Geochemistry of the Paleocene Tartan Formation
in the Great South Basin, New Zealand

By

Dylan James Meadows

Submitted in fulfilment
of the requirements for
the degree of Graduate Diploma in Science
(Petroleum Geology & Geochemistry)

Victoria University of Wellington
February 2008
ABSTRACT

The Late Teurian (Paleocene) Tartan Formation is an organic rich mudstone up to 57 m thick that has been identified in five of the eight petroleum exploration wells drilled in the Great South Basin.

In this study, the geochemistry of five wells from the Great South Basin of New Zealand (Takapu-1A, Toroa-1, Kawau-1A, Hoiho-1C and Pakaha-1) were investigated using EA-IRMS and Rock-Eval analyses on selected sidewall core and cuttings samples.

All wells except Takapu-1A showed geochemical characteristics that allowed recognition of the Tartan Formation. The formation is characterised by enrichments in TOC (generally above 4%), and $^{13}$C (generally $\delta^{13}$C ratios are between -21 and -17‰), indicating a significant marine contribution. C/N ratios recorded within Tartan Formation samples are all above 20, which suggest that the organic matter contains a significant contribution from terrestrial and/or altered marine material.

Geochemical changes that are characteristic of the Tartan Formation are recognised below the lithological base of the formation in some wells and thus a geochemical facies is proposed for the total interval. This is referred to as the Tartan geochemical facies (TGF).

The underlying Wickliffe and overlying Laing formations have TOC contents generally below 2%, isotopically light $\delta^{13}$C values (generally between -25 to -28‰), and a wide range of C/N ratios (ranging from 3.9 to 64.2). The latter suggests that there were varying degrees of preservation of the deposited organic matter within these formations. The low TOC contents recorded in the enclosing formations of the Tartan Formation suggest that there was a profound change in the conditions under which the formation (and TGF) was deposited, with respect to the deposition of the enclosing formations. Conditions for the preservation and accumulation of organic matter were more favorable prior to deposition of the Tartan Formation than following it.

Geochemical evidence from samples within the Tartan geochemical facies suggests that it contains a mixture of marine bacterial/plant/algal, $C_3$ and $C_4$ terrestrial plant source components. Organic matter within enclosing formations appears to be derived from a combination of $C_3$ land plants and marine material. This is consistent with the findings of Killlops et al. (2000), who reported from biomarker studies that the organic matter of some Great South Basin samples contained organic matter derived from a marine source with varying degrees of terrestrial contribution.

The enrichment of $^{13}$C and the high TOC contents within the TGF are consistent with that of the mid to Late Teurian Waipawa Formation that has been identified throughout many of New Zealand’s major sedimentary basins (See Section 2.1). However, samples from Hoiho-1C (1554 m; -15.8‰) and Kawau-1A (2264 m; -17.4‰) have $\delta^{13}$C values that exceed those previously reported for the Waipawa Formation. It is likely that the oceanographic environmental conditions that caused the geochemical changes of the Tartan and Waipawa formations (with respect to enclosing formations) were synchronous. The Tartan Formation appears to be equivalent to the mid and upper part of the Waipawa Formation, whereas the Tartan geochemical facies is equivalent to the entire Waipawa Formation.
ACKNOWLEDGEMENTS

I would like to thank both my supervisors, A/Prof John Collen (VUW) and Dr. Karyne Rogers (GNS Science), for their time and valuable discussions that made this study possible. In particular I would like to thank John for his excellent supervision and editing throughout this study. I would also like to give special thanks to Karyne who assisted me during the preparation stages and ran all the mass spectrometry samples. Both supervisors greatly assisted my understanding of some of the more complicated aspects of this project.

I would also like thank Dr. Poul Schioler of GNS Science for his contribution and communications during this project. GNS Science contributed greatly to this project in several other ways. The costs of mass spectrometry and Rock-Eval analyses were supported by the NZ FRST program through NPR contract COSXO3O2 to Dr. Chris Hollis and Mr. Richard Sykes. The Rock-Eval results relevant to this study were provided to the author by Dr. Chris Hollis and Mr. Richard Sykes, who also provided several plots of the Rock-Eval data that were modified by the author and used in this study (Figures 6.6.1, 6.6.2, 6.6.3 [original version], and 7.8.6).

The following VUW staff also assisted me during this project:

Dr. Joel Baker and Michael Killick who let me use their laboratories to prepare samples, and Ms. Gillian Ruthven for assistance with formatting and finalisation of this project.

And finally, no dissertation would be complete without the acknowledgement of my parents, Colin and Natalie, and my Great Uncle, Bob. All of you aided me during this project and I cannot thank each of you enough.
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CHAPTER 1

Introduction

1.1 Aim and significance of study

This study is a geochemical investigation of the Tartan Formation in the Great South Basin, New Zealand.

The Tartan Formation is Late Teurian (Paleocene) in age and is of interest to the petroleum exploration industry because it is considered to be a lateral equivalent of the mid to Late Teurian Waipawa Formation, that is widely distributed throughout most of New Zealand’s major sedimentary basins (see Section 2.1). The Waipawa Formation is considered to be an important hydrocarbon source rock, especially in the East Coast Basin.

This study focuses on correlation and characterisation of geochemical signatures of the Tartan Formation in the Great South Basin. Correlations to the Waipawa Formation in the East Coast region are made. Discussion of the Tartan Formation as a source rock is beyond the scope of the present study.

This is the first geochemical study performed on a specific formation within Great South Basin wells that examined the total organic carbon (TOC) content, nitrogen content, C/N ratio and δ¹³C values of cuttings and sidewall core samples. The TOC concentrations of the samples are of prime importance to this study, as the organic richness of the samples allows formation boundaries to be identified and constrained, as well as the assisting in identification of the characteristically organic-rich Tartan Formation, where present. The nitrogen content for each sample was also recorded; the main purpose of this was to be used in conjunction with the TOC results to give C/N ratios. The C/N ratios are important for determining the type and source of the organic matter in the Tartan Formation.

Carbon stable isotope geochemistry is also of great importance to the present study. Stable isotope fractionation in chemical reactions is dependant on the bond strength between atoms. Bond strength is dependant on the mass of the atoms on each end of the bond; hence slight mass differences between isotopes will result in bond strength variations in a molecule. This effect causes equilibrium and kinetic differences in a given reaction, with the lighter or heavier isotopic system being preferentially favoured over the other, resulting in fractionation (Anbar and Rouxel, 2007). The type of carbon isotopic fractionation of relevance to this study is biological kinetic fractionation by photosynthesising plants and
Chapter 1. Introduction

algae. Implications of this to source determinations of the organic content in samples are discussed in Sections 7.8 and 7.9.

$\delta^{13}$C ratios are used here to identify and define geochemical boundaries within the wells investigated and to allow isotopic characterisation of the Tartan Formation. These data can also provide insight into the source of the organic matter present, as different plants, algae and marine bacteria have distinctive isotopic characteristics. $\delta^{13}$C studies can also provide insight into the timing and extent of past environmental perturbations, and indicate how conditions have varied throughout geological time.

Geochemical data recorded throughout this study are compared to gamma ray logs taken during drilling, and differences between lithological and geochemical boundaries are discussed and interpreted. These geochemical characteristics of the Tartan Formation are used for correlation with the Waipawa Formation present in other New Zealand sedimentary basins.

1.2 Area of study

The Great South Basin lies off the southeast coast of the South Island of New Zealand (Fig 1.2). The basin covers an area of approximately 100,000 km$^2$, with water depths ranging from 100 m to 1250 m and with a mean depth of 700 m. The northern limit of the basin is taken as 46°S, and the southern limit is 50°S. The westernmost part of the basin lies at 168°E, and extends east to 172°E (Cook et al. 1999).

1.3 Exploration history

The Great South Basin was defined by geophysical surveys carried out by the Sea Hunt exploration group. Between 1968 and 1983 more than 30,000 line km of seismic reflection data were collected (Cook et al. 1999), with eight petroleum exploration wells drilled between 1976 and 1984. During 1976 and 1977, the Sea Hunt consortium drilled four wells in License 863 (Toroa-1, Pakaha-1, Kawau-1A, and Hoito-1C). In 1978 Petrocorp drilled two further wells; Tara-1 and Takapu-1A. The Placid Oil Company drilled Rakiura-1 and Pukaki-1 in 1983 and 1984 respectively.
Chapter 1. Introduction

Figure 1.2 Location map and distribution of petroleum exploration wells of the Great South Basin (Crown Minerals, 2008).
1.4 Previous studies of the Great South Basin

The first comprehensive published accounts of the Great South Basin were compiled by Carter (1988a, b). Carter (1988a) defined a formal stratigraphic framework for the eastern South Island and placed the Great South Basin stratigraphy within this framework (Cook et al. 1999).

Beggs (1993) proposed a revised stratigraphy for the Great South Basin, and Raine et al. (1993, 1994) provided a comprehensive review of the foraminiferal and palynological biostratigraphy for seven of the petroleum exploration wells in the basin.

Killops et al. (1997) used geochemistry to report the petroleum potential and oil-source correlation in the Great South and Canterbury basins.

Cook et al. (1999) have published a compilation of the Great South Basin petroleum industry exploration data and information from petroleum reports, including well logs, as one of the IGNS Cretaceous-Cenozoic geology monograph series.

1.5 Outline of this study

Chapter 1 provides a brief introduction into the aim and significance of this study and a basic history of exploration and research of the Great South Basin. Ages are discussed in terms of both international and local subdivisions (Fig 1.5). Chapter 2 is a compilation of data that details the stratigraphy and a brief structural history of areas of the basin relevant to this study. The general stratigraphy of the East Coast Basin is included in here, and used as a comparison to the stratigraphy of the Great South Basin and a basis for discussion in later chapters. Changes in the environmental conditions that are likely to have contributed to the deposition of the Tartan and Waipawa formations and equivalents found elsewhere in New Zealand are described in Chapter 3. Chapter 4 outlines the processes of organic matter preservation and accumulation and the significant role anoxia plays in these processes, and its association to the depositional environments of the Waipawa Formation. Methods and analytical procedures employed in this study are described in Chapter 5. The results from mass spectrometry and Rock-Eval analyses are described and compared in Chapter 6. The main discussion and implications for the geochemical data are compared to other literature and are interpreted in Chapter 7. Important findings from this study are summarised in Chapter 8.
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Figure 1.5 International Geochronological and New Zealand Geological Timescales. Modified from Geological and Nuclear Sciences (2003).
Geological setting of the Great South Basin and distribution of the Waipawa Formation

2.1 Regional distribution of the Waipawa Formation

The Waipawa Formation and stratigraphically equivalent formations have been identified in several sedimentary basins around New Zealand. These are the Great South Basin (GSB), (Raine *et al.* 1993; Killops *et al.* 1997), the Canterbury Basin (Gibbons and Fry, 1986; Field and Browne, 1989; Killops *et al.* 1997), the East Coast Basin (ECB), from the Te Hoe River and East Cape in the northern region of the ECB to the Hawkes Bay-Wairarapa in the southern region of the ECB (Moore, 1988b, 1989; Field *et al.* 1997), Northland (Isaac *et al.* 1994), northern Taranaki (Killops *et al.* 1994; King and Thrasher, 1996), Marlborough (Strong *et al.* 1995), and possibly southern Westland (Nathan, 1976) (Fig 2.1).

![Regional distribution of the Waipawa Formation around New Zealand's sedimentary basins](image)

Figure 2.1 Regional distribution of the Waipawa Formation around New Zealand's sedimentary basins (From Killops *et al.* 1996; Killops *et al.* 2000).
Chapter 2. Geological setting of the GSB and distribution of the Waipawa Formation

Outcrops of Waipawa Formation in the East Coast Basin show the contact with the underlying Whangai Formation to be conformable and typically gradational over centimeters to meters, and the contact with the overlying Wanstead Formation to be sharp but conformable, as reported by Moore (1986, 1988b, and 1989) and Killlops et al. (2000). Correlatives of the Wanstead and Whangai formations are recognised in exploration wells in the Great South Basin in which a Waipawa Formation equivalent, the Tartan Formation, is present and in the Canterbury Basin, where the Waipawa Formation is also present. As in the East Coast Basin, there is a gradual change in sedimentological characteristics at the Whangai/Waipawa boundary (Killlops et al. 2000).

Whangai Formation equivalents occur in the Northland Basin, with a conformable, gradational boundary with the overlying Waipawa Formation (Isaac et al. 1994), and an equivalent formation appears to be present in the Ariki-1 exploration well in the Taranaki Basin. In both Northland and Taranaki basins, the Waipawa Formation is overlain by deep-water facies that resemble the Wanstead Formation (Killlops et al. 2000).

The Tartan Formation has been identified in five exploration wells in the Great South Basin: Toroa-1 (63 m thick), Pakaha-1 (48 m thick), Hoiho-1C (47 m thick), Kawau-1A (44 m thick), and is also represented in Takapu-1A (20 m thick) (Cook et al. 1999). In comparison, Waipawa Formation equivalents encountered in exploration wells in other basins are generally thinner, such as in the Canterbury Basin; Clipper-1 (35 m thick), Endeavour-1 (40 m thick), Galleon-1 (10 m thick) and in the Taranaki Basin, where only one exploration well has a Waipawa Formation equivalent (Ariki-1; 10 m thick) (Fig 2.1). Moore (1988b, 1989) has stated that the Waipawa Formation in East Coast Basin outcrops rarely exceed a thickness of 50 m.

2.2 Stratigraphy of the Great South Basin

The Great South Basin is a mid to Late Cretaceous intra-continental rift basin that formed as a result of regional extension in association with the opening of the Tasman Sea and separation of Australia from Antarctica (Fig 2.2.1) (Olson, 1996).
Chapter 2. Geological setting of the GSB and distribution of the Waipawa Formation

74 Ma

Figure 2.2.1 Paleogeographic reconstruction depicting the opening of the Tasman Sea and separation of Australia from Antarctica 74 Ma. Modified from Olson (1996).

The Great South Basin is made up of a series of NE-SW trending grabens and half grabens formed between the South Island and the Campbell Plateau. Figure 2.2.2 is a schematic of the Great South Basin that displays the position of the petroleum exploration wells drilled within the basin and the sediment thickness distribution of the basin.

Figure 2.2.2 Sediment thickness distribution and location of exploration wells of the Great South Basin. Modified from Olson (1996).
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The structural history of most of the Great South Basin consists of a fault-controlled subsidence followed largely by Tertiary thermal subsidence. The basin sediment fill consists of a mid-Cretaceous, syn-rift and Late Cretaceous, post-rift fluvial-deltaic sequence. Since the Tertiary, regional subsidence and diminishing clastic sedimentation resulted in progressive deepening of water across the basin (Olson, 1996).

A detailed account of the stratigraphy and structural evolution of the Great South Basin can be found in Cook et al (1999), the following is a summary of the more important points from Cook et al. (1999) that are relevant to this study.

Figure 2.2.3 is a generalised representation of the stratigraphy of the Great South Basin.

Cook et al. (1999) have divided the stratigraphy of the Great South Basin into four lithostratigraphic groups: the Hoiho, Pakaha, Rakiura and Penrod groups.
Chapter 2. Geological setting of the GSB and distribution of the Waipawa Formation

2.2.1 Hoiho Group

The Hoiho Group is the oldest group recognized in the Great South Basin and is inferred to be of mid to Late Cretaceous [Ngaterian (Cn) to Piripauan (Mp)] age, although older and younger boundaries are possible. The group is represented by a lithology consisting of sandstones, shales, conglomerates and coals.

The Hoiho Group consists of a succession of non-marine clastic facies that can be subdivided into three time components: the Clarence Series, Raukumara Series and the Piripauan Stage. The Clarence Series represents the lowermost unit and, based upon seismic mapping, is characterised by variable-amplitude reflectors with a discontinuous and wedge shaped geometry suggesting fluvial valley fill, and adjacent high-amplitude, steeply dipping reflectors that are interpreted to be fault scarp fans along the graben margins.

The middle unit is the Raukumara Series and seismic facies within the unit are highly variable which is interpreted to indicate a dominance of terrestrial paleoenvironments. The low-amplitude, discontinuous reflectors are proposed to be lacustrine facies, while medium to high-amplitude and variably continuous reflectors are interpreted as coal measures.

The upper unit of the Hoiho Group, the Piripauan Stage, has a chaotic, variable-amplitude seismic facies in the Eastern-Flank sub-basin (Fig 2.2.4), which has been interpreted to be deposits formed of reworked and winnowed earlier Cretaceous sediments that resulted from a deficiency of sediment supply coupled with wave and tidal action during transgressions.

The deposition of the Hoiho Group took place in a series of normal faulted depressions and sub-basins. Steeply dipping reflectors close to faults are indicative of widespread alluvial fan sedimentation. Distal fault scarps, fluvial and coal measure facies are interpreted to be the result of deposition in braided floodplain and lacustrine environments.
2.2.2 Pakaha Group

The Pakaha Group ranges from Late Cretaceous to Paleocene (Piripauan to top of Teurian) and consists of several formations. The base of the Pakaha Group is the Kawau Sandstone, overlain by the Wickliffe Formation followed by the Taratu Formation, which is in turn overlain by the Tartan Formation at the top of the group.

