THE STRATIGRAPHY, SEDIMENTOLOGY AND THERMAL HISTORY OF THE EARLY CAMBRIAN HEATHERDALE SHALE, FLEURIEU PENINSULA

Matthew W. Carson B.Sc.

This thesis is submitted as partial fulfilment for the Honours Degree of Bachelor of Science.

November 1994



The University of Adelaide
The Department of Geology and Geophysics

Australian National Grid Reference Barker Sheet (SI 54-13) 1: 250 000

ABSTRACT

A detailed study of the stratigraphy, sedimentology and thermal history of the Heatherdale Shale, the youngest unit of the Early-Mid Cambrian Normanville Group (Fleurieu Peninsula, South Australia), was undertaken to elucidate its petroleum source rock potential and collect data crucial to the prospectivity of the Stansbury Basin.

Stratigraphic and sedimentologic observations from the upper section of the Normanville Group delineated potential source beds and enabled reconstruction of their depositional environment. The focus of this study was a typical marine black shale facies, the Upper Heatherdale Shale. It is carbonaceous, fissile, pyritic and phosphatic, implying anoxic, deep water sedimentation (100+ m water depth), conducive to source rock development.

Total organic carbon values in the range 0.73–2.57% (mean = 1.73%) were obtained for the Upper Heatherdale Shale consistent with the presence of potential petroleum source rocks. The thermal maturity of the unit was determined using three maturation indicators. The primary indicator, kerogen H/C atomic ratio, rated the samples as overmature (H/C = 0.22–0.36). However, the carbon isotopic composition of the kerogen (δ^{13} Cpdb = -32.4 to -30.9%) showed no sign of metamorphic alteration. The Methylphenanthrene Index, a particulary useful maturity indicator for sediments deposited prior to the evolution of land plants (i.e. pre-Devonian) provided calculated vitrinite reflectance values of 2.50–2.56%.

Two offshore locations representing thermal maturation end-member scenarios within the Stansbury Basin were selected for quantitative thermal modelling. A calculated vitrinite reflectance of 2.5% was modelled 15 km NNW of Carrickalinga Head and a value of 1.2% was used in a second model 20 km E of Kangaroo Island. The above organic geochemical maturation parameters were combined with stratigraphic information and modelled using the *BasinMod* computer package. Results have shown that liquid hydrocarbons expelled by the source rocks between 518 and 500 Ma, if retained in an unbreached reservoir would exist today as both oil and gas.

TABLE OF CONTENTS

Abstract List of Figures List of Plates

| 1. INTRODUCTION 1.1 Background and Rationale 1.2 Regional Geology 1.3 Previous Investigations | 1 1 1 2 |
|---|--|
| 2. STRATIGRAPHY AND SEDIMENTOLOGY 2.1 Introduction 2.2 Stratigraphy of the Normanville Group 2.3 Stratigraphy of the Lower Heatherdale Shale 2.4 The Concretion Enigma 2.5 Stratigraphy of the Upper Heatherdale Shale 2.6 Depositional Model | 3 3 3 5 7 9 |
| 3. SOURCE ROCK STUDIES 3.1 Introduction 3.2 Organic Richness 3.3 Kerogen Type 3.4 Thermal Maturity 3.4.1 Kerogen H/C Atomic Ratio 3.4.2 Kerogen Isotopic Analysis 3.4.3 Methylphenanthrene Index | 13 13 13 15 16 16 17 18 |
| 4. THERMAL MODELLING 4.1. Introduction 4.2. Carrickalinga Head 4.3. Kangaroo Island | 19 19 20 21 |
| 5. SUMMARY | 22 |
| REFERENCES CITED | |
| ACKNOWLEDGEMENTS | |
| APPENDICES I Stratigraphic Logs II Sedimentology and Mineralogy III Analytical Techniques IV Results V Basin Analysis | · |

LIST OF FIGURES

| Figure No. | Title | On/between page/s |
|--------------|--|-------------------|
| 1. | Geology of the Sellick Hill-Carrickalinga Head | 1-2 |
| • | region | |
| 2. | Normanville Group stratigraphy | 3-4 |
| 3. | Sellick Hill study area, Inset 1 | 5-6 |
| . 4. | Carrickalinga Head study area, Inset 2 | 5-6 |
| · 5 . | Diagenetic zones and concretion growth | 8 |
| 6. | Heatherdale Shale depositional model | 12-13 |
| 7. | Source potential plots | 14-15 |
| 8. | Van Krevelen diagram | 16 |
| 9. | Crossplot of $\partial^{13}C$ vs. H/C ratio | 18 |
| 10. | RIC Trace of tri-aromatic hydrocarbons | 18-19 |
| 11. | Thermal modelling of the Heatherdale Shale | 20-21 |
| 12. | Fraction of oil remaining after heating | 21 |
| 13. | Thermal modelling of the Mt McDonnell Formati | |

LIST OF PLATES

| <u>Plate No.</u> la lb lc ld | Title On Fork Tree Limestone-Heatherdale contact Lower Heatherdale incompetent folding Lower Heatherdale later folding Lower Heatherdale crystalline carbonate | <u>/between page/s</u> 5-6 5-6 5-6 5-6 |
|--|---|--|
| le,1f | Lower Heatherdale Shale ovoid hollows | 5-6 |
| 2a 2b 2c 2d 2e 2f,2g | Serrated Lower Heatherdale Hyolithids in ribbon limestone Gentle folding in Carrickalinga Creek Spheroidal concretion Ellipsoidal concretion Sellick Hill concretions | 7-8 7-8 7-8 7-8 7-8 |
| 3a 3b 3c 3d 3e 3f,3g | Upper Heatherdale Shale type section Upper Heatherdale Shale concretionary horizon Cambrian thrust faulting Weathered coastal outcrop Heatherdale Shale wavecut platform Trilobite trails in tuff layer | 10-11 10-11 10-11 10-11 10-11 |
| 4a , 4b | Thin section photograph of Lower Heatherdale Shale Thin section photograph of Upper Heatherdale Shale | App. II App. II |

1. INTRODUCTION

1.1 Background and Rationale

The Early-Mid Cambrian Stansbury Basin lies mainly beneath Gulf St Vincent. The preserved basin margins are delineated by outcrop on the Yorke Peninsula (to the west), Kangaroo Island (to the south) and Fleurieu Peninsula (to the east) (Hibburt, 1994). Oil traces in Cambrian rocks recovered from the south-western Arrowie Basin in 1956-57 and an appraisal of the oil and gas prospects of the St Vincent Gulf graben by Sprigg (1961) indicated that the province had genuine hydrocarbon potential. Recent seismic acquisition and reconnaissance geochemical analyses have given rise to an increased exploration interest in the Cambrian succession.

Seismic interpretation has led to the delineation of a series of prospective structures for drilling by Canyon Australia Ltd, generous sponsors of the present project. Subsurface information obtained from three deep exploration wells on the Yorke Peninsula led to the recognition of a potential primary reservoir (Kulpara Limestone) and seal (Parara Limestone) for petroleum hydrocarbons (Hibburt, 1994). The probable source rock is the Heatherdale Shale (McKirdy, 1993). Source rock studies are an integral part of petroleum exploration. Seismic, stratigraphic and sedimentological studies may be able to delineate potential petroleum reservoirs, traps and seals. However, should source rocks be absent, immature or occur at an incorrect stratigraphic level, there is no means of charging the reservoir (Powell, 1985).

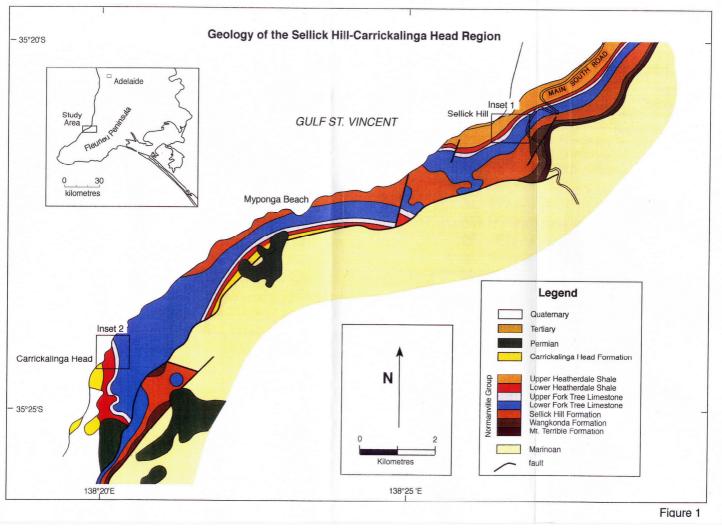
With these considerations in mind this project aims to study the Heatherdale Shale where it is exposed along the eastern margin of the Stansbury Basin, and determine:

- the stratigraphic location and cumulative thickness of petroleum source beds;
- the organic richness, quality and thermal maturity of the source beds;
- an appropriate model for source bed deposition; and
- the thermal history of the formation, as an aid to understanding the timing of hydrocarbon generation.

The last objective is crucial to any rigorous evaluation of the prospectivity of the Stansbury Basin.

1.2 Regional Geology

The Sellick Hill-Carrickalinga Head region, situated on the northern Fleurieu Peninsula (Figure 1, adapted from Abele and McGowran, 1959), forms part of the southern Adelaide Fold Belt (also known as the Adelaide Geosyncline: Preiss, 1990).



The entire fold belt extends from Kangaroo Island in the south, northwards through Fleurieu Peninsula and the Mt Lofty and Flinders Ranges, to Olary, spanning a distance of over 1100 km (Mancktelow, 1990). The belt comprises rocks of late Proterozoic age, deposited in response to repetitive lithospheric attenuation and thermal subsidence, followed by a thick carbonate and turbiditic Cambrian succession (Jenkins, 1990).

The regional disconformity between the Proterozoic and Cambrian successions, ascribed to the Duttonian folding event (Thomson, 1970), was followed by a renewed period of thermal subsidence, and resulted in the deposition of three transgressive cycles separated by Type 1 sequence boundaries (Gatehouse *et al.*, 1990; Jago *et al.*, 1994). Cycle 1 comprises the Normanville Group in the Stansbury Basin. Cycles 2 and 3 make up the Kanmantoo Group for which the depocentre was the adjacent Kanmantoo Trough.

Geosynclinal sedimentation was terminated in late Cambrian-Early Ordovician times by the compressional deformation of the Delamerian Orogeny. This major tectonic event resulted in the uplift, folding and exposure of the sedimentary sequence. Rejuvenation of Delamerian structures and tectonic elements during the Tertiary period gave rise to the Flinders and Mt Lofty Ranges and depression of the surrounding basins, e.g. Gulf St Vincent (Preiss, 1990), providing the fold belt with its present day configuration.

1.3 Previous Studies

The geology of the Cambrian succession on the Fleurieu Peninsula has been extensively studied on various scales since the late 1890's. Pioneering work by Howchin (1897), followed by that of Madigan (1925, 1927) and Mawson (1925), provided accurate descriptions of the predominantly carbonate sequence.

Increasingly detailed regional mapping, stratigraphic interpretation and structural studies were undertaken by Campana *et al.* (1954), Abele and McGowran (1959) and Daily (1963). Later studies of lead-zinc geochemical anomalies (Wright, 1967; 1968; 1970) contributed to our understanding of the economic geology of the region.

Previous studies involving the Heatherdale Shale, the primary subject of this thesis, have been of a general nature, forming a small part of the stratigraphic description of the Normanville Group. Studies of the Carrickalinga Head (Cernovskis, 1983; Scholefield, 1983) and Sellick Hill (Cooper, 1985) localities have described the formation in this context. Specific aspects of the Heatherdale Shale have been addressed in a series of palaeontological papers (Jago et al., 1984; Foster *et al.*, 1985; Jenkins and Hasenohr, 1989) and several organic geochemical reconaissance investigations summarised in McKirdy (1993) and Hibburt (1994).

2. STRATIGRAPHY and SEDIMENTOLOGY

2.1 Introduction

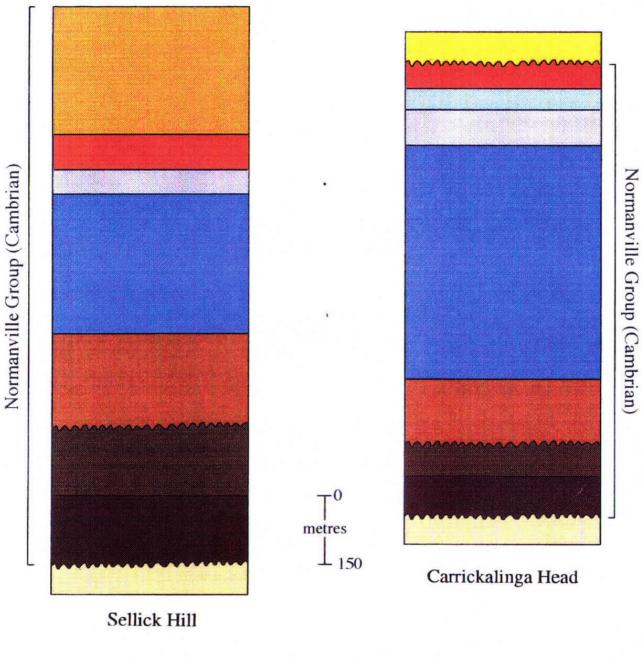
Field observations and a comprehensive literature survey are combined in this chapter to establish a depositional model for the Heatherdale Shale. A number of factors are considered to produce the model. A brief overview of Normanville Group stratigraphy is outlined to illustrate its depositional environment, within the Stansbury Basin. Detailed logging of the Heatherdale Shale was undertaken at two locations: Sellick Hill and Carrickalinga Head (Appendix 1). The resulting stratigraphic analysis of the unit is supported by a sedimentological description of its constituent rocks. Both are important in understanding the depositional environment.

2.2 Stratigraphy of the Normanville Group

The Normanville Group sediments represent the deeper water, ramp to basinal facies of the Stansbury Basin. The equivalent units, seen on the Yorke Peninsula to the west, are the shallow water shelf carbonate sequences closer to the margin of the basin (Alexander and Gravestock, 1990). Normanville Group stratigraphy as observed in the Sellick Hill-Carrickalinga Head region is summarised in Figure 2. The Group has been categorised as three sequences (C 1.1 - C 1.3) of sandy to shaley clastics and various limestones which together represent two Early Cambrian transgressive cycles (Hibburt, 1994) Evidence of these two complete cycles: lowstand systems tract, followed by transgression and culminating in highstand systems tract are readily observed in the field study area.

Presented below is a brief summary of the stratigraphic nomenclature, lithological description and environmental analysis of the group's five formations. The following papers and theses were consulted as a back up to my field observations: Abele and McGowran (1959), Daily (1963), Daily et al. (1976), Cernovskis (1983), Scholefield (1983) and Jago et al. (1986). A more comprehensive detailing of the sedimentology and mineralogy of selected samples is found in Appendix II.

The oldest unit of the Normanville Group, the Mt. Terrible Formation, disconformably overlies the Marinoan sediments and signifies the begining of the first of two transgressive cycles. The unit comprises a series of basal Cambrian sheet sands, which form part of a lowstand wedge, that onlapped onto the Gawler Craton and extended seaward to the southeast (Hibburt, 1994). The appearance of worm burrows in the basal arkose unit clearly distinguishes it from the subjacent Precambrian sequence.



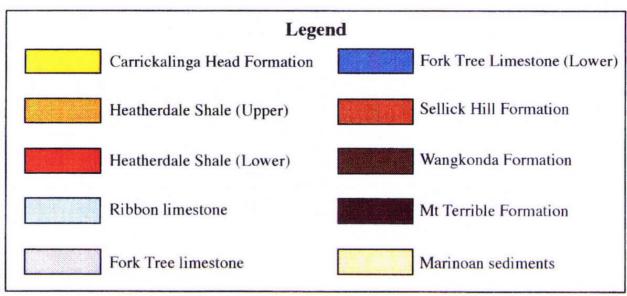


Figure 2: The stratigraphy of the Normanville Group in the Sellick Hill and Carrickalinga Head regions.

The middle part of the formation consists of dark grey siltstone with an upward increasing carbonate content. The upper *Hyolithes* sandstone member contains abundant fossils, e.g. molluscs, gastropods, conodonts and sponge spicules, indicative of shallow marine conditions. The continuation of the lowstand systems tract, resulted in the deposition of the carbonate-rich Wangkonda Formation. Conformably overlying the Mt Terrible Formation, it comprises two shallowing upward cycles of calcareous siltstone, mottled limestone and an unfossiliferous pale grey limestone.

Lying disconformably over the Wangkonda Formation is the Sellick Hill Formation. Its basal coarse sandy facies represents the upper part of the lowstand tract that encompasses the aforementioned units of the sequence C 1.1 (Hibburt, 1994). The rest of the formation comprises sediments deposited in a deeper water environment, the result of basin subsidence in response to the development of a hinge zone across central Yorke Peninsula (Hibburt, 1994). A calcareous shale (transgressive tract) passes upwards into dark grey mottled and banded limestone and calcareous shale (highstand tract) that weathers to a characteristic "serrated" appearance. Although the unit contains abundant fossils in its basal and topmost portions, the dark colouration of some stratigraphic intervals provide the first evidence of basin stagnation.

