3.1 Introduction

Since the residence time of strontium in the world oceans is orders of magnitude longer (≥ 4 million years; Veizer, 1989) than the estimated mixing time for world ocean water (around 5000 years; Holland, 1978), $^{87}Sr/^{86}Sr$ in seawater at any one time is the same worldwide. Therefore changes in the $^{87}Sr/^{86}Sr$ in well dated, unaltered limestones that incorporate the seawater $^{87}Sr/^{86}Sr$ without fractionation can serve in global correlation (Burke et al., 1982; Veizer, 1989; Brand, 1991; Smalley et al., 1994; Denison et al., 1994). The most useful portions of the Phanerozoic $^{87}Sr/^{86}Sr$ seawater curve for correlation occur when $^{87}Sr/^{86}Sr$ in seawater changed rapidly.

The Permian to Early Triassic was such a time with rapid changes in $^{87}Sr/^{86}Sr$ in unaltered marine limestones including cements and the calcitic components of organisms (Popp et al., 1986b; Smalley et al., 1994; Denison et al., 1994).

In North America the $^{87}Sr/^{86}Sr$ minimum of 0.70672 (Fig. 3.1) at the Ochoan/Guadalupian stage boundary in the Ochoan Castile Formation (incorrectly referred to the Salada Formation, Denison et al., 1994, p. 148) overlies a sample with $^{87}Sr/^{86}Sr$ of 0.70682 from the Lamar Member of the Bell Canyon Formation at the top of the Guadalupian (Denison et al., 1994, p. 162). The location of the $^{87}Sr/^{86}Sr$ minimum in Australian sediments therefore indicates a Guadalupian/Ochoan age.

Modern brachiopod shells equilibrate with the Sr of the seawater in which they have grown without biologically controlling the $^{87}Sr/^{86}Sr$ incorporated into the shell (Brand, 1989), and it is assumed ancient brachiopods did also. Samples from Permian brachiopod shells found in Australian sedimentary basins that were unaltered (nonluminescent under a cathodo-luminescence (C.L.) microscope) were analysed in an attempt to calibrate Australian biostratigraphical schemes by locating the $^{87}Sr/^{86}Sr$ minimum.

3.2 Sample selection

Samples for a $^{87}Sr/^{86}Sr$ chronostratigraphic profile ideally come from a single well-controlled stratigraphic sequence. This is not available in the Australian Permian sequences so samples from four fully cored diamond drill holes from the Bowen Basin, Eastern Australia (GSQ Eddystone 1, GSQ Eddystone 5, GSQ Taroom 10 and GSQ Springsure 19; locations listed in Appendix 2.0, shown on Fig. 2.17) were supplemented by outcrop samples. The locations of outcrop samples is listed in Table 3.1.

Table 3.1 Sample localities.

Sample locality No.	BASIN	SUB-BASIN	Locality Description; formation.
HB11	Canning	Fitzroy Trough	Lat. 19°5' 36", Long. 125°9' 45" Cherruban Mbr, Mt Hardman.
UQ L2421	Bowen	Denison Trough	Mantuan Horizon, Peawaddy Fm, Reids Dome Rd, 3.25 km from the Rewan-Rolleston Rd.
UQ L3543;	Bowen	Denison Trough	Lat. 20°50' approx.; Long. 147°42' approx. Scottsville Mbr., Blenheim Fm.
UQ L5124 = NE L1229	Sydney		Hunter Valley, western end of road cut on Kurri Kurri-Mulbring Rd, Elderslie Fm.
UQ L5129	Sydney		Hunter Valley, east end of railway cut west of road overpass at Branxton, Fenestella Shale.

UQ = University of Queensland fossil locality. NE = University of New England fossil locality.

Analyses of $^{87}Sr/^{86}Sr$ were made on 33 nonluminescent Spiriferacean and Productacean brachiopod shells from Australian sediments of late Early to latest Late Permian age (Artinskian to Djulfian) based on brachiopod (Briggs, 1989) and palynology biostratigraphical schemes (Price, 1983; Helby et al. 1987). Nonluminescent brachiopod shells were used because calcite from nonluminescent fabric-retentive brachiopod shells is likely to preserve original $^{87}Sr/^{86}Sr$ seawater ratio values (Popp et al., 1986b; Grossman et al., 1991). The shells selected for analysis were predominantly enclosed in shale and hence would be enriched in Mn and Fe if they had undergone reprecipitation whereas unaltered marine calcite is enriched in Sr and Mg (Brand and Veizer, 1980). Under a C.L. microscope Mn in concentrations > 100 ppm causes luminescence (Myers, 1974; Machel, 1985) so C.L. inspection screens samples for alteration.

3.3 Methods

Thick sections (0.5 to 1 mm) of the brachiopods were studied by C.L and polarising microscope to determine retention of primary fabric. Nonluminescent fabric-retentive shell areas were microsampled with a fine dental drill under a stereomicroscope. Subsamples of 0.5 to 2 mg were reacted with 104% phosphoric acid polymer at 25°C for 4 to 12 hours in vacuum-sealed analysis bottles before determination of $\delta^{13}C$ and $\delta^{18}O$ on a Finnigan Mat 252 mass spectrometer (see Appendix 3.1 for full method description). A selection of samples with $\delta^{13}C_{CO3} > 2‰$ and $\delta^{18}O_{CO3} > -3.5$ ‰, typical for the Late Permian (Grossman, 1994), were analysed for $^{87}Sr/^{86}Sr$.