Sediments in the Pakaha Group were deposited after most normal faulting had begun to subside quickly and as a result, marine transgression continued. To the west of the basin was an eastward progression of depositional environments ranging from fluvial and coastal plain with extensive coal swamps, paralic, to shallow marine conditions. The major drainage systems formed alluvial fan complexes. The eastern margin gradually subsided to shelf depths (Cook et al. 1999; Enclosure 1, maps 5 and 6), and in the East Flank sub-basin, carbonates began to accumulate as a result of reduced sediment supply.

The Kawau Sandstone is a white to grey, medium coarse, friable sandstone. It ranges in age from Piripauan to Haumurian (Raine et al. 1993). The formation is interpreted to have been deposited in a shallow marine, nearshore setting.

The Wickliffe Formation is bound by unconformities at both the base and the top, and ranges in age from Piripauan to Late Teurian (Raine et al. 1993). The formation generally consists of soft to firm, fissile, light grey shales and clays with subordinate darker brown shale and is glauconitic in places. Based on fossil faunas identified in the south and west of the basin within the Wickliffe Formation, a nearshore to inner-shelf marine environment,
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generally with restricted circulation depositional environment is inferred (Raine et al. 1993). The most widespread marine conditions seem to have been in about the Late Cretaceous, followed by shallowing to coastal environments during the Paleocene. The Wickliffe Formation has similar characteristics to the Whangai Formation found on the East Coast region of the North Island.

The top of the Taratu Formation is defined by the transition to marine facies of the Wickliffe Formation which interfingers laterally with the Taratu Formation. The Taratu Formation consists of interbeds of quartzose grit, pebble conglomerates, sandstone and shales with common coal measures. The sandstones are light brown, and fine to coarse grained, while the shale is chocolate brown, firm to blocky, micaceous and very carbonaceous. The coals range in rank from lignite to sub-bituminous. The base of the formation is at least Piripauan in age and possibly Late Haumurian at the top of the formation. Its deposition in the Great South Basin is inferred to have taken place on a lower coastal plain, and it is possible that some of the coal measures were influenced by brackish conditions (Raine et al. 1994; Wilson and McMillan, 1996).

The formation of most importance to this study is the Late Paleocene (Late Teurian) Tartan Formation. It is a dark brown, firm, carbonaceous, slightly calcareous, highly micaceous, and slightly glauconitic shale. The Tartan Formation very closely resembles the Waipawa Black Shale widely found in many basins around New Zealand (see Section 2.1) and is interpreted to be its equivalent. Deposition of the Tartan Formation is likely to have been similar to that of the Waipawa Formation but it was possibly deposited in a shallower environment in the Great South Basin than in other basins around New Zealand (see Section 4.7).

2.2.3 Rakiura Group

The Rakiura Group was deposited during the Eocene (with the lowermost formation deposited in the Waipawan and the uppermost formation during the Runangan). The group is made up of the Laing and Tucker Cove formations.

In southern parts of the basin, the group is defined by an unconformity, or the base of a condensed section. In central parts of the basin the correlative surface lies immediately above the Tartan Formation, and is typically characterised by a sharp upward increase in carbonate content. The top of the group is marked by a regional unconformity close to the
present shelf edge, with overlying Penrod Group sediments progressively onlapping it from the west. In the Central sub-basin, the boundary is characterised by a change in lithology from siltstones and clays of the Laing Formation to chalks or foraminiferal oozes of the Penrod Group. In the southeastern part of the basin, the Tucker Cove Formation overlies the Laing Formation and there is a change from the limestone of Tucker Cove Formation to foraminiferal oozes and chalks of the overlying Penrod Group.

Seismic facies appearing in the Rakiura Group are interpreted to represent slope-basin floor fans and turbidite fans, bathyal carbonates and clastics, and submarine canyon deposits.

The base of the Rakiura Group corresponds to the transition from restricted marine circulation with organic-rich shale deposition in the Late Paleocene to open ocean conditions. Pelagic carbonate sediments of the Tucker Cove Formation were deposited in the southeast of the basin during the earliest Eocene, and extended progressively to the west. From the Early Eocene, a broad prograding wedge formed at the eastward-curving shelf margin, from which a slope-basin floor fan complex developed, probably in outer shelf to upper bathyal depths (Raine et al. 1993). Submarine canyon and valley systems appeared at bathyal depths from at least the Early Eocene.

The base of the Laing Formation is defined by the regional unconformity at the base of the Rakiura Group and is interpreted to be of Late Teurian age. Siltstones in the formation are laterally continuous with marls of the Tucker Cove Formation. In central and southeastern parts of the basin, there is an upward transition from the Laing Formation to the Tucker Cove Formation which is defined by a change from clastic to carbonate-dominated sedimentation.

The Laing Formation extended over most of the Great South Basin in the Early Eocene but by the end of the Eocene, clastic sedimentation was restricted to areas in the west of the basin. The Laing Formation in western parts of the basin consists of interbedded sandstones and siltstones, which are moderately calcareous, and contain glauconite and traces of pyrite. To the east, the formation consists of shales and calcareous clays. The Laing Formation is interpreted to have been deposited in a shelf to upper bathyal setting. Raine et al. (1994) provide evidence for gradual deepening from inner to mid-shelf depositional settings to the west of the basin during the Early Eocene, whereas an outer shelf to upper bathyal setting was present in the east of the basin.
Chapter 2. Geological setting of the GSB and distribution of the Waipawa Formation

The base of the Tucker Cove Formation is defined as the base of carbonate-rich marls and foraminiferal limestones which overlie the unconformity recognised near Late Paleocene strata. The top of the formation is the regional unconformity that separates the Rakiura Group from Penrod Group sediments. The Tucker Cove Formation consists of soft to firm, white to light grey, fine-grained, foraminiferal limestone with chert nodules and traces of pyrite and glauconite. The unit ranges in age from Waipawan to Runangan. Deposition of the formation ranged from outer-shelf to mid-bathyal depths with open oceanic conditions in surface waters.

2.2.4 Penrod Group

The Penrod Group is the uppermost stratigraphic unit in the Great South Basin, with the upper limit of the unit representing the present sea floor. The lower boundary is a regional unconformity that is of Late Eocene or earliest Oligocene age. Oligocene strata lap onto the western margin where moderate to high-amplitude, continuous, slightly wedge-shaped seismic facies suggest deposition in deep water with restricted clastic sediment supply.

The depositional environment in the southern and eastern parts of the basin is inferred to have been under bathyal depths. Along the northwestern margin of the basin, increased sediment supply during Miocene-Recent time formed a thick (<800 m) shelf wedge.

2.3 Stratigraphy and structure of petroleum exploration wells sampled

The basin floor that upper Cretaceous and Tertiary sediments were deposited upon was a peneplained series of anticlinal mountains of Triassic and Jurassic age. Periodic structural uplift throughout the Tertiary resulted in uplift and drape of the Tertiary sediments over the buried lower and mid-Mesozoic mountains that had a NW-SE trend. Seismic mapping shows that the greatest uplift, and hence structural drape, took place in the lower Tertiary.

2.3.1 Toroa – 1 Stratigraphy

The Toroa-1 petroleum exploration well is located in approximately 490 m of water just off the edge of the old Pleistocene continental shelf. The structure has more than 160 km² of area and shows structural uplift from the sea floor downward through upper Tertiary, through a possible unconformity of presumed mid-Tertiary and deeper into the lower
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Tertiary or Cretaceous. This NE-SW trending faulting is thought to be associated with the subsidence and continued depositional changes of the steep west flank of the Great South Basin. A deep-seated fault block seems to be the controlling feature of the Toroa structure (Fig 2.3.1) (Hunt International Petroleum, 1977c). Figure 2.3.2 shows the gamma ray log of Toroa-1 and the depths at which samples were taken with respect to the gamma ray log.

Figure 2.3.1 Seismic cross-section of the Toroa-1 petroleum exploration well.
Figure 2.3.2 Gamma Ray log and stratigraphy of the Toroa-1 petroleum exploration well. Scanned and modified from Cook et al. (1999). Blue arrows indicate depths at which sidewall core samples were taken, and red arrows indicate depths at which cuttings samples were taken.
2.3.2 Pakaha – 1 Stratigraphy

The Pakaha-1 petroleum exploration well is located on the SW extension of the trough that forms the centre of the Great South Basin, in approximately 670 m of water. The structure has an area of more than 80 km$^2$ and shows up to 180 m of structural uplift from Late Tertiary down through the mid to Late Cretaceous. Cretaceous and Tertiary sediments are draped over an old deep-seated horst structure that was uplifted by a NE-SW trending fault system thought to be associated with subsidence and continued depositional changes of the Great South Basin (Fig 2.3.3) (Hunt International Petroleum, 1977b). Figure 2.3.4 shows the gamma ray log of Pakaha-1 and the depths at which samples were taken with respect to the gamma ray log.

Figure 2.3.3 Seismic cross-section of the Pakaha-1 petroleum exploration well.
Figure 2.3.4 Gamma Ray log and stratigraphy of the Pakaha-1 petroleum exploration well. Scanned and modified from Cook et al. (1999). Blue arrows indicate depths at which sidewall core samples were taken, and red arrows indicate depths at which cuttings samples were taken.
2.3.3 Kawau – 1A Stratigraphy

The Kawau-1A petroleum exploration well is located on the southeastern flank of the Great South Basin, in approximately 680 m of water. The Kawau structures appear to be drape rejuvenation features but it is possible that they are controlled by early to mid-Cretaceous tectonics related to the overall subsidence of the Great South Basin itself. The Kawau uplift shows some faulting, most likely normal but possibly reverse, in the deep-seated Cretaceous beds. Latest Cretaceous, Paleocene and Eocene strata are raised and/or structurally draped over this horst-type uplift (Fig 2.3.5) (Hunt International Petroleum, 1977a). Figure 2.3.6 shows the gamma ray log of Kawau-1A and the depths at which samples were taken with respect to the gamma ray log.

Figure 2.3.5 Seismic cross-section of the Kawau-1A petroleum exploration well.
Figure 2.3.6 Gamma Ray log and stratigraphy of the Kawau-1A petroleum exploration well. Scanned and modified from Cook et al. (1999). Blue arrows indicate depths at which sidewall core samples were taken, and red arrows indicate depths at which cuttings samples were taken.
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2.3.4 Hoiho – 1C Stratigraphy

The Hoiho-1C petroleum exploration well is located on the southeastern flank of the Great South Basin, in approximately 660 m of water. The prominent structure appears as depositional drapes and uplift of deep-seated folds and fault blocks. This suggests pre-Tertiary, and possibly pre-mid Cretaceous structural trends on a general NE-SW alignment. Hoiho is a long, NE-SW trending anticline and has an area of 100 km² within the mapped closure around the top of the Paleocene (Fig 2.3.7) (Hunt International Petroleum, 1978a). Figure 2.3.8 shows the gamma ray log of Hoiho-1C and the depths at which samples were taken with respect to the gamma ray log.

![Figure 2.3.7 Seismic cross-section of the Hoiho-1C petroleum exploration well.](image)

Dylan Meadows. Tartan Formation Geochemistry, Great South Basin
Figure 2.3.8 Gamma Ray log and stratigraphy of the Hoiho-1C petroleum exploration well. Scanned and modified from Cook et al. (1999). Blue arrows indicate depths at which sidewall core samples were taken.
2.3.5 Takapu – 1A Stratigraphy

The Takapu-1A petroleum exploration well is in less than 60 m of water depth and is located approximately 19 km offshore. The long narrow structure is a turn over of Late Cretaceous and Tertiary beds against a deep-seated NE-SW trending thrust fault, and has an area of approximately 65 km$^2$. There is up to 150 m of closure against the fault. To the SE, the Late Cretaceous and Tertiary beds rapidly increase in thickness as they plunge steeply towards the deep centre of the Great South Basin (Fig 2.3.9) (Hunt International Petroleum, 1978b). Figure 2.3.10 shows the gamma ray log of Takapu-1A and the depths at which samples were taken with respect to the gamma ray log.

![Takapu-1A Seismic Cross-Section](image)

Figure 2.3.9 Seismic cross-section of the Takapu-1A petroleum exploration well.
2.4 Biostratigraphy and Age of the Tartan Formation in Great South Basin

2.4.1 Toroa – 1

The top of the Tartan Formation in the Toroa-1 petroleum exploration well was reported to be at 2137 m and the base at 2200 m by Cook et al. (1999). This interval given by Cook et al. (1999) implies that most of the Tartan Formation was deposited during the Late Teurian with a small portion having been deposited during the earliest Waipawan Stage. The Teurian interval occurs between 2150 m-2863 m and the Waipawan Interval between 1350 m-2150 m in Toroa-1 (Raine et al. 1993).
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A sidewall core from 2206.8 m, approximately the depth that Cook et al. (1999) give as the base of the Tartan Formation, shows a moderately rich dinoflagellate assemblage with the first appearance of Palaeocystodinium golzowense, indicating the Late Teurian P. golzowense Zone. The same sidewall sample contains Phyllocladidites mawsonii-dominated assemblages of miospores, in which some restricted Cenozoic taxa, including Nothofagus waipawaensis (which is restricted to the Teurian), occur.

Palynofloras and foraminifera agree in giving a Teurian age at around 2200 m, but above this level there is some doubt of the age, due to the occurrence of the foraminifera Bolivinopsis spectabilis in a sidewall sample taken from 1847 m. B. spectabilis is of Waipawan age, above the limits of the upper Teurian. The dinoflagellate Apectodinium homomorphum from 2094 m also suggests Waipawan age (Raine et al. 1993).

Cyclammina spp. is a characteristic Waipawa Black Shale species, and has been identified from about 2150 m through 2260 m. Below 2260 m, faunas are still dominated by a Cyclammina-Budashevaella association, indicating a Late Teurian age, but there is a tendency for declining abundance (Raine et al. 1993).

2.4.2 Pakaha – 1

Cook et al. (1999) report the top of the Tartan Formation in the Pakaha-1 petroleum exploration well to be at a depth of 2503 m and the base at a depth of 2551 m. Raine et al. (1993) have designated the interval 2055 m-2485 m to belong to the Waipawan Stage, while the Teurian Stage occurs between 2485 m and 3167 m. Comparison of the data from both Cook et al. (1999) and Raine et al. (1993) shows that deposition of the Tartan Formation occurred during the latest Teurian.

A sidewall core from 2252 m contains a dinoflagellate-dominated palynoflora with an A. homomorphum or W. spinulosa Zone assemblage, of Early to mid-Waipawan age. Another sidewall sample from 2473 m was dated from nannofossils to be of upper Teurian to basal Waipawan age (Hornibrook and Edwards, 1977).

The approximate positioning of the top of the Teurian is suggested, by the occurrence of the foraminifera Bolivinopsis spectabilis at 2463 m. Bulimina kickapooensis, Alabamina creta and Anomalinoideas piripana have the highest occurrence in the sidewall core from 2554 m, and are considered to be more definitive species for the determination of the upper boundary of the Teurian Stage (Raine et al. 1993).
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A sidewall core examining dinoflagellates from 2505 m contains fairly abundant *Palaeocystodinium golzowense* and rare *Cassidium fragile*, indicating Late Teurian.

Raine *et al.* (1993) state that the Teurian/Waipawan boundary lies between sidewall samples at 2505 m and 2474 m, with a depth of 2485 m being chosen to represent the boundary.

The upper Teurian is characterised by a Waipawa Black Shale lithofacies, primarily comprising agglutinated foraminiferal fauna typified by *Budashevaella multicamerata* and *Cyclammina elegans*, with minor calcareous benthics, in particular *Bulimina kickapooensis* and *Alabamina creta* (Raine *et al.* 1993).

2.4.3 Kawau – 1A

The top of the Tartan Formation as published by Cook *et al.* (1999) is at a depth of 2220 m, while the base is reported to be 2264 m. Raine *et al.* (1993) state that the Teurian interval is between a depth of 2140 m-2850 m. Thus the Tartan Formation in Kawau-1A is entirely of upper Teurian age.

The top of the Teurian is placed by Raine *et al.* (1993) at the highest occurrence of the foraminifera *Cyclammina elegans*, in a cutting sample taken from 2140 m.

The foraminiferal fauna primarily consists of agglutinated forms. Principle taxa are *Cyclammina elegans*, *Budashevaella multicamerata* and *Haplophragmoides* sp.

2.4.4 Hoiho – 1C

The top of the Tartan Formation in Hoiho-1C is placed at 1545 m, while the base is at a depth of 1592 m (Cook *et al.* 1999). Raine *et al.* (1993) has placed the Teurian Stage between 1545 m-1735 m. Thus the Tartan Formation here was deposited during the very latest Teurian. The top of the Teurian Stage is placed at the highest occurrence of *Bolivinopsis spectabilis* together with the tentatively identified *Cyclammina elegans*, in a fauna from a cuttings sample from 1545 m. The highest occurrence of the typical Teurian foraminiferan *Budashevaella multicamerata* was identified in a cuttings sample from 1554 m.

All samples are characterised by sparse to moderately abundant, low diversity assemblages consisting primarily or entirely of agglutinated taxa. No planktics were observed.
Agglutinated taxa are dominated by *Bolivinopsis*, *Cyclammina elegans*, *Budashevaella multicamerata*, *Haplophragmoides* spp., and *Karreriella aegra* (Raine *et al.* 1993).