A rapid marine regression following the deposition of the Sellick Hill Formation, led to the growth of the bioherms of the Fork Tree Limestone on the outer ramp during a new lowstand tract (C 1.2) (Hibburt, 1994). The lower member of the formation is a pure, grey-blue, archaeocyathal limestone deposited in a shallow marine environment. A renewed transgression (marking the onset of the second of the Normanville Group transgressive cycles, sequence C 1.3) brought about the deposition of mottled lime muds that make up the Upper Fork Tree Limestone. The unit grades from a diagenetically "brecciated" limey-siltstone into a uniformly interbedded limey-shale or "ribbon" limestone.

The youngest unit of the Normanville Group, the Heatherdale Shale, is a deep water facies deposited under fluctuating oxic-anoxic seafloor and sub-seafloor conditions conformably overlying the Upper Fork Tree Limestone (Hibburt, 1994). The Lower Heatherdale Shale is a buff coloured, calcareous shale which contains large ovoid carbonate concretions and phosphate nodules. The Upper Heatherdale Shale is a well cleaved, pyritic, black shaley-siltstone, which contains abundant phosphate and is essentially carbonate free. Its high organic carbon content is indicative of a sub-oxic to anoxic depositional environment, a key factor in the development of petroleum source potential. Extensive observation, recording and sampling of the Heatherdale Shale was undertaken during a three week field season in April this year. The two localities provided an interesting comparison, displaying both numerous similarities and some significant differences. For a more detailed analysis of this unit see Sections 2.3 and 2.5.

2.3 Stratigraphy of the Lower Heatherdale Shale

The Lower Heatherdale Shale was studied at Sellick Hill (Figure 3, inset 1) in the two creeks immediately south of Mt Terrible Gully (Appendix I) and in the small cove to the north of Carrickalinga Head (Figure 4, inset 2). This member in the Sellick Hill region is a variably carbonate-rich, finely laminated, tan-brown shale, commonly weathered to a light purple-pink colour. The fine laminations dominate the texture of the rock in thin section, which also reveals a simple, but uniform mineralogy. Extremely fine (3-5 μ m) quartz makes up 50% of the sample and elongate calcite approximately 35%. The remaining 10% comprises opaques (detrital organic fragments and phosphate), disseminated throughout the rock. XRD analysis confirmed this bulk mineralogy, but did not detect the opaque fraction (Appendix 2).

The contact with the underlying Fork Tree Limestone is sharp and conformable (Plate 1a). Two episodes of folding can be recognised in the lower half of the unit. Small scale incompetent folding (Plate 1b) is apparent in the basal 10m of this unit, the result of soft sediment deformation of strata during a regional structural event. A much later event, most likely associated with Tertiary tectonics has produced a series of reverse faults and associated folds (Plate 1c). An increase in carbonate content is evident approximately 20m from the base of this unit, with the appearance of a horizon of carbonate concretions and a subsequent 3m thick layer of pure crystalline carbonate (Plate 1d). Alternating carbonate and shale beds make up the middle section of the sequence, with the upper 20m of the unit being dominated by carbonate concretions. The concretions occur in a matrix of calcareous shale, and whilst the upper level shows an overall increase in carbonate content, discrete beds of crystalline limestone, such as that seen in the lower portion of the unit, have not formed.

Phosphate nodules and stringers were recorded at various stratigraphic levels within the Lower Heatherdale Shale (Appendix I). The existence of phosphate within the stratigraphy provides useful information regarding palaeoenvironments. Phosphate nodules are a primary sedimentary characteristic, formed diagenetically by precipitation of calcium phosphates, derived from organic phosphorous. They form in reducing environments where loss of phosphate by diffusion into overlying waters is minimised (Waples, 1982). Phosphate enrichment on a continental shelf environment is commonly linked to upwelling waters (Demaison and Moore, 1980). A large nutrient influx promotes increased biological productivity in the surface water, providing a ready supply of organic matter to the seafloor where anoxic conditions favour its preservation. This close link between phosphate enrichment and high organic carbon content of the sediment also has important implications for petroleum exploration. An understanding of the environment of deposition of phosphaterich shales and subsequent discoveries of them, may lead exploration ventures to potential petroleum source rocks.

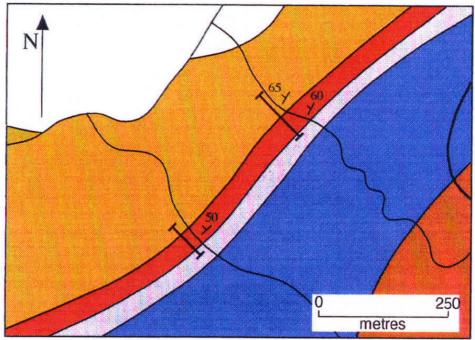
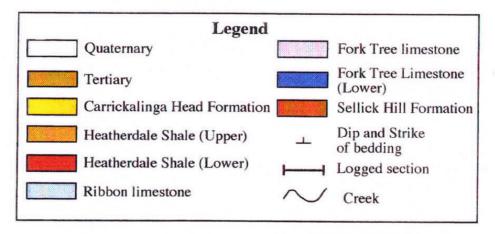


Figure 3: Inset showing Sellick Hill study area.



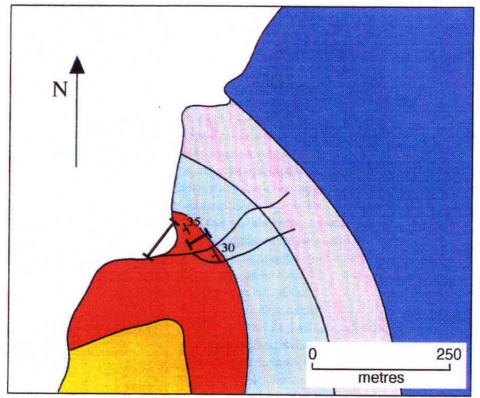
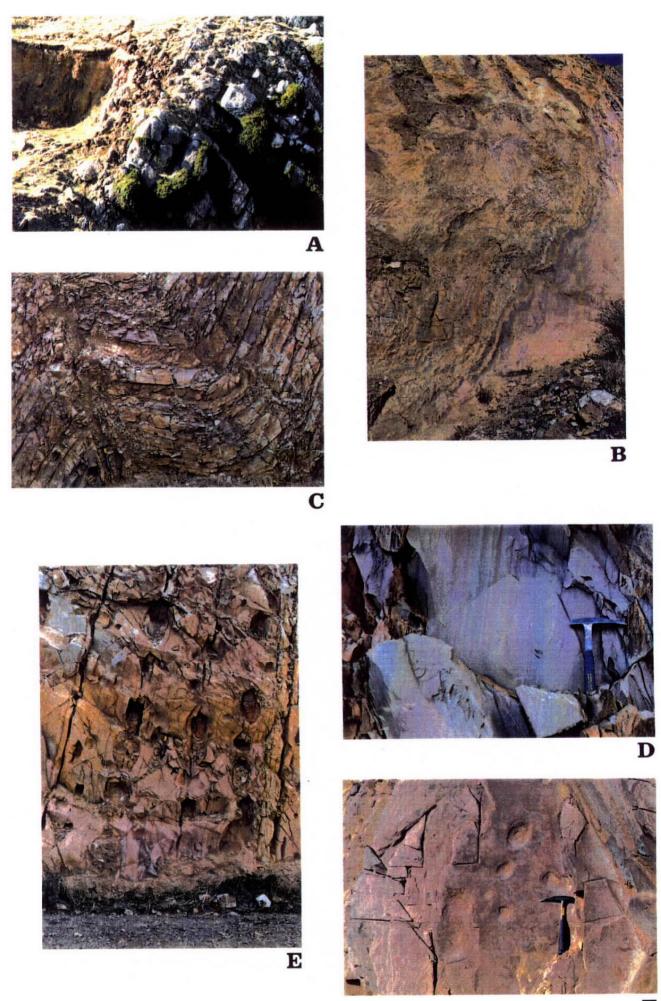


Figure 4: Inset showing the Carrickalinga study area

PLATE 1

- A The sharp contact between the Lower Heatherdale Shale and the Upper Fork Tree Limestone, Sellick Hill. The photo is 30 m across.
- B The basal 10 m of the Lower Heatherdale Shale showing small scale incompetent folding, Sellick Hill. The photo is 8 m across.
- C A later deformation event in the Sellick Hill region, most likely during the Tertiary, produced a series of reverse faults and associated folds.
- D A 3m thick pure, crystalline carbonate layer, 20 m from the base of the Lower Heatherdale Shale at Sellick Hill.
- E,F Extremely weathered Lower Heatherdale Shale, where the carbonate concretions have been completely removed, leaving remnant ovoid hollows. E shows a cross section of beds, F is looking at the surface of the bedding plane.



 \mathbf{F}

Although both sections studied at Sellick Hill conform to this stratigraphy, the creek due south of Mt Terrible Gully, Waterfall Creek (Appendix I) was highly weathered. Here the shale in general was non-calcareous and crumbly, and the carbonate concretions completely removed by weathering, leaving remnant ovoid hollows in the creek bed (Plates 1e, 1f).

The Lower Heatherdale Shale at Carrickalinga Head is a sequence of uniformly interbedded blue-purple calcareous shale and pink calcareous siltstone. The shale at this location has a "serrated" appearance (Plate 2a), a feature common to certain members of the Normanville Group, and contrasting to the more "massive" beds seen at Sellick Hill. The lower contact with the Upper Fork Tree Limestone differs from the sharp contact seen to the ENE, giving rise to conjecture as to the exact nature of this boundary. A 50 m sequence of ribbon limestone, separating the Lower Heatherdale Shale and Upper Fork Tree Limestone can be seen outcropping in the northern portion of Carrickalinga Cove. The limestone is similar to its neighbouring units, being an interbedded siltstone-carbonate facies, but it can be categorised as an individual entity for two reasons. It is darker than the Upper Fork Tree Limestone, indicative of increasing oxygen depletion at the sediment-water interface; and yet it is more carbonate-rich than the Heatherdale Shale, thus qualifying as a typical transitional lithology. A conspicuous layer in the limestone shows a series of aligned Hyolithid fossils, their configuration a result of wave action (Plate 2b). This indicates that the depositional environment, although tending towards deeper marine, was not below storm wave base.

Stratigraphic logging of the Lower Heatherdale Shale exposed at Carrickalinga Head was more difficult than the previous sections as the entire region is gently folded (Plate 2c). However once this was taken into consideration, an accurate section was established (Appendix I). The overall unit here was more organic-rich than at Sellick Hill, with a maximum TOC of 2.14% being recorded. No direct comparison with the lower member from Sellick Hill is possible as the weathered appearance of the latter in hand specimen indicated its unsuitability for organic geochemical analysis. Generally, concretion quantity and phosphate nodule abundance were analogous with Sellick Hill outcrop, although the concretions showed a greater variety of shapes than previously seen. The majority of the concretions were ellipsoidal (as at Sellick Hill), although spheroidal (Plate 2d) and elongate (Plate2e) concretions were also noted. Highly strained phosphate stringers associated with the elongate concretions, are direct evidence of what is arguably the highest strain increment (although difficult to quantify) seen in the Heatherdale Shale on the Fleurieu Peninsula. "Strain markers" recorded in previous studies are indicative of soft sediment, incompetent folding, whereas this "stretching" is most likely to be a later, competent feature, unrelated to earlier, regional deformation events.

2.4 The Concretion Enigma

In the Upper Heatherdale Shale carbonate concretions occur along a single bedding plane 2 m above the contact with the lower member. This confines the concretions to a 50 m thick stratigraphic interval, indicating something unusual or specific about the environment of deposition of the Lower Heatherdale Shale. A comprehensive literature survey, combined with the present field observations, reveals that carbonate concretions are somewhat enigmatic. Potentially themselves the subject of a detailed scientific study, it is essential in the context of this thesis to understand their palaeoenvironmental significance. In the absence of much pertinent analytical data, information from the literature has been used to determine the likely origins of the Heatherdale concretions.

Carbonate concretions are a ubiquitous product of the diagenesis of ancient siliciclastic sediments rich in organic carbon (Raiswell, 1987). Carbonate concretions form during early diagenesis in uncompacted sediment, under locally alkaline conditions produced by the anaerobic decay of organic matter. Early diagenesis can be divided into four zones (Figure 5). Concretions begin nucleating in zones 2 and 3, and "grow" mostly in zone 3 where the porewater becomes saturated by HCO₃- generated by microbiological redox reactions.

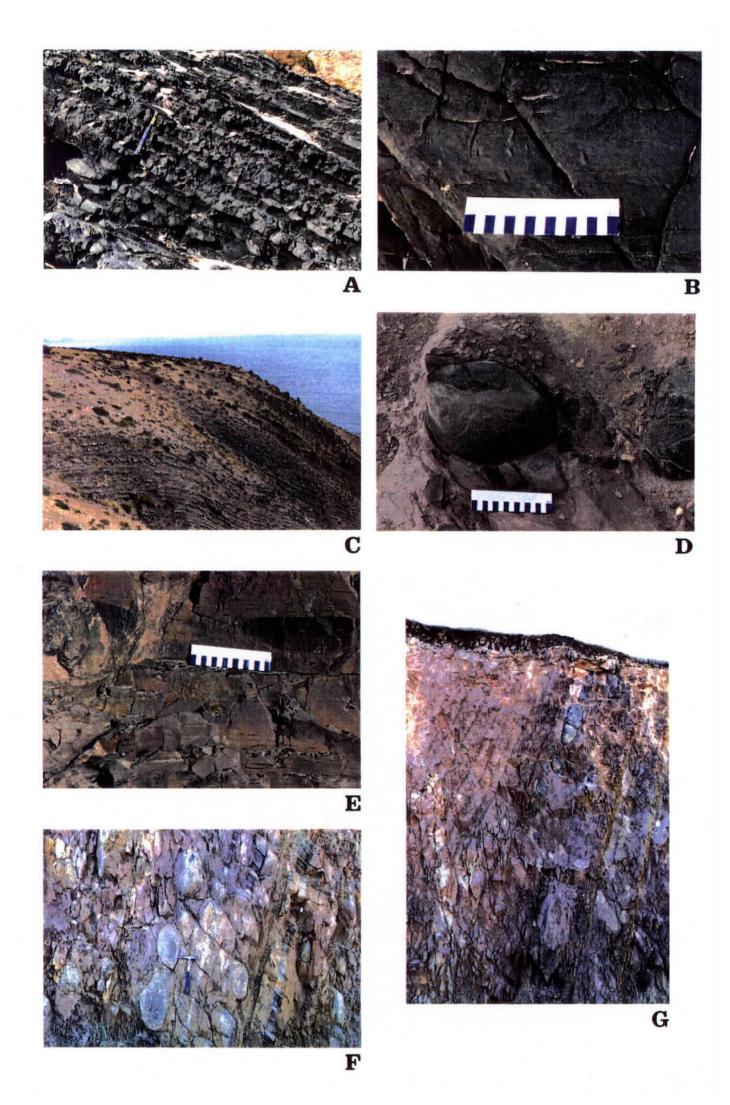
The alkaline conditions induce the precipitation of CaCO₃. Likewise, decaying organisms can provide nucleation sites for carbonate concretions. Weeks (1953) described South American Cretaceous concretions which contain entire, perfectly preserved fish. The carbonate precipitates in situ within the upper, porous layers of the sediment column and incorporates the host sediment rather than replacing it (Allison, 1990). Studies by Raiswell (1976) and Coleman and Raiswell (1981) have shown that original porosity estimates of the host sediment can be accurately obtained by dissolving the carbonate fraction of the concretion. High porosities (up to 90%) are direct evidence of concretionary growth only metres below the sediment-water interface.

Concretions outcrop in spectaular fashion along bedding planes in the Lower Heatherdale Shale at both Sellick Hill (Plate 2f, 2g) and Carrickalinga Head. They range from 10 cm to 1 m in diameter. Their predominantly ellipsoidal shape is controlled by sediment porosity. In argillaceous sediments porosity tends to be greater in the horizontal direction and thus concretions tend to be slightly elongate parallel to bedding (Allison, 1990). The occurence of multiple concretions along single bedding planes, and the sparsity of "outlier" concretions, is direct evidence of a stratigraphically controlled phenomenon. As previously stated, the concretions form in alkaline diagenetic environments (Figure 5). This localised alkaline environment requires time to evolve and establish itself as a site of carbonate precipitation and concretion growth.

PLATE 2

- A The serrated appearance of the Lower Heatherdale Shale at Carrickalinga Head.
- B A Hyolithid rich layer in the ribbon limestone at Carrickalinga Head. Fossil alignment is the result of wave action.
- C Gentle folding evident in the Lower Heatherdale Shale at Carrickalinga Creek.
- D Spheroidal carbonate concretion at Carrickalinga Head.
- E Elongate, highly strained concretion in Carrickalinga Cove.
- F,G Carbonate concretion-dominated bedding in the Lower Heatherdale Shale at Sellick Hill

The scale bar is in cm.



| POREWATER SYSTEM OP CL | ZONE DEPTH (m) | Sedimentation V V V V V | DIAGENETIC ZONE |
|------------------------------|-------------------|---|---|
| | 0.1 | $CH_2O+O_2 \longrightarrow CO_2+H_2O$ | Z-1 AEROBIC OXIDATION |
| | | • | Z-2 SULPHATE REDUCTION |
| | | $2CH_2O+SO_4^2-\longrightarrow 2HCO_3^-+H_2S$ | Microalkaline conditions establishing. |
| | | $2Fe_2O_3+8SO_4^2-+15CH_2O \longrightarrow 4FeS_2+15HCO_3^2+7H_2O+OH^2$ | Zone of pyrite formation. |
| | | · | Initial concretion formation. |
| | | | Z-3 ANAEROBIC METHANE OXIDATION |
| | | | Sulphate reduction continues. |
| | | $CH_4+SO_4^2 \longrightarrow HCO_3^-+HS^-+H_2O$ | CH ₄ diffusion from Z-4 provides a nucleation site. |
| | | diffusion | Optimum conditions for concretion growth. |
| | | 1 1 1 | |
| | 10 | | Z-4 METHANOGENESIS The CH ₄ produced in Z-4 diffuses into Z-3. |
| | | $2CH_2O+H_2O \longrightarrow 2CO_2+4H_2$ | |
| | | $4H_2+CO_2 \longrightarrow CH_4+2H_2O$ | |
| | | | As the pore water system closes fluid dynamics slow and concretions are unable to form. |

Figure 5: The zones of Diagenesis and Concretion Growth. The porewater system trends from open (OP) in the upper portion of the sediment to closed (CL) further down in the column.