Anomalous $\delta^{18}O$ indicates alteration because fluids interacting with the calcite generally have a $\delta^{18}O$ significantly different from that of the primary calcite (Marshall, 1992). Experience in this study has shown that samples apparently altered (non-fabric retentive, luminescent) have $\delta^{18}O$ values more negative than fabric retentive, nonluminescent samples from the same stratigraphic horizon, or subsamples taken from adjacent unaltered areas within the shell (Table 3.2). The $\delta^{18}O$ of calcite is sensitive to diagenetic alteration because during interaction with pore fluids the dominant oxygen source is in the pore water not that contained within the solid calcite (Marshall, 1992). Re-equilibration of oxygen from the calcite with the pore water oxygen can therefore alter the $\delta^{18}O$ of a sample. Brachiopod shells that appear unaltered and nonluminescent, yet show $\delta^{18}O$ significantly more negative than samples immediately higher or lower in the section (> 2 ‰ different) were not analysed for $^{87}Sr/^{86}Sr$.

Determination of $^{87}Sr/^{86}Sr$ from a nonluminescent (0.70689) and luminescent (0.70692) shell from 864.5 m in Eddystone-5, gave a higher $^{87}Sr/^{86}Sr$ in the luminescent shell. Lavoie (1993), Banner and Kaufman (1994) and Hallam (1994) found similar results.

Analytical methods are more fully described in Appendices 3.1 and 3.2.

Table 3.2 Comparison between $\delta^{13}C_{CO3}$ and $\delta^{18}O_{CO3}$ from cathodoluminescent and nonluminescent portions of brachiopod or bivalve shells.

Location	Depth m	$\delta^{13}C$ ‰ lum	$\delta^{13}C$ ‰ nonlum	$\delta^{18}O$ ‰ lum	$\delta^{18}O$ ‰ nonlum
Taroom 10	890.7	1.90	5.50	-5.92	-1.98
Taroom 10	897.2	4.42	6.96	-5.21	-1.19
Taroom 10	946.45	4.87	7.46	-4.33	-1.08
Eddystone 5	1256.2	-3.70	3.50	-11.90	-5.20
Eddystone 5	1219.3	4.02	4.40	-4.50	-2.26

lum - luminescent, nonlum - nonluminescent.

3.4 Results

Results of analyses are listed in Table 3.3 and shown in individual coreholes in Figs 3.2-3.4.

