases with increasing calcite content. Pure calcites (100% calcite) contain about 2% Mg in them.

### Strontium and Sodium

The plot of Sr versus calcite contents (Fig. 8) indicates that Sr content increases with increasing amount of calcite and 100% calcite has Sr contents of about 3,200ppm, which is identical to the average Sr content in bryozoans (Land and Hoops, 1972; Rao, 1981b; Rao and Adabi, 1992). Samples that lie above HMC regression line contain more Sr than that can be attributable for by HMC. These samples contain aragonite in them because aragonite contains between 8,000 to 10,000ppm Sr (Kinsman, 1969; Milliman,

1974), which is much higher concentration of Sr than that in bryozoans. Samples that lie below HMC-regression line contain lower Sr concentrations than bryozoans because the samples contain low-Mg calcite (LMC), which contains about 1300ppm Sr in it (Rao, 1981b and Rao and Adabi, 1992).

The plot of Na versus calcite contents (Fig. 9) illustrates that Na content increases with increasing amount of HMC, with 100% calcite having around 4,000ppm Na, which is similar to the amount of Na in bryozoans (Land and Hoops, 1972; Rao, 1981b; Rao and Adabi, 1992). Samples that lie above the HMC-regression line contain aragonite, whereas those that lie below this line contain low-Mg calcite because aragonite contains about 2,700ppm Na whereas low-Mg calcite contains only 270ppm Na (Rao, 1981b; Veizer, 1983).

The plot of Na and Sr contents (Fig. 10) shows that these two elements are positively correlated with a correlation coefficient of 0.7 (Table 2). The slopes of Na:Sr that pass through the data mostly range from 1.3: 1 to 1: 1 (Fig. 9). The Na:Sr slope of 1.3: 1 corresponds to values of 25 to 100% bryozoans with 100% bryozoa consisting of 4,000 ppm Na and 3,200ppm Sr. The samples that lie above 1.3: 1 slope contain more Na and samples below 1.3:1 line contain more Sr than can be attributable to bryozoans alone. Samples that fall away from this bryozoa-line may be due to occurrence of different faunal elements, biochemical fractionation and cementation of aragonite, calcite or vaterite. All these need to be later investigated.

### Manganese and Iron

Manganese and Fe concentrations are positively correlated (0.8) and the concentrations of Fe are 20 to 60 times higher than Mn contents (Fig. 11). Both Fe and Mn values are positively correlated with Mg (0.6 and 0.5 respectively; Table 2). Earlier studies (Rao, 1981b; Rao, 1990a; Rao and Adabi, 1992) also indicated that Fe and Mn contents are positively correlated with Mg due to their incorporation in calcite in a reducing marine environment. During meteoric diagenesis, in a reducing environment, Fe and Mn values increase with decreasing Mg contents in calcite (Lohmann, 1988), which is not the case in King Island samples because these sediments are unaffected by meteoric diagenesis.

## STABLE ISOTOPES

The  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  field of King Island of bulk sediments overlaps isotope fields of bryozoa, benthic foraminifera and brachiopods of eastern Tasmania (Rao, 1993; Rao and Stait, 1993). All these fields are dissected by both trendlines of seafloor diagenesis and upwelling water (Fig. 12) because the bulk sediments and fauna are in equilibrium with marine waters. The seafloor diagenesis

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IR%	1							
Carbonate%	-1	1						
13C‰	-.249	.249	1					
18O‰	-.156	.156	.2	1				
Ca%	-.955	.955	.242	.171	1			
Mg%	-.634	.634	.305	.059	.533	1		
Na ppm	-.678	.678	.056	-.16	.583	.405	1	
Fe ppm	-.094	.094	-.072	-.295	-.077	.564	.288	1
Mn ppm	-.241	.241	-.162	-.107	.095	.486	.278	.834
Sr ppm	-.666	.666	.046	-.312	.6	.445	.71	.156
Aragonite%	-.076	.076	-.095	-.15	.148	-.468	.321	-.165
Calcite %	-.905	.905	.275	.02	.809	.843	.589	.333
Quartz%	.956	-.956	-.255	.023	-.877	-.732	-.7	-.295
Depth, m.	-.502	.502	.518	.23	.527	.579	-.006	-.053
	Mn ppm	Sr ppm	%Arag	%Calc	%Quar	Depth		
Mn ppm	1							
Sr ppm	.205	1						
Aragonite%	-.115	.186	1					
Calcite%	.394	.637	-.246	1				
Quartz%	-.372	-.71	-.039	-.959	1			
Depth, m.	-.089	.198	-.239	.555	-.502	1		