This is achieved by a complete cessation of sediment accumulation, or sharp reduction in sedimentation rate, which stabilizes the formation zone at a fixed distance below the sediment-water interface (Raiswell, 1987). This has direct implications for the depositional model of the Lower Heatherdale Shale, indicating that sedimentation occurred in discrete pulses or episodes, and was not entirely continuous.

Studies of the mineralogical, trace element and isotopic composition of concretions have been both extensive and comprehensive resulting in papers by Raiswell (1971,1976), Dickson and Barber (1976), Irwin *et al.* (1977), Hudson (1978), Coleman and Raiswell (1981) and Mozley and Burns (1993). Carbonate concretions worldwide show a series of common, but not necessarily diagnostic, compositional trends.

Marine concretions are composed mainly of siliciclastics (original host sediment), calcite and pyrite. XRD analysis of several concretions from Carrickalinga Head supports this, showing that they comprise mostly calcite with minor quartz and pyrite (Appendix II). Studies have shown that pyrite is typically concentrated at the rim of the concretion, directly implicating sulphate-reducing bacteria in the later stages of its formation, and that pure calcite is concentrated at the core. Isotopic studies have indicated that the carbonate is biogenic (displaying highly negative δ^{13} C values), and that two different forms of pyrite are present reflecting variations in porewater chemistry during the course of diagenesis. These studies are far more complex than what has briefly been described here. The reader is referred to a companion study of the Heatherdale Shale by Turner (1994) for more information on the composition of its concretions.

The growth rate of carbonate concretions must at least be considered when determining their depositional environment. Confinement of growth rate to a particular time scale would potentially provide information on the duration of diagenesis or sediment accumulation. Unfortunately, there are as yet no satisfactory estimates for the rate of concretion growth, with evolutionary events being hard to date, relatively or absolutely (Hudson, 1978). Raiswell (1988) rejects the attempt by Berner (1968) to quantitatively describe the growth rate by diffusive mechanisms, in favour of a surface-reaction controlled regime. Thus, for the time being at least, carbonate concretions are not proving to be useful as a means of establishing the duration of diagenesis in marine, organic-rich shales.

2.5 Stratigraphy of the Upper Heatherdale Shale

The Upper Unit of the Heatherdale Shale was studied at various locations in the Sellick Hill region. A precise thickness was difficult to determine, due to increasing structural complexity and outcrop extending below sea level. However, a minimum thickness of 280m was estimated. The upper member of the formation does not exist at Carrickalinga Head, as shown in Figure 2. At this location the basal unit of the Kanmantoo Group, the Carrickalinga Head Formation, overlies the Lower Heatherdale Shale, along what has been hitherto commonly and illogically mis-reported in the literature as a conformable contact. In fact, a disconformable contact is evident from the large lateral disparities in unit thickness and, in places, the complete absence of the Upper Heatherdale Shale.

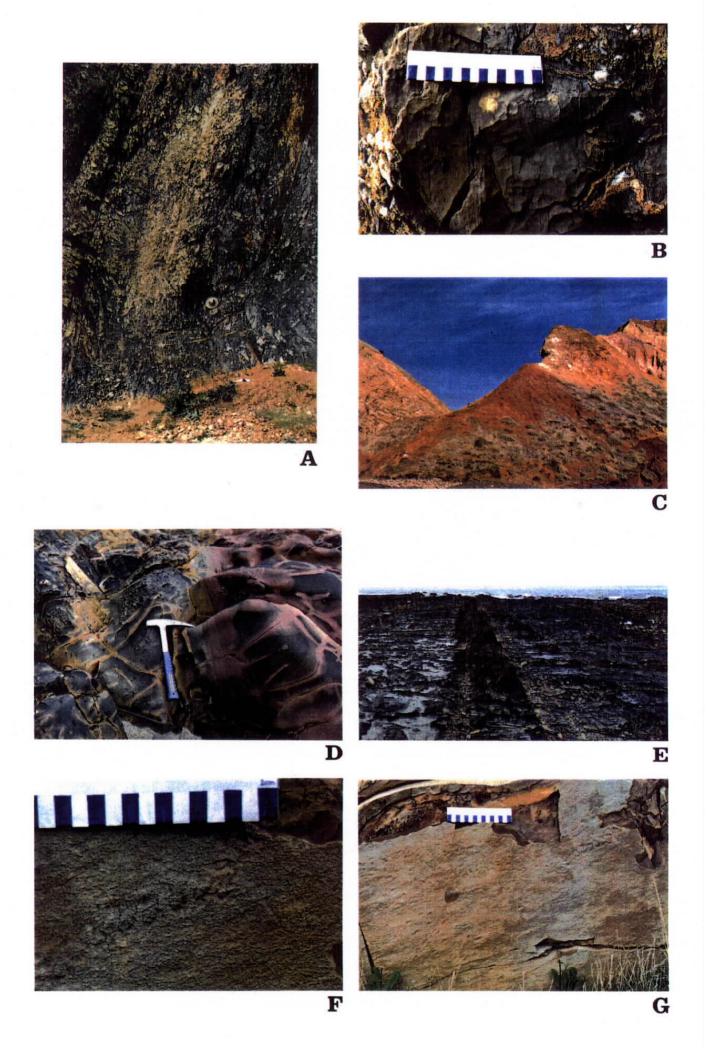
Such observations are clearly indicative of an erosional surface between the Heatherdale Shale and Carrickalinga Head Formation. Jago et al. (1994) now corroborate the latter hypothesis in a comprehensive paper documenting the nature of the contact between the Normanville and Kanmantoo Groups.

The "type section" of the Upper Heatherdale Shale is 55 m thick (Appendix I) and crops out in the middle tier of Waterfall Creek, due south of Mt Terrible Gully (Figure 3, Plate 3a). In this location it is a dark, carbonaceous, fissile silty-shale, rich in pyrite and phosphate, but lacking carbonate, and corresponds to the black shale facies of Curtis (1980). Thin section analysis showed the upper member to have a coarser grain size than the lower member. The predominant mineral quartz, is bimodally distributed, with 48% of the sample as sub-angular grains 12-16 µm across, and 2% of 30-50 µm size. Opaques are far more evident, comprising 45% of the sample. They are direct evidence of the increase in dispersed organic matter (kerogen) as well as higher pyrite and phosphate concentrations (Appendix II). The fissility is an important characteristic, enabling correct identification of the rock unit being studied. Curtis (1980) ascribes the development of fissility to fine scale lamination of the sediment (arising from the alternation of organic and pyrite rich layers and clay-rich layers), rather than to preferred alignment of clay minerals. Thin section analysis supports this theory (Appendix II). Laminated or "varved" sediments are found in modern stagnant marine waters, undisturbed by benthic marine fauna (Guclear and Gross, 1964). They indicate anoxic environmental conditions. Thus the "type section" of the Upper Heatherdale Shale represents deposition in an anoxic marine setting.

The upper unit shows a compositional uniformity, with a high concentration of pyrite and phosphate throughout. The abundance of phosphate nodules and stringers is suggestive of upwelling waters, combined with stagnant conditions enabling the precipitation of phosphate from enriched waters. Pyrite formation occurs in the sulphate reduction zone of the sediment during early diagenesis (Figure 5). The presence of abundant pyrite indicates the maintenance of stable anoxic conditions, an adequate supply of ferric iron species among the particulate mineral matter, and diffusion of dissolved sulphate into the sediment from the overlying water column. The lack of carbonate and disappearance of concretions (only one concretionary horizon was seen, 2 m above the base of this unit: Plate 3b) implies a sudden change in environment. It is likely that increased concentration and preservation of organic matter within the sediment resulted in an increased permeability, certainly higher than in an average shale. This in turn increased the likelihood of chemical exchange between the diagenetic zones, leading to an overall increase in acidity, and preventing the development of alkaline micro-environments. Resumption of sedimentation (albeit slow) may also have contributed to the loss of the physiochemical conditions required for concretion growth.

PLATE 3

- A The type section of the Upper Heatherdale Shale in Waterfall Creek, Sellick Hill.
- B The lone concretionary horizon in the Upper Heatherdale Shale. Bedding and phosphate stringers within the concretion are parallel to host sediment bedding.
- C Cambrian Heatherdale Shale (yellow-brown) thrust over Tertiary sediments (red-brown) at Sellick Hill.
- D Weathered Upper Heatherdale Shale at Sellick Hill, phosphate nodules are still prominent.
- E The Upper Heatherdale Shale forming a wavecut platform, approximately 2km south of the Sellick's Beach township.
- F,G Trilobite trails in crystalline tuff layer within the Upper Heatherdale Shale in a road cutting 1.5 km south of the Victory Hotel, Main South Road.



The type section described above is atypical of the Upper Heatherdale Shale in the region. The remainder of the unit is variably weathered and structurally deformed, thus deemed unsuitable for stratigraphic logging. A series of thrust faults may be seen, the most spectacular being one in which Cambrian rocks are thrust over Tertiary sediments at the mouth of Waterfall Creek (Plate 3c). Although coastal outcrop is intensely weathered, phosphate abundance is still evident (Plate 3d), and a wavecut platform extends seaward for 50 m (Plate 3e). At first sight the rocks comprising the platform resemble the black shale in the type section. However, a closer inspection reveals its leached and weathered state.

Trilobite discoveries in the Heatherdale Shale (Jago et al., 1984; Jenkins and Hasenohr, 1989) add an interesting variable to the palaeodepositional equation. Previous studies and observations indicated an anoxic depositional environment for the shale. However two specimens of concoryphid trilobites (genus Ivshiniellus) and well-preserved arthropod trails on a bedding plane (Plate 3e, 3f) indicate oxic to sub-oxic conditions at or just above the seafloor. The trilobite trails are preserved in a tuff layer, the lower surface of which forms a record of depressions in the shale made by the organisms (Jenkins and Hasenohr, 1989). The tuff layer is also important as it fortuitously provides the Heatherdale Shale with an accurate age of 526 +/- 4 Ma (Cooper et al., 1992). A recent review of this date indicates it could be some 6 or 7Ma less than the originally calculated age, with a much smaller error margin (R.J.F. Jenkins, pers comm.). The resulting conclusion is that the bottom waters of the Heatherdale Shale environment were clearly not uniformly anoxic and must have been at least intermittently oxygenated to sustain large invertebrates (Jenkins and Hasenohr, 1989).

2.6 Depositional Model

Inferences made regarding the depositional environment of the Heatherdale Shale are based on the complex interplay of factors described above. Clearly evident differences between the upper and lower units of the formation, as well as disparities between the two study locations (Carrickalinga Head and Sellick Hill), will be accounted for.

The facies change from the Fork Tree Limestone (a low stand tract) to the Heatherdale Shale (a transgressive tract) represents an increased siliciclastic input, and greater oxygen depletion in a prograding sequence (Figure 6), during the second transgressive sequence aluded to in Section 2.2. The pure, archaeocyathal Lower Fork Tree Limestone was deposited in a shallow, low turbidity, open marine environment with little terrigenous input. The mottled upper member was deposited in a less oxic, deeper water environment. It shows the first episode of rhythmic sedimentation and oxygen minimum layer expansion, processes caused by the onset of marine transgressive conditions. These effects become more pronounced in the Lower Heatherdale Shale as the transgressive cycle continues. The contact between the Lower Heatherdale Shale and Upper Fork Tree Limestone is gradational, a feature clearly visible at Carrickalinga Head and to a lesser degree, Sellick Hill.

The deep water deposition of the Lower Heatherdale Shale on the outer part of a carbonate ramp exhibits evidence of increasing clastic input. The rhythmic nature of the sedimentation is observed in the form of carbonate concretions and the "serrated" appearance of the regularly interbedded calcareous shale and limestone. The carbonate concretions, as discussed in section 2.4 represent "pauses" in sedimentation, a feature common to both the Sellick Hill and Carrickalinga Head sections of the formation, but uncommon elsewhere in the Normanville Group.

More pronounced at Carrickalinga Head, the blue-purple interbeds within the serrated lower unit are indicative of alternating suboxic-anoxic conditions, as a result of a fluctuating oxygen minimum layer. Although there is a trend to increasing anoxia, the numerous fossils within the unit (including hyolithids, gastropods and sponge spicules) are proof of extended oxic periods.

The Sellick Hill section, despite not having the "ribbon" or "serrated" appearance of Carrickalinga Head sequence still shows rhythmicity. The unit is slightly mottled for the first 10 m and then grades into a series of interbedded shale and crystalline carbonate horizons. The formation at this locality also shows significantly less fluctuation of the oxygen minimum layer. Deeper water sedimentation is more clearly evident in the fine, bedding parallel laminations of the calcareous shale.

The Upper Heatherdale Shale accumulated in a deep, basinal environment (high stand tract) where stable anoxic or suboxic conditions prevailed during deposition (Figure 6). The anoxic conditions enhanced the preservation of organic matter and led to the formation of diagenetic minerals such as pyrite. Sedimentation was dominated by a uniform siliciclastic input in a slow, continuous mode. Fine laminations within the shale, often highlighted by visible pyrite mineralisation, is characteristic of a deep water environment where the sediment-water interface is below storm wave base (100+ metres deep). The higher concentration of phosphate, both as stringers and nodules supports the model. Cold, upwelling waters, rich in nutrients increase the level of primary photosynthetic productivity and lead ultimately to sediments that are both organic-rich and phosphate-rich. The rare trilobite fossils in this unit represent occasional lowering of the suboxic/anoxic boundary to just above the seafloor.

Pronounced tectonic activity (the Kangarooian Movements) ended Normanville Group sedimentation and brought about a new sequence of syndepositional uplift and erosion. During this period the Kanmantoo Trough was initiated, the vast extension creating space to accommodate massive volumes of siliciclastic sediment (Kanmantoo Group), transported from the Gawler Craton. Outcrop in Carrickalinga Cove preserves this sequence of events, with basinal shale sediments stripped, and alluvial and fan delta sediments deposited disconformably on top of the erosional surface.

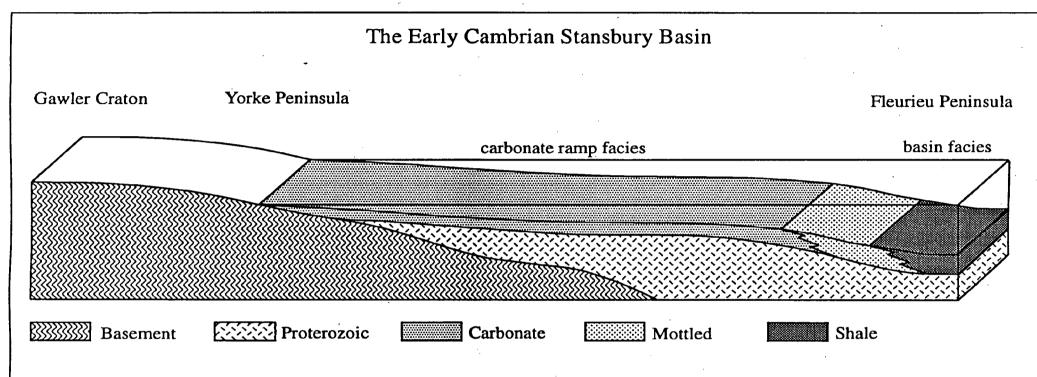


Figure 6: Depositional model for the upper portion of the Normanville Group.

The diagram illustrates the final stage (high stand tract) of the second transgressive sequence of the Normanville Group (C 1.3). The deep water shale facies, the upper member of the Heatherdale Shale progrades over previously deposited mottled sediments. The nature of the mottled sediments: the lower unit of the Heatherdale Shale, the Lower Fork Tree Limestone and ribbon limestone provide the first evidence of the expansion of the oxygen minimum layer in response to relatively higher sea levels. From the diagram it is clear that during a regressive period the carbonate platform would be in shallow water, enhancing the formation of carbonate facies, such as the Fork Tree Limestone and the carbonate rich sediments seen on the Yorke Peninsula.

3. SOURCE ROCK STUDIES

3.1 Introduction

The recognition of the Upper Heatherdale Shale as a black shale facies (Section 2.5) provides a substantial reason for a full evaluation of its petroleum source rock potential. The three parameters: **amount**, **type** and **maturity** of organic matter, form the basis of all source rock studies. The organic richness is measured by Total Organic Carbon (TOC) analysis, and the organic matter type by elemental analysis of isolated kerogen. The most important parameter (at least in the context of the present study) is thermal maturity, which has been assessed using the H/C atomic ratios and δ^{13} C value of kerogen and Methylphenanthrene Index (MPI) of the coexisting aromatic hydrocarbons. Calculations of equivalent vitrinite reflectance were then used to model the thermal evolution of the Stansbury Basin, discussed in Chapter 4.