### 2.4.5 Foraminifera commonly identified in the Waipawa Formation of the East Coast Basin

The Waipawa Formation contains sparse foraminifera; however, Moore (1988b; table 2) reported those that are commonly identified include *Bathysiphon* sp., *Haplophragmoides* sp., *Haplophragmoides* spp., *Bolivinopsis spectabilis*, *Budashevaella multicamerata*, *A.* sp., and *Trochammina* sp. The Waipawa Formation is described by Moore (1988b) as being entirely of Teurian age.

### 2.5 Stratigraphy of the East Coast Basin

The stratigraphy of the East Coast Basin is included here because of the importance of correlation between the Tartan Formation of the Great South Basin and the Waipawa Formation of the East Coast Basin. This correlation will be discussed in more detail in Section 7.9.

The Whangai Formation is a siliceous mudstone ranging from Late Piripauan/Haumurian (Late Cretaceous) to Early Teurian (Paleocene) in age. The formation is widely distributed through the eastern North Island, and is also present in other parts of New Zealand.

The formation is made up of five members: Rakauroa, Upper Calcareous, and Porangahau members, and two members with more local distribution, the Kirks Breccia and the Te Uri Member (Moore, 1988b) (Fig 2.5). Whangai Formation in almost all exposures is conformably overlain by Waipawa Formation (also termed Waipawa Black Shale) (Moore, 1989).
The Late Piripauan-Early Haumurian Kirks Breccia is the lowermost member of the Whangai Formation. It contains poorly sorted, matrix to clast-supported breccia beds 30 m to 200 m thick. Clasts consist of fine sandstone, light and dark grey mudstone and concretions in a micaceous and gritty mudstone matrix (Moore, 1988b).

The next unit of the Whangai Formation is the Rakauroa Member. The member is primarily of Haumurian age, though some basal sediments may be Late Piripauan. The unit ranges from 40 m to 400 m in thickness but tends to average 200 m-300 m. The Rakauroa Member comprises hard, typically very poorly bedded, rusty weathering, bioturbated, medium grey, non-calcareous, micaceous mudstone that has also has thin glauconitic sandstone beds, and scattered pyrite nodules and calcareous concretions. Fine laminations are present near the base the member, consisting of alternating light grey and dark grey siltstone and mudstone. Some areas are more strongly laminated than others (Moore, 1988b).

The Upper Calcareous Member is of Haumurian to Early Teurian age. The unit ranges in thickness from 50 m to 200 m and is a hard, generally very poorly bedded, light bluish-grey weathering, medium grey, slightly to moderately calcareous, bioturbated, laminated micaceous mudstone. The unit contains sporadic concretions, pyrite nodules, glauconitic
sandstone beds and rare breccias, and the carbonate content generally increases upward (Moore, 1988b).

Overlying this is the Early Teurian Porangahau Member, with a thickness of 20 m to 300 m. The unit consists of mainly hard, well bedded, light grey, slightly to highly calcareous mudstone, which is usually moderately to highly bioturbated. Glaucconitic sandstone beds are common (Moore, 1988b). The unit is commonly termed the “zebra facies”, based on thin alternating light and darker grey mudstone layers through the Porangahau Member.

The Te Uri Member consists of approximately 35 m of interbedded glauconitic sandstone and hard, light grey, glauconitic, slightly calcareous, laminated siltstone, which disconformably overlies the Upper Calcareous Member. The Te Uri Member has a similar composition to the underlying Whangai mudstone, with the only major lithologic difference being the higher glauconite proportion of the Te Uri Member. The member is most likely Early Teurian in age. Moore (1988b) stated that the Te Uri Member appears to be a lateral equivalent, in part, of the Waipawa Formation.

Waipawa Formation conformably overlies the Whangai Formation and is widely distributed throughout the East Coast Basin. The formation is of mid-Late Teurian age and rarely exceeds a thickness of 50 m. The Waipawa Formation consists primarily of very poorly bedded, hard to moderately soft, dark brown-grey to brownish black, non-calcareous micaceous siltstone. Locally, there is a high proportion of glauconitic sandstone, and also some intervals of Whangai-like calcareous mudstone. In some places the shale is highly bioturbated, but contains very few macrofossils other than small bivalves and rare gastropods (Moore, 1988b, 1989). Upper and lower contacts are relatively sharp, although the basal contact with the Whangai Formation is commonly gradational over a few centimeters to several meters.

Waipawa Formation overlies different facies of the Whangai Formation across the East Coast region. Moore (1988b, 1989) stated that this is due to the base of the Waipawa Formation probably being diachronous; however, Rogers et al. (2001) interpreted this observation as evidence for the upper members of the Whangai Formation to be diachronous, and facies dependent rather than the Waipawa Formation.

Waipawa Formation is conformably overlain by Wanstead Formation, which is of Teurian to Runangan age (Late Paleocene-Eocene). The formation consists of poorly bedded, moderately hard, light grey to greenish-grey weathering, micaceous, slightly calcareous
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mudstone. The mudstone is intensively bioturbated and contains isolated glauconitic sandstone beds. The Wanstand Formation has a maximum thickness of 490 m (Leckie et al. 1992) but is poorly exposed, and thus accurate thickness determinations are difficult.

Wanstand Formation is conformably overlain by Weber Formation. This consists of up to 370 m of primarily fine-grained, hard, light-grey, bioturbated, calcareous mudstone with minor interbeds of glauconitic sandstone. Ages range from Whaingaroan (Early Oligocene) to likely Duntroonian-Waitakian (Late Oligocene-Early Miocene) (Leckie et al. 1992).
CHAPTER 3

Environmental conditions during the Late Paleocene-Early Eocene

3.1 Late Paleocene-Early Eocene warming

Records from the Ocean Drilling Project (ODP) indicate a period of rapid climate change culminated in a brief transient climate. This transient climate, referred to as the Late Paleocene Thermal Maximum (LPTM), was a time of global warming that began to develop during the mid-Paleocene. The LPTM climate extreme was not stable and lasted only a few 100 ka. This is possibly the result of a climatic overshoot because of timing, direction and rate of change, causing a climatic state that had briefly passed equilibrium (Zachos et al. 1993).

The Paleocene-Eocene boundary was a time of global transgression and also the warmest period of the Cenozoic, with temperatures climaxing at the Paleocene-Eocene boundary (Field et al. 1997). Paleontologic proxies indicate that high latitude marine and terrestrial environments experienced near sub-tropical conditions (Zachos et al. 1993).

During the Early Paleogene, significant Antarctic warmth combined with inferred higher precipitation may have caused a large reduction in deep waters derived from the high latitudes and polar sources (Kennett and Stott, 1991). The highest temperature of the deep oceanic water was around 11-15°C during the Early Eocene.

During the latest Paleocene, deep waters warmed to temperatures close to those at the ocean surface. This deep ocean warming temporarily eliminated the vertical temperature gradient between deep and surface waters, and carbonate records show decreases in both $\delta^{18}O$ and $\delta^{13}C$. The oceanic temperature gradient was re-established 30 ka after the initial isotopic excursion (Zachos et al. 1993).

The LPTM transient climate was accompanied by a re-organisation in ocean circulation and was marked by reduced oceanic turnover, decreases in marine productivity and global $\delta^{13}C$. Benthic foraminiferal oxygen isotopic records show that from Late Paleocene to Early Eocene, deep sea temperatures warmed from 8°C to 12°C as depicted in Fig 3.1.
Chapter 3. Environmental conditions during the Late Paleocene-Early Eocene

During this time, surface water temperatures increased by 5-6°C, with maximum temperatures exceeding 20°C (Zachos et al. 1993). This transition appears to have taken place in less than 10 ka and did not persist. Following this period of extraordinary warmth, temperatures almost immediately began to decrease, gradually cooling over the next 100 ka but remaining 1-2°C higher than before the beginning of the excursion (Zachos et al. 1993; Kennett and Stott, 1991).

3.2 Paleoceanographic conditions at the Paleocene – Eocene boundary

Warm, saline seas coupled with foraminiferal extinctions and dysaerobia suggest that a sluggish oceanic circulation existed during the Late Paleocene to Early Eocene (Killops et al. 2000). These waters were the least ventilated in the entire Cenozoic (Thomas, 1990), and were poorly oxygenated compared to today’s oceans (Kaiho et al. 1993).

Deep ocean oxygen concentrations are primarily controlled by deep water formation processes. In the modern ocean, almost all dense, oxygen rich waters are produced at high latitudes as a result of cold temperatures in combination with moderately high salinity (Kennett and Stott, 1991).

Thomas (1990) suggested that during the LPTM there was a change from the formation of sinking, high latitude deep waters to the formation of deep to intermediate waters in the oceans by evaporation at lower latitudes. It is possible that these deep waters may have formed at sub-tropical latitudes, where evaporation strongly exceeds precipitation. As a
result, heavy, dense, warm, saline deep waters could have formed. This water would have likely been depleted in oxygen due to the lower solubility of oxygen at higher temperatures.

Today’s oceanic circulation is thermohaline, which is essentially driven by the temperature differences between cold, well oxygenated, high latitudinal water. Zachos et al. (1993) stated that because the LPTM was a time of high temperatures and significant warmth, there would have been smaller planetary temperature gradients between high and low latitudes. During this time, deep sea water temperatures were similar to high latitudinal surface waters. The contribution of warm, saline waters to the overall deep circulation was likely to have been small, but as the higher latitudes began to warm during the mid-Paleocene and climaxing in the Early Eocene, the density distribution of the ocean should have changed, shifting the ratio of deep water formation between high and low latitudes. At some threshold, deep ocean circulation may have changed into a form closer to a halothermal mechanism, driven by heavier, more dense, warm, saline surface waters originating from low to mid latitudes around 20-30° (Zachos et al. 1993; Kaiho et al. 1993). These surface waters would have been heavier and more dense than contemporaneous high latitudinal surface waters (Kaiho et al. 1993). There was a global dysaerobic event in the oceans associated with this change was that is thought to have resulted from the switch from thermohaline to halothermal circulation (Killops et al. 2000). ODP data from the Southern Ocean suggest there was a short period of non-production of deep waters at high Southern latitudes at the Paleocene-Eocene boundary (Thomas, 1990).

During the LPTM, surface water temperatures had maximum temperatures surpassing 20°C. At the same time, bottom waters increased to 15°C (Zachos et al. 1993; Kaiho et al. 1993). Warm, saline, shallow surface waters from mid to low latitudes may have sank to the bottom of the ocean to drive slow circulation (Kaiho et al. 1993). When deep water temperatures reach or exceed 10°C, deep water circulation originating at high latitudes must disappear because heavy, cold water will not be produced at this temperature (De boar, 1986). Thus deep water oxygen levels would have declined if production was constant due to increasing oxygen consumption by biological activity (Fig 3.2). If circulation was slower this oxygen consumption would have been augmented (Kaiho et al. 1993).
Chapter 3. Environmental conditions during the Late Paleocene-Early Eocene

Figure 3.2 Low oxygen conditions of bottom waters during the LPTM (from Kaiho, 1991).

It is possible that if oxygen consumption was intense enough, bottom waters may have become anoxic. However, there is no record of the existence of total anoxia (Zachos et al. 1993).

Associated with the Late Paleocene-Early Eocene warming were major benthic foraminiferal extinctions. The process that caused the widespread extinctions was rapid (≤ 3 ka) and had the capacity to affect great volumes of deep ocean very quickly. The extinctions were thought to have occurred at about the rate of replacement time of the Early Paleogene oceans, which is suspected to have been slower than the present day oceanic rate of replacement of around 1 ka (Kennett and Stott, 1991).

The absence of significant planktonic extinctions with respect to vast benthic extinctions and the nature of carbon and oxygen isotopic records have been suggested to reflect a decoupling of shallow and deep water ecosystems (Zachos et al. 1993). Elimination of ocean temperature gradients indicates vertical ocean mixing and homogenisation of nutrient distributions. Whole ocean δ13C decreased by 2.5-3‰ in less than 10 ka during the Paleocene-Eocene warming episode. Such a rapid reduction in oceanic carbon composition requires an abrupt change in the flux of depleted carbon either to or from the ocean. A possible explanation (Zachos et al. 1993) is that lower global temperature gradients leads to a decline in the vigor of atmospheric circulation, thus dampening wind driven upwelling, amplifying the reduction in nutrient flux to the oceans photic zone. As the result of vertical mixing and deep water turnover, nutrient fluxes would have declined, lowering the production and export of particulate carbon to and from the mixing layer.
3.3 Isotopic and biological variations during the LPTM

The LPTM was marked by reduced oceanic turnover and decreases in global $\delta^{13}$C and marine productivity. During this time $\delta^{18}$O and $\delta^{13}$C records show a global dysaerobic event that is associated with the Paleocene warming. This dysaerobia affected benthic taxa but not surface planktonic species (Field et al. 1997; Zachos et al. 1993; Kennett and Stott, 1991). The climatic warming event was recognised in a pelagic sequence from the Maud Rise in the Atlantic sector of the Southern Ocean (Kennett and Stott, 1991).

$\delta^{18}$O analyses of foraminifera revealed abrupt, brief warming of deep ocean, high latitude surface waters coincident with a major extinction of benthic epifaunal foraminifera (Fig 3.3.1).

Figure 3.3.1 Lower Tertiary benthic epifaunal foraminifera variations at ODP 690.

Modified from Zachos et al. (1993).

Thomas (1990) has stipulated that benthic foraminiferal diversity dropped by 50% over a period of less than 25 ka during the latest Paleocene, this is corroborated by other authors such as Kennett and Stott (1991) who report benthic communities deeper than continental shelf (>100 m depth) declined. During the widespread benthic epifaunal decline at the peak of the LPTM there were no extinctions of surface dwelling or terrestrial organisms on a comparable magnitude. This warming period was a time of low overall extinction rates (Thomas, 1990).

Kennett and Stott (1991) state the lack of bioturbation by burrowers and epifaunal species early on in the warming excursion confirm the mass extinction of benthic communities.
Kaiho et al. (1993) suggested that the extinction event at the Paleocene-Eocene boundary is characterised by the extinction of *inter alia* *Stensioenia beccoriiformis*.

From the Late Paleocene to the Eocene, high latitudinal planktonic foraminiferal faunas and nannofossils became increasingly more diverse. Characteristic subtropical fauna and flora appeared in the Southern Oceans by Late Paleocene and reached peak abundance during the Early Eocene. These subtropical species slowly disappeared by the mid-Eocene as the temperature cooled to slightly higher than levels before the Paleocene warming (Stott et al. 1990; Zachos et al. 1993).

Abundance records from the Late Paleocene to Early Eocene show deep sea benthic foraminifer species encountered mass extinctions and epifaunal taxa disappeared. However, at the same time, planktonic infaunal biota diversity increased. This change is thought to have resulted from a reduction of oxygen in bottom waters. The turnover in benthic species composition was abrupt, with most disappearances occurring just below the Paleocene-Eocene boundary (Zachos et al. 1993).

Thomas (1990) has proposed that deep sea benthic foraminiferal fauna reflect the characteristics of deep waters. The benthic extinction event was likely due to changes in the oceanic conditions, with the replacement of a cold, well oxygenated water mass originating from high latitudes, with warm, heavy, saline, oxygen depleted water from mid to low latitudes, brought on by a change in water circulation patterns due to the LPTM warming (Field et al. 1997). Isotopic data from benthic foraminifera and suggested that there was a short period of intense warm-saline water production during the Late Paleocene (Thomas, 1990).

Surface to deep water δ¹³C gradients, as reconstructed from planktonic and benthic foraminifera, briefly declined to near zero in less than 10 kyr during the peak of the LPTM event (Zachos et al. 1993). Killops et al. (1996) stated that because benthic extinctions occurred at high latitudes and the main effect of the extinctions was encountered at intermediate depths, there was a loss in the oceanic temperature gradient between deep and surface waters. Kennett and Stott (1991) present data that support this (Fig 3.3.2).
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Figure 3.3.2 Late Paleocene $\delta^{18}O$ and $\delta^{13}C$ records from ODP site 690. Modified from Kennett and Stott (1991).

$\delta^{13}C$ levels immediately preceding the extinction event are the highest in the entire Cenozoic. $\delta^{13}C$ Benthic foraminiferal values at 57.32 Ma are almost identical to contemporaneous surface water planktonic records, and there is usually a 2‰ gradient between surface and deep waters. Zachos et al. (1993) suggest a decrease of over 3‰ in the $\delta^{13}C$ records took place at this time.

From ODP research, Thomas (1990) concluded that the epifaunal benthic extinctions occurred over less than 25 ka and were followed by approximately 350 ka of low diversity and a strong dominance of infaunal planktonic species. This short interval is characterised by extremely low $\delta^{18}O$ and $\delta^{13}C$ values in benthic foraminiferal records. The dominance of infaunal species following the epifaunal reduction suggests the extinctions may have been caused by an increase in surface productivity, causing a strong increase in the abundance of infaunal biota. Such fauna appear to indicate high productivity of primary producers in the surface waters, good preservation of organic matter, and hence a lack of oxidation, or a combination of these. Dominance of infaunal taxa has been recorded from areas with a high flux of organic carbon to the ocean floor, or with low dissolved oxygen in the bottom waters.
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As oceanic circulation during the LPTM was slow, more of the oxygen in deep waters must have been consumed by bacteria (Figures 3.2 and 3.3.3; Kaiho et al. 1993) and epifaunal species could not survive in such an oxygen-depleted environment.