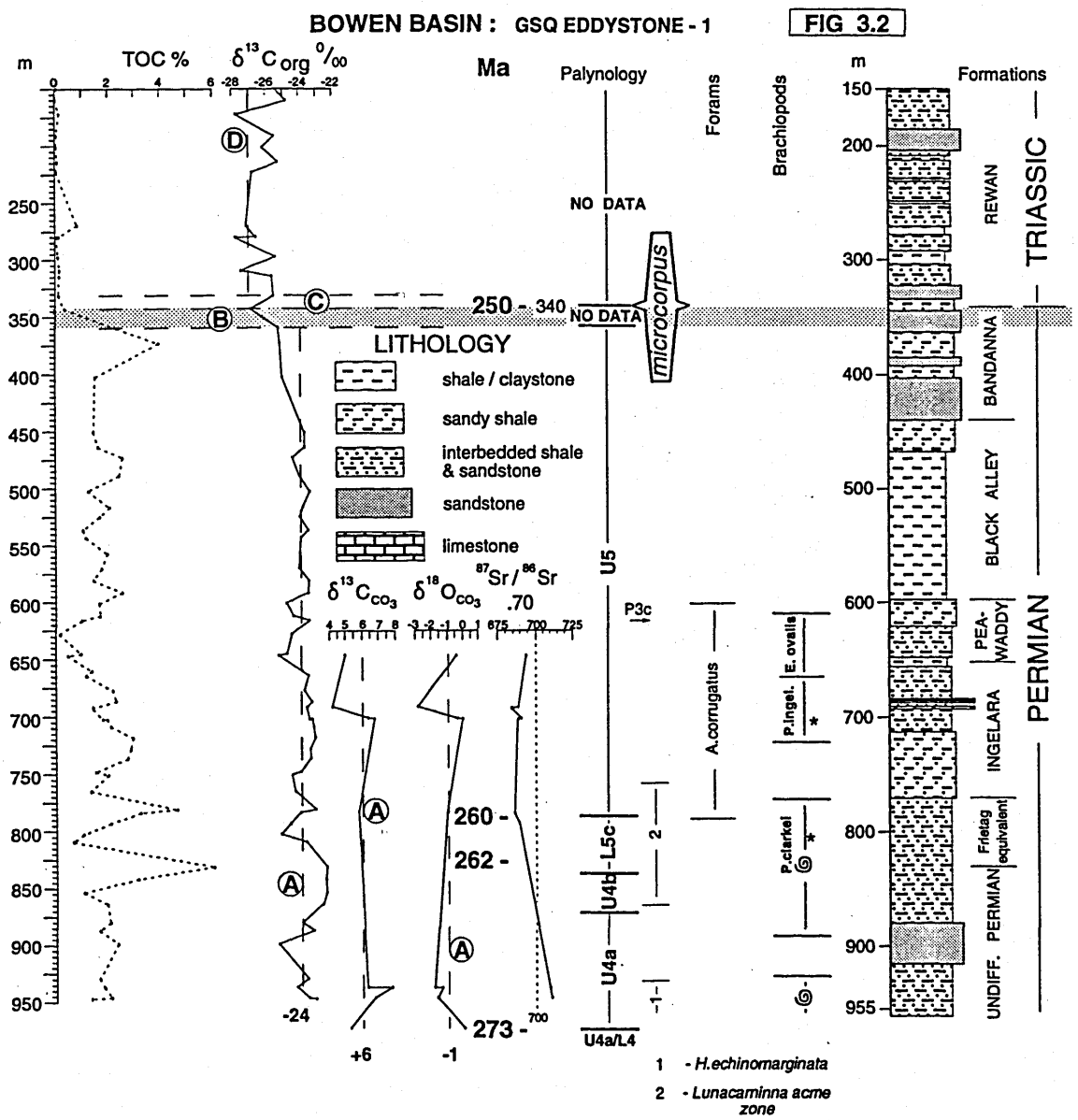

Figure 3.2 Eddystone-1, Bowen Basin, eastern Australia. Total organic carbon (TOC), $\delta^{13}C_{org}$, $\delta^{13}C_{CO3}$, $\delta^{18}O_{CO3}$, $^{87}Sr/^{86}Sr$, palynological zones (McKellar, 1978), foraminifera zones (Palmieri,1983), brachiopod zones (D. Briggs pers. comm., 1992), lithological log, and formations (Heywood, 1978). Determinations on carbonate samples are from non-cathodoluminescent brachiopods. The negative $\delta^{13}C_{org}$ excursion is between values of -24‰ for the Permian and -27‰ for the Triassic. The line at 340 m is my pick of the Permian-Triassic boundary, and it coincides with the base of the Rewan Formation and the first determined sample of the Tr1a (= *P. microcorpus*) Zone (McKellar, 1978).