3.2 Organic Richness

The quantity of organic matter within a sediment is measured by weight percent TOC. A total of 42 samples were sent to Amdel Limited Petroleum Services for this purpose. The results are presented in Appendix IV and Figure 7. The 22 samples from the Lower Heatherdale Shale at Carrickalinga Head include several carbonate concretion-host shale pairs. The results obtained revealed TOC values in the range 0.19-2.14% (mean = 0.79%). Some of the higher values were particularly encouraging. The concretion-host shale pairs were also interesting, with the concretions consistently being far less organic-rich than the surrounding shale. Initial speculation, based on the "dark" colour of the concretions, was that the concretionary TOC values would be equivalent to the original TOC value of the sediment. It was thought that non-replacive growth of the concretion had enveloped the organic matter within the confines of the concretionary structure, preserving it from the ravages of subsequent weathering. This is not so; instead what appears to have happened is that carbonate precipitation has diluted the dispersed organic matter. The 19 samples of the Upper Heatherdale Shale from Sellick Hill gave TOC values ranging from 0.73-2.57% (mean = 1.73%). As predicted these dark, pyritic shales are considerably richer than the sediments comprising the lower member.

The organic richness of the source beds can be quantified by correlating ranges of TOC values with degrees of source potential. Both Tissot and Welte (1984) and Waples (1979) suggest that a minimum TOC value of 0.5% in a source bed is required for hydrocarbon expulsion to occur, and Hunt (1972) stated that the average TOC for a shale is 1%.

With these considerations in mind, it is appropriate to use an adaption of the source rock richness scheme suggested by Waples (1984). TOC values between 0.5-1% are designated fair, 1-2% moderate and above 2% good. The scheme is employed in Figures 7.1, 7.2 and 7.3 where TOC values are plotted in correct stratigraphic context allowing source bed richness and thickness to be determined.

The major focus of this study, in terms of source rock studies, was the Upper Heatherdale Shale. Thus any source rock potential recognised in the lower member is an unexpected bonus. The Carrickalinga Cove results from this perspective are interesting. Although missing the top most portion (1-10 m) of the Lower Heatherdale Shale and all of the upper member (discussed in section 2.5), the formation at this locality clearly shows a trend of increasing source potential towards the top of the preserved sequence (Figure 7.1). A minimum of 8 m of moderate source rock, and 1 m with good source richness are apparent. The majority of the formation is rated as fair, with the ribbon limestone at the base of the section being particularly poor despite its dark appearance in outcrop. The TOC results from the Carrickalinga Creek section (Figure 7.2) show little or no correlation with the Cove data. The creek was logged with the intention of producing a composite section, representative of the entire Heatherdale Shale stratigraphy at Carrickalinga Head. Unfortunately this was not possible because of a lack of consistency in the data. Minor, but significant, structural disruptions and intense weathering account for this disparity (Appendix I). A few metres of shale with moderate source potential were recorded at the base of the section where samples collected from the creekbed are less affected by weathering processes.

TOC results from the Upper Heatherdale Shale at Sellick Hill show a far greater source richness (Figure 7.3). Some 26 m of good source rock has been delineated, with the remaining 29 m of the section rating as moderate source rock. There is a positive correlation with pyrite and phosphate concentration, traditional indicators of black shale facies.

As shown, the TOC results have corroborated previous investigations (e.g. McKirdy, 1993) by confirming the status of the Heatherdale Shale as a potential petroleum source rock. Despite intense weathering of much of the upper member, which prevented a full evaluation of its true source richness, the 55 m of "type" section studied provides a minimum estimate of effective source bed thickness.

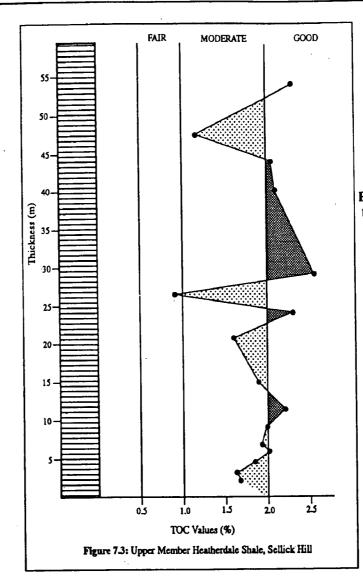
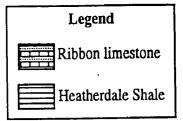
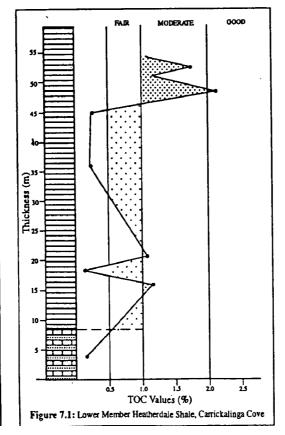
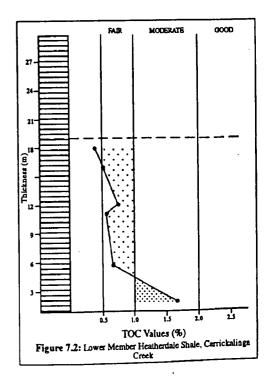


Figure: 7 illustrates TOC values in their correct stratigraphic context, allowing source bed richness and thickness to be determined.







3.3 Kerogen Type

The second stage of the source rock evaluation of the Heatherdale Shale involves determination of its kerogen type. Kerogen is the insoluble portion of the organic matter within sedimentary rocks (Dow, 1977). Kerogen forms during diagenesis, the period in which a sedimentary system tends to approach equilibrium under conditions of shallow burial (Tissot and Welte, 1984). The diagenetic phase involves only mild increases in temperature and pressure so that inorganic and organic transformations occur at slow rates. Continuing sedimentation and accumulation of overburden result in substantial increases in temperature and pressure, and the delineation of a new phase of evolution, catagenesis. Catagenesis is associated with temperatures of 50-150°C and pressures of 3-10 Kbars (Tissot and Welte, 1984), disrupting the equilibrium of diagenesis. Organic matter undergoes a spectacular transition, with kerogen producing liquid petroleum, wet gas and condensate. The onset of metagenesis comes after the termination of hydrocarbon expulsion. Here the sediments are placed under extreme temperatures and pressures that are close to those of metamorphism. Residual kerogen increases in aromaticity and takes on a graphitic composition and appearance.

The standard procedure for kerogen typing is elemental analysis which has the capability of classifying kerogens according to their ability to generate oil and gas at depth (Durand and Monin, 1980). For the purpose of this study, 9 kerogen samples were isolated, using a methodology described by B. Michaelsen (pers comm.) (Appendix III) and then sent to National Analytical Laboratories in Melbourne for microanalysis. The results obtained were weight percent C, H, N and ash (Appendix IV). Such elemental data are traditionally represented on a van Krevelen diagram (Figure 8) which plots H/C against O/C. The value of the van Krevelen diagram is undeniable in that it immediately gives information on kerogen type, and thermal maturity (Section 3.4.1). The Heatherdale Shale kerogens, as shown by the range bars on the left hand side of Figure 8, all have H/C values below 0.36 and plot in the zone of metagenesis. Although maturity information is obtained, the type of organic matter cannot be determined because, by this stage of thermal maturation the evolution pathways of all three kerogen types have converged. A Type II kerogen composition may be assumed for the marine Heatherdale Shale. Type II kerogen is formed in marine environments where autochthonous organic matter, derived from a mixture of phytoplankton, zooplankton and bacteria, has been deposited in a reducing environment (Tissot and Welte, 1984). This compares with relatively rare Type I kerogen formed in lacustrine environments and Type III kerogen derived from terrestrial plant matter. For the purpose of this study a Type II composition is assumed for the organic matter originally preserved in the Heatherdale Shale on the basis of its Early Cambrian age, marine biota and the anoxic depositional setting implied by TOC values in excess of 2.57%. Moreover, such organic matter is decidedly oil prone, i.e. capable of generating oil (as well as some gas) during its passage through the oil window.

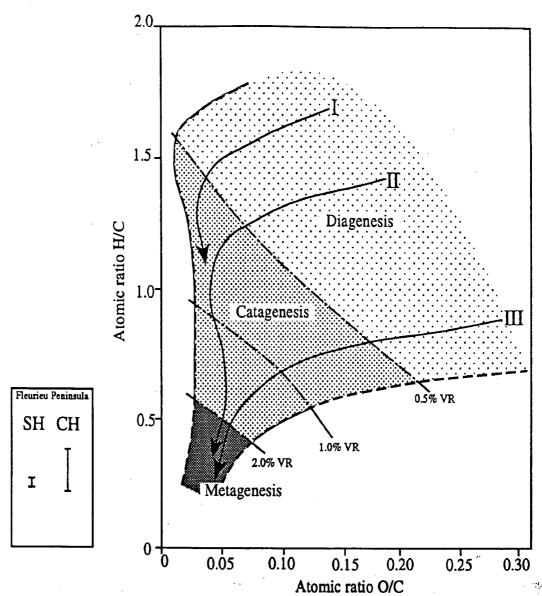


Figure 8: van Krevelen diagram
The box on the left indicates the range of H/C results attained from Sellick Hill (SH) and
Carrickalinga Head (CH).

3.4 Thermal Maturity

3.4.1 Kerogen H/C Atomic Ratio

As discussed in Section 3.3, a preliminary estimate of the degree of thermal maturation can be derived from the van Krevelen diagram. The H/C values of kerogens from both Carrickalinga Head and Sellick Hill place them in the zone of metagenesis, or thermal overmaturity (Figure 8). The lower H/C values of the Sellick Hill samples (H/C = 0.23-0.24) is due to a combination of greater structural deformation in the Sellick Hill region and a greater amount of burial.

Importantly, the results show that the organic matter has at some stage passed through the oil window, (0.5-1.35% VR: Figure 8) potentially forming an economic hydrocarbon resource. The realisation of this potential resource is dependent on the formation of appropriate structural traps, delineated in seismic sections, as well as the presence of appropriate cap rocks (seals). As these results represent overmature, "end-member" examples of Heatherdale source beds along the western margin of the Fleurieu Peninsula, it is hypothesised that less mature organic matter can be found offshore in the Stansbury Basin beneath Gulf St Vincent.

3.4.2 Isotope Analysis

The high level of thermal maturity indicated by Figure 8 implies that the Heatherdale Shale has undergone substantial heating. Study of the stable carbon isotopic composition of the kerogen can help to distinguish the influence of metamorphism from that of "natural" burial. Five kerogen samples were chosen for stable carbon isotope studies (Appendix III). The results are given as δ^{13} C values, expressed as per mil difference from the Peedee Belemnite (PDB) standard (Appendix IV). Baker and Claypool (1970) and McKirdy and Powell (1974) suggested that stable carbon isotopic composition of kerogen changes during thermal maturation. The changes in δ^{13} C are most pronounced in samples with H/C values of less than 0.30 (McKirdy and Hahn, 1975), and thus are an applicable indicator for the the Heatherdale Shale.

A study of the Tindelpina Shale Member of the late Neoproterozoic Tapley Hill Formation by McKirdy et al. (1975) divided kerogen samples into graphitic and sub-graphitic categories by plotting H/C against δ^{13} C values. A comparison of these results with the Heatherdale Shale samples shows that the new data are significantly removed from the sub-graphitic Tindelpina Shale kerogens. A second study by McKirdy and Hahn (1975), using the same approach with additional samples produced a curve which showed how the isotopic composition of kerogen changes with the atomic H/C ratio. The results were also used to delineate a metamorphic threshold (Figure 9), below which overmature samples are said to have entered the zone of metamorphism. The metamorphic threshold aligns with the H/C value of 0.2, where the average curve suddenly trends from sub-horizontal to vertical. It is evident that the Heatherdale Shale kerogens plot above the metamorphic threshold.

This set of results indicates that the Heatherdale Shale in the study area has not undergone metamorphism. A modelled peak metagenetic temperature of 220°C (Chapter 4) is less than the temperature required for biotite or chlorite zone metamorphism (lower greenschist facies) assigned to the Fleurieu Peninsula by Offler and Fleming (1968). It is likely therefore that a combination of mild regional heating (the most probable source being the Delamerian Orogeny) and sediment burial has resulted in the observed maturity level of this Early Cambrian sequence.

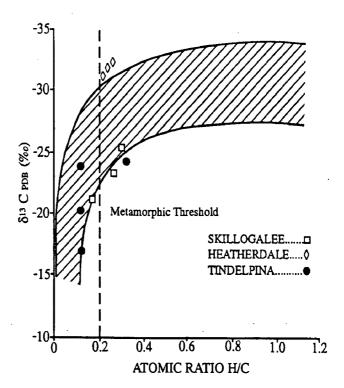


Figure 9: A crossplot of kerogen stable isotopic composition and atomic H/C ratio showing the relationship to the metamorphic threshold.

3.4.3 Methylphenanthrene Index

The Methylphenanthrene Index (MPI) is a relatively new maturity indicator, used increasingly in basin analysis over the last twelve years. It is a replacement for the conventional vitrinite reflectance, which cannot readily be applied to ancient sediments, such as the Heatherdale Shale, deposited prior to the appearance of vascular plants (Summons et al., 1994). Studies on aromatic hydrocarbon fractions have shown that the distribution of methylphenanthrene homologues is strongly controlled by thermal maturation processes (Radke and Welte, 1983; Radke, 1988). Furthermore the MPI, based on phenanthrene and the four isomers of methylphenanthrene, exhibits a close correlation with measured vitrinite reflectance values in younger rocks.

Four shale samples from strategic stratigraphic positions were chosen for analysis. The samples were prepared by extracting the soluble organic matter from the rock powder and then using column chromatography to separate it into three fractions: saturates, aromatics and polar compounds (Appendix III). The aromatic fraction was then analysed on a Varian 3400 gas chromatograph (GC) coupled with a Finnegan TSQ mass spectrometer (MS).

Unfortunately, only one of the samples yielded sufficient aromatic hydrocarbons for analysis (viz. sample C-17 from Carrickalinga Head: Figure 10). This sample gave an MPI of 0.90 and a calculated vitrinite reflectance (VRcalc) of 2.50 % (for full calculations see appendix IV). This result agrees with the other maturation indicators discussed in Sections 3.4.1 and 3.4.2.

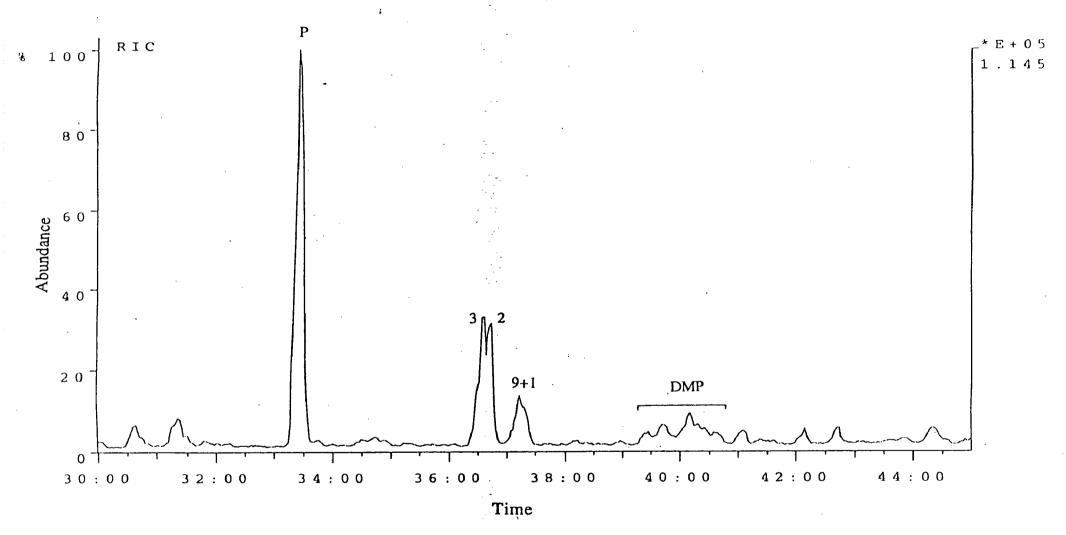


Figure 10: GC-MS trace of m/z 178, 192 and 206 (RIC). Explanation of symbols: P = phenanthrene; 3,2,9 and 1 refer to 3-MP, 2-MP, 9-MP and 1-MP respectively, where MP = methylphenanthrene; DMP = dimethylphenanthrenes.

4. THERMAL MODELLING

4.1 Introduction

The BasinMod computer package (at the National Centre for Petroleum Geology and Geophysics) models the thermal evolution of the source rocks of a sedimentary basin with the aims of 1) constraining the timing of hydrocarbon generation, 2) correlating this with trap formation and, 3) assessing the likelihood of preservation of any hydrocarbons generated. Realisation of these aims for the Stansbury Basin required an assessment of its geologic history.

An important aspect of the geological history in thermal modelling is recognising when erosion could have occurred. Two major periods of erosion, one during the Cambro-Ordovician Delamerian Orogeny and the other linked to the Permian glaciation, removed thick sequences of Cambrian sediments. Of these two events, erosion associated with the Delamerian Orogeny is considered to have been much greater. The Permian sediments clearly have not been subjected to so great a depth. Thus post Permian erosion is of little relevance to the maturation observed in the Cambrian sediments.

The parameters required for this basin modelling exercise include: the thickness of the stratigraphic units present now (determined by field observation and stratigraphic interpretation), and vitrinite reflectance values, kerogen type and average TOC values of the source rocks. The aim of the modelling exercise was to produce a logical combination of parameters that best suit the known geology of the Stansbury Basin. The equivalent vitrinite reflectance values were used to constrain maximum temperatures and the thickness of the section that has been removed by erosion.