![Graph showing low oxygen in the world's ocean compared with δ18O records. Modified from Kaiho et al. (1993).](image)

Thomas (1990) later proposed that the benthic extinctions were most likely neither the result of an increase or decrease in surface productivity, rather the main cause was due to the deep ocean changes at the Paleocene-Eocene boundary.
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CHAPTER 4

Organic matter accumulation and preservation

4.1 Anoxia and sources of organic carbon

The anoxic aquatic environment is a mass of water in which almost all biologic activity has been terminated due to that water being so severely depleted in oxygen that most organisms cannot survive. Anoxia occurs when the oxygen saturation in water is below 0.5 ml/L (millilitre of oxygen per litre of sea water). Above 0.5 ml/L the environment is said to be oxic; thus, the 0.5 ml/L level is proposed as the boundary between potentially good or poor qualitative and quantitative preservation of organic matter in sediments (Demaison and Moore, 1980).

Anoxic conditions occur when the demand for oxygen in a water column exceeds supply. Oxygen demand relates to surface-biologic (primary) productivity, whereas oxygen supply below the depth of surface mixing depends on water circulation (Demaison and Moore, 1980).

Increased primary production in the surface layers of the ocean increases the flux of organic carbon delivered to the sea floor, owing to degradation and other sedimentary factors, discussed in Section 4.5. The primary source of organic matter in the ocean is phytoplankton, predominantly made up of unicellular algae that inhabit the uppermost layer of water illuminated by sunlight (photic zone). The main limiting factor to planktonic productivity, in addition to sunlight, is the availability of mineral nutrients, such as nitrates and phosphates, which are in short supply in the photic zone due to consumption by phytoplankton (Pedersen and Calvert, 1990; Demaison and Moore, 1980). Phytoplankton is intensively foraged by zooplankton, both of which are consumed by larger invertebrates and fish.

4.2 Mechanism for the biochemical degradation of organic matter

The breakdown of organic matter in marine sediments follows a sequence of oxidation reactions that involve different electron acceptors/oxidants.

Bacterial degradation proceeds rapidly and efficiently in well oxygenated, aerobic water. Anaerobic degradation is thermodynamically less efficient than aerobic decomposition, and
thus results in a more lipid-rich and subsequently more reduced, hydrogen-rich organic residue compared to that of aerobic degradation. The first step in the oxidation of dead organic matter involves oxygen acting as the oxidant, and is generalised by the following reaction scheme that has been modified from Demaison and Moore (1980) using general reaction equations from White (2001).

1. \[(\text{CH}_2\text{O}) + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}\]

When the oxygen supply becomes exhausted, oxidation continues, but organic matter is now degraded by anaerobic bacteria that use nitrates as the oxidant. This is shown by:

2. \[5(\text{CH}_2\text{O}) + 4\text{NO}_3^- \rightarrow \text{CO}_2 + 3\text{H}_2\text{O} + 4\text{HCO}_3^- + 2\text{N}_2\]

Once nitrates become exhausted, anaerobic sulfate reducing bacteria break down the organic matter. In environments with free H\(_2\)S in the water or in pore waters of the sediments, oxidation is evidently proceeding as indicated by the presence of the sulfide (S\(^2\)) by-product. The following generic reaction scheme illustrates this reaction:

3. \[2(\text{CH}_2\text{O}) + \text{SO}_4^{2-} \rightarrow 2\text{HCO}_3^- + \text{H}_2\text{S}\]

The above reaction schemes (1-3) show that even in the absence of oxygen in sediments and stagnant water bodies, oxidation continues without oxygen acting as the oxidant. Only once all of the oxidants (oxygen, nitrates and sulfates) have been completely exhausted does oxidative degradation of deposited labile organic matter stop. Under these conditions the final and least efficient step in anaerobic metabolism, known as fermentation (methanogenesis; methane generating), takes place. This process occurs in environments where the oxygen saturation of the bottom water is below 0.1 ml/L. Fermentation utilises carboxyl groups and organic acids that have been produced from the degradation of the deposited organic matter itself or from bacterial breakdown as the oxidants in the reaction. Below 0.5ml/L, low diversity, highly stressed suspension feeding epifaunal taxa can survive above the sediment/water interface, but below 0.5-0.3 ml/L bioturbation from burrowers is almost eliminated and the overall benthic community is sharply reduced (Demaison and Moore, 1980). Pedersen and Calvert (1990) have summarised this well by stating that the preservation of organic matter in marine sediments depends on the degree to which
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sediment dwelling bacteria are able to metabolise the constituent components of the organic matter that have been deposited within the sediments.

4.3 Oxygen supply and demand in the ocean

The maximum oxygen saturation in the ocean is around 6-8.5 ml/L, depending on temperature and salinity. Oxygen is supplied to water masses by two physical processes: a) downward flow of well oxygenated water from the aerated surface waters as oxygen is supplied to the surface layers by exchange from the atmosphere and by photosynthetic oxygen producers, and b) the upward movement of oxygen-rich, colder, denser bottom water into intermediate water zones.

As previously mentioned in Chapter 3, oxygen-rich waters are denser, colder and more saline than oxygen-depleted warm waters. Oxygen-rich waters sink to the bottom of the water column and circulate; this water acts as an aerating undercurrent resulting in multilayered vertical stratification. Modern oceans would be anoxic at depth without aeration of their basins by colder, more dense oxygen-rich bottom waters mainly derived from high southern latitudes (Demaison and Moore, 1980).

The most common cause of anoxia in the oceans is the inability of the oxygen supply in water to meet the biochemical demand. Oxygen minima in the oceanic water column occur at depths where the concentration of dissolved oxygen has been reduced by bacterial decomposition of settling organic matter in a layer that slowly advects and has had no interaction with the atmosphere for a long period of time (Pedersen and Calvert, 1990). The small portion of organic matter that has escaped total degradation and has sunk to the sea floor continues to create a demand for oxygen and, if continued demand is not replenished by deep water circulation, the water column will become anoxic. Areas with a normal oxygen supply can become anoxic. This occurs in areas of very high primary productivity, where the oxygen supply near the sea floor cannot deal with the amount of organic detritus that settles on to the ocean floor (Demaison and Moore, 1980).

4.4 Oxic and anoxic environments

Under an oxic water column (defined as having an oxygen saturation above 0.5 ml/L) the benthic fauna on the sea floor actively rework the organic detritus that falls through the water column (Fig 4.4.1). In shallow waters the sunlight penetrates to the sea floor, resulting
in very little primary productivity in the surface layers of the ocean and most of the organic matter at the benthic boundary is consumed. In an oxic environment these bottom muds are extensively disrupted by oxygen resiping invertebrates (e.g. polychaete worms and bivalves). This bioturbation of sediments allows the diffusion of oxidants within the sediment, ultimately leading to poorer preservation of organic matter resulting in lower quality organic matter with a low total organic carbon (TOC) content, generally between 0.2-4%, as summarised in the following schematic:

**OXIC ENVIRONMENT**

**Biological reworking is enhanced by:**
- presence of animal scavengers at sediment/water interface
- bioturbation by worms etc facilitates diffusion of oxidants (O₂, SO₄) in sediments
- lesser organic complexation with toxic metals

**Poorer OM preservation Lower quality OM**

![Diagram of Oxic Environment](image)

Figure 4.4.1 The oxic water column. Modified from Demaison and Moore (1980).

Under an anoxic water column (Fig 4.4.2) (oxygen saturation below 0.5 ml/L), oxygen depletion depresses and eventually eliminates benthonic metazoan life forms. The lack of bioturbation acts as a limiting factor to diffusion of oxidants into the sediment. The sediment/water interface has no animal scavengers and thus no bioturbation due to the restricted diffusion of oxidants. The lack of sediment aeration by bioturbation at the sea floor in an anoxic setting leads to enhanced preservation and higher quality organic matter with TOC contents ranging from 1-25%, much higher than that of sediments deposited under oxic waters (Fig 4.4.1). Anaerobic bacteria in anoxic environments utilise lipids from the deposited organic matter to a lesser extent than in oxic environments. Thus sediments deposited under anoxic conditions tend to produce a lipid-rich, hydrogen-rich, more reduced
organic product than those accumulated under oxic waters, as shown by the following illustration:

**ANOXYC ENVIRONMENT**

Biological reworking is slowed by:
- absence of animal scavengers at sediment/water interface
- restricted diffusion of oxidants (SO₄) into undisturbed sediments
- lesser utilization of lipids by anaerobic bacteria

**Better OM preservation**
- 1 - 25% TOC
**Higher quality OM**

Figure 4.4.2 The anoxic water column. Modified from Demaison and Moore (1980).

Bioturbated sediments under oxic waters tend to be homogenised whereas those deposited under anoxic conditions will be varied or laminated with an absence of burrowing and deposit feeding infauna.

**4.5 The influence of sedimentation rate on the preservation of organic matter**

The concentration of organic carbon in marine sediments is regulated by its rate of supply (bulk accumulation rate), the extent of preservation after burial and the degree of dilution by other sedimentary components. Pedersen and Calvert (1990) state that only a small fraction of the organic matter produced in the photic zone is exported and ultimately settles into deeper water. This is due to several factors including the degradation of the organic matter by oxidation, consumption by benthic feeders and continued degradation in the sediment, while the remaining organic residue is buried.

Organic matter that has a long residence time in the water column prior to sedimentation is more likely to suffer biological attack and hence its preservation will be adversely affected.
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Thus the depth of the water column as well as the size of the organic particles affects both the quality and quantity of the organic input into the sediment (Demaison and Moore, 1980).

4.6 Upwelling causing anoxia

Upwelling is a process of vertical water motion in the ocean where deep nutrient-rich waters rise towards the surface (Fig 4.6).

Anoxia in oceanic waters caused by upwelling can only occur when the oxygen concentration in deep water cannot meet the demand for oxygen required from biologic primary productivity. Dysaerobic conditions develop in these deep water layers beneath the upwelling. An upwelling can be described as a countercurrent system that acts as a trap in which nutrients will tend to accumulate; hence upwelled water that is rich in nutrients promotes high biologic productivity in the water column (Demaison and Moore, 1980). The photic zone typically has a very low concentration of nutrients due to consumption by phytoplankton. Continued planktonic production can only take place if nutrients are supplied to the photic zone, either by vertical mixing (upwelling) or if deposited for example by aeolian transport. Vertical mixing is controlled by the vertical stability of the water column and to what extent it allows vertical mixing (Pedersen and Calvert, 1990). Oxygen depletion creates conditions favorable for enhanced preservation of organic matter in the underlying sediments. The concentration of this organic matter is further enhanced by the lack of significant water circulation in the stratified water column.

Anoxia resulting from upwelling is more common during times of worldwide transgression, and occurs around coastal regions at shallow depths of 200 m or less, as coastal regions are commonly associated with high primary productivity.

The sediments deposited under areas of upwelling are typically laminated, bituminous, dark-brown shales and laminated, hard, siliceous, dark-brown, often diatomaceous shales (Demaison and Moore, 1980).
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Figure 4.6 Schematic of a coastal upwelling system. Modified from Encyclopædia Britannica Concise (2008). After A. Carroll, based on an original drawing by R.T. Barber, copyright National Geographic Society 1984 in T.Y. Canby, National Geographic (February, 1984).

4.7 Depositional environment of the Waipawa Formation

During deposition of the Waipawa Formation, ocean surface waters were warmer than immediately prior to deposition of the formation (see Chapter 3).

The global dysaerobic event that occurred during the latest Paleocene at the Teurian-Waipawan boundary, 55.5 Ma is defined by extinctions and carbon and oxygen isotopic excursions in benthic foraminifera at high latitudes in the Southern hemisphere oceans (Kennett and Stott, 1991; Zachos et al. 1993; Thomas, 1990).

It is possible that the characteristic high organic content of the Waipawa Formation is the result of changes in oceanic circulation patterns prior to the benthic extinctions of the Late Paleocene warming (Field et al. 1997) (see Chapter 3 and 4 discussions).

The Waipawa Formation is interpreted to represent a condensed section that was likely to have been deposited at the peak of marine transgression or highstand of sea-level following a major lowering of the Late Paleocene sea-level (Haq et al. 1987; Strong et al. 1995; Rogers et al. 2001) during a period of global warming that began in the mid-Paleogene and climaxned during Late Paleocene to Early Eocene time (Zachos et al. 1993). Paleogeographic reconstructions (Fig 4.7) show the Waipawa Formation was deposited widely over the New Zealand landmass (Field et al. 1997).
Dysaerobia during the deposition of the Waipawa Formation may have been brought on by high biological oxygen demand in the water column due to biological scavenging and reworking of descending organic matter. The biochemical degradation of this organic matter would have resulted in reduced oxygen saturation levels within the water. Killops et al. (2000) stated an important point, in that the change in circulation pattern from a thermohaline to halothermal system would create an oxygen-depleted water body below a depth of 200 m, which may have also contributed to or had a profound influence on dysaerobic conditions during the deposition of the Waipawa Formation.

From the wide distribution of the Waipawa Formation and its equivalents throughout New Zealand it is unlikely that it was deposited contemporaneously in a number of basins with restricted bottom water circulation (Field et al. 1997). Wind-driven upwelling may have had a partial influence on the nature of the Waipawa Formation in some places, but was unlikely to have been the cause of distinctive features of the formation such as the sterane content and its paleodistribution around much of the New Zealand landmass (Killops et al. 1996; Killops et al. 2000; Field et al. 1997). The Waipawa Formation is likely to have been associated with the changes in oceanic circulation during the Late Paleocene, 55.5 Ma (Killops et al. 2000).
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It is probable that the degradation of a significant amount of organic matter below an area of high phytoplankton productivity, resulting from upwelling, led to sediments rich in organic content being deposited over a large part of the New Zealand region (Field et al. 1997).

To produce almost entirely anoxic bottom waters in an open, well-oxygenated marine setting from the aerobic decomposition of organic matter would require exceptionally high productivity in the surface waters, and this unusually high productivity would have had to have taken place over a large area to account for the distribution of the Waipawa Formation. Field et al. (1997) pointed out that there is no clear evidence that the Waipawa Formation is associated with such extreme high productivity, although the authors concluded that the high organic content of the formation suggests that high productivity was involved. In some places, biogenic reworking and degradation has prevented the preservation of organic carbon in equivalent condensed stratigraphic intervals, such as in the East Coat Basin. A likely example of this is documented by Rogers et al. (2001) at Tawanui. The presence of greensands of the Te Uri Member in Tawanui rather than the coeval black shale of the Waipawa Formation observed in the nearby Angora Stream, approximately 10 km away, suggest that conditions were oxygenated enough for biologic degradation of organic matter deposited in Tawanui, but not oxygenated enough for degradation of organic matter at Angora Stream.

Abundant sulfur and its large range of isotopic fractionation, shown by negative $\delta^{34}S$ values for kerogen and bitumen samples, suggest sulfate reduction with an unrestricted supply of fresh sulfate, which is typical of anoxia in an open marine system was likely to have taken place during the deposition of the Waipawa Formation (Killops et al. 2000).

28, 30-Dinorhopane is abundant in some Waipawa Formation samples. It is believed to be synthesised by bacteria utilising CO$_2$ (Shoell et al. 1992). The likely source of CO$_2$ in the Waipawa Formation is in the sulfate reduction reaction that liberates CO$_2$ as well as hydrogen sulfide (see Section 4.2). Waples and Machihara (1991) mention that sediments containing large amounts of 28, 30-Dinorhopane are often indicative of deposition under anoxic conditions. There is a very high abundance of 28, 30-Dinorhopane in some wells in the Great South Basin, such as Pakaha-1 and Kawau-1A. This is suggested to be evidence of anoxic conditions developing rapidly within the sediments (Cook et al. 1999; Grantham et al. 1980). Killops et al. (2000) concurs, stating that anaerobia must have developed rapidly
within the sediments based on the sulfur isotopic composition and content, benthic faunal abundances and γ-ray logs of samples analysed from the Waipawa Formation.

The Waipawa Formation has an unusually high abundance of 24-n-propylcholesteranes. Killops et al. (2000) stated that surface water conditions must have favoured phytoplankton that preferentially synthesised the C₃₀ sterol precursors. Deposition of the Waipawa Formation coincides with a sharp increase in the abundance of 24-n-propylcholesteranes; however, the relative abundance of 24-n-propylcholesteranes began increasing gradually prior to the deposition of the Waipawa Formation earlier in the Teurian, during the deposition of the Upper Calcareous Member (UCM) of the Whangai Formation (Killops et al. 2000).

Deposition of the Waipawa Formation under dysaerobia is marked by very limited bioturbation in most exposures and low abundances of benthic microfossil (Killops et al. 2000). It is likely that the water immediately above the sediment/water interface was not completely anoxic due to the presence of bioturbation within the Waipawa Formation.

The Waipawa Formation has very poor preservation of foraminifera; however, there is some evidence for changes in the foraminiferal assemblages through time. Below the Waipawa Formation sediments are dominated by benthic species, while the formation above the Waipawa Formation primarily contains planktonic species. Within the Waipawa Formation, faunas are poor but most are planktonic species together with some calcareous and agglutinated benthics (Strong et al. 1995).