Table 2. Correlation matrix of King Island data.

trendline corresponds to seawater with 0‰ of both  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ ; whereas upwelling water trendline corresponds to water with -1‰  $\delta^{18}\text{O}$  and 1‰  $\delta^{13}\text{C}$  (Rao, 1993). The 'inverted J-trend' characteristic of meteoric diagenesis (Lohmann, 1988) is absent because of lack of meteoric diagenesis of King Island sediments.

The ambient water temperatures calculated from  $\delta^{18}\text{O}$  values (Fig. 12) using the equation of Shackleton and Kennett (1977) indicate a range of temperatures of about 10 to 15°C considering  $\delta w=0$ , which is the narrowest range in Tasmanian whole sediments and also warmer than whole samples from other Tasmanian localities (Rao and Green, 1983; Rao and Nelson, 1992). These temperatures decrease by -4°C if  $\delta^{18}\text{O} = -1$  of upwelling water is considered. Measured surface sea water temperatures around King Island range from 13 to 14°C in winter to 16 to 18°C in summer (Edwards, 1979). About 3°C cooler sea water temperatures obtained from oxygen isotope thermometry than measured surface temperatures may be due to strong seasonal effects and a slight enrichment of  $\delta^{18}\text{O}$  values up to 1‰ due to aragonite and high-Mg calcite mineralogy (Rao and Green, 1983; Rao and Adabi, 1992).

### GEOLOGIC SIGNIFICANCE

The type of carbonate minerals in modern sediments is related to water temperature. Aragonite and high-Mg calcite are the main minerals in skeletal fragments from tropical carbonates (Milliman, 1974; Morse and MacKenzie, 1990). Predominantly high-Mg calcites with some aragonite occur in modern warm temperate carbonates (Collins, 1988), whereas a complete spectrum of high-Mg to low-

Mg calcites with minor aragonite occur in modern cool temperate carbonates (Rao and Adabi, 1992). Entirely low-Mg calcite sediments occur in subpolar carbonates (Rao, 1981a; 1991). The King Island mineralogical data are mainly high-Mg calcite with aragonite and minor low-Mg calcite, and thus, provide a mineralogical data base for areas between cool-temperate to warm temperate regions.

	Factor 1	Factor 2	Factor 3
IR%	-.958	.162	-.142
Carbonate%	.958	-.162	.142
13C‰	.299	-.48	-.301
18O‰	.037	-.558	-.295
Ca%	.883	-.303	.212
Mg%	.795	.164	-.515
Na ppm	.707	.26	.458
Fe ppm	.301	.816	-.363
Mn ppm	.376	.747	-.277
Sr ppm	.725	.176	.395
Aragonite%	-.033	-.005	.829
Calcite%	.964	.026	-.168
Quartz%	-.984	-.026	-.068
Depth, m.	.549	-.505	-.409

Table 3. Factor matrix of King Island data.

Originally calcitic carbonates are abundant in the geological record, particularly during the Early and Middle Paleozoic and Jurassic (Wilkinson, 1982; Sandberg, 1975; Tucker, 1984). During the Permian, aragonite dominated in the tropics (Given and Lohmann, 1985), high-Mg calcite in temperate carbonates (Rao, 1988a) and low-Mg cal-

cite carbonates in cold, polar settings (Rao, 1981a). The marine, meteoric and burial diagenesis of originally calcitic carbonates can be better understood by using baseline data of modern calcitic temperate carbonates rather than with modern tropical aragonitic carbonates (James and Bone, 1989, 1992). Many Paleozoic limestones contain abundant bryozoans, foraminifera and echinoderms (Wilson, 1975). These limestones are not associated with warm-water indicators, such as chlorozoan assemblages, aragonitic nonskeletal grains, aragonite cements and evaporites, and could be of non-tropical origin. This possibility of non-tropical origin is also indicated by the occurrence elsewhere of originally aragonitic coeval Ordovician (Rao, 1990b, 1991) and Jurassic (Adabi and Rao, 1991) carbonates.