Two locations were modelled along Canyon's 92-5 seismic line: shot point 2420, 15 km NNW of Carrickalinga Head and shot point 620, 20 km to the ENE of Kangaroo Island (Appendix V). These two locations were specifically chosen as end member scenarios, with calculated vitrinite reflectance values of 2.5% and 1.2% respectively. The Kangaroo Island modelling utilised core samples and data from the Mount McDonnell Formation in Investigator-2 (McKirdy, 1994). The top of the Mount McDonnell Formation correlates with the base of the Heatherdale (Hibburt, 1994). Carrickalinga Head calculated vitrinite reflectance data came from outcrop samples. Modelling assumed the offshore portion of the Heatherdale Shale had the same maturity as its onshore equivalent.

4.2 Carrickalinga Head

A vitrinite reflectance value of 2.5% for the Heatherdale Shale at Carrickalinga Head would require approximately 10 km of overburden to generate the heating needed, under normal geothermal gradients (approximately 25° C per km) for this level of thermal maturity. However, the total preserved section onshore on Fleurieu Peninsula places the Heatherdale Shale under 2300 m of overburden. This suggests that either vast amounts of sediment have been removed at some stage over geologic time or an external heat source has "cooked" the source rock, or a combination of both. The lack of metamorphism (Section 3.4.2) indicates that the former alternative is more likely. The mechanism most likely to have deposited and removed the massive quantities of sediment required to achieve such a high maturation level involved the deposition of the Kanmantoo Group (after the Kangarooian Movements), followed by the action of the Delamerian Orogeny. The preferred model (Figure 11) suggests that a maximum sediment thickness of 7 km was present by the late Cambrian (Kanmantoo Group) and, prior to the onset of the Delamerian Orogeny. The geothermal gradient, with 8km of burial still falls short of the heat requirements of the model. Therefore, it is assumed that the granites at Victor Harbor with high grade contact aureoles are proximal enough to potentially increase the magnitude of the regional geothermal gradient. During the Early and Middle Cambrian between 518 and 500 Ma, the Heatherdale Shale was buried to depths of approximately 8 km, and its kerogen passed through the oil and gas generation windows. This is clearly shown on Figure 11, which enables an accurate constraint to be placed on the timing of the successive phases of hydrocarbon generation.

A temperature curve, which tracks the temperature changes within the Heatherdale Shale during basin evolution, indicates a maximum temperature of 220°C for this formation (Appendix V), just prior to the onset of Delamerian erosion. Assuming that its generated petroleum was trapped in a contiguous reservoir, e.g. within the updip Kulpara Formation, it can be seen from Figure 12 that gas would be the most likely hydrocarbon product to have survived to the present day, its retention dependant on appropriate structure. Evidence from the seismic section shows a sparsity of nearby structure. However recent work by Flöttmann et al. (1994) indicates a series of nearshore fault blocks that could act as traps for hydrocarbons. The maintenance of trap integrity is vitally important, as hydrocarbons may escape a breached reservoir.

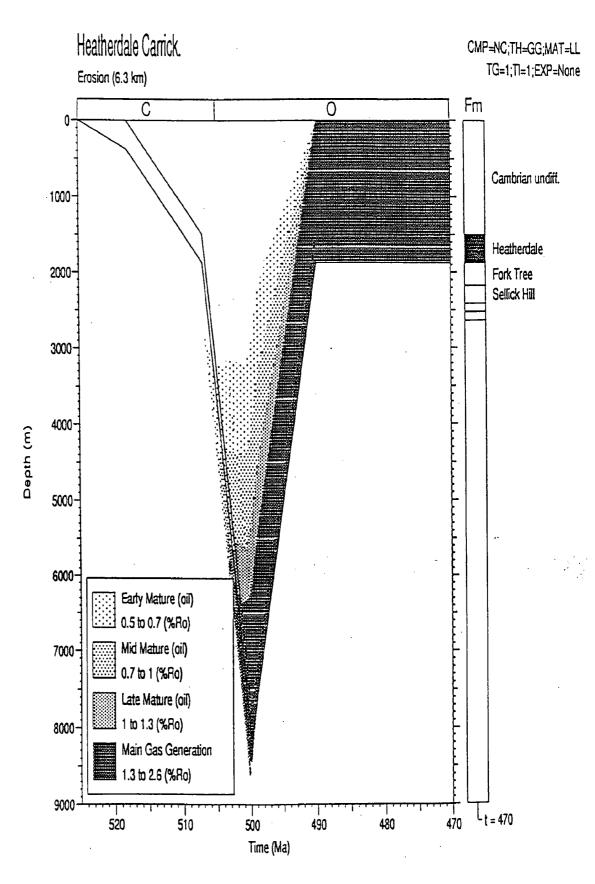


Figure 11: Thermal modelling of the Heatherdale Shale, Carrickalinga Head. The diagram tracks the vertical movement of the Heatherdale Shale from the Late Cambrian to Early Ordovician period. A maximum burial depth of 8.5 km at 500 Ma, the onset of the oil window at 506 Ma and the dominance of the gas generative phase are the dominant features of the figure. The assumed geothermal gradient is 25° C per km.

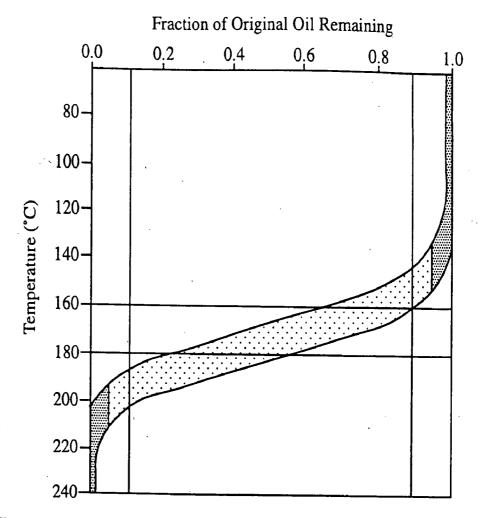


Figure 12: Fraction of oil remaining in a reservoir as a function of reservoir temperature (Pepper, A.S. and Dodd, T.A. In press.)

4.2.2 Kangaroo Island

The Mount McDonnell Formation modelling is of extreme importance, as it is close to a major exploration target identified by Canyon Australia Ltd. from their seismic interpretation. Allowing for similarities within the basin, an analogous set of parameters to the Carrickalinga Head model was used in the Kangaroo Island model. The lower calculated vitrinite reflectance value of 1.2% was an immediate indicator that a lesser thickness of overburden was required to achieve the level of thermal maturation measured. A thickness of 4 km of sediment, deposited in the Cambrian prior to the Delamerian Orogeny, and subsequently removed is suggested by the model (Figure 13). The corresponding temperature curve in this case is vastly different to its Carrickalinga counterpart (Appendix V). A maximum temperature of 165°C, implies that approximately 60% of any oil that charged the adjacent structure is still present as oil, the remainder has been cracked *in situ* to gas. This has exciting implications for Canyon's exploration program as the seismic section clearly delineates a potential anticlinal trap.

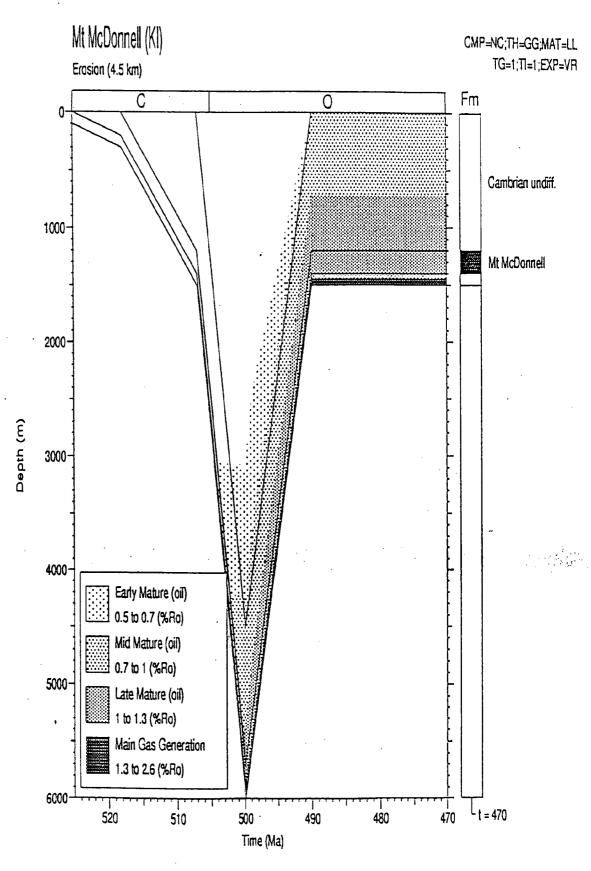


Figure 13: Thermal modelling of the Mt. McDonnell Formation, Kangaroo Island. A lower calculated vitrinite reflectance and lesser depth of burial result in a vastly different scenario to that seen at Carrickalinga Head. The dominance of the oil phase and less "severe" burial depth are apparent from the diagram. The assumed geothermal gradient is 25° C per km.

5. SUMMARY

- 1. The Heatherdale Shale is the youngest formation of the Early-Mid Cambrian Normanville Group, Fleurieu Peninsula. It can be divided into an Upper and Lower Member. The formation represents the transition from ramp to basinal facies deposition at the end of a marine transgressive cycle.
- 2. The characteristics displayed by the Upper Heatherdale Shale a carbonaceous, pyritic, phosphatic silty-shale delineate it as a potential petroleum source rock.
- 3. The unit has a minimum thickness of 280 m in the Sellick Hill region, and has been removed by erosion in the Carrickalinga Head area. The majority of the Upper Heatherdale Shale is variably weathered and structurally deformed. A type section 55 m, out of a minimum unit thickness of 280 m was the focus of source rock studies.
- 4. TOC analysis of the Upper Heatherdale Shale (mean = 1.73%) rated its source richness as moderate to good. Similar analysis of the Lower Heatherdale Shale from Carrickalinga Head was undertaken (mean = 0.79%) and the resultant richness rating was fair to moderate.
- 5. Atomic H/C analysis of the kerogen isolated from whole rock samples showed that the Heatherdale Shale was overmature.
- 6. Although overmature, the Heatherdale Shale has not been metamorphosed, as indicated by its pristine stable carbon isotopic composition. A comparison of isotopic composition and H/C ratios indicated that the samples were above the metamorphic threshold.
- 7. The most reliable maturity indicator of pre-landplant organic matter, the Methylphenanthrene Index, confirmed the overmature status of the Heatherdale Shale. This parameter also enabled the calculation of an equivalent vitrinite reflectance (2.5%).
- 8. Thermal modelling, utilising the maturity data gathered, provided end-member thermal maturation scenarios for the major source rocks in the Stansbury Basin.
- 9. Between 518 and 500 Ma, Heatherdale Shale (Carrickalinga Head) kerogen reached a maximum temperature of 220° C illustrating that the liquid hydrocarbons produced would have undergone *in situ* cracking. Hence gas is the most likely hydrocarbon product to be remaining today in any adjacent traps.
- 10. At a similar time, Mount McDonnell kerogen reached a maximum temperature of 165° C, indicating that of the liquid hydrocarbons produced, only 40% have cracked into gas. This model is further enhanced by the appearance of an appropriate structural trap on seismic sections.
- 11. The data indicate that the Early Cambrian sequence within the Stansbury Basin is potentially oil and gas bearing which has important implications for exploration strategies.

REFERENCES CITED

- Abele, C. and McGowran, B. 1959. The geology of the Cambrian south of Adelaide (Sellick Hill to Yankalilla). Transactions of the Royal Society of South Australia 82, 301-320.
- Alexander, E.M. and Gravestock, D.I. 1990. Sedimentary facies in the Sellick Hill formation, Fleurieu Peninsula, South Australia. In: Jago, J.B. and Moore, P.S. (eds.) The Evolution of a Late Precambrian-Early Palaeozoic Rift Complex: The Adelaide Geosyncline. Geological Society of Australia, Special Publication 16, 269-289.
- Allison, P.A. 1990. Carbonate Nodules and Plattenkalks. In:Briggs, D.E. and Crowther, P.R. (eds.) *Palaeobiology, a Synthesis*, pp 250-253.
- Baker, D.R. and Claypool, G.E. 1970. Effects of incipient metamorphism on organic matter in mudrock. *American Association of Petroleum Geologists Bulletin* 54, 456-468.
- Berner, R.A. 1968. Calcium carbonate concretions formed by the decomposition of organic matter. *Science* 159, 195-197.
- Campana, B., Wilson, R.B. and Whittle, A.W.G. 1953. The geology of the Jervis and Yankalilla Military sheets. Report of Investigation of the Geological Survey of South Australia 3.
- Cernovskis, A. 1983. A sedimentological approach to the geology of the Carrickalinga Head Area, Fleurieu Peninsula. BSc Honours thesis, Flinders University (unpublished).
- Coleman M.L. and Raiswell, R. 1981. Carbon, Oxygen and Sulphur isotope variations in concretions from the Upper Lias of NE England. Geochimica et Cosmochimica Acta 45, 329-340.
- Cooper S.J. 1985. The geology of the Sellick Hill-Myponga Beach Area. Graduate thesis, School of Applied Geology, South Australian Institute of Technology (unpublished).

- Cooper, J.A., Jenkins, R.J.F., Compston, W. and Williams, I.S. 1992. Ion probe zircon dating of a Mid-Early Cambrian tuff in South Australia. *Journal of the Geological Society* 149, 185-196.
- Curtis, C.D. 1980. Diagenetic alteration in Black Shales. Journal of the Geological Society of London 137, 189-194.
- Daily, B., Firman, J.B., Forbes, B.G. and Lindsay, J.M. 1976. Geology. In: Twidale, C.R., Tyler, M.J. and Webb, B.P. (eds.) Natural History of the Adelaide Region, Royal Society Of South Australia.
- Daily, B. 1963. The fossiliferous Cambrian succession on Fleurieu Peninsula, South Australia. Records of the South Australian Museum 14, 579-601.
- Demaison, G. J. and Moore, G.T. 1980. Anoxic environments and oil source bed genesis. American Association of Petroleum Geologists Bulletin 64, 1179-1209.
- Dickson, J.A.D. and Barber, C. 1976. Petrography, chemistry and origin of early diagenetic concretions in the Lower Carboniferous of the Isle of Man. Sedimentology 23, 189-211.
- Dow, W.G. 1977. Kerogen Studies and Geological Interpretation. *Journal of Geochemical Exploration* 7, 79-99.
- Durand, B. and Monin, J.C. 1980. Elemental analysis of kerogens (C, H, O, N, S, Fe). In: Durand, B. (ed.) Kerogen-insoluble organic matter from sedimentary rocks, 113-142.
- Flöttmann, T., James, P., Rogers, J. and Johnson, T. 1994. Early Palaeozoic foreland thrusting and basin reactivation at the Palaeo-Pacific margin of the southeastern Australian Precambrian Craton: a reappraisel of the structural evolution of the Southern Adelaide Fold-Thrust Belt. *Tectonophysics* 233, 1-22.
- Foster, C.B., Cernovskis, A. and O'Brien, G.W. 1985. Organic walled microfossils from the Early Cambrian of South Australia. *Alcheringa* 9, 259-268.

- Gatehouse, C.G., Jago, J.B. and Cooper, B.J. 1990. Sedimentology and Stratigraphy of the Carrickalinga Head Formation (low stand fan to high stand systems tract), Kanmantoo Group, South Australia. In: Jago, J.B. and Moore, P.S. (eds.) The Evolution of a Late Precambrian-Early Palaeozoic Rift Complex: The Adelaide Geosyncline. Geological Society of Australia, Special Publication 16, 351-368.
- Guclear and Gross, M.G. 1964. Recent Marine Sediments in Saanich Inlet, a stagnant marine basin. Limnology and Oceanography 9, 358-376.
- Hibburt, J. (compiler) 1994. Stansbury Basin. In: Petroleum Exploration and Development, 9th edition, Department of Mines and Energy, South Australia.
- Howchin, W. 1897. On the occurrence of Lower Cambrian fossils in the Mount Lofty Ranges. Transactions of the Royal Society of South Australia 21, 74-86.
- Hudson, J.D. 1978. Concretions, isotopes, and the diagenetic history of the Oxford Clay (Jurassic) of Central England. Sedimentology 25, 339-370.
- Hunt, J. M. 1972. Distribution of carbon in crust of Earth. American Association of Petroleum Geologists Bulletin 56, 2273-2277.
- Irwin, H., Curtis, C. and Coleman, M. 1977. Isotopic evidence for source of diagenetic carbonates formed during burial of organic-rich sediments. *Nature* 269, 209-213.
- Jago J.B., Dyson, I.A. and Gatehouse, C.G. 1994. The nature of the sequence boundary between the Normanville and Kanmantoo Groups on Fleurieu Peninsula, South Australia. Australian Journal of Earth Science 41, 445-453.
- Jago, J.B., Gehling, J.G. and Daily, B. 1986. Cambrian sediments of the Sellick Hill-Carrickalinga Head, Fleurieu Peninsula. In: Parker, A.J. (compiler) One day geological excursions of the Adelaide Region: including the Barossa Valley, Mt Lofty Ranges and Fleurieu Peninsula., pp 67-81.