Strong et al. (1995) has proposed that Haplophragmoides-dominated assemblages that are commonly recovered may indicate environmental stress that could have resulted from low oxygen/high organic matter deposition. The elongate nodosariids are indicative of dysaerobia (Kaiho, 1991) and the presence of Alabamina is considered to be an indicator of deposition under a sub-oxic environment (Kaiho, 1994).

Strong et al. (1995) stated that there is no evidence for a major depth change at the time of deposition, suggesting that the Waipawa Formation was deposited under bathyal conditions. Killops et al. (2000) reached a similar conclusion and suggested that the open marine depositional environment, beyond the neritic zone, was associated with the deposition of the underlying Whangai and the overlying Wanstead formations. Waipawa Formation deposition corresponds to inner shelf or basal slope/abyssal environments (Killops et al. 1996; Killops et al. 2000). Field et al. (1997) and Cook et al. (1999) also conclude that the Waipawa Formation
was deposited in fairly deep water, below the limit of wave action (>200 m) and possibly on the upper continental slope.

Deposition in the Great South Basin appears to have taken place in a relatively shallow, restricted marine environment.

The upwelling event that is associated with the deposition of the Waipawa Formation would have provided nutrients to the surface waters around the shelf break and could have caused shoaling of the oxygen minimum layer so that it impinged on the upper continental slope (Killops et al. 1996; Killops et al. 2000). The high primary productivity that accompanied the deposition of the Waipawa Formation could have occurred during a period of high sea-level that followed a glacio-eustatic fall. This period is marked by dropstones in the Upper Calcareous Member of the upper Whangai Formation that underlies the Waipawa Formation (Leckie et al. 1995).

At some locations where the Waipawa Formation is present, two organic-rich black mudstone units are separated by a less organic-rich and more calcareous unit (Killops et al. 1996). The organic-rich layers may correspond to more intense episodes of upwelling (Field et al. 1997). Degradation of large amounts of organic detritus sinking through the water column would have intensified dysaerobia, enhancing preservation of the organic matter in the formation.

The differences between the Tartan Formation of the Great South Basin and the Waipawa Formation (discussed in Chapter 7) of the East Coast region are likely related to the deposition of the Tartan Formation in relatively shallow water behind a near-surface ridge that was present from the Late Cretaceous to the Paleocene. This ridge was present immediately to the west of and extended along the line of wells in the Great South Basin from which the Tartan Formation has been identified (Killops et al. 1996; Killops et al. 2000; Cook et al. 1999).
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Geochemical analyses were performed on cuttings and sidewall core samples from five wells from the Great South Basin. Mass spectroscopy was undertaken at the GNS National Isotope Centre (Gracefield, Lower Hutt) using an elemental analyser isotope ratio mass spectrometer (EA-IRMS) to determine the total organic carbon (TOC) content, nitrogen content, and the carbon stable isotope ratio ($\delta^{13}C$) of each sample. Rock-Eval analyses were performed on selected sidewall core samples by two independent laboratories: Applied Petroleum Technologies (APT), Norway, and Geological Survey of Canada (GSC). Each laboratory used a Rock-Eval 6 appliance and the results were made available to the present study by GNS Science.

5.1 Sampling

Washed cuttings and sidewall cores were collected from the national core and cuttings archive in at Gracefield. 42 cuttings samples were taken from four wells (Kawau-1A, Takapu-1A, Pakaha-1 and Toroa-1); 33 sidewall cores were also taken from four wells (Kawau-1A, Hoiho-1C, Pakaha-1 and Toroa-1). Samples were taken to approximately 200 m above and below the Tartan Formation interval, with a nominal sampling interval of 50 m. Within the Tartan Formation, closer sampling intervals of 10 m were collected where possible. Due to previous studies of the Great South Basin petroleum exploration wells, many of the cuttings samples had little material remaining. Thus many of the desired intervals could not be analysed in this study, and as a result there are many large sampling gaps in the data set.

In the present study, cuttings sample depths are not represented as a depth range (for example, Kawau-1A; 2030-2037 m); instead, the depth intervals are given as the middle value of the depth range in order to clarify graphical interpretations and referencing (for example, Kawau-1A; 2030-2037 m is represented as 2034 m).

5.2 Sample preparation
Coarse cuttings fragments were hand picked using a microscope in order to select the most suitable fragments of that particular cuttings sample. Both cuttings and sidewall core samples were ground to fine powder using a mortar and pestle. This was then demineralised by placing the powder into 50 mL sample tubes, followed by the addition of approximately 10 mL of 1 mol HCl to remove the inorganic carbon (CO$_3^{2-}$). The tubes were shaken vigorously and the acid left in the tube for at least 24 hours. Next, the samples were neutralised by adding approximately 50 mL of distilled water and centrifuging at 300 rpm for 10 minutes. This neutralisation process was repeated and the powdered sediment allowed to dry in an oven at around 35-40 °C.

5.3 Mass Spectrometry

In this study carbon isotopic ratios, nitrogen contents and organic contents were measured by Dr K. Rogers of GNS Science using a Europa Geo 20-20 isotope ratio mass spectrometer, interfaced to an ANCA-SL elemental analyser in continuous flow mode (EA-IRMS). Around 6-80 mg of demineralised, powdered sediment was weighed in duplicate into tin capsules. The tin capsules were tightly crimped to avoid any trapping of air that would disturb the combustion process. After O$_2$ injection, each capsule was dropped individually into a catalytic combustion furnace at a temperature around 1040 °C. When O$_2$ is introduced, tin oxidation creates an exothermic ‘flash combustion’ at 1800 °C, ensuring complete combustion and oxidation of the sample (Grassineau, 2006). The carbon dioxide and nitrogen gases were resolved using gas chromatographic separation on a column at 60 °C, and analysed simultaneously for isotopic abundance as well as total organic carbon (TOC) and nitrogen (%N). Standards and blanks were included during the run for internal calibration. The analytical precision of the carbon isotopic measurements are ±0.1‰. The final carbon isotopic ratio measurements are expressed using the standard δ notation (see equation 5.3, White, 2001), as per mil (‰) deviations relative to the Pee Dee Belemnite (VPDB) standard for carbon.

\[
\delta^{13}C = 1000 \times \left( \frac{^{13}C/^{12}C_{\text{sample}}}{^{13}C/^{12}C_{\text{standard}}} - 1 \right)
\]

C/N ratios were calculated by dividing the TOC content by the total nitrogen content (TN or %N) and multiplying by 14 (the atomic number of nitrogen) over 12 (the atomic number of carbon). Thus, \(C/N = (\text{TOC}/\text{TN}) \times (14/12)\).
5.4 Rock-Eval pyrolysis

Rock-Eval pyrolysis is performed using temperature programmed heating (100° - 850° C) of a small amount of sample (~ 100 mg) in an inert atmosphere. The temperature controlled heating procedure is used to determine the quantity of free hydrocarbons present in the sample (S1 peak), and the amount of hydrocarbon and oxygen containing compounds (CO₂) that are produced by the thermal cracking of kerogen in the rock (S2 and S3 peaks). Of principle importance to this study was the TOC content of the samples analysed. The TOC content of a rock is determined by oxidation of the residual carbon after pyrolysis (S4 peak). The S4 peak is determined by the sum of the CO (S4CO) and CO₂ (S4CO₂) peaks that are measured up to 650°C (Lafargue et al. 1998).
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CHAPTER 6

Results

Geochemical analyses of five petroleum exploration wells from the Great South Basin were undertaken using cuttings and sidewall core samples. 42 cuttings and 33 sidewall core samples were selected, prepared (see Methods, Chapter 5) and analysed in duplicate for their TOC, δ\textsuperscript{13}C and nitrogen contents using an EA-IRMS (see Section 5.3 and 5.4).

Graphical summaries of geochemical results are presented in Figures 6.1 to 6.5.2 for each well examined in this study, and Appendix 1 contains a complete list of all TOC, %N, C/N and δ\textsuperscript{13}C values for each sample analysed.

6.1 Takapu-1A

Figure 6.1 Geochemical results from GNS mass spec analyses of Takapu-1A cuttings.

TOC – Cuttings

Results from analyses of Takapu-1A cuttings samples show no clear pattern or consistency. There is no clear trend in the TOC results from the ten samples analysed from Takapu-1A. The deepest two samples from 865 m and 810 m have moderate TOC contents of 1.4 and 0.9% respectively. The sample from 762 m has a relatively high TOC content of 2.3%. This correlates to the δ\textsuperscript{13}C result of the same sample, which is one of the heaviest δ\textsuperscript{13}C values. The six samples from 709 m through 535 m, including those that intersect the Tartan
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Formation interval proposed by Cook et al. (1999), have low to moderate TOC contents ranging from 0.8 to 1.4%. The shallowest sample analysed from 490 m has the highest TOC content of the sample set in this well, with a value of 3.3%.

Nitrogen percentage- Cuttings

No clear pattern exists within this set of results. All ten samples have low nitrogen contents ranging between 0.03 and 0.06%. Samples from 762 m and 490 m have the highest nitrogen contents of 0.06% and the four samples from 709 m through 636 m have nitrogen contents of 0.05%.

Carbon/Nitrogen Ratio – Cuttings

The deepest sample examined from 865 m has a high C/N ratio of 54.44. This is followed by a ratio of 26.25 in the next sample from 810 m, and the sample from 762 m has a high C/N ratio of 44.72. The following six samples from 709 m through 535 m all have similar C/N ratios that range from 23.33 to 32.67. The two samples from 700 m and 691 m that Cook et al. (1999) determined to be of Tartan Formation depth have identical C/N ratios of 25.67. The shallowest sample analysed in this well has the highest C/N ratio, with a value of 64.17.

δ¹³C - Cuttings

As with the TOC and nitrogen contents, no trends are observed in the δ¹³C results. The first sample analysed from 865 m has the most isotopically heavy δ¹³C value of -25.2‰. This is the deepest cuttings sample analysed from Takapu-1A in this study, and is much deeper than the proposed base of the Tartan Formation. The next two samples from 810 m and 762 m have δ¹³C values of -26.8 and -25.6‰. The three samples from around the Tartan Formation interval have moderately light isotopic values ranging from -26.2 to -27.0‰. These are followed by an isotopically light sample from 636 m (-27.8‰). The two samples from 590 m and 535 m have δ¹³C values of -26.1 and -26.7‰ respectively. The most shallow sample examined from 490 m has one of the heaviest δ¹³C values (-25.8‰).
6.2 Hoiho-1C

Figure 6.2 Geochemical results from GNS mass spec analyses of Hoiho-1C sidewall cores.

**TOC - Sidewall cores**

Samples analysed from 1646 m and 1614 m have low TOC contents of 0.7 to 1.3% respectively. There is a significant increase in TOC content in the sample from 1582 m (8%), which is the first sample to display an elevated TOC content. A further increase in the TOC content was recorded from the next sample from 1578 m (17.1%), which is the maximum TOC content of all samples examined from Hoiho-1C. This is followed by the final elevated TOC content of the sample taken from 1558 m (3%). The shallowest samples examined from 1554 m through 1524 m have low to moderate TOC contents ranging from 0.5 to 1.5%.

**Nitrogen percentage –Sidewall cores**

Sidewall core samples from 1646 m and 1614 m have low nitrogen contents of 0.02 and 0.06% respectively. The next sample taken from 1582 m is the first to exhibit a significant increase nitrogen percentage (0.26%). The peak nitrogen percentage occurs in the sample taken from 1578 m (0.45%). There is a decrease in nitrogen content in the next sample...
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examined from 1558 m (0.1%). Samples from 1554 m through 1524 m have low nitrogen contents ranging from 0.02 to 0.05%.

Carbon/Nitrogen Ratio – Sidewall Cores

The deepest sample analysed in Hoiho-1C from 1646 m has a high C/N ratio of 40.83. The next sample from 1614 m has a C/N ratio of 25.28. The following three samples from 1582 m through 1558 m, all of which lie within the Tartan Formation interval, have C/N ratios that range from 35.00 to 44.33. The sidewall core sample from 1578 m has the highest TOC content and the heaviest δ\text{13}C value in this well, and also has the highest C/N ratio (44.33). These three samples have a high average C/N ratio of 38.4. The C/N data from Fig 6.3 show that the three samples that are within the Tartan Formation interval display a similar excursion to the δ\text{13}C and TOC results, as the samples immediately above and below these three Tartan Formation samples have comparatively lower C/N values. The shallowest three samples from 1554 m through 1524 m have C/N ratios ranging from 29.17 to 35.00.

δ\text{13}C – Sidewall cores

Samples analysed from 1646 m and 1614 m have moderately light δ\text{13}C values of -26.4 and -26.6‰ respectively. There is a 32 m gap between the sample taken from 1614 m and the next point analysed above from 1582 m, which is the first sample to exhibit a significant isotopically heavy excursion with a δ\text{13}C value of -19.7‰. The next sample taken from 1578 m has the heaviest δ\text{13}C value (-15.8‰) of all samples recorded in Hoiho-1C. There is a 20 m sampling gap between this maximum heavy excursion and the next sample from 1558 m, which is the last sample to exhibit a moderately heavy δ\text{13}C excursion of -25‰. Samples analysed from 1554 m through 1524 m exhibit similar light δ\text{13}C values, ranging from -26.3 to -27.1‰.
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6.3 Kawau-1A

**Kawau-1A Cuttings**

![Graph showing geochemical results for Kawau-1A cuttings](image)

Figure 6.3.1 Geochemical results from GNS mass spec analyses of Kawau-1A cuttings.

**Kawau-1A Sidewall Core**

![Graph showing geochemical results for Kawau-1A sidewall cores](image)

Figure 6.3.2 Geochemical results from GNS mass spec analyses of Kawau-1A sidewall cores.

TOC – Cuttings

Dylan Meadows. Tartan Formation Geochemistry, Great South Basin
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The TOC contents from the deepest sample from 2511 m through to the sample from 2302 m are relatively consistent, ranging from 1.0 to 1.9%. The first sample to display an elevated TOC content is from 2292 m (3.5%). There is a gradual increase in the TOC content over the next three samples from 2282 m (3.8%), 2273 m (7.9%), and the maximum value recorded in the sample from 2264 m (11%). There are small TOC decreases in the following samples from 2255 m (10.8%), and 2246 m (7.6%), with the final elevated TOC excursion recorded from 2237 m (5%). Samples from 2182 m through 2034 m have low to moderate TOC contents ranging from 0.2 to 1.6%, these appear to have lower TOC contents on average than prior to the excursion at 2292 m (Fig 6.3.1).

There is a 55 m sampling gap between 2237 m and 2182 m, thus a more accurate determination of the sharpness of this TOC increase, and subsequently the top of the geochemical changes of the Tartan Formation, is not possible.

**TOC – Sidewall cores**

Samples taken from 2387 m through 2301 m have low and consistent TOC content ranging from 1.2 to 1.3%. The first sample to exhibit a significantly elevated TOC content is from 2263 m (4.7%). There is an increase in the TOC content in the following sample from 2240 m, which has highest TOC percentage from the entire sidewall core set sampled from Kawau-1A (9.3%). This is also the shallowest sample to display an elevated TOC content in this well. Samples from 2218 m up to the shallowest sidewall core examined from 2107 m have a relatively low TOC contents, ranging from 0.4 to 1%, which is lower on average than that of the samples prior to the first positive excursion from 2263 m (Fig 6.3.2).

There is a 22 m gap between the sample with the last elevated TOC content and the first overlying sample with a low TOC percentage. This gap is smaller than the 55 m gap between the equivalent two samples from the cuttings samples, thus potentially constraining the top of the geochemical changes of the Tartan Formation within this 22 m gap between 2240 m and 2218 m in Kawau-1A.

**Nitrogen percentage – Cuttings**

Samples examined from 2511 m through 2302 m contain low to moderate nitrogen percentages ranging from 0.05 to 0.13%. The nitrogen percentage begins to gradually
increase from 2292 m (0.18%) through 2264 m, which has the maximum nitrogen content of 0.45%. The next three samples above 2264 m begin to gradually decrease from 0.42% recorded in the sample from 2255 m to 0.2% in the sample from 2237 m. Samples from 2182 m through 2034 m have low nitrogen contents ranging from 0.02 to 0.05%.

**Nitrogen percentage – Sidewall cores**

The deepest sample taken from 2387 m has a high nitrogen content of 0.2%. From 2376 m to 2301 m, the nitrogen percentages are low (0.05% each). At 2263 m the nitrogen content increases to 0.19%, followed by the sample with the highest nitrogen percentage from 2240 m (0.38%). Samples from 2218 m through 2107 m return to low nitrogen percentages that range from 0.02 to 0.03%, but remain lower than prior to the first increase in nitrogen content below 2263 m (Fig 6.3.2).

**Carbon/Nitrogen Ratio – Cuttings**

The deepest two samples analysed from 2511 m and 2456 m have similar C/N ratios of 25.7 and 23.3 respectively. The following three samples from 2410 m through 2302 m all have C/N values below 20, ranging from 17.1 to 19.8. The next seven samples from 2292 m through 2237 m, all of which lie within the Tartan Formation interval, have relatively similar C/N ratios that range from 22.7 to 30.6, with an average of 27.5. The two samples immediately above the Tartan Formation interval from 2182 m and 2145 m have ratios of 35.0 and 37.3 respectively. The two shallowest samples analysed from 2081 m and 2034 m have low C/N ratios of 17.5 and 11.7 respectively.