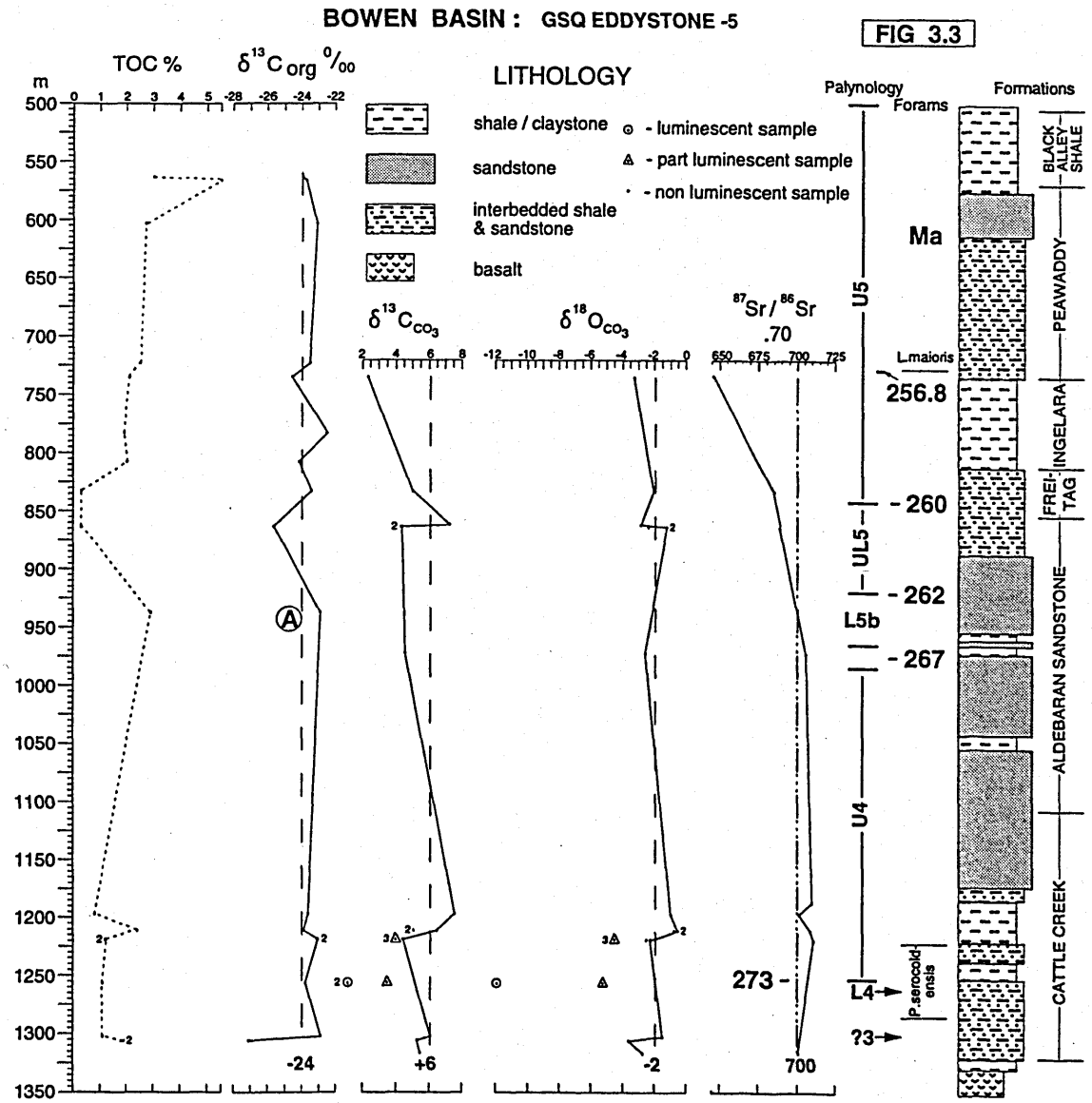

Figure 3.3 Eddystone-5, Bowen Basin, eastern Australia. Total organic carbon (TOC), $\delta^{13}C_{org}$, $\delta^{13}C_{CO3}$, $\delta^{18}O_{CO3}$, $^{87}Sr/^{86}Sr_{CO3}$, palynological zones (Jones, 1986), foraminifera zones (Palmieri,1983), brachiopod zones (Briggs pers. comm., 1992), lithological log, and formations (Draper & Green, 1983). Determinations on carbonate samples are from non-luminescent (nlum) brachiopods, except at 1219.3 m which was a partly luminescent (plum) specimen.

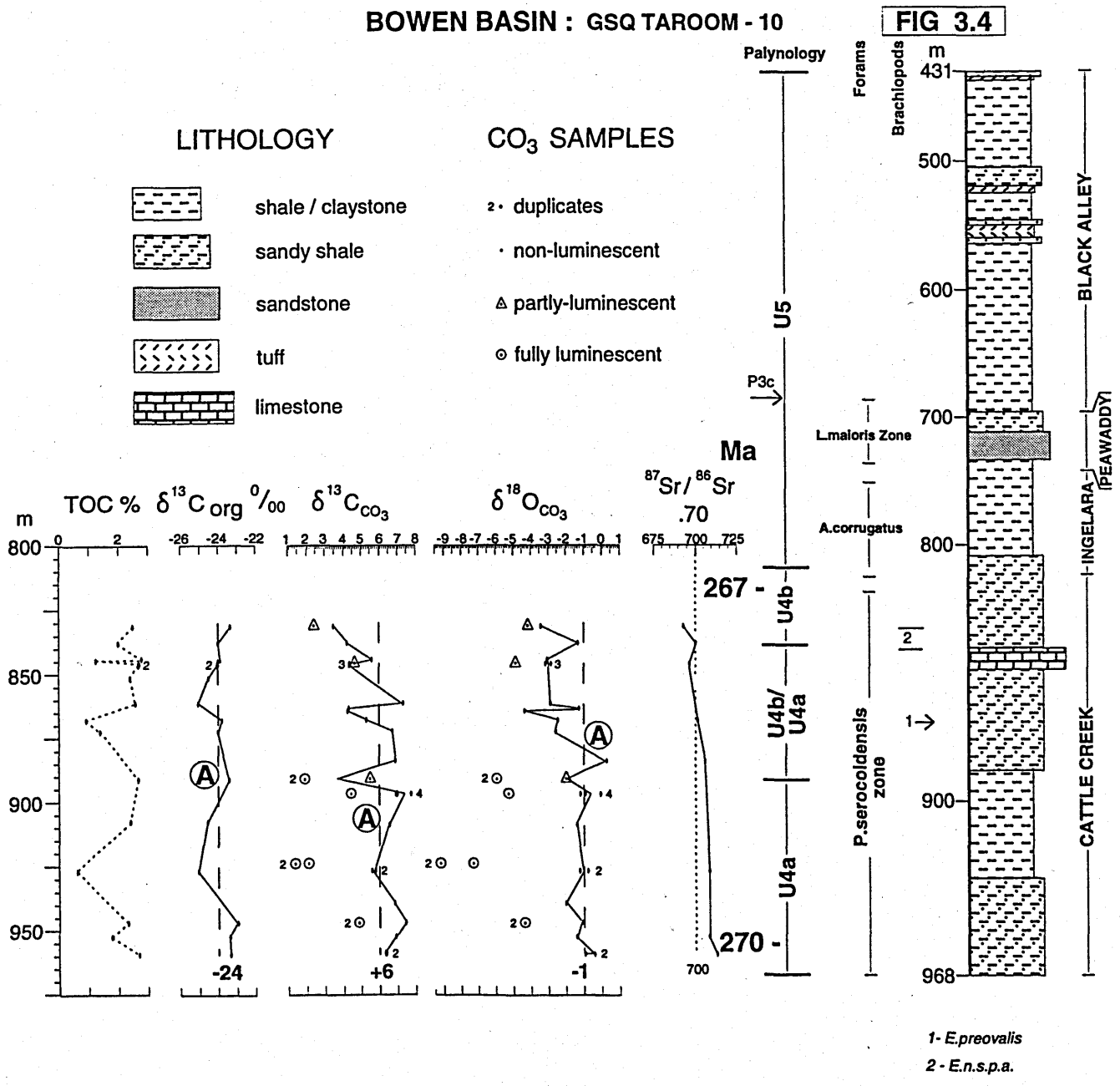

Figure 3.4 Taroom-10, Bowen Basin, eastern Australia. Total organic carbon (TOC), $\delta^{13}C_{org}$, $\delta^{13}C_{CO3}$, $\delta^{18}O_{CO3}$, (relative to PDB), $^{87}Sr/^{86}Sr_{CO3}$, palynological zones (McKellar, 1978), foraminifera zones (Palmieri,1983), brachiopod zones (Briggs pers. comm., 1992), lithological log and formations (Draper & Green, 1983).