- Jago, J.B., Daily, B.D., Von Der Borch, C.C., Cernovskis, A. and Saunders N. 1984. First reported trilobites from the Lower Cambrian Normanville group, Fleurieu Peninsula, South Australia. Transactions of the Royal Society of South Australia 108, 207-211.
- Jenkins, R.J.F. 1990. The Adelaide Fold Belt: Tectonic reappraisal. In: Jago, J.B. and Moore, P.S. (eds.) The Evolution of a Late Precambrian-Early Palaeozoic Rift Complex: The Adelaide Geosyncline. Geological Society of Australia, Special Publication 16,396-420.
- Jenkins, R.J.F. and Hasenohhr, P. 1989. Trilobites and their trails in a black shale: Early Cambrian of the Fleurieu Peninsula, South Australia. Transactions of the Royal Society of South Australia 113, 195-203.
- Madigan, C.T. 1925. The geology of the Fleurieu Peninsula. Part 1-The coast from Sellick's Hill to Victor Harbour. Transactions of the Royal Society of South Australia 49, 198-212.
- Madigan, C.T. 1927. Organic remains from below the Archaeocyathinae Limestone at Myponga Jetty. Transactions of the Royal Society of South Australia 50, 31-35.
- Mancktelow, N.S. 1990. The structure of the Southern Adelaide Fold Belt, South Australia. In: Jago, J.B. and Moore, P.S. (eds.) The Evolution of a Late Precambrian-Early Palaeozoic Rift Complex: The Adelaide Geosyncline. Geological Society of Australia, Special Publication 16, 269-289.
- Mawson, D. 1925. Evidence and indications of algal contributions in the Cambrian and Precambrian limestones of South Australia. Transactions of the Royal Society of South Australia 50, 186-190.
- McKirdy, D.M. and Powell, T.G. 1974. Metamorphic alteration of carbon isotopic composition in ancient sedimentary organic matter: new evidence from Australia and South Africa. *Geology* 2, 591-595.
- McKirdy, D.M., Sumartojo, J, Tucker, D.H. and Gostin, V. 1975. Organic, mineralogic and magnetic indications of metamorphism in the Tapley Hill Formation, Adelaide Geosyncline. *Precambrian Research* 2, 345-373.

- Jago, J.B., Daily, B.D., Von Der Borch, C.C., Cernovskis, A. and Saunders N. 1984. First reported trilobites from the Lower Cambrian Normanville group, Fleurieu Peninsula, South Australia. Transactions of the Royal Society of South Australia 108, 207-211.
- Jenkins, R.J.F. 1990. The Adelaide Fold Belt: Tectonic reappraisal. In: Jago, J.B. and Moore, P.S. (eds.) The Evolution of a Late Precambrian-Early Palaeozoic Rift Complex: The Adelaide Geosyncline. Geological Society of Australia, Special Publication 16,396-420.
- Jenkins, R.J.F. and Hasenohhr, P. 1989. Trilobites and their trails in a black shale: Early Cambrian of the Fleurieu Peninsula, South Australia. Transactions of the Royal Society of South Australia 113, 195-203.
- Madigan, C.T. 1925. The geology of the Fleurieu Peninsula. Part 1-The coast from Sellick's Hill to Victor Harbour. Transactions of the Royal Society of South Australia 49, 198-212.
- Madigan, C.T. 1927. Organic remains from below the Archaeocyathinae Limestone at Myponga Jetty. Transactions of the Royal Society of South Australia 50, 31-35.
- Mancktelow, N.S. 1990. The structure of the Southern Adelaide Fold Belt, South Australia. In: Jago, J.B. and Moore, P.S. (eds.) The Evolution of a Late Precambrian-Early Palaeozoic Rift Complex: The Adelaide Geosyncline. Geological Society of Australia, Special Publication 16, 269-289.
- Mawson, D. 1925. Evidence and indications of algal contributions in the Cambrian and Precambrian limestones of South Australia. Transactions of the Royal Society of South Australia 50, 186-190.
- McKirdy, D.M. and Powell, T.G. 1974. Metamorphic alteration of carbon isotopic composition in ancient sedimentary organic matter: new evidence from Australia and South Africa. *Geology* 2, 591-595.
- McKirdy, D.M., Sumartojo, J, Tucker, D.H. and Gostin, V. 1975. Organic, mineralogic and magnetic indications of metamorphism in the Tapley Hill Formation, Adelaide Geosyncline. *Precambrian Research* 2, 345-373.

- McKirdy, D.M. and Hahn, J.H. 1975. The composition of kerogen and hydrocarbons in Precambrian rocks. In Holland, H.D. and Schidlowski, M. (eds.) Mineral Deposits and the Evolution of the Biosphere, pp 123-154.
- McKirdy, D.M. 1993. Cambrian source rock geochemistry, Stansbury basin. Report for Canyon (Australia) Pty. Ltd. (unpublished).
- McKirdy, D.M. 1994. Cambrian source rock Geochemistry, Stansbury Basin: 3. Thermal maturity of Early Cambrian Mount McDonnell Formation in Investigator-2, Northern Kangaroo Island. Report for Canyon (Australia) Pty. Ltd. (unpublished).
- Mozley, P.S. and Burns, S.J. 1993. Oxygen and carbon isotopic composition of marine carbonate concretions-an overview. *Journal of Sedimentary Petrology* 63, 73-83.
- Offler R. and Fleming P.D. 1968. A synthesis of folding and metamorphism in the Mt. Lofty Ranges, South Australia. *Journal of the Geological Society of Australia* 15, 245-266.
- Padley, D., Michaelsen, B.H. and McKirdy, D.M. 1991. Organic Geochemical Procedures: A Protocol of Preparative Geochemistry, 2nd edition (unpublished).
- Pepper, A.S. and Dodd, T.A. 1994. Simple kinetic models of petroleum formation, Part 2: oil-gas cracking. *Marine and Petroleum Geology* (in press).
- Powell, T.G. 1985. Applying geochemical concepts to play analysis and basin evaluation. *PESA Journal* 6, 25-39.
- Preiss, W.V. 1990. A stratigraphic and tectonic overview of the Adelaide Geosyncline, South Australia. In: Jago, J.B. and Moore, P.S. (eds.) The Evolution of a Late Precambrian-Early Palaeozoic Rift Complex: The Adelaide Geosyncline. Geological Society of Australia, Special Publication 16, 1-33.
- Radke, M. 1988. Application of aromatic compounds as maturuty indicators in source rocks and cude oils. *Marine and Petroleum Geology* 5, 224-236.

- Radke, M. and Welte, D.H. 1983. The Methylphenanthrene Index (MPI): A Maturity parameter based on Aromatic hydrocarbons. In Bjoroy, M. et al. (eds.) Advances in Organic Geochemistry, 1981, Wiley, Chichester, 504-512.
- Raiswell, R. 1971. The growth of Cambrian and Liassic concretions. Sedimentology 17, 147-171.
- Raiswell, R. 1976. The microbial formation of carbonate concretions in the Upper Lias of NE England. *Chemical Geology* 18, 227-244.
- Raiswell, R. 1987. Non steady state microbiological diagenesis and the origin of concretions and nodular limestones. In: *Diagenesis of Sedimentary Sequences*. Geological Society Special Publication 36, 41-54.
- Raiswell, R. 1988. Evidence for surface reaction-controlled growth of carbonate concretions in shales. Sedimentology 35, 571-575.
- Scholefield, T. 1983. Geology of the Carrickalinga Area. Graduate thesis, School of Applied Geology, South Australian Institute of Technology. (unpublished).
- Sprigg, R.C. 1961. The oil and gas prospects of the St. Vincent Gulf Graben. APEA Journal 1, 71-88.
- Summons, R.E., Taylor, D. and Boreham, C.J. 1994. Geochemical tools for evaluating petroleum generation in middle Proterozoic sediments of the McArthur Basin, Northern Territory, Australia. *APEA Journal* 34, 692-706.
- Thomson, B.P. 1970. A review of the Precambrian and Lower palaeozoic tectonics of South Australia. Transactions of the Royal Society of South Australia 94, 193-221.
- Tissot, B.P. and Welte, D.H. 1984. Petroleum Formation and Occurence, 2nd edition. Springer-Verlag, Berlin.
- Tucker, M.E. 1991. Sedimentary Petrology, 2nd Edition. Blackwell Scientific Publications, William Clowes Ltd, London, 260pp.

- Turner, B.L. 1994. Cambrian black shales in the Karinya Syncline: stratigraphic distribution, sedimentology and kerogen composition. Honours thesis, University of Adelaide (unpublished).
- Waples, D.W. 1979. Simple Method for Oil Source Bed Evaluation. American Association of Petroleum Geologists Bulletin 63, 239-248.
- Waples, D.W. 1982. Phosphate-rich sedimentary rocks: significance for organic facies and Petroleum Exploration. *Journal of Geochemical Exploration* 16, 135-160.
- Waples, D.W. 1985. Geochemistry in Petroleum Exploration. International Human Resources Development, Boston, 232pp.
- Weeks, L.G. 1953. Environment and mode of origin and facies relationships of carbonate concretions in shales. *Journal of Sedimentary Petrology* 23, 162-173.
- Wright, R.G. 1967. Geological and geochemical report on the Sellick Hill Area.

 Mineral Resources Review, South Australia 126, 21-32.
- Wright, R.G. 1968. Second geological and geochemical report on the Sellick Hill Area. Mineral Resources Review, South Australia 128, 119-126.
- Wright, R.G. 1970. Third geological and geochemical report on the Sellick Hill Area.

 Mineral Resources Review, South Australia 132, 110-120.

ACKNOWLEDGEMENTS

My Honours year has been the culmination of a very enjoyable and rewarding University career. I would sincerely like to thank all the people who have invested their precious time in offering me advice, technical assistance, and friendship over the year.

Firstly my sincerest thanks go to my supervisor Dr David McKirdy who had the faith in me to fulfil the ambituous aims of this project. His continued advice and exacting red pen treatment of my written work have been invaluable.

I would like to thank Canyon Australia Ltd for their financial support of this study.

A big thank you to my fellow organic geochemists, Chris Hepplewhite and Bronwyn Turner, for their companionship, field assistance and willingness to have a chat when things started to get a bit out of hand.

The support of Bernd Michaelsen as lab mentor and zero-hour proof-reader has been immensely appreciated.

Many thanks to Dr Peter Tingate and Dr Thomas Flöttmann at various stages of the year, for giving me insights into their respective areas of expertise, thermal modelling and structural geology.

Thanks to the technical and assistance staff: Sherry, Geoff and Wayne, Keith, Rick and Rosemary for their neverending patience and tolerance throughout the year.

A highlight of my fieldwork was the fantastic accommodation that I was lucky enough to attain. Thanks to Jill and Ash Hallandal for the use of their luxurious beach house at Sellicks, and to Sue and Malc Jones for the use of their van at Nuriootpa.

A BIG thanks to the rest of my colleagues who have ridden the Honours rollercoaster with me. Their friendship, support and positive attitude have made life easier during the year and really enjoyable. My sincerest best wishes for the future to all of them in their chosen fields.

The biggest vote of thanks go to my family. I am indebted to their ever present patience, financial and emotional support without which the opportunities that have presented themselves to me over the years would not have been forthcoming.

APPENDIX I

Stratigraphic Logs

| | UNIN | ÆRS | ITY O | F AD | ELAI | DE - HONOURS | GEOL | OGY | Sheet1 of3 |
|--------------|---------|--------|-------|------|--------|-------------------------|------------|-------------|---|
| STR | | | _ | | | HC LO | | | HEET From0. m to .25 m |
| Locati | | | | | | | | | eatherdale Shale Upper Member Measured by MC/BT |
| | ke] | Pur | pur | nd | lay | Analytical | samp | les denoted | d with # Strike / dip of beds03.0/65.W |
| Metres | Gravel | C.sand | M.s | F.sa | silt/c | Analytical Litho log | • | Structure | Shale Siltstone Sandstone Carbonate |
| | | | | | Ī | ם ם ם | S28# | | |
| _ | | | | | | | 320# | | |
| | | | | | | | | | |
| - | | | | | | | | | · |
| | | | | | | | | | |
| | | | | | | | | | |
| _ | | | | | | | S27# | | |
| | | | | | | \$-\$-\$ | | | |
| 20 - | | | | | | | | | |
| | | | | | | | | | |
| - | 1 | | | | | | | | |
| - | | | | | | | S26 | | |
| 1 | | | | | | | | | |
| - ∤ | | | | | | 0.00 | | | · |
| | | | | | | | | | |
| - | | | | | | | | İ | |
| 15_ | | | | ٠, | | | S25# | ł | • |
| | | | ļ | | | | | | |
| - | | | | ١ | | | | | Uniform black shale/siltstone The mock is fissile, the angle between bedding and |
| E _ | | | | | | X X X | | | The rock is fissile, the angle between bedding and cleavage is approximately 30° |
| Jess |] | | | | | | 1 | 1 | |
| hickness (m) | | | | | | | 1 | | · |
| F | | | | | | | S24/ | 4 | |
| - | 1 | | | | | | | | |
| 10- | | | | | | | | | |
| 10- | | | | | | | S234 | A | · |
| - | ļ | | | | I | 0.0.0 | | | |
| | , | | | | ı | | 1 | | |
| - | | | | | I | | 1 | | |
| İ _ | | ļ | | | | |] S22# | # | · |
| - |] | | | | | | | | |
| - | - | | | | | | S21 | * | |
| | | | | | | | 1 | | Phosphate stringers aligned along bedding |
| 5- | 1 | | | | | | | | |
| _ | | | | | | \$-\$-\$ | S20/ | 7 | Uniform black shale/siltstone with pyrite laminations |
| | | | | | | | S19 | , | |
| - | \cdot | | | | | <u> </u> | 1 | | |
| | | | | | | ,4,4,-,-,-,- | S186 | | Black, pyritic shale/siltstone |
| - | 1 | | | | | | S17 | # | prime, prince summering |
| _ | | | ' | | | COOT | S16 | | The carbonate concretionary layer at the 1m mark of this section |
| | | | | | | \$-\$-\$ | S15 | 1 | corresponds to the 2m mark above the contact between the Lower and Hoper Members of the unit (plate 3a) |

| | LINI | VERS | TY O | FADEL | AIDE - HONOURS | GEOL | OGY | | - | Sheet2. of3 |
|---------------|------|-------|-------|-------|--------------------------------|------|--------------------------|-------------------|----------------------|--|
| STE | | | | | HIC LO | | | HEET | | From .25 m to .50 m |
| Local | | | | | 71 | | | atherdale Shale U | pper Member | Measured by MC/BT Strike / dip of beds 030/65W |
| Metres | Grav | C.san | A.san | Sand | Analytical : | samp | les denoted Structure | | Siltstone | Sandstone Carbonate |
| Metres | | Ť | | | S S S | | Saucime | | <u> </u> | |
| _ | | | | | | | | | | ı |
|] | | | | ` | | | | | | |
| - | | | | | | | | | | |
| | | | | | | S37# | | | | |
| - | 1 | | | | | S36 | | | | |
| - | | | | | | | | The shale subjets | acatains the absent | Shoto is slightly lighter in colour |
| | ļ | | | | | | | The shale which | of pyrite tends to c | phate is slightly lighter in colour correspond to an equivalent |
| 45- | | | | I | | | | decrease in phos | pnate | |
| _ | | | | | | | | | | |
| | | | | | | S35# | • | | | |
| - | 1 | | | | | | | A comparison w | ith the TOC graph | (fig. 7) shows that the greater source te is most concentrated |
| _ | | | | | | | | bed richness occ | curs where phospha | ate is most concentrated |
| | | | | | | | | - | | |
| - | 1 | | | | | S34 | | | | |
| 40_ | | | | | | S33# | | | | |
| | | | | | | 055 | | | | |
| - | 1 | | | | | | | : | | |
| 1 1 1 | | | | | | | | | | • " |
| ness | | | | | | | | | • | |
| Thickness (m) | 1 | | | | | | | , | | |
| | | | | | | | | | | |
| | | | | | | S29c | | | | |
| 35- | ł | | | | | S29b | | | | • |
| | | | | | | S29a | | Phosphate densi | ty increases | |
| |] | | | | | | | | | |
| - | ł | | | | | | | | , | |
| | | | | | | | | | · | , |
| - | 1 | | | | | S31 | | | | • |
| - | ┨ | | | | | 931 | | | | |
| | | | | | | | | | | |
| 30- | 1 | | | | | | | | | |
| - | ┨ | | | | ⊘ - ⋄ - ⋄ | S30# | | Pyrite laminatio | ns reappear, coinci | ding with disappearance of phosphate |
| | | | | | | | | | , | |
| - | 1 | | | | | | ! | | | |
| _ | - | | | | | | | | | |
| | | | . | | | S32# | | | | |
| - | 1 | | | | | | | Rapid increase i | n phosphate occure | ence, both as nodules and stringers |
| 1 | 1 | l | 1 | - 11 | | | l | I . | | |

| | | | | | | DE - HONOURS | | | Sheet3. of3 |
|---------------|------|------|------|----------|----------|-------------------------|-------------|-------------|---|
| STR | 'A | ΓI | GF | R | PH | HC LO | GG | ING SI | HEET From .50. m to .55. m |
| Locati | on . | Sel | lick | Hil | <u>l</u> | | Ro | ck Unit Hea | atherdale Shale Upper Member Measured by MC/BT |
| | /el | pu | pu | 힏 | lay | Analytical | samp | les denoted | with # Strike / dip of beds .030/65.W |
| Metres | Gra | C.sa | M.sa | F.sa | silvo | Analytical Litho log | | Structure | Shale Siltstone Sandstone Carbonate |
| Thickness (m) | | | | | | | | | At the 55m mark a combination of increased weathering, structural complexity and dangerous outcrop restricted the continuation of this log The unit was followed perpendicular and parallel to strike in order to gain the most accurate thickness and observe any major fluctuations. The unit has a minimum thickness of approximately 250m (hard to determine as outcrop extends below sea level) |
| 55- | | | | | | | 0204 | | |
| - | | | | | | | S39# S38 | | Laminated organic rich shale/siltstone with phosphate Increasing degree of weathering, crumbly outcrop, pale in colour |

| | | | | | | SING S | |
|---------------------|------|------|------|-------------------------|----------|--------------|--|
| | | | | e <u>k</u> | | | therdale Shale Lower Member Measured by MC/BT |
| | avel | sand | sand | Analytical Litho log | sam | oles denoted | d with # Strike / dip of beds 040/60W |
| Metres | Ö | Ü | Σ̈́ | Litho log | | Structure | |
| | | | | | S5 S4 | | Sudden transition into a well cleaved, organic rich shale/silstone, termed the Upper Heatherdale Shale |
| 70 — | | | | 0.000 | | | Well laminated fine brown shale |
| 65 _ | | | | 8.8 9.0 | | | |
| 60 – | | | | 8989 | | | Ovoid hollows common betwen the 56-69m mark They are evenly spaced over approximately 1m intervals Small phosphate stringers interbedded every 2.5m Hollows range in size from 15-50cm in length |
| 55 - | | | | 8050 | S9 | , | |
| 50- | | | | | S3 | · | Abundant phosphate between the 48-53m mark Nodules range in size from 0.5-10cm in length |
| 45 — | | | | | | | Extremely weathered tan-brown shale, over a 20m |
| 40 (m) seems (m) | | | | | | | range, indicating a long period of continuous sedimentary deposition |
| 30- | | | | 8888 | S2 | | Thin dark layer (potential remnant organic rich layer) Regular ovoid hollows |
| | | | | 89.88 **** | S1 | | |
| 25 — | | | | 8888 8888 | S8 | | |
| 20 – | | | | | | | The shale is non-calcareous, were expecting a calcareous lower member as described in literature |
| 15_ | | | | 0.000 | | | Phosphate occurring as nodules rather than continous stringers Occurrence of ovoid hollows-weathered remnants of concretions Highly weathered red-brown shale, finely laminated |
| 10 – | | | | | | | Logging started at an estimated 8m above the contact between the Heatherdale and Fork Tree Limestone |
| 5 — | | | | | | 25 | Two problems encountered were: 1. the contact was covered by soil/scree 2. the start of the outcrop was weathered and folded on a small scale |