**Carbon/Nitrogen Ratio – Sidewall Cores**

The deepest sidewall core analysed from 2387 m has a very low C/N ratio of 7.6. The two following samples from 2376 m and 2301 m have C/N values of 30.3 and 28.0 respectively. The two samples that lie within Tartan Formation interval from 2263 m and 2240 m have very similar C/N ratios of 28.9 and 28.6 respectively. The next three samples from 2218 m through 2193 m have similar C/N ratios that range from 23.3 to 27.2. The two shallowest samples examined in this study from 2180 m and 2107 m exhibit elevated C/N ratios relative to other samples in Kawau-1A with values of 31.1 and 38.9 respectively.
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$\delta^{13}C$ - Cuttings

Samples analysed from 2511 m through 2302 m exhibit highly to moderately isotopically light $\delta^{13}C$ values ranging from -25.1 to -27.6‰. The first isotopically heavy $\delta^{13}C$ value is recorded in the sample from 2292 m (-20.4). This is followed by a series of samples that gradually become heavier from 2282 m (-20.2‰), and 2273 m (-18.4‰), with the heaviest sample having been recorded in the sample from 2264 m (-17.4‰). The next three samples from 2255 m, 2246 m and 2237 m have gradual decreases in $\delta^{13}C$ values of -17.7, -19.6, and -21.3‰ respectively. The sample analysed from 2237 m is the final sample to display a heavy $\delta^{13}C$ value in Kawau-I1A. Samples analysed from 2182 m through 2034 m range from -26.3 to -27.3‰.

The 55 m sampling gap between 2237 m and 2182 m makes it difficult to constrain the upper geochemical changes of the Tartan Formation within this interval; the lower contact, however, appears to be clearer. There is a 10 m sample gap between the first significant isotopically heavy $\delta^{13}C$ excursion from 2292 m and the last isotopically light $\delta^{13}C$ sample from 2302 m. This may indicate that the base of the geochemical changes of the Tartan Formation lie within this 10 m sampling gap.

$\delta^{13}C$ – Sidewall cores

The samples analysed from 2387 m through 2301 m exhibit isotopically light $\delta^{13}C$ values ranging from -27.2 to -27.6‰. The first indication of a heavy $\delta^{13}C$ value appears in the sample taken from 2263 m (-21.4‰), followed by heaviest sample recorded from 2240 m (-18.2‰). Above this, $\delta^{13}C$ values gradually become isotopically lighter, with samples from 2218 m and 2201 m having recorded moderately heavy values of -24.5 and -25.6‰ respectively. The sample from 2201 m possibly represents the final isotopically heavy $\delta^{13}C$ value, and may represent the top of the geochemical changes of the Tartan Formation (see Chapter 7 for detailed interpretation). Samples analysed from 2193 m through 2107 m range from -26.6 to -28.5‰.

6.4 Pakaha-1
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**Pakaha-1 cuttings**

Figure 6.4.1 Geochemical results from GNS mass spec analyses of Pakaha-1 cuttings.

**Pakaha-1 Sidewall Core**

Figure 6.4.2 Geochemical results from GNS mass spec analyses of Pakaha-1 sidewall cores.

**TOC – Cuttings**

Cuttings samples from 2807 m through 2706 m exhibit moderate TOC contents ranging from 0.9 to 1.4%. There is a very large sampling gap between the point from 2706 m and the
following cuttings sample from 2560 m, which is the first sample to display an elevated TOC content, with a value of 5.9%. There is an increase in TOC content in the next sample from 2551 m (6.5%), which has the highest recorded value of this set of results. Samples from 2496 m through 2377 m exhibit moderate TOC contents ranging from 0.7 to 1.9%. This is slightly higher on average than below the first increase in TOC content in samples analysed from 2807 m through 2706 m (Fig 6.4.1).

TOC – Sidewall cores

The three samples from 2838 m through 2638 m exhibit moderate TOC contents ranging from 1.5 to 1.6%. The next sample from 2576 m has the only significant TOC content of all seven sidewall core samples analysed, with a value of 5.3%. The sample from 2505 m has a moderate TOC content of 1.1%, followed by two samples from 2474 m and 2252 m which have low TOC contents of 0.42 and 0.36% respectively. This is slightly lower on average than below the first increase in TOC content in samples analysed from 2838 m through 2638 m (Fig 6.5.2).

Nitrogen percentage – Cuttings

Cuttings samples analysed from 2807 m through 2706 m exhibit moderate nitrogen contents between 0.09 and 0.14%. The next sample examined from 2560 m is the first to display an elevated nitrogen content and has the highest nitrogen content of all seven sidewall core samples in Pakaha-1, with 0.33%. The sample analysed from 2551 m has a high nitrogen content, with a value of 0.31%. Samples examined from 2496 m through 2377 m exhibit low nitrogen contents that range from 0.07 to 0.08%. This is a lower average nitrogen content than below the first high nitrogen content sample from 2560 m (Fig 6.4.1).

Nitrogen percentage – Sidewall cores

Sidewall core samples from 2838 m through 2638 m exhibit moderate nitrogen contents between 0.12 and 0.15%. The sample from 2576 m is the only sidewall core sample analysed that has a high nitrogen content, with a value of 0.29%. Samples from 2505 m though 2252 m have low nitrogen contents ranging between 0.04 to 0.09%. This is a lower average nitrogen content than below the high nitrogen content sample from 2576 m.
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Carbon/Nitrogen Ratio – Cuttings

The deepest three samples from 2807 m through 2706 m all have low C/N ratios ranging from 11.67 to 14.0. The two samples from 2560 m and 2551 m that lie within the Tartan Formation interval have higher C/N ratios of 20.86 and 24.46 respectively. The average C/N ratio for Tartan Formation samples is 22.66. The first sample above the Tartan Formation from 2496 m has a low C/N ratio of 11.67, which is similar to values below the formation. The shallowest two samples from 2478 m and 2377 m have C/N ratios of 21.88 and 31.67 respectively.

Carbon/Nitrogen Ratio – Sidewall Cores

The deepest three samples analysed from 2838 m through 2638 m all have low and similar C/N ratios that range from 12.44 to 14.58. The one sample from 2576 m that lies within the Tartan Formation interval has the highest C/N ratio of all sidewall core samples examined from this well with a value of 21.32. This high C/N ratio sample also has the highest TOC and heaviest δ¹³C values of all Pakaha-1 sidewall core samples. The C/N plot in Fig 6.4.2 shows an increase in the C/N ratio from samples around the Tartan Formation. The three samples above the Tartan Formation from 2505 m through 2252 m all have relatively low C/N ratios that range from 9.8 to 14.26.

δ¹³C - Cuttings

Samples from 2807 m through 2706 m exhibit moderately light δ¹³C values ranging from -25.8 to -26.8‰. Cuttings samples available for analysis within Pakaha-1 are scarce, and there is a 146 m sampling gap to the next sample from 2560 m, which has a heavy δ¹³C value of -19.7‰, followed by the sample from 2551 m which has the heaviest isotopic excursion in this well with a value of -19.3‰. This is the shallowest sample to exhibit a heavy δ¹³C excursion. The next sample available from 2496 m has a moderately light δ¹³C value -26.4‰. The final samples from 2478 m and 2377 m have moderately heavy δ¹³C values of -25.5 and -23.6‰ respectively.

δ¹³C – Sidewall cores
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Sidewall core samples that were available for analysis in Pakaha-1 were very scarce and as a result there were only seven samples analysed in the 2838 m to 2252 m interval. The first two samples from 2838 m and 2658 m have $\delta^{13}C$ values of -26.0 and -27.0‰ respectively. The next sample from 2638 m shows a slightly heavy isotopic excursion with respect to other samples analysed in Pakaha-1 with a value of -25.9‰. The next sample, some 62 m above the previous, from 2576 m is the only significantly isotopically heavy $\delta^{13}C$ sample in this set of analysis, with a $\delta^{13}C$ value of -20.7‰.

Unfortunately samples at depths close to the sidewall core from 2576 m were not available for analysis; hence it is likely that the sample point from 2576 m was the only sample that was from the Tartan Formation interval. The following sample from 2505 m has a moderately light $\delta^{13}C$ value of -26.4‰. The final two samples from 2474 m and 2252 m have very isotopically light $\delta^{13}C$ values of -27.7 to -27.9‰ respectively.

6.5 Toroa-1

[Graph showing Geochemical results from GNS mass spec analyses of Toroa-1 cuttings]

Figure 6.5.1 Geochemical results from GNS mass spec analyses of Toroa-1 cuttings.
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**Figure 6.5.2** Geochemical results from GNS mass spec analyses of Toroa-1 sidewall cores.

**TOC – Cuttings**

Cuttings samples analysed from Toroa-1 all exhibit low to moderate TOC contents. The maximum TOC content of 1.4% was recorded from the sample from 2246 m. All other samples range from 0.23 to 0.95% (Fig 6.5.1).

**TOC – Sidewall cores**

The first sample taken from 2260 m has a moderately high TOC content of 1.9%; however, this sample is well below the inferred depth of the base of the Tartan Formation. The next two sidewall cores taken from 2235 m and 2233 m both have low TOC contents of 0.5 and 0.9% respectively. The next sample from 2207 m has a moderate TOC content of 1.6%. Following this sample there is a 45 m gap to the next sample from 2162 m, which has the only significant TOC content of the sidewall cores analysed (Fig 6.5.2), with a value of 7.2%. The shallowest samples examined from 2160 m through 2079 m have low TOC contents that range from 0.07 to 0.23%.

**Nitrogen percentage – Cuttings**
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As with the TOC results analysed from cuttings in Toroa-1 there are no samples with significant nitrogen contents. All samples range from 0.01 to 0.06%, with the maximum 0.06% recorded in the sample taken from 2246 m, which also has the peak TOC value of the Toroa-1 cuttings samples.

Nitrogen percentage – Sidewall cores

Samples from 2260 m through 2207 m have low nitrogen contents that range from 0.04 to 0.1%. The sidewall core sample from 2162 m has the only high nitrogen content in this data set, with a value of 0.38%. Samples from 2160 m through 2079 m have low nitrogen contents that gradually decrease from 0.04 to 0.02% over the three samples.

Carbon/Nitrogen Ratio – Cuttings

All eight cuttings samples analysed from Toroa-1 have similar C/N ratios that range from a minimum of 20.42 to a maximum of 30.33. The average C/N ratio for all cuttings samples in Toroa-1 is 26.3.

Carbon/Nitrogen Ratio – Sidewall Cores

The deepest sample analysed from 2260 m has the highest C/N ratio of all sidewall cores examined in this well, with a value of 24.63. The following three samples from 2235 m through 2207 m have relatively low C/N ratios that range from 14.58 to 18.67. Of the two samples that lie within the Tartan Formation interval, the sample from 2162 m has a C/N ratio of 22.11 and the sample from 2160 m has an extremely low value of 6.71. The two shallowest samples examined above the Tartan Formation from 2124 m and 2079 m have the lowest C/N ratios of all samples analysed in this study, with values of 3.89 and 4.08 respectively.

$\delta^{13}C$ - Cuttings

The most isotopically light sample was recorded at the greatest depth of the sample set from 2438 m (−27.4‰). The next two samples from 2438 m and 2346 m gradually become slightly heavier, with $\delta^{13}C$ values of -26.3 and -26.0‰ respectively.
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Unfortunately, due to scarce sample availability, few samples were collected and analysed from within the Tartan Formation interval. The heaviest $\delta^{13}C$ value was recorded in the sample from 2246 m (-24.5‰). All samples from 2118 m through 1962 m exhibit a gradually increasingly light isotopic tendency.

$\delta^{13}C$ – Sidewall cores

Samples analysed from 2260 m through 2207 m have $\delta^{13}C$ values that range from -25.5 to -27.0‰. Sample availability from sidewall cores around the Tartan Formation interval is poor, but slightly better than the availability of cuttings samples; however there is a 45 m gap to the next sample from 2162 m, which has the only isotopically heavy $\delta^{13}C$ value, with -21.0‰. Samples analysed from 2160 m through 2079 m have fairly light isotopic $\delta^{13}C$ values that range from -26.2 to -26.6‰.

6.6 TOC data from Rock-Eval results (from Applied Petroleum Technology and Geological Survey of Canada)

A total of 30 sidewall core samples were sent to Applied Petroleum Technology (APT), Norway for Rock-Eval analyses (See Appendix 4 for full list of TOC data from Rock-Eval analyses). The analyses were intended to check the TOC results obtained from the mass spectrometry analyses performed by GNS Science for this study and to verify the validity of the results of these analyses. For the purposes of this study, TOC results from APT Rock-Eval analyses were made available by GNS Science.

Only sidewall core samples were sent to APT, as these allow greater accuracy than cuttings samples which are often contaminated by well cavings from shallower depths. Thus sidewall cores offer greater precision and allow tighter constraints to be placed on any interpretations involving depth intervals that maybe made.

Comparison of the APT and GNS data (Fig 6.6.1) shows that there is a difference between the two data sets. The x-axis represents the data recorded by GNS, and the y-axis represents the results from APT. The line that bisects the plot is the 1:1 ratio line, which is a theoretical line that would represent a 1:1 correspondence of results if the same data were plotted on both the x- and y-axes. The closer the actual results plot to this line, the closer the data sets are to one another.
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![Figure 6.6.1 Comparison of GNS and APT data.](image)

There is close correlation between results from both APT and GNS (Fig 6.6.1) when the TOC content is 2% or less. Values above 2% TOC display a decreasing correlation. All such samples lie below the 1:1 ratio line, which equates to lower TOC values being recorded by APT. As these are all samples with high TOC contents, it is generally the samples that lie within the Tartan Formation interval that display a weaker correlation between the APT and GNS results.

Although the APT and GNS data share almost identical TOC excursions and trends within the wells examined, the APT data generally have lower TOC values than corresponding samples analysed by GNS.

As a result of the low degree of reproducibility between APT and GNS analyses of samples with TOC contents above 2%, GNS Science sent 11 sidewall core samples to the Geological Survey of Canada (GSC) for further Rock-Eval investigation, and again, made the TOC results of these analyses available to the author for this study. The samples that were sent to GSC were also required to confirm any possible poor sample preparation or calibration errors of the GNS mass spectrometer and/or the APT Rock-Eval 6 appliance.
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The results from the GSC analyses are compared with the GNS data in Fig 6.6.2. The TOC results on the x-axis are those from the GNS analyses, while the y-axis represents the data recorded by GSC.

![Interlab comparison between GNS and GSC](image)

Figure 6.6.2 Comparison of GNS and GSC data.

It is evident from inter-laboratory comparison in Fig 6.6.2 that the data from both GNS and GSC lie very close to the 1:1 ratio line. This indicates that the values for samples with TOC contents above 2% recorded by GNS mass spectrometry analyses are very close to those measured by GSC, rather than to those reported by APT. Figure 6.6.3 compares all three sets of results and it is evident that the GNS/GSC data fit the 1:1 ratio line best.
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![Inter-Laboratory TOC comparison](image)

Figure 6.6.3 Inter-laboratory comparison of APT, GNS and GSC data.

The high TOC data recorded by GNS Science agree with corresponding samples by GSC. Comparison of the GNS vs. APT plot (Figures 6.6.1 and 6.6.3) indicates a trend of decreasing correlation amongst the higher TOC samples. A possible explanation for this could be a calibration error of the APT Rock-Eval 6 appliance.

As only 11 of the sidewall core samples were submitted to GSC for Rock-Eval analyses, and 30 were sent to APT, the final Rock-Eval results combine both sets of data. The samples that were not analysed by GSC all have low TOC contents below 2%. As previously mentioned, the APT results for samples containing less than 2% TOC lie close to the 1:1 ratio line (see Figures 6.6.1 and 6.6.3). All GSC results are used in the final Rock-Eval data, as they agree with the values recorded by GNS Science, whereas the samples not analysed by GSC that were analysed by APT are used to complete the final Rock-Eval data, and from this point on the combined final Rock-Eval data from both APT and GSC are referred to as ‘Rock-Eval’ data. The overall TOC data from Rock-Eval are plotted against the final GNS data in Fig 6.6.4. The points of the plot lie very close to the 1:1 ratio line, thus verifying
agreement between the Rock-Eval results and the mass spectrometry results from the present study.

Figure 6.6.4 Final GNS mass spec TOC data vs. final Rock-Eval TOC data.

The final data are presented in Appendix 4 alongside the TOC and δ¹³C data from GNS.

6.7 Hoiho-1C

The deepest sample analysed in from 1646 m has a low TOC content of 0.71%. The next sample from 1614 m has a moderate TOC content of 0.94%. There is a 32 m gap to the following sample examined from 1582 m, which is the first sample to exhibit an elevated TOC content, at 7.35%. The sample from 1578 m has the peak value of this data set, with a TOC content of 15.15%. The sidewall core analysed from 1558 m is the final sample to exhibit an elevated and relatively high TOC content, with 2.84%. Samples analysed from 1554 m through 1524 m have low to moderate TOC contents that range from 0.46 to 1.2%.
Chapter 6. Results

6.7.1 Comparison between Rock-Eval and GNS mass spec TOC results for Hoiho-1C

The overall trend between the two sets of analyses is very similar. All samples have similar excursions. For example, there is an increase in TOC content from 1646 m to 1614 m, then further increases from 1614 m to 1582 m and 1578 m in both sets of results.