Table 3.3 Strontium isotope results.

Sample	$^{87}Sr/^{86}Sr$	Formation	Palynological zone	$\delta^{18}O$ ‰	$\delta^{13}C$‰
E-1-647	0.70693	Peawaddy	U5	-0.43	5.00
E-1-692	0.70680	top third Ingelara	U5	-2.81	4.16
E-1-693.8	0.70684	top third Ingelara	U5	-1.31	4.50
E-1-701.8	0.70691	top third Ingelara	U5	-0.25	6.40
E-1-702	0.70688	top third Ingelara	U5	0.03	6.83
E-1-784	0.70686	Freitag equivalent	U5a-b?	-0.98	5.82
E-1-793.1	0.70689	Freitag equivalent	U5a-b?	-3.31	4.25
E-1-937	0.70710	undifferentiated	U4a	-1.76	6.34
E-1-947	0.70709	undifferentiated	U4a	-1.56	6.76
E-5-735	0.70646	top Ingelara	bottom U5b	-3.27	2.36
E-5-735	0.70651	top Ingelara	bottom U5b		
E-5-833	0.70687	Freitag	U5a-b?	-2.03	5.03
E-5-864.35	0.70689	top third Aldebaran	L5c	-2.34	4.40
E-5-972.59	0.70706	middle Aldebaran	U4	-2.54	4.60
E-5-1196.84	0.70711	middle Cattle Creek	U4	-0.97	7.60
E-5-1210.6	0.70709	middle Cattle Creek	U4	-0.73	6.52
E-5-1219.3	0.70711	lower third Cattle Ck	U4	-2.51	4.38
E-5-1316.2	0.70719	bottom Cattle Ck.	Stage 3	-2.65	5.50
S19-514.25	0.70689	top Peawaddy *	U5b	-2.68	5.249
T-10-831.25	0.70693	top Cattle Creek	U4b	-3.45	3.50
T-10-838.2	0.70700	top Cattle Creek	U4b	-1.28	4.22
T-10-845.25	0.70696	top Cattle Creek	U4b/U4a	-2.82	4.29
T-10-868.8	0.70705	middle Cattle Creek	U4b/U4a	-2.41	5.29
T-10-884.4	0.70706	middle Cattle Creek	U4b/U4a	0.30	6.90
T-10-897.2	0.70706	middle Cattle Creek	U4a	-1.19	6.96
T-10-926.8	0.70710	lower third Cattle Ck	U4a	-0.08	5.62
T-10-952.39	0.70709	bottom Cattle Ck	U4a	-1.38	6.89
T-10-959.9	0.70713	bottom Cattle Ck	U4a	-0.96	6.33
UQ L2421	0.70695	top Peawaddy *	U5c	-0.58	4.78
UQ L3543	0.70695	Scottsville Mbr.	L5c	-3.26	5.15
UQ L5124	0.70708	Elderslie Fm.	bottom U4b	1.46	5.46
UQ L5129	0.70698	Fenestella Shale	top U4b	-0.51	4.70
HB11-1	0.70716	Cherrabun Mbr	U5c	0.10	5.70
HB11-2	0.70715	Cherrabun Mbr	U5c	-1.40	2.80

E-1 - GSQ Eddystone -1, E-5 - GSQ Eddystone -5, T-10 - GSQ Taroom-10, S-19 - GSQ Springsure-19, UQ - University of Queensland fossil localities, HB - Cherrabun Member, Hardman Fm, Canning Basin. Formations in GSQ Eddystone -1 and GSQ Taroom-10 from Gray et al., (1980), palynology from M^{c}Kellar, (1977; 1978); GSQ Eddystone -5 formations (Draper and Green, 1983), palynology Jones (1986); GSQ Springsure-19 formations (Green, 1982), palynology interpolated from Briggs (1993b). UQ samples' palynology by interpolation from Briggs' (1993b) brachiopod zones. Locality of HB samples from J.M.Dickins (pers. comm., 1994), palynology from Paradise Cores (Morante et al., 1994). $\delta^{13}C$ and $\delta^{18}O$ values are expressed relative to PDB. Standard NBS 987 $^{87}Sr/^{86}Sr = 0.710257 \pm 0.0032\%$ 2σ pop., $n = 41$)

3.5 Discussion

The late Early to early Late Permian of the Bowen Basin is marked by fall in $^{87}Sr/^{86}Sr$ from about 0.70720 in sediments of palynological zone Lower Stage 4, interpreted as Artinskian, to a minimum of 0.70647 in Upper Stage 5.

In Eddystone-1 (Fig. 3.2) $^{87}Sr/^{86}Sr$ falls to the base of the Peawaddy Formation at 652 m and rises thereafter. A sample from 647 m within the Peawaddy Formation has a $^{87}Sr/^{86}Sr$ of 0.70693. This sample is stratigraphically below a palynology sample from 616.57 m identified as belonging to the P3c acritarch zone of Upper Stage 5 (McKellar, 1978). Other samples between 947and 642 m show decreasing $^{87}Sr/^{86}Sr$ with decreasing depth.