UNIVERSITY OF ADELAIDE - HONOURS GEOLOGY Sheet ..l.. of ..l.. STRATIGRAPHIC LOGGING SHEET From Rock Unit Heatherdale Shale Lower Member Location Sellick Hill (NEW) Measured by MC/BT C.sand M.sand F.sand Strike / dip of beds 035/50W Gravel Analytical samples denoted with # Siltstone Sandstone Carbonate Shale Litho log Structure Metres The Upper Member is not exposed at this locality above the 75 mark. The contact between the two Heatherdale units is clear, with an increased cleavage and phosphate concentration 70 0.0.0.0 65 Concretion density increases towards the top of the section This is indicative of a change in environment 60 Carbonate rich shale 55 0.0.0.0 50 $\sigma \sigma \sigma c$ 45 Interbedded shale and carbonate Thickness (m) Concretionary layers (plate 2c) 30 25 Crystalline carbonate horizon (plate 1c) First concretions flattened along bedding 20 . 15 Phosphate nodules and hyolithids layer 10 1 metre of small scale intrafolial folds (plate 1b) Slight "serration" indicative of resistant/non-resistant layers Sharp contact between the Lower Heatherdale Shale and the Upper Fork Tree Limestone (plate 1a)

UNIVERSITY OF ADELAIDE - HONOURS GEOLOGY Sheet ...l.. of ...l.. STRATIGRAPHIC LOGGING SHEET From ..Q. m to .65, m Location Carrickalinga Head Cove Rock Unit . Heatherdale Shale Lower Member Measured by ...MC/BT..... Strike / dip of beds ...150/35W C.sand Gravel F.s and Analytic samples denoted with # Shale Siltstone Sandstone Carbonate Litho log Metres Structure C12 Carrickalinga Head formation, green-brown sand C13 Boundary with lower Heatherdale an erosional unconformity spanning potentially 2-3m 65 Disconformable contact between the Normanville Group J. D. D. D. andoverlying Kanmantoo Group 0.0.0.0 Dark, organic rich sediment with phospate nodules 0.0.0.0 Carbonate concretions occuring consistantly at 1-2m intervals 60 Concretions range in size from 15 to 50cm 8 0 0 0 B Spheroidal concretions (plate 2c) 55. Highest TOC at this location, 2.14% 50. 0.0.0.0 0.0.0.0. 0 0 0 45 Shale becoming lighter, most likely due to increased weathering Q.Q.Q.Q C21 C22 **o.a.o.**|C23# 40 0.0.0.0 The Shale is a uniformly interbedded blue-purple € calcareous shale and pink calcareous siltsone Concretions are strained (plate 2d) 30 0.0.0.0 0000 Shale becoming darker once more Increasing amount of phosphate The darkest looking rocks seen at Carrickalinga 25. 20 Phosphate rich zone close to termination of the ribbon limestone, indicative of a sudden change in environment 15 Sharp transition from a ribboned limestone to typical Heatherdale Shale Ribbon Limestone: interbedded shale-limestone on a 10-15cm scale 10 Hyolithids layer at 8.5m 5 .

Section measurement ceased after 65 m of logging due to inaccessible outcrop

| | _ | _ | | | | | | | |
|-----------------|-------|------|------|-------|--------|---|---------------------|-------------|--|
| | | | | | | DE-HONOURS | | | Sheetl ofl From0. m to .22. m |
| Locati | ion (| Carr | icka | din | ga.H | lead.Creek | I | Rock Unit . | Heatherdale Shale Lower Member Measured by MC/BT |
| | /el | pur | pur | D D | :lay | Analytical | samp | les denoted | C+11-111 140 h ave |
| Metres | Gra | C.sa | M.s | F.sau | silt/c | Analytical Litho log | | Structure | The second of th |
| | | | | | | | | | Carrickalinga Head Formation (Kanmantoo Group) |
| 29 — | | | | | Τ | | | | |
| 25 — | | | - | | | | | | |
| | | | | | | | | | |
| Thickness (m) O | | | | | | | | | |
| Thickne | | | | | | 0000 | C 11# | | |
| | | | | | | 0000 0000 | | | Moving towards the contact, the formation decreases in carbonate content The carbonate rich bands disappear 20m from the contact of the two Cambrian units This decrease in carbonate content is anticipated |
| 10 - | | | | | | 0000 | C18 C 78 C 68 | | |
| | | | | | | | | | |
| 5 | | | | | | 0000 | C 5# | ļ. | |
| | | | | | | • | C 3# | ŧ | Black, pyrite rich shale (creek pavement) Base of Creek |

.

4

APPENDIX II

Sedimentology and Mineralogy

SEDIMENTOLOGY AND MINERALOGY

Sample number: S-10

Locality: Waterfall Creek, Sellick Hill

Type: Surface outcrop

Formation: Fork Tree Limestone, Lower Member

Stratigraphic position: 250 m from the base of formation

Hand specimen: A grey-light blue, massive crystalline limestone. Bulk mineralogy (XRD): Dominant calcite and a trace of quartz.

Comments: Although abundantly rich in archaeocyatha, the fossils are poorly preserved due to recrystallisaton. The fossils are best observed on weathered surfaces. The mineralogy combined with the abundance of archaeocyatha suggest a shallow water, platformal environment of deposition.

Sample number: S-11 Locality: Sellick Hill

Type: Freshly quarried subsurface sample

Formation: Fork Tree Limestone, Upper Member

Stratigraphic position: 15 m from the base of formation

Hand specimen: The specimen is composed of two distinct lithologies, comprising angular dark grey-black clasts of fine grained limestone in an orange-brown shaley matrix. The samples' conglomeratic appearance is due to deformation during diagenesis, thus the terminology "diagenetic breccia". The components of the breccia are the same as the interbeds that form the overlying ribbon limestone facies.

Bulk mineralogy (XRD): The shale member is dominantly quartz and calcite with minor K-feldspar. The limestone is dominantly calcite.

Comments: The conformable transition from the Fork Tree Limestone to the Heatherdale Shale is well illustrated through mineralogy. The limestone clasts in the Upper Fork Tree Limestone have a similar composition to the massive, archaeocyathal limestone, and the shale portion of the Upper Member is equivalent to the Lower Heatherdale Shale. This is also documented in the description of S-12.

Sample number: S-12

Locality: Sellick Hill (NEW)

Type: Surface outcrop

Formation: Heatherdale Shale, Lower Member

Stratigraphic position: 12 m from the base of formation

Hand specimen: An interbedded light brown, fine calcareous shale and dark grey crystalline

limestone. The contact between the interbeds is sharp, each interbed is 10 cm thick.

Bulk mineralogy (XRD): The shale is predominantly quartz with minor calcite and clay mineral, the limestone comprises an equal distribution of quartz and calcite.

Comments: This sample has the same mineralogy as the underlying unit, the Upper Fork Tree Limestone however, there is an obvious increase in clastic input. The shale consists of only minor calcite, and the limestone fraction is far more quartz rich. The interbedding is distinctly linear, with no evidence of the brecciation seen in the sample 50 m lower in the stratigraphic section (S-11).

Sample number: S-9

Locality: Waterfall Creek, Sellick Hill

Type: Surface outcrop

Formation: Heatherdale Shale, Lower Member

Stratigraphic position: 52 m from the base of formation

Hand specimen: A pink-purple, well laminated, fine grained calcareous shale, with phosphate nodules aligned along bedding planes. Bedding is well defined by dark purple laminae.

Thin section: The fine laminations, depicted by dark purple bands in hand specimen are readily seen under the microscope (Plate 4a). The phosphate nodules are dark, elongate and aligned with bedding. Extremely fine grain quartz (3-5 μ m) is the dominant mineral making up 60% of the sample, with the accessories calcite (30%) and opaques (10%). The opaque fraction comprises pyrite, organic detritus and phosphate.

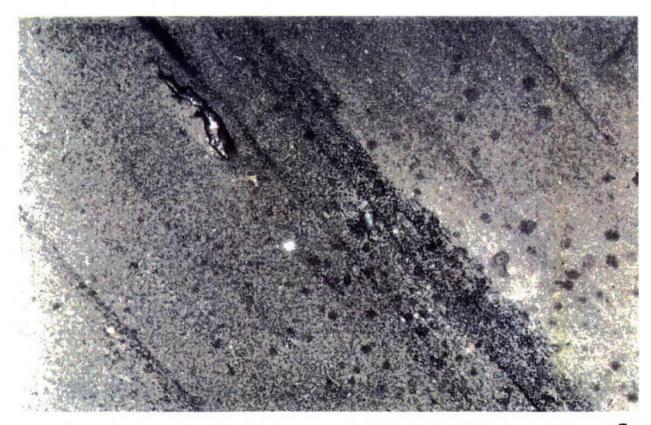
Bulk mineralogy (XRD): Quartz is dominant, with minor calcite and clay minerals.

Comments: Although highly weathered, fine laminae are readily apparent in both hand specimen and thin section. This is evidence for a deeper water environment of deposition. The sudden increase in clastic content is also supportive of deep water sedimentation.

PLATE 4

- A Fine laminations in the Lower Heatherdale Shale (sample S-9) depicted by dark purple bands in thin section. The dark mass seen in the sample is a phosphate nodule.
- B Fine pyrite laminations in the Upper Heatherdale Shale (sample S-21).

The field of view for both sections is 15 mm.



A



Sample number: C-19A

Locality: Carrickalinga Head Cove

Type: Outcrop sample, carbonate concretion

Formation: Heatherdale Shale, Lower Member

Stratigraphic position: 55 m from the base of formation

Hand specimen: The ovoid carbonate concretion was dissected to reveal a uniform, dark

grey crystalline limestone with cross-cutting calcite veining.

Thin section: The sample is very fine-crystalline with a uniform matrix grain size of 30-40 μ m. The matrix comprises 70% quartz and 10% disseminated opaques, closely packed in by a calcitic cement (20%). The opaques are both angular (pyrite) and amorphous (detrital organic matter).

Bulk mineralogy (XRD): Calcite and quartz are the two dominant minerals.

Comments: Concretion growth is non-replacive, thus it is expected that a large component of the concretion is remnant host sediment. This is far more evident in thin section than the XRD analysis. The high percentage of quartz also indicates that the initial sediment was highly porous.

Sample number: S-21

Locality: Waterfall Creek, Sellick Hill

Type: Surface outcrop

Formation: Heatherdale Shale, Upper Member

Stratigraphic position: 6 m from the base of formation

Hand specimen: A dark black, massive siltstone with pyrite laminae and abundant

phosphate.

Thin section: The mineral quartz makes up 50% of the sample, opaques the other major contributor with approximately 45%. The quartz has a bimodal distribution, being mostly subangular grains of 12-16 μ m, however a distinct percentage is 30-50 μ m in size. The very fine laminations are evident in plate 4b, indicating a deep water environment of deposition with a high clastic input.

Bulk Mineralogy (XRD): The major components are quartz and clay minerals, with minor pyrite.

Comments: The higher concentration of opaques in this sample is a direct indicator of its deeper water deposition. The increased organic matter content and pyrite formation are both features expected in the anoxic zone. With the exception of the 55m of type section (Section 2.5), the majority of the upper member is variably weathered and leached of its organic content.

APPENDIX III

Analytical Techniques

ANALYTICAL TECHNIQUES

Sample Preparation

Forty-eight samples from Sellick Hill, Myponga Beach and Carrickalinga Head were initially selected for organic geochemical analysis. Each sample (200-400 g) was crushed using a Siebtechnik chrome-steel mill. The resultant powders were used for a variety of procedures: TOC analysis, kerogen isolation, and solvent extraction.

TOC Analysis

Forty-two samples were selected for TOC analysis. Approximately 2 g of each sample was sent to Amdel Limited Petroleum Services at Thebarton for this purpose.

Kerogen Isolation

Nine samples from strategic stratigraphic locations were chosen for kerogen isolation. This was achieved using a methodology described by B. Michaelsen (pers. comm). 150 g of powdered whole rock was placed in a 500 ml teflon beaker. The following steps were then undertaken:

- 1. 250 ml of 16% hydrochloric acid (HCl) was added to remove the carbonate fraction of the sample. The beaker was placed on a hot plate at 50° C for 24 hours and stirred 2 or 3 times during this period.
- 2. The suspension was left to settle and the spent reagent was then decanted. The remaining organic residue/sediment mix was then rinsed with distilled water in a centrifuge to attain a neutral pH.
- 3. 375 ml of 33% hydrofluoric acid (HF) was added to digest silica. In HF, silica and silicates are converted to silicon tetrafluoride (SiF_4) and fluorosilicic acid (H_2SiF_6). The beaker was then placed on a hot plate at 50° C for 48 hours and stirred 2 or 3 times during this period.
- 4. Repeat of step 2.
- 5. 200 ml of deionised water was added to the organic residue, and 3 pellets of sodium borohydride (NaBH₄) were then placed carefully in the beaker. The addition of this saturated solution assisted in the breakdown of unwanted pyrite (from the original whole rock sample) and fluorosilicate compounds that may have formed during step 3.
- 6. Repeat of step 2.
- 7. Repeat of steps 1–6.

- 8. After final rinsing the sample was left to settle overnight in 150 ml of deionised water. The kerogen was easily discerned as it floated on the water surface and formed a dark layer on top of the remnant sediment. The beaker was slightly agitated, suspending the kerogen in the water column. The water containing the kerogen was centrifuged and the kerogen collected and placed on a watchglass and allowed to dry for 48 hours.
- 9. A small amount of cotton wool was placed in the neck of a Pasteur pipette and the dry kerogen placed on top of this. Remaining soluble organic matter was then removed by flushing the kerogen with methanol and dichloromethane. The sample was then left to dry for 12 hours. 10. The kerogen sample was placed in a small glass vial and dried in a vacuum desiccator for 24 hours.

Stable Carbon Isotopes

Stable carbon isotopic composition of the isolated kerogen was determined using a procedure developed by K. Turnbull and summarised by Bernd Michaelsen:

- 1. 4 mg of isolated kerogen, 400 mg of pelletised copper oxide and 25 mm of silver wire were placed in a pyrex tube, then evacuated and sealed on the sulphur-vacuum line.
- 2. The sealed tubes were then reacted in a furnace at 900° C overnight.
- 3. The evolved carbon dioxide was purified on the sulphur-vacuum line.
- 4. The carbon isotopic ratios were then analysed on a Micromass 602E mass spectrometer and the δ^{13} C ratio calculated using the following formula:

$$\delta^{13}$$
C (‰) = $\left(\frac{^{13}\text{C}/^{12}\text{C sample}}{^{13}\text{C}/^{12}\text{C standard}} - 1\right)$ x 1000

The results are expressed as parts per million, as compared with the international Peedee Belemnite (PDB) standard.

Preparation of carbon dioxide (steps 1–3 above) was undertaken by B. Michaelsen and B. Turner. Measurement of the δ^{13} C value (step 4) was performed by K. Turnbull.