6.8 Kawau-1A

The deepest three samples from 2387 m through 2301 m have low TOC contents ranging from 0.23 to 0.71%. The sidewall core from 2263 m is the first sample to display a high TOC content, with a value of 3.73%. This is followed by the sample from 2240 m, which has the highest TOC content of this set of analyses, with a value of 8.65%, and is the shallowest sample to display an elevated TOC content. The next sample from 2218 m has a very low TOC content of 0.29%. The following sample from 2201 m has a TOC content of 0.60%. The final three samples from 2193 m through 2107 m have low to moderate TOC contents ranging from 0.86 to 1.01%.
Chapter 6. Results

6.8.1 Comparison between Rock-Eval and GNS mass spec TOC results for Kawau-1A

![Diagram showing comparison between Rock-Eval and GNS mass spec TOC results for Kawau-1A](image)

Figure 6.8 Comparison between Rock-Eval and GNS mass spec results for Kawau-1A.

There are many similarities between the Rock-Eval and GNS mass spectrometry data sets for Kawau-1A; however, these data would appear to be the least correlative overall of those investigated by both Rock-Eval and GNS Science.

The greatest difference between data sets comes in the deepest four samples analysed. The two deepest samples from 2387 m and 2376 m have low TOC contents of 0.71 and 0.62% respectively for the Rock-Eval analyses, and moderately high TOC contents of 1.3 and 1.3% respectively in the GNS mass spectrometry analyses. Rock-Eval analyses of the sample taken from 2301 m yielded a low TOC content of 0.23% compared to the GNS result of 1.2%. Rock-Eval recorded the sample from 2263 m as having a TOC content of 3.73%, whereas GNS mass spectrometry analyses yielded a value of 4.7%. This is the first sample to exhibit a significant increase in TOC content in both Rock-Eval and GNS Science results. The sample from 2240 m has a TOC content of 8.65% for the Rock-Eval analyses and 9.3% for the GNS Science results. The sidewall core taken from 2218 m has a similar TOC content in both data sets. The next two samples at 2201 m and 2193 m both have low TOC contents of 0.29 and 0.6% for the Rock-Eval analyses, while GNS recorded values of 0.4 and 0.7% for the same samples respectively. The two shallowest samples from 2180 m and 2107 m are very similar in both sets of data.
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6.9 Pakaha-1

The deepest three samples analysed in Pakaha-1, from 2838 m through 2638 m have moderate TOC contents that range from 1.1 to 1.49%. The peak TOC content of 4.85% was recorded in the sample from 2576 m. The final two sidewall core samples taken from 2505 m and 2473 m have low TOC contents of 0.8 and 0.39% respectively.

6.9.1 Comparison between Rock-Eval and GNS mass spec TOC results for Pakaha-1

Figure 6.9 Comparison between Rock-Eval and GNS mass spec results for Pakaha-1.

On comparison of the Rock-Eval and GNS data sets, a very similar trend is observed between the two. Both sets of data share a very similar pattern, with the greatest TOC content having been recorded from the sample analysed from 2576 m in both sets of results.

6.10 Toroa-1

The deepest sample analysed from 2260 m has a moderately high TOC content of 1.47%. The two samples from 2235 m and 2233 m have low TOC contents of 0.37 and 0.69% respectively. In the next sample, some 45 m shallower from 2207 m, there is an increase in TOC content to 1.41%. The sample above from 2162 m has the highest TOC content in this set of results from Toroa-1, with 6.32%. The sidewall core taken just 2 m above the peak TOC sample from 2160 m has a low TOC content of 0.27%.
Chapter 6. Results

6.10.1 Comparison between Rock-Eval and GNS mass spec TOC results for Toroa-1

The data from Rock-Eval and GNS mass spectrometry analyses closely resemble one another, with identical trends observed throughout the two sets of samples.
Chapter 7. Discussion

CHAPTER 7

Discussion

Correlations between each of the exploration wells investigated in this study are discussed based upon gamma ray logs (defining the lithological interval of the Tartan Formation) and geochemical data from the present study. These define differences between lithologic and geochemical boundaries over the intervals studied. Possible sources of the organic matter are also discussed. A definitive explanation for the organic matter source in the Tartan Formation is beyond the scope of this study; however, interpretations as to the source of organic matter present in the Tartan Formation based upon the geochemical data from this study are described in this Chapter.

7.1 Gamma Ray logs of Great South Basin wells

Gamma ray logs covering the Tartan Formation were derived from the original logs taken by Hunt International Petroleum Co. during the drilling of the exploration wells.

Gamma ray logs are lithology logs that measure the natural radiation of a formation. Sandstones and carbonates have low concentrations of radioactive material, and thus emit low levels of gamma ray radiation. Shales characteristically concentrate radioactive material, thus emitting high levels of gamma ray radiation. As the shale content of a formation increases so does the gamma ray response, due to the increasing concentration of radioactive material. Shale-free strata may also produce high gamma ray readings if, for example, there are potassium feldspars, micas, glauconite, or uranium-rich waters present. The use of gamma ray logs run in conjunction with a Spectralog (Dresser Industries Inc.) can discriminate these types of radioactive materials (Asquith, 1983).

Reports by Cook et al. (1999) and Schioler, (Pers comm, 2008) define the top and base of the Tartan Formation based upon the gamma ray excursion that is produced by the formation. There are minor differences between the positioning of the tops and bases of the formation between the two authors, but they generally recognise similar intervals (Table 7.1).
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One notable difference between the studies of Cook et al. (1999) and Schioler (Pers comm, 2008) relates to the Tartan Formation in Takapu-1A (Table 7.1). Cook et al. (1999) proposed a Tartan Formation thickness of 20 m, between 700 m and 680 m, whereas Schioler found no evidence for the existence of the formation in this well. The geochemical results from the present study also provide no evidence for the presence of the Tartan Formation in Takapu-1A. The two cuttings samples analysed that were taken from 700 m and 691 m lie within the depth interval of the Tartan Formation as recognised by Cook et al. (1999), but neither of these samples shows the geochemical characteristics of the Tartan Formation that are present in the other wells investigated here. It is possible that the Tartan Formation in Takapu-1A is present and is very thin, and thus not easily identified on the gamma ray log, or that the formation was not encountered during sampling due to the sampling gaps between cuttings.

### 7.2 Tartan geochemical facies

As previously mentioned, reports by Cook et al. (1999) and Schioler, (Pers comm, 2008) define the Tartan Formation by its gamma ray response to lithology. Sidewall core and cuttings samples also show changes in lithology, from the light grey shales and clays of the underlying Wickliffe Formation to the dark brown, highly micaceous shales of the Tartan Formation, which is in turn overlain by siltstones and calcareous clays of the Laing Formation. The suite of geochemical analyses performed in this study agree with the gamma ray data in defining the top of the Tartan Formation; however, the geochemical data from some wells demonstrate changes that appear below the recognised base of that formation, in the top of underlying Wickliffe Formation. For this reason, a geochemical facies termed the Tartan geochemical facies (TGF) is here proposed for this interval. The TGF covers the interval of the Tartan

<table>
<thead>
<tr>
<th>Well</th>
<th>Cook et al. (1999)</th>
<th>Schioler (Pers comm, 2008)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Top (m)</td>
<td>Base (m)</td>
</tr>
<tr>
<td>Takapu-1A</td>
<td>680</td>
<td>700</td>
</tr>
<tr>
<td>Hoiho-1C</td>
<td>1545</td>
<td>1592</td>
</tr>
<tr>
<td>Kawau-1A</td>
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<td>2264</td>
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<tr>
<td>Pakaha-1</td>
<td>2503</td>
<td>2551</td>
</tr>
<tr>
<td>Toro-1</td>
<td>2137</td>
<td>2200</td>
</tr>
</tbody>
</table>

Table 7.1 Top and base depths of the Tartan Formation from gamma ray excursions.
Chapter 7. Discussion

Formation, but in some cases is more extensive, including part of the upper Wickliffe Formation.

Figure 7.2 correlates the gamma ray logs of each well to the TOC and $\delta^{13}$C data recorded in the present study. The figure clearly demonstrates the difference between the base of the Tartan Formation, as defined by its gamma ray excursion and the base of the Tartan geochemical facies.
Figure 7.2 Comparison of gamma ray logs and geochemical properties of the Great South Basin exploration wells examined in the present study.
Chapter 7. Discussion

All wells (with the exception of Takapu-1A) show close correlation between the gamma ray and geochemical data in defining the top of the Tartan Formation (Fig 7.2). The geochemical data from Hoîho-1C and Toroa-1 match the gamma ray log base of the formation as determined by Schioler (Pers comm, 2008). There are differences between the gamma ray and geochemical excursions in Kawau-1A and Pakaha-1 as to the positioning of the base of the Tartan Formation. The gamma ray excursion from these wells begins above the geochemical base of the formation (Fig 7.2). It is possible that cavings from shallower depths have had a small influence on the depth of the TGF base in Kawau-1A; however a sidewall core sample from 2576 m (below the base of the Tartan Formation given by Cook et al. and Schioler) in Pakaha-1 also has the very high TOC content and heavy δ¹³C value that appears characteristic of the Tartan Formation in other Great South Basin wells. Thus the sample from 2576 m in Pakaha-1 lies within the TGF.

As the gamma ray log is a lithology log, changes in the properties of the strata encountered during the drilling of a well influence the gamma ray response depending upon the amount and distribution of the natural radiation present in a formation. The TOC and δ¹³C values obtained in this study measure the quantity and type of organic carbon present in the formation. It is possible that the onset of the event associated with the deposition of the Tartan Formation (that led to increased deposition and preservation of organic matter) began prior to the change in lithology from the light grey shales and clays of the Wickliffe Formation to the dark brown, highly micaceous shales of the Tartan Formation. This would explain why the geochemical data change in some wells before the gamma ray log excursions (i.e. in older sediments).

7.3 Tartan Formation and TGF depth interval comparison

Based upon the first and last signs of changes in the geochemical results from the data obtained from analysis of the five Great South Basin wells examined in this study, thickness intervals for the Tartan geochemical facies (TGF) can be estimated.

There appears to be a similar trend throughout four of the five wells examined in this study. All but Takapu-1A have common TOC, δ¹³C and nitrogen content excursions. It is possible that Takapu-1A has this excursion also, but it is not possible to identify due to the poor sample availability and natural variation between samples that were examined within the well, unlike the more distinct excursions present from the results of other wells investigated. The
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top of the Tartan geochemical facies can be reasonably determined in Hoiho-1C. There is a 4 m gap between the first sample to exhibit a major change in TOC, δ¹³C and nitrogen content at 1558 m and the sample above it at 1554 m that has relatively negative δ¹³C and low TOC and nitrogen contents. The position of the TGF base with respect to the Tartan Formation in Hoiho-1C is not as easy to determine, as there is a sampling gap between the deepest sample that has been interpreted as being Tartan Formation at 1582 m and the next sample below it at 1614 m. Cook et al. (1999) considered the Tartan Formation in Hoiho-1C to be 47 m thick (1545 m-1592 m), while Schioler (Pers comm, 2008) proposed a thickness of 40 m (1556 m-1596 m). Thickness estimates based upon the results of this study place a maximum value of 60 m (1554 m-1614 m) and a minimum thickness of 24 m (1558 m-1582 m) for the TGF. See Tables 7.1 and 7.3.

<table>
<thead>
<tr>
<th>Well</th>
<th>Depth Top Max (m)</th>
<th>Min (m)</th>
<th>Depth Base Max (m)</th>
<th>Min (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hoiho-1C</td>
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<td>1558</td>
<td>1614</td>
<td>1579</td>
</tr>
<tr>
<td>Kawau-1A</td>
<td>2218</td>
<td>2237</td>
<td>2301</td>
<td>2292</td>
</tr>
<tr>
<td>Pakaha-1</td>
<td>2496</td>
<td>2551</td>
<td>2639</td>
<td>2576</td>
</tr>
<tr>
<td>Toroa-1</td>
<td>2072</td>
<td>2162</td>
<td>2346</td>
<td>2246</td>
</tr>
</tbody>
</table>

Table 7.3 Upper and lower limits of the TGF, based upon results from this study.

Kawau-1A was the well with the most samples available for analysis for this study. The top of the Tartan geochemical facies is difficult to accurately determine due to a lack of samples around that depth range, but is considered to lie between 2218 m and 2237 m. The base appears to be more clearly defined, with δ¹³C evidence from both sidewall cores and cuttings suggesting that the TGF base extends to a maximum depth between 2292 m and 2301 m. Cook et al. (1999), and Schioler (Pers comm, 2008) proposed a thickness of 44 m for the Tartan Formation, between 2220 m and 2264 m. The author has constrained the thickness of the Tartan geochemical facies to a maximum thickness of 83 m (2218 m-2301 m) and a minimum thickness of 55 m (2237 m-2292 m). See Tables 7.1 and 7.3.

Sampling around the Tartan Formation interval in Pakaha-1 was incomplete, due to a lack of cuttings and sidewall core material, and thus thickness estimates are somewhat ambiguous. Cook et al. (1999) proposed a thickness of 48 m (2503 m-2551 m) for the Tartan Formation interval in Pakaha-1, while Schioler, (Pers comm, 2008) has suggested a thickness of 36 m (2510 m-2546 m). From the data obtained in this study from both cuttings and sidewall core
samples, the TGF has a maximum thickness of 143 m (2496 m-2639 m), and a minimum thickness of 25 m (2551 m-2576 m). See Tables 7.1 and 7.3.

Determination of the depth interval for the Tartan geochemical facies in Toroa-1 is very difficult, and has very limited precision due to a severe lack of sample availability. There was only one, possibly two, samples from both cuttings and sidewall cores that are interpreted to have been within the Tartan geochemical facies interval. Cook et al. (1999) proposed a 63 m thickness (2137 m-2200 m), and Schioler (Pers comm, 2008) suggested a thickness of 57 m (2138 m-2195 m) for the Tartan Formation. Very uncertain estimates in the present study indicate a maximum thickness of 274 m (2072 m-2346 m) and a minimum thickness of 84 m (2162 m-2246 m) for the TGF. As there is only one clear sample of Tartan geochemical facies depth in this study, the thickness could be much less than 84 m, it could be close to the gamma ray thicknesses proposed by Cook et al. (1999), and Schioler (Pers comm, 2008). See Tables 7.1 and 7.3.

7.4 Correlation of TOC contents between wells across the Great South Basin

Total Organic Carbon data provide a measure of how much organic matter is present in sediments. TOC data recorded by GNS Science and Rock-Eval (APT and GSC) are of principle importance to this study. The processes that control organic matter accumulation and preservation are discussed in Chapter 4 and will not be further discussed here.

Samples from Takapu-1A generally display moderate organic richness (with the exception of the shallowest sample from 490 m with a relatively high TOC content of 3.3%), that range in TOC from 0.8 to 2.3%, with a mean value of 1.3%. There is no gradual increase or trend in the plot of TOC vs. depth in Takapu-1A, as is present in other wells examined (Fig 7.4), and there are also no elevated TOC results from samples around the inferred Late Paleocene to Early Eocene sediment depths (approximately 700 m to 680 m). This is further evidence to support the absence of the Tartan Formation in Takapu-1A.
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Figure 7.4 Well by well comparison of TOC content from cuttings and sidewall core samples.

There are three sidewall core samples from Hoiho-1C with high organic contents. These samples from 1582 m, 1578 m, and 1558 m have values of 8, 17.1, and 3% TOC respectively (Fig 7.4). The exceptionally high value of 17.1% recorded in the sample from 1578 m is the highest recorded TOC value of all 75 samples analysed in this study (both sidewall cores and cuttings). Samples taken from the underlying Wickliffe and overlying Laing formations show low to moderate TOC contents ranging from 0.5 to 1.5%. This establishes that there was a profound change in the conditions under which the Tartan Formation was deposited, with respect to the immediately underlying and overlying formations. There was a change from low organic input and/or poor organic matter preservation in the underlying Wickliffe Formation, to good preservation of the deposited organic matter, likely combined with increased organic input into seafloor sediments during the deposition of the Tartan Formation. This change in bottom water conditions was unlikely to have persisted for a prolonged period of time, as the thickness of the Tartan Formation is only approximately 40 m (and is of similar thickness in other wells examined, where present), representing deposition during the latest Teurian in Hoiho-1C. A return to poor organic matter preservation and/or low organic input into the deposited sediments of the overlying Laing Formation follows the deposition of the Tartan Formation.