In Eddystone-5 (Fig.3.3) the minimum $^{87}Sr/^{86}Sr$ recorded at 735 m (0.70647, the lowest reported in the Phanerozoic) occurs at the topmost Ingelara Formation one metre below the Peawaddy Formation (Draper and Green, 1983) in a sequence where V. Palmieri (pers. comm., 1992) has identified Kazanian Foraminifera. This extreme minimum (Fig. 3.3) is much lower than that reported by Denison et al. (1994) at 0.70672 (Fig 3.1) and is possibly due to unusual diagenetic alteration. Although the sample appeared nonluminescent the $\delta^{13}C_{CO3}$ and $\delta^{18}O_{CO3}$ are negative compared with other samples above and below in the section (Table 3.3). A repeat analysis of a sample from 735 m in Eddystone-5 on a different shell yielded $^{87}Sr/^{86}Sr$ of 0.70651 (the second lowest reported in the Phanerozoic) which is measurably different from the earlier determination but still very low. These samples do not apparently represent altered $^{87}Sr/^{86}Sr$ so they are tentatively used in the best estimate of $^{87}Sr/^{86}Sr$ seawater curve for Australian Permian sediments (because they are so much lower than any other seawater $^{87}Sr/^{86}Sr$ reported from the Phanerozoic). They define the minimum point on the $^{87}Sr/^{86}Sr$ curve.

In GSQ Springsure-19 a sample from the topmost Peawaddy Formation within the Mantuan Productus beds at 514.25 m has a $^{87}Sr/^{86}Sr$ ratio of 0.70689 higher than the 0.70647 in Eddystone-5.

Above the Ingelara/Peawaddy Formation boundary, $^{87}Sr/^{86}Sr$ rises in all samples determined to be younger by relative stratigraphic position. These younger samples were obtained from outcrop and core from Eddystone-1 and Springsure-19 (Table 3.3).

$^{87}Sr/^{86}Sr$ values of outcrop samples (Table 3.3) from the Denison Trough and Sydney Basin compare with values from a similar stratigraphic level in core. Where supplementary these values follow a trend similar to the $^{87}Sr/^{86}Sr$ curve of Denison et al. (1994). A $^{87}Sr/^{86}Sr$ of 0.70716 has been determined for an outcrop sample in late Upper Stage 5 of the Cherrabun Member, top Hardman Formation, Canning Basin (Table 2.7), presumed to be of Djulfian age (Table 3.3) by association with *Cyclobus persulcatus* (Glenister et al., 1990) and hence younger than the topmost samples analysed from the Bowen Basin.

3.6 Conclusions

The fall and rise in $^{87}Sr/^{86}Sr$ of late Early to latest Permian brachiopods from Australia is similar to that recorded during this time interval in four published Phanerozoic $^{87}Sr/^{86}Sr$ seawater curves (Burke et al., 1982; Popp et al., 1986; Denison et al. 1994; Smalley et al. 1994). The $^{87}Sr/^{86}Sr$ seawater minimum defined by these Australian $^{87}Sr/^{86}Sr$ analyses is correlated to the Guadalupian/Ochoan Stage boundary of the Late Permian of North America (Denison et al., 1994). This minimum occurs in a lithostratigraphic position around 300 m lower in Bowen Basin

sequences than the negative $\delta^{13}C$ excursion that is correlated with the Chinese stratotype Permian-Triassic boundary at Meishan Section D (Baud et al., 1989; Chen et al., 1991).

In the Bowen Basin the $^{87}Sr/^{86}Sr$ minimum is in sediments from Upper Stage 5 and occurs about the base Peawaddy Formation. The Ingelara/ Peawaddy Formation boundary is a major sequence boundary (Briggs, 1993). A major sequence boundary also marks the Guadalupian/Ochoan Stage boundary of North America reinforcing a correlation between North America and the Bowen Basin at the $^{87}Sr/^{86}Sr$ minimum (Ross and Ross, 1994). The Ochoan sediments are assigned a Djulfian or younger age by Ross and Ross (1994). The Upper Stage 5 Zone therefore includes the Guadalupian/Ochoan Stage boundary and persists until the Permian-Triassic system boundary.

The Peawaddy Formation contains the youngest Foraminifera zones of Palmieri (1990) that are as young as early Midian (= Longtanian). The $^{87}Sr/^{86}Sr$ minimum is therefore interpreted as top Kazanian age (= top Capitanian).

The $^{87}Sr/^{86}Sr$ values from Australian sediments with the exception of the extreme minimum detected at 735 m in Eddystone -5 are within the bounds of, or slightly lower than, values on the seawater curves of Burke et al. (1982), Smalley et al. (1994), and Denison et al. (1994) which are predominantly based upon whole rock limestones and compare favourably with other results from nonluminescent brachiopods (Popp et al., 1986b).

The well known Bowen Basin biostratigraphic marker, the P3c acritarch zone, is constrained to be younger than the Guadalupian and older than the Permian-Triassic boundary because of its placement between the $^{87}Sr/^{86}Sr$ minimum and the $\delta^{13}C$ negative excursion (Figs 3.2).

The uppermost Ingelara and lowermost Peawaddy Formation are of Guadalupian/Ochoan age (and hence Capatanian/Longtanian; Harland et al., 1990, p. 48).