Elemental Analysis

The 9 kerogen samples were sent to National Analytical Labs in Melbourne for elemental analyses. C, H, N and ash weight percentages were determined. Atomic H/C ratios were plotted on Van Krevelen Diagram (Fig. 8) and compared with δ^{13} C values in Figures 9 and 10.

Solvent Extraction

Solvent extraction was undertaken using a version of the procedure described in Padley et al. (1991). Four samples were selected for this analysis. Analytical reagent grade solvents were distilled through a 60 cm fractionating column prior to their use in the extraction process. All glassware used was thoroughly solvent cleaned and dried prior to analytical work.

Soxhlet extraction was employed to remove any extractable organic matter (EOM) in the samples. This was achieved by placing 150 g of crushed sample into a pre-extracted thimble, plugged with cotton-wool. The thimble was placed in the Soxhlet apparatus and extracted for 72 hours with an azeotropic mixture comprising of 372 ml of dichloromethane (DCM) and 28ml of methanol. Prior to extraction both activated copper turnings (for remove of elemental sulphur incorporated within the sediment) and silica bumping chips were added to the solvent.

Upon completion of the solvent extraction, excess solvent was removed using a rotary evaporator and the concentrated EOM transferred to pre-weighed vials. Residual solvent in the vials was evaporated in the fume hood and the total EOM recorded. The vial was sealed and stored in preparation for column chromatography.

Column chromatography

Column chromatography was undertaken using a version of the procedure described in Padley et al. (1991). A 40 cm glass column was plugged with cotton wool, filled with 80 ml of petroleum ether and packed with a slurry of activated silica and petroleum ether. Approximately 1 g of activated silica was then added to the top of the packed column. The EOM was redissolved in DCM and then transferred dropwise to 2 g of activated alumina. After the DCM had evaporated from the alumina, the sample was carefully transferred to the top of the prepared column.

Separation of the EOM into aliphatic, aromatic and polar fractions was carried out by eluting with 80 ml of the following solvents: aliphatics with 100% petroleum ether; the aromatics with a 30:70 petroleum ether-DCM mixture; and the polars with a 35:65 mixture of DCM and methanol. Excess solvent from each fraction of the EOM was removed with a rotary evaporator and the residue transferred to pre-weighed vials. The mass of each fraction was recorded.

GC-MS of the aromatic fraction

The gas chromatography-mass spectrometry (GC-MS) analysis of aromatic hydrocarbons was undertaken using a Varian 3400 gas chromatograph interfaced with a Finnigan TSQ 70 mass spectrometer. The gas chromatograph was fitted with a 60 m x 0.25 mm i.d. fused silica column (DB-1, 0.25 μ m film thickness; J&W Scientific). Helium was used as the carrier gas at an inlet pressure of approximately 22.5 psi. The program of the oven was as follows: 50° C for 2 min, 50° C to 120° C at 8° C per minute, 120° C to 300° C at 4° C per minute and then held at 300° C for 35 minutes. Mass spectrometer operating parameters included an ionization voltage of 70 eV, a filament current of 200 μ A and a photomultiplier voltage of 1100 V. Aromatic fractions in DCM were injected on-column. The injector was held at 50° C for 10 seconds then ramped to 300° C at 180° C per minute, and held at 300° C for 5 minutes. The mass spectrometer was programmed (MID mode) to monitor mass to charge ratio (m/z) 178 (phenanthrene), m/z 192 (methylphenanthrenes) and m/z 206 (dimethylphenanthrenes). These analyses were performed by Bernd Michaelsen.

| Sample Code | TOC | Elemental | Isotope | MPI |
|-------------|-----|-----------|---------------------------------------|--------------|
| S-12 | * | | zotopo | IVIL 1 |
| S-13 | * | | | |
| S-14 | * | | · · · · · · · · · · · · · · · · · · · | |
| S-17 | * , | * | * | |
| S-18 | * | | | |
| S-20 | * | | | |
| S-21 | * | | | |
| S-22 | * | | | |
| S-23 | * | | | |
| S-24 | * | * | * | |
| S-25 | * | | | |
| S-27 | * | | | · · · |
| S-28 | * | | | * |
| S-30 | * | * | | |
| S-32 | * | | | |
| S-33 | * | * | | |
| S-35 | . * | | | |
| S-37 | * | | | |
| S-39 | * | * : | | * |
| | | | | |
| M-3 | * | | | |
| | | | | |
| C-3 | * | * | | |
| C-5 | * | | | |
| C-6 | * | * | * | |
| C-7 | * | | | |
| C-8 | * | | | |
| C-9 | * | | | |
| C-10 | * | | | |
| C-10A | * | | | |
| C-11 | * | | | |
| C-15 | * | | | |
| C-16 | * - | | | |
| C-17 | * | | | * |
| · C-18A | * | | | |
| C-18C | * | | | |
| C-19A | * | * | * | |
| C-19B | * | * | * | |
| C-20 | * | | | |
| C-23 | * | | | |
| C-27 | * | | | * |
| C-28 | * | | | |
| C-29 | * | | | |
| C-31 | * | | | |

This table is a summary of the Organic Geochemical analyses performed on the Heatherdale Shale samples.

APPENDIX IV

Results

| Sample Code | Location | Rock Unit | TOC (%) |
|-------------|--------------------|---------------------------|---------|
| S-12 | Sellick Hill | Heatherdale Shale (Upper) | 0.83 |
| S-13 | | | 1.09 |
| S-14 | | | 0.73 |
| S-17 | | | 1.62 |
| S-18 | | | 1.60 |
| S-20 | | | 1.85 |
| S-21 | | | 2.03 |
| S-22 | | | 1.99 |
| S-23 | | | 2.03 |
| S-24 | | | 2.22 |
| S-25 | | | 1.94 |
| S-27 | | | 1.57 |
| S-28 | | | 2.28 |
| S-30 | | | 2.57 |
| S-32 | | | 0.91 |
| S-33 | | | 2.11 |
| S-35 | | | 2.05 |
| S-37 | | | 1.18 |
| S-39 | | | 2.33 |
| 14.2 | | | |
| M-3 | Myponga Beach | Heatherdale Shale (Lower) | 0.37 |
| C-3 | Carrickalinga Head | Heatherdale Shale (Lower) | 1.66 |
| C-5 | | · | 0.63 |
| C-6 | | | 0.55 |
| C-7 | | | 0:77 |
| C-8 | - | | 0.55 |
| C-9 | | | 0.77 |
| C-10 | | | 0.47 |
| C-10A | | | 0.52 |
| C-11 | | | 0.4 |
| C-15 | | | 0.46 |
| C-16 | | | 1.07 |
| C-17 | | | 1.75 |
| C-18A | | | 1.16 |
| C-18C | | | 0.56 |
| C-19A | | | 0.72 |
| C-19B | | | 2.14 |
| C-20 | | | 0.25 |
| C-23 | | | 0.24 |
| C-27 | | | 1.05 |
| C-28 | | | 0.19 |
| C-29 | | | 1.16 |
| C-31 | | | 0.21 |

| Sample Code | TOC | %C d.a.f. | H/C | 13C |
|-------------|--------|-----------|------|--------|
| S-17 | 1.62 | 71.5 | 0.23 | -30.94 |
| S-24 | 2.22 | ND | ND | ND |
| S-30 | 2.57 | ND | ND | ND |
| S-33 | 2.11 | ND | 0.24 | ND |
| S-39 | . 2.57 | 83.2 | ND | ND |
| C-3 | 1.66 | ND | 0.36 | ND |
| C-6 | 0.55 | 83.6 | 0.22 | -31.38 |
| C-19A | 0.72 | ND | ND | -31.16 |
| C-19B | 2.14 | ND | 0.25 | -32.37 |

This table is a summary of the analyses performed on the nine samples chosen for kerogen isolation. Unfortunately the H/C atomic ratio data obtained in some cases were misleading, due to unacceptably high ash contents.

MPI and calculated vitrinite reflectance

The Methylphenanthrene Index (MPI) was calculated for sample C-17 from Carrickalinga Head using the following equation and peak areas determined from the RIC trace (Figure 10);

$$MPI = \frac{1.5 (2-MP + 3-MP)}{P + 1-MP + 9-MP}$$

A response factor of 0.6 was applied to the phenanthrene peak.

The MPI value was calculated to be 0.9016. A calculated vitrinite reflectance was then obtained using the following calibration (after Radke and Welte, 1983);

$$Rc = -0.55 MPI + 3.0\%$$

The result was an Rc value of 2.50%.

Although 3 other samples were prepared: C-27, S-28 and S-39, the aromatic fraction collected was negligible and further analysis was deemed futile.

APPENDIX V

Basin Analysis

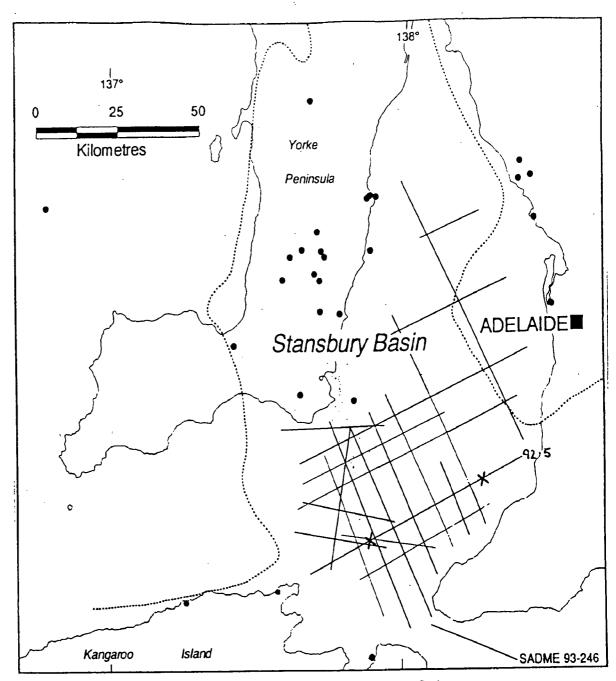
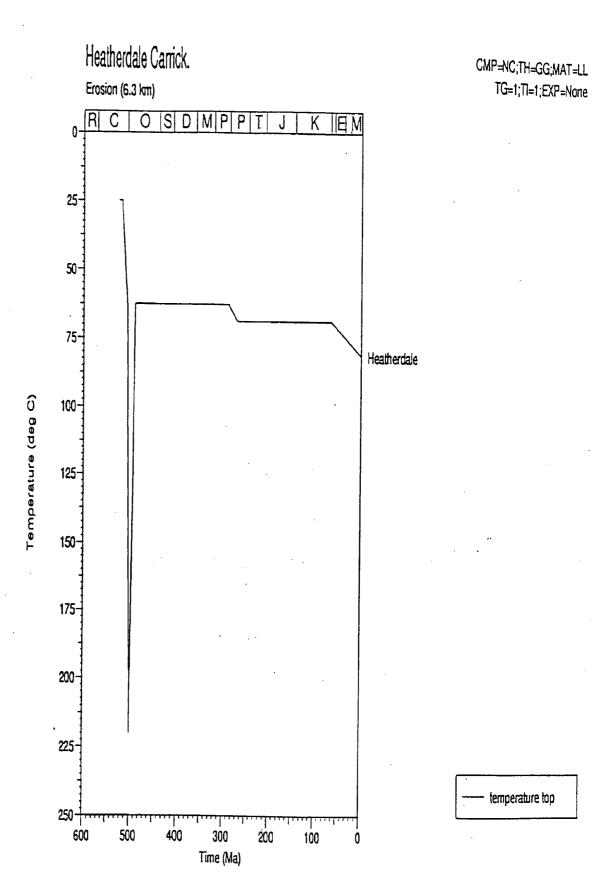
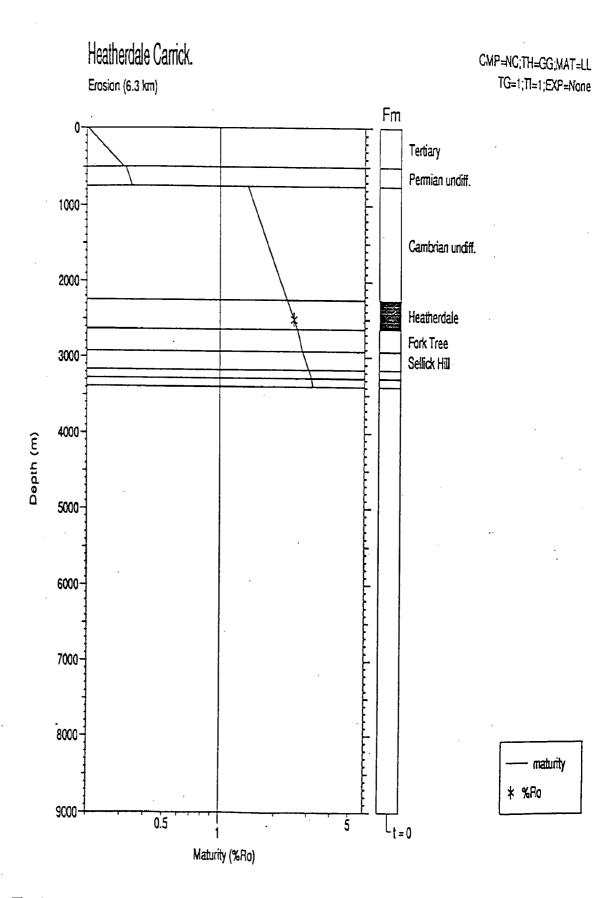


Figure 77. Seismic lines recorded from 1980 to 1992 inclusive, covering the Stansbury Basin.

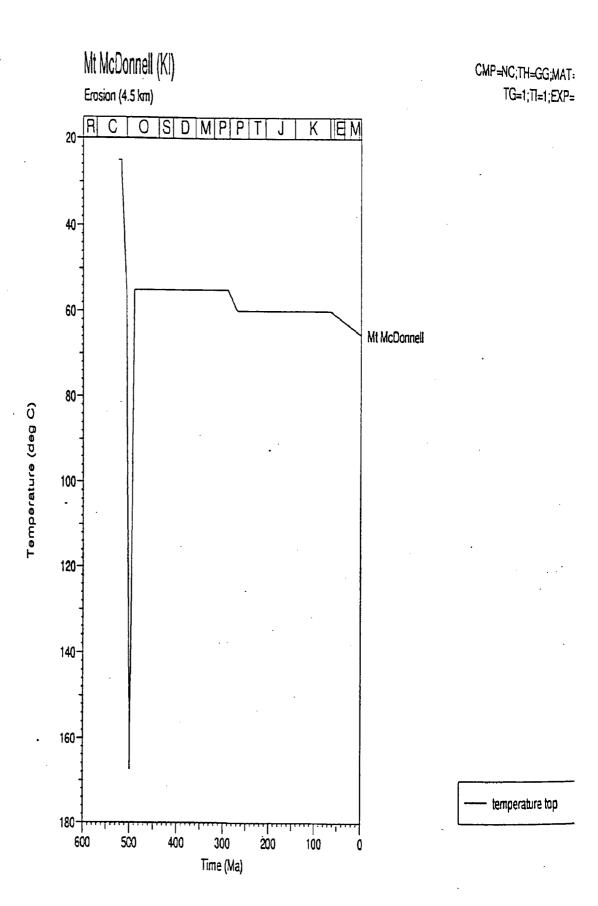
This map (taken from Hibburt, 1994) shows the location of the two shotpoints chosen for the thermal modelling exercise.



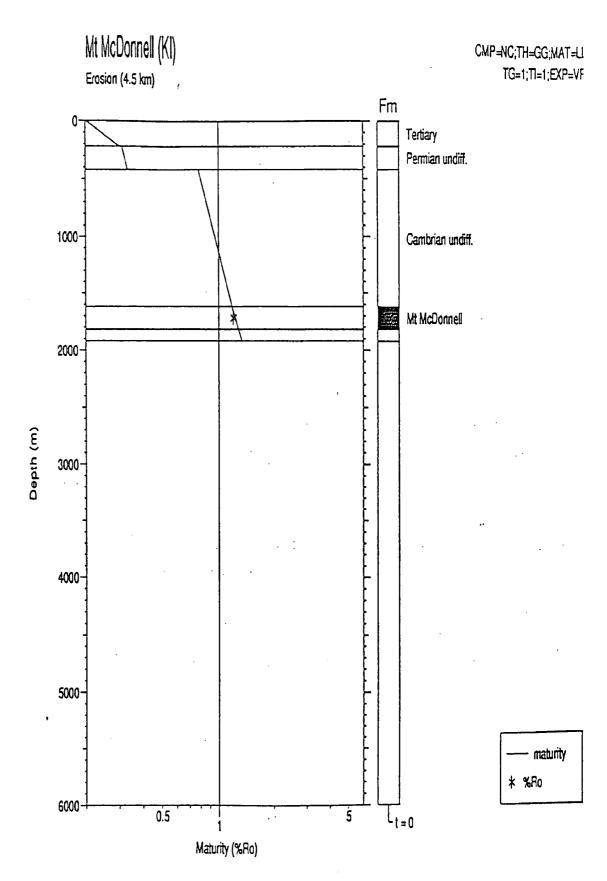
Temperature evolution curve for the Heatherdale Shale, providing information on the timing and magnitude of maximum temperatures.



The thermal model tracking the evolutionary path of vitrinite reflectance values with respect to the current stratigraphic configuration. Displacement of the line corresponds to erosional activity.



Temperature evolution curve for the Mt. McDonnell Formation, providing information on the timing and magnitude of maximum temperatures.



The thermal model tracking the evolutionary path of vitrinite reflectance values with respect to the current stratigraphic configuration. Displacement of the line corresponds to erosional activity.