The occurrence of originally calcitic mineralogy in the Early and Middle Paleozoic and Jurassic is attributed to differences in atmospheric CO<sub>2</sub> levels and resulting differences in seawater chemistry (MacKenzie and Pigott, 1981; Wilkinson, 1982; Sandberg, 1983). The evaluation of atmospheric CO<sub>2</sub> concentrations based on marine δ<sup>13</sup>C values indicate that during the Ordovician (Rao and Wang, 1990) and Jurassic (Adabi and Rao, 1991) atmospheric CO<sub>2</sub> levels were similar to present day values. Therefore, originally calcitic mineralogy in carbonates formed during these periods may be due to cooler water temperatures. Carbonate minerals are now forming at different pCO<sub>2</sub> levels as evidenced by the occurrence of mainly aragonite in shallow marine tropics, which are in equilibrium with atmospheric CO<sub>2</sub>, whereas mainly calcite occurs in shallow marine temperate carbonates and in deep marine carbonates both of which are now in equilibrium with low pCO<sub>2</sub> bottom waters (Rao and Green, 1983; Rao and Nelson, 1992). Similar pCO<sub>2</sub> differences in surface and bottom waters may have also caused formation of different carbonate minerals in the past.

Low Mg contents in ancient limestones might be either due to originally low Mg levels due to aragonite or calcite contents. The Mg in high-Mg calcite decreases during meteoric and burial diagenesis. The variations of Sr, Na, Mn and Fe with Mg provide means of assessing diagenetic changes from high-Mg to low-Mg calcite. Decrease of Sr, Na values and increase of Mn and Fe values with decreasing Mg concentrations are due to meteoric diagenesis (Brand and Veizer, 1980; Rao, 1990b). Uniform Sr and Na contents and increase of Fe and Mn values with increasing Mg concentrations are due to marine diagenesis (Rao, 1990a). The Sr concentrations are lower and Na concentrations are higher in temperate biogenic carbonates. The ratio of Sr/Na is ~1 in temperate carbonates which is much lower than the Sr/Na ratios of 3-4 in tropical aragonitic carbonates. These ratios are preserved in ancient tropical to polar carbonates (Rao, 1991) despite prolonged diagenesis and thus are significant in the recognition of non-tropical carbonates. Geochemical differences exist between tropical, temperate and polar carbonates (Rao, 1981c; 1991)

and combined with petrographic features they can be used to differentiate non-tropical carbonates from their tropical counterparts.

## CONCLUSIONS

The present study illustrates mineralogy and geochemistry of temperate carbonates occurring in a region between cool and warm temperate settings. These carbonates have the following characteristics:

1. Carbonates consist mainly of bryozoan sand grains with minor intragranular CaCO<sub>3</sub> cement.
2. Carbonate minerals in particles are mainly high-Mg calcite and aragonite with minor amounts of low-Mg calcite.
3. Ca, Mg, Sr, Na, Fe and Mn are in carbonate fractions and these are inversely related to quartz and insoluble residue contents and to particle type.
4. Sr and Na are positively correlated and increase with increasing high-Mg calcite and aragonite content. The ratio of Sr/Na is 1, unlike ratios >3 in shallow tropical aragonitic carbonates.
5. Fe and Mn contents are positively correlated with Mg contents in calcite.
6. The δ<sup>18</sup>O and δ<sup>13</sup>C isotope field of bulk sediments overlaps with other temperate fauna and all these fields are dissected by trendlines of both seafloor diagenesis and upwelling as temperate carbonates are in equilibrium with bottom waters.
7. The δ<sup>18</sup>O determined ambient water temperatures range from 10 to 15°C and these are 3°C lower than measured surface water temperatures due to seasonal effects and carbonate mineralogy.

Originally calcitic bryozoan, foraminifera and echinoderm ancient carbonates are abundant in the stratigraphic sequences and their diagenesis and geochemistry can be better understood by comparing them with modern calcitic temperate carbonates. The possibility exists that most of these originally calcitic ancient carbonates are of temperate origin due to the occurrence of coeval originally aragonitic carbonates elsewhere. As the present is the key to the past, we can expect to find extensive occurrences of ancient nontropical carbonates.

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