The Black Alley Shale is interpreted as Late Longtanian or Early Changxingian because it immediately overlies the Peawaddy Formation, interpreted as early Longtanian because of its stratigraphic position with respect to the $^{87}Sr/^{86}Sr$ minimum.

The negative $\delta^{13}C$ excursion in Eddystone-1 (Fig. 3.3) constrains the timing of the $^{87}Sr/^{86}Sr$ minimum to within the Late Permian and confirms it does not occur at the Permian-Triassic boundary as suggested by Holser and Magaritz (1987) and Gruszczynski et al. (1992).

APPENDIX 3.1

Strontium isotope analysis techniques.

Chemical separation of samples was accomplished by the dissolution of calcite samples (2- 10 mg) in 1 ml of 1M acetic acid in a 5 ml polypropylene centrifuge tube. Samples were left overnight to equilibrate then were centrifuged and the leachate removed taking care not to disturb any discernible undissolved residue. The leachate was dried in a teflon beaker and 3 ml 6M HCl added and then dried down. The residue was dissolved in 1 ml 6M HCl and loaded onto a preconditioned 4 ml capacity cation exchange column (AG50W-X8/-400 mesh ion exchange resin, Bio Rad Econo Columns). Sr was eluted with 2.5 ml of 6M HCl after washing with 7.5 ml of 6M HCl. The Sr fraction was dried then 1 drop of concentrated HNO_3 added at 210°C to remove organic residues derived from the column. Samples were stored in sealed teflon beakers prior to loading onto the mass spectrometer.

Sr mass spectrometry. Samples were loaded onto single Ta filaments with H_2O and H_3PO_4 and oxidised in air. The isotopic compositions were measured on a VG 354 thermal-ionisation mass spectrometer fitted with 7 collectors. Samples were run in dynamic mode with an ion-beam intensity of $3 * 10^{-11}$A of ^{88}Sr. Six blocks of nine $^{87}Sr/^{86}Sr$ were measured yielding 54 ratio determinations. $^{87}Sr/^{86}Sr$ was normalised to $^{86}Sr/^{88}Sr = 0.1194$ using an exponential correction law. Rubidium concentrations were negligible so no Rb corrections were necessary.

The precision of the $^{87}Sr/^{86}Sr$ at 95% confidence limits is calculated as 2 standard errors of the mean (2 sem) where:

$$2\ \text{sem} = 2\sigma / \sqrt{n},$$

where σ is the standard deviation and n is the number of determinations (usually 54).

This estimate, known as the *internal precision*, is a measure of the quality of a mass spectrometer's performance on particular sample on a particular day; it is used as a measure of the acceptability of a particular analysis and is not used to set errors. An internal precision of <0.0010- 0.0020% is generally accepted as adequate. All samples in this study had internal precision scores within this range.

Standardisation and Error Analysis.

Measured $^{87}Sr/^{86}Sr$ are referred to a determination of a standard for two reasons:

1) Every mass spectrometer has its own measurement bias and different mass spectrometers rarely yield exactly the same isotope determination on the same material. By reference to the standard it is possible to make interlaboratory comparison of results. For the $^{87}Sr/^{86}Sr$ of NBS 987 standard most laboratories quote values around 0.71020- 0.71030.

2) To indicate analytical precision an *external precision* can be estimated from repeated analysis of the same sample. The external precision at the 95% confidence limits is calculated as 2 standard deviations of the population of individual analyses. The external precision provides an effective lower limit to the real precision whereas the internal precision often underestimates analytical uncertainties. As a result of this the number of $^{87}Sr/^{86}Sr$ measured during the analysis of an unknown sample is effectively determined such that the internal precision is well within the external precision limits derived from the replicate analyses of a standard. External precision is a measure of the reproducibility of analyses and is used to decide if different samples have the same

$^{87}Sr/^{86}Sr$. During the interval of this project the $^{87}Sr/^{86}Sr$ were standardised to NBS SRM 987 $^{87}Sr/^{86}Sr$ for which a ratio of 0.710257 has been determined (41 ratios, 0.0016%, 2σ at 0.0032%, *external precision*).

APPENDIX 3.2

Calcite isotopic analyses.

Thick sections of brachiopods approximately 0.5mm thick were prepared and inspected with plane polarised light to determine fabric retention before examination with a cathode luminescing microscope. Photomicrographs were taken of shell areas to assist in identification of nonluminescent portions to be sampled. Sampling was by a fine dentist drill and the resulting calcite powder was re-examined with the cathode luminescing microscope to ensure nonluminescence of the sample. Typical sample size was of the order of 1-5 mg.

Carbon and oxygen isotopes in low magnesium calcite from brachiopod shells that were nonluminescent under a cathode luminescing microscope were analysed by the conventional phosphoric acid method at 25°C (McCrea, 1950). The samples were placed in in-house designed reaction vessels with a side arm to accommodate the 104% phosphoric acid polymer. The reaction vessels were evacuated for 40 minutes before sealing and being placed in a thermostatically controlled water bath at 25°C for at least 4 hours. The vessels were then tipped to allow the phosphoric acid to react with the calcite at 25°C for at least 4 hours. The CO_2 produced in the reaction was then analysed on a Finnigan Mat 252 mass spectrometer.

APPENDIX 3.3

Cathode luminescence microscopy

Thick sections (500 to 1000 micrometres) of brachiopods enclosed in fine grained shaley matrix were examined using a cold cathode luminescence 8200 MkIII unit attached to a Nikon petrological microscope with a Nikon AFX-DX 35 mm camera attachment in order to screen calcite shell material for evidence of diagenisis.

Sections were initially screened to determine suitability for isotope analysis on the basis of fabric retention of shell structure by visual examination of the shell material under plane polarised light. Shells that were not fabric retentive and showed evidence of calcite recrystallisation were rejected.

Fabric retentive shells were examined under cathodoluminescence for evidence of diagenetic alteration. Photographs of the specimens under plane polarised light and cathode luminescing conditions were taken to identify suitable shell areas for sampling by micro-drilling at a later point. Photographic exposure times were generally on the order of 60 seconds using Kodak Ektar 1000 ASA print film. Nonluminescent shell material appears deep blue when photographed using Kodak Ektar 1000 ASA colour print film whereas luminescent material appears red to bright orange (Figure 3.5). The red to orange luminescence is due to the presence of Mn^{2+} ions in excess of 100 ppm and is interpreted to indicate alteration and hence possible loss of the primary isotopic signature (Machel, 1985). Luminescent shell areas were not sampled except for a few samples analysed to test whether the luminescent shell material was isotopically equilibrated compared to nonluminescent shell.

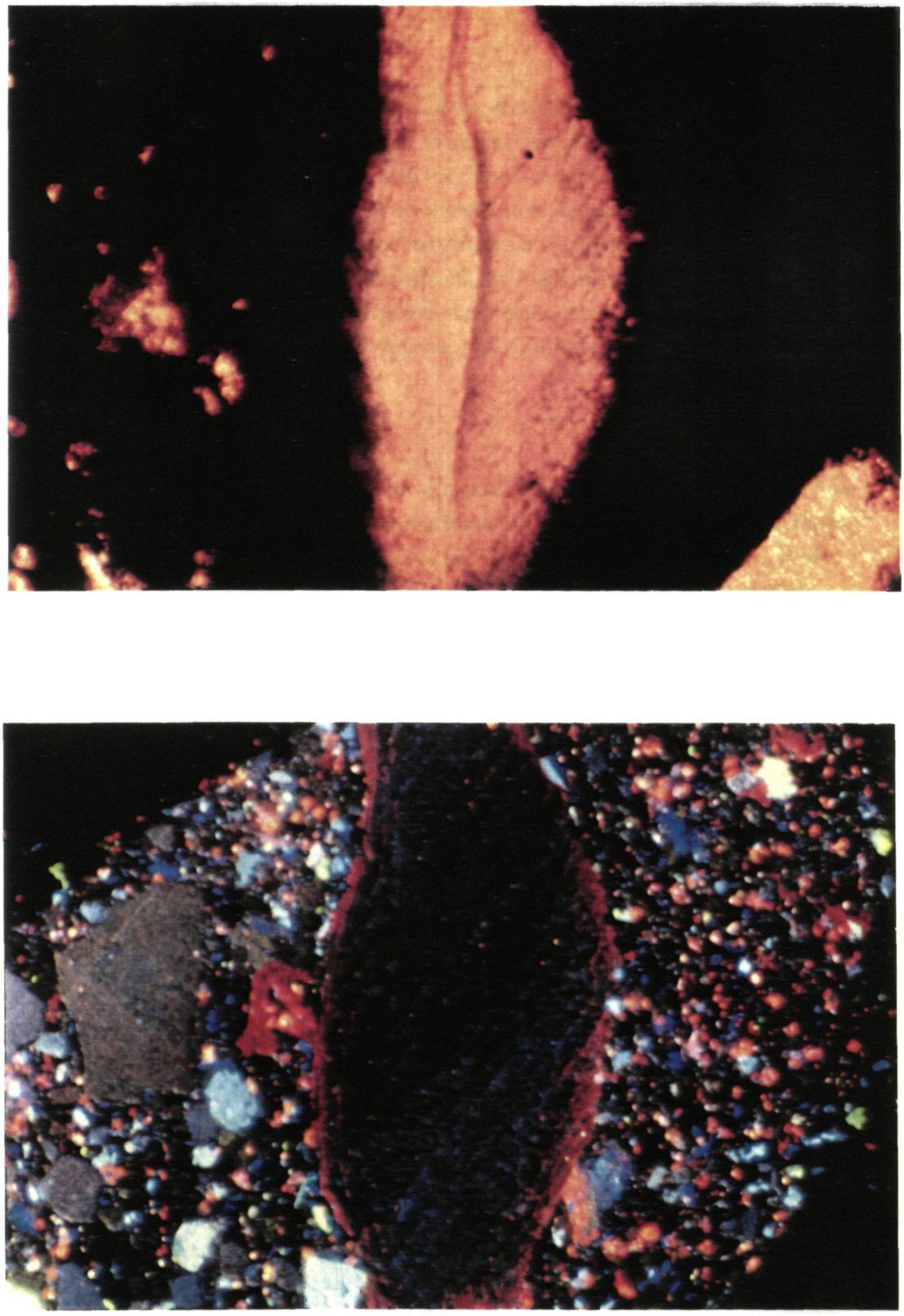

Figure 3.5 Plane polarised light and C.L. micrographs of a fabric retentive nonluminescent brachiopod. Sample GSQE-5 1219.3m. Non-cathodoluminescent area is blue, primary shell layer luminesces red.