Sampling of the Tartan geochemical facies in Kawau-1A yielded two sidewall cores and seven cuttings samples that have high TOC contents. Examination of the cuttings data (Fig 7.4) shows a gradational increase in TOC content from the first significantly elevated sample
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from 2292 m (3.5%) to the peak value recorded in the sample from 2264 m (11%). Following this peak TOC value, there is a gradual decrease over the next three Tartan Formation/TGF samples, with the final elevated TOC sample having been recorded from 2237 m (5%). It is possible that the environmental changes associated with the deposition of the Tartan geochemical facies in Kawau-1A were less pronounced during the initial and final stages of deposition, but were most prominent towards the mid stages of deposition, coinciding with the two high TOC contents of 11 and 10.8% recorded from 2264 m and 2255 m respectively. Another possibility relates to the preservation and input of organic matter into the sediments during the deposition of the Tartan Formation/TGF. The two high TOC values may represent a time in which conditions for accumulation and preservation of organic matter were most favorable, whereas the other samples of Tartan Formation/TGF depth above and below these peak values represent slightly less favorable conditions for the preservation and accumulation of organic matter.

Data from the sidewall cores are not as well-defined as those of cuttings samples as there were fewer samples available for analysis around the Tartan Formation/TGF depth interval. Only two samples are recorded from the Tartan Formation interval, and thus it is difficult to infer the conditions under which the formation was deposited. However, examination of the underlying Wickliffe Formation from both sidewall core and cuttings samples shows moderate organic contents (Fig 7.4, Appendix 1), with TOC values ranging from 1 to 1.9%, with an average of 1.3%. The overlying Laing Formation generally has lower TOC values than the underlying Wickliffe Formation, with TOC contents ranging from 0.2 to 1.6%, with a mean value of 0.7%. From this data, it would appear that conditions for the preservation and accumulation of organic matter were more favorable prior to the deposition of the Tartan Formation than following it.

Two sidewall cores and a single cuttings sample represent the Tartan Formation in Pakaha-1 (one sample actually lies outside the Tartan Formation but within the TGF). The TOC contents recorded from these three samples are not as high as samples from Hoiho-1C and Kawau-1A; however, it possible that there are samples from Pakaha-1 that have similarly high TOC contents but were not available for geochemical analyses. The three high TOC samples range from 5.3 to 6.5%. As in Hoiho-1C and Kawau-1A, the underlying Wickliffe and overlying Laing formations generally have moderate TOC contents, with a mean value of approximately 1.1%.
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Sample availability for the Tartan Formation in Toroa-1 is very poor. There was a single sidewall core that exhibited a high TOC content of 7.2% (2162 m), and possibly one cuttings sample from 2246 m (1.4%) that possibly represented the TGF. Due to such large sampling gaps in the Toroa-1 data, it is difficult to ascertain the nature of deposition of the Tartan Formation from this well. However, based upon the limited data set, and by examining the data from the enclosing formations, it seems likely that a similar scenario for the deposition of the Tartan Formation occurred around Toroa-1 as in the previously mentioned wells.

7.5 Correlation of nitrogen content between wells across the Great South Basin

The nitrogen content of each sample was recorded along with the TOC and δ¹³C data by GNS Science using EA-IRMS analyses (see Chapter 5: Methods). Fig 7.5 shows the nitrogen variation between samples examined in each well. The data points and excursions generally follow closely those of the TOC data (Fig 7.4).

![Figure 7.5 Comparison of nitrogen content from cuttings and sidewall core samples.](image)

For the purposes of this study, the nitrogen contents were primarily recorded and used in conjunction with the TOC data to calculate the C/N ratio for each sample. The nitrogen content data are not discussed individually; instead; Section 7.6 details the importance of these data when combined with TOC data.

7.6 C/N correlation between wells across the Great South Basin

C/N ratios can be used to distinguish between marine and terrestrial origins in sedimentary organic matter (Meyers, 1994). Fresh, unaltered algae typically have atomic C/N ratios
between 5-8 (Emerson and Hedges, 1988; Meyers, 1994), whereas vascular land plants have C/N ratios of ≥ 20 (Meyers, 1994). This distinction is caused by the absence of cellulose in algae and its abundance vascular plants (Meyers, 1994), and also the protein richness of algal organic matter (Rau at al. 1987; Twichell et al. 2002). Meyers (1994) has stated that C/N ratio variability can result from changes in the proportions of C₃ and C₄ plant material.

Meyers (1992) suggested that elevated C/N ratios maybe associated with high rates of marine productivity, possibly under conditions of low nitrogen availability. Elevated C/N ratios have been identified in modern sediments deposited under areas of high productivity (Meyers et al. 2006). The organic matter produced under these conditions would be lipid-rich and nitrogen-poor. Organic-rich strata may have elevated C/N ratios as a result of selective loss of nitrogenous organic compounds (Rau et al. 1987). Verardo and MacIntyre (1994) have proposed that high C/N ratios can indicate faster loss of nitrogen over carbon during the sinking of marine organic matter from the photic zone. They reasoned that nitrogen-containing proteinaceous matter is more readily utilised by microbes than carbohydrate compounds. Meyers (1997) made a similar point in that partial degradation of algal organic matter during sinking can selectively reduce proteinaceous compounds, thus raising the C/N ratio. Van Mooy et al. (2002) stated that degradation of organic matter is different under oxic and suboxic conditions. They concluded that suboxic microbial degradation by denitrification preferentially utilises nitrogen-rich amino acids, leaving a larger portion of the nitrogen-poor organic components intact than under an oxic environment, and thus the C/N ratios of the surviving organic matter are higher.

Selective degradation of organic matter components during early diagenesis can modify C/N ratios of organic matter in sediments (Meyers, 1997). The C/N source signature of subaqueous sediments is generally well preserved despite the large reduction of the total amount of organic matter during sinking. Both C/N and δ¹³C values appear to experience little diagenetic change through time once deposited on the seafloor (Meyers, 1994; Twichell et al. 2002), and thus the source information gathered from C/N ratios in sub-aqueous sediments is generally reliable (Meyers, 1997).

There are circumstances where the C/N ratios impart misleading indications of bulk organic matter origins. The majority of sediments contain low inorganic nitrogen (IN) concentrations compared to the organic nitrogen content and thus C/N ratios usually represent organic matter concentration closely. However, in some sediments that contain low organic matter
concentrations, where the TOC content is less than 0.3%, the proportion of inorganic nitrogen can occasionally constitute a large fraction of the residual nitrogen, and so C/N ratios based on residual nitrogen could be artificially low (Meyers, 1997). Rau et al. (1987) made a similar point, and further suggested that C/N ratios may also be depressed because of significant adsorbed inorganic nitrogen from bacterial degradation of organic material. Rogers (Pers comm, 2008) also mentioned that samples containing low organic contents (below 0.3%) become more difficult to accurately detect using the present analytical methods, hence analytical errors become larger.

The C/N ratios calculated from the TOC and nitrogen contents in this study are of particular importance. Previous studies of the Waipawa Formation by Killops et al. (1996) and Killops et al. (2000) have stated that the formation had a predominantly marine origin with variable terrestrial components incorporated. Killops et al. (2000) stated that there are terrestrial components in many samples examined from the Waipawa Formation in the East Coast Basin, and traces of black, coaly material are also present in samples examined from the Great South Basin; Kawau-1A, Pakaha-1 and Toroa-1.

Of all samples analysed in this study that lie within the Tartan Formation and TGF intervals, none have a C/N ratio below 20 (Fig 7.6.1).

As mentioned earlier in this section, typical unaltered algal organic matter has low C/N ratios between 5-8, and C/N ratios of 20 or greater are associated with vascular land plants. Samples that have C/N ratios between 10-20 are considered to have a mixed marine/terrestrial
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source. Fig 7.6.2 shows the peak and average C/N values from this study for both sidewall core and cuttings samples from TGF across the Great South Basin. As a general trend, C/N ratios appear to increase as the well site becomes further from the inferred paleo-shoreline (see Cook et al. 1999; Enclosure 1, map 6 for petroleum exploration well site positions during the Paleocene).

Figure 7.6.2 Peak and average C/N ratios for wells examined in this study across the GSB.

Meyers et al. (2006) stated that elevated C/N ratios are typical of black shales, and indicate depressed organic matter degradation associated with suboxic conditions in the water column, which preferentially favours preservation of carbon-rich forms of marine organic matter over nitrogen-rich components. Meyers et al. (2006) also mentioned that C/N values between 20 and 40 in black shales are unusual for marine organic matter but are common in mid-Cretaceous black shales (Rau et al. 1987; Meyers, 1989; Dumitresca and Brassell, 2006).

The C/N results (Fig 7.6.1) of samples from within the TGF indicate that the organic matter of the facies is derived from a terrestrial source, and/or a marine source that has elevated C/N ratios due to preferential nitrogen loss during biological degradation. Fig 7.6.1 shows that 33 of 42 cuttings samples examined have C/N values above 20, and all have values above 10. Similar results were recorded from sidewall core samples, with 20 of 33 having ratios above 20 and 28 of 33 having C/N values above 10. Of the five sidewall core samples that have C/N ratios below 10, three have very low TOC contents of 0.1 or lower. These three low values could possibly be the result of residual inorganic nitrogen depressing the C/N signal for samples, or the greater analytical uncertainties associated with samples containing a low organic content.
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Many of the sidewall core samples from Pakaha-1 and Toroa-1 have C/N values between 10 and 20, indicating a mixed marine and terrestrial source of organic matter, whereas Hoihoo-1C and Kawau-1A samples generally contain C/N ratios that exceed 20, indicating primarily a terrestrial source. Cuttings samples from Toroa-1 have C/N values that all exceed 20, which indicates a terrestrial source, different from the mixed marine and terrestrial source suggested by the sidewall core samples. The differences between sample types could be caused by caving from shallower depths, contaminating the cuttings. The cuttings samples from Pakaha-1 generally have similar C/N ratios to those recorded from the sidewall cores. Takapu-1A samples contain some of the highest C/N ratios, and have an overall average ratio of 35.8, which is almost certainly derived from terrestrial organic matter.

7.7 $\delta^{13}C$ correlation between wells across the Great South Basin

Carbon isotopic ratios are useful for distinguishing between marine and continental plant sources of organic matter and for identifying different types of land plant contributions in marine sediments (Meyers, 1994, 1997).

Biochemical fractionation of carbon isotopes is primarily a kinetic process (White, 2001) and occurs during photosynthesis (Meyers, 1994). In marine plants such as phytoplankton, carbon isotopic fractionation is controlled by many factors such as; temperature, availability of CO$_2$ (aqueous), light intensity, nutrient availability, pH, and physiological factors, such as cell size and growth rate etc (Hoefs, 2004). Most photosynthetic plants incorporate carbon into organic matter using the C$_3$ Calvin-Benson metabolic pathway, which biochemically discriminates against $^{13}C$ to produce a $\delta^{13}C$ shift of approximately -20‰ from the isotopic ratio of the inorganic carbon source (Meyers, 1994). Approximately 90% of modern plants utilise the Calvin-Benson metabolic pathway, producing C$_3$ plants. These include most trees and shrubs, algae and autotrophic bacteria and most cultivated vegetation. Isotopic ranges for organic matter of C$_3$ type marine plants are approximately -20‰ for bacterial carboxylation and -29‰ for higher plant species (White, 2001). Organic matter produced from atmospheric CO$_2$ ($\delta^{13}C \sim -7‰$) by land plants using the C$_3$ pathway consequently has average $\delta^{13}C$ values between -29 and -26‰ (PDB) (Meyers, 1994).

Some plant species incorporate carbon into organic matter using the C$_4$ Hatch-Slack pathway, which creates less carbon isotopic fractionation and has heavier $\delta^{13}C$ values (White,
Chapter 7. Discussion

2001). Meyers (1994) stated that organic matter derived from C$_4$ type plants have $\delta^{13}$C values around -14‰. Modern C$_4$ plant types include many grasses, corn and sugarcane (White, 2001).

Hayes (1993) concluded that the $\delta^{13}$C content of each biomolecule depends primarily on four factors: (1) the $\delta^{13}$C content of the carbon source, (2) isotopic effects associated with the assimilation of carbon, (3) isotopic effects associated with metabolism and biosynthesis (i.e. during respiration and uptake of CO$_2$), and (4) cellular carbon budgets at each branch point (at each point within the cellular reaction network, distribution of carbon among products will affect isotopic compositions). White (2001) suggested that $\delta^{13}$C compositions become slightly heavier moving up the food chain. The carbon isotopic compositions of organic matter reflect principally the dynamics of carbon assimilation during photosynthesis and the isotopic composition of the source (Hayes, 1993).

Marine algae (all C$_3$ type plants; White, 2001) and bacteria are isotopically heavier than C$_3$ land plants (Meyers, 1994), as the main chemical compounds (lipids and carbohydrates) in terrestrial plants are usually isotopically lighter than those of marine plants (Tissot and Welte, 1978). Hayes (1993) stated that lipids contain less heavy $^{13}$C than other products of biosynthesis and hence are isotopically lighter. The distinction between marine and terrestrial organic matter reflects the isotopic composition of the carbon source for photosynthesis; marine plants utilise dissolved carbonate components in seawater, whereas terrestrial plants use atmospheric CO$_2$, with an isotopically lighter $\delta^{13}$C ratio (Tissot and Welte, 1978). Freshwater algae utilise dissolved CO$_2$, which is usually in isotopic equilibrium with atmospheric CO$_2$. The source of inorganic carbon for marine algae is dissolved bicarbonate, which, with a $\delta^{13}$C value of approximately 0‰ (Meyers, 1994), is heavier than atmospheric CO$_2$ ($\delta^{13}$C ~ -7‰). Thus marine organic matter is generally isotopically heavier than terrestrial organic matter.

Late Cretaceous black shales are commonly isotopically lighter than Cenozoic organic-rich marine sediments. Dean et al. (1986) concluded, based on carbon isotopic studies, that the isotopic differences between Cretaceous black shales (-29 to -26‰) and Neogene organic-rich sediments (-23 to -16‰) were the result of dissolved CO$_2$ availability to marine algae. They reported that CO$_2$ availability during the Late Cretaceous was higher than in the Neogene, thus resulting in isotopically lighter $\delta^{13}$C ratios in Cretaceous black shales.

Carbon isotope results from this study will be discussed initially as a well by well investigation and the discussion in Section 7.8 will integrate all relevant geochemical data.
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providing an overall interpretation of the possible sources and conditions surrounding the deposition of the organic matter present in the TGF.

δ\textsuperscript{13}C results from Takapu-1A show little variation with respect to those of other wells examined in this study (Fig 7.7; note narrow δ\textsuperscript{13}C scale on the Takapu-1A plot compared to other wells examined). All ten samples are isotopically light, ranging from -27.8 to -25.2‰. Based upon this small isotopic range, it is likely that the source of the organic matter was consistent throughout deposition of the sampled section of this well. It probable that the organic matter contained within samples taken from Takapu-1A had a significant contribution from terrestrial plants, most likely those that utilised the C\textsubscript{3} Calvin-Benson metabolic pathway.

![Figure 7.7 Comparison of δ\textsuperscript{13}C values from cuttings and sidewall core samples.](image)

Results from sidewall core analysis of Hoiho-1C show an isotopic excursion over three samples from 1582 m, 1578 m and 1558 m (Fig 7.7). These three samples have δ\textsuperscript{13}C values of -19.7, -15.8 and -25.0‰ respectively. White (2001) stated that carbon isotopic values around -20‰ for C\textsubscript{3} type plants is common for organic matter (marine) derived from bacterial carboxylation. Fig 1 from Meyers (1994) demonstrates that C\textsubscript{3} marine algae and C\textsubscript{3} land plants can have δ\textsuperscript{13}C values around -20‰; however, C\textsubscript{3} terrestrial plants average approximately -27‰, and are not as isotopically heavy as -15.8‰ (Hoiho-1C, 1578 m). From Fig 1 (Meyers, 1994), it is unlikely that a C\textsubscript{3} marine contribution alone could have caused the heavy δ\textsuperscript{13}C values. Fry et al. (1977) stated that the isotopic source signal can be complicated by areas that receive or contain combinations of organic matter derived from marine and/or C\textsubscript{3} and C\textsubscript{4} vascular plant origins. It is possible that there is some contribution from isotopically heavier C\textsubscript{4} land plant.
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types in the sidewall core from 1578 m; this would help to explain the isotopically heavy nature of the sample. This will be discussed further in Section 7.8.

The five samples analysed from above and below the three Tartan Formation/TGF samples in Hoiho-1C have relatively light isotopic values that range from -27.1 to -26.3‰, which is typical of organic matter with a C₃ land plant contribution.

There were 16 cuttings samples examined from Kawau-1A and seven of these samples from 2292 m through 2237 m exhibit heavy δ¹³C values that range from -21.3 to -17.4‰ (Fig 7.8). These seven samples lie within the boundary of the Tartan geochemical facies recognised in this study (see Section 7.3). There were also ten sidewall core samples examined, in which two from 2263 m and 2240 m display significantly heavy δ¹³C values of -21.4 and -18.2‰ respectively. There is one sidewall core sample from 2218 m that lies 2 m above the top of the Tartan Formation boundary that has a moderately heavy carbon isotopic value of -24.5‰. It is possible that this sample represents the very top of the Tartan geochemical facies; however in this study it is not considered to represent the Tartan Formation or TGF.

To explain the observed carbon isotopic ratios of the TGF in Kawau-1A (based only on δ¹³C data), it is possible that the source of the organic matter contained within the heaviest δ¹³C samples with values around -18‰ and greater, is derived, in part, from C₃ land plants and marine bacteria/plants, with possibly some contribution from C₄ land plants. Possible origins of these isotopically heavy samples are discussed in more detail in Section 7.8.

Sidewall core and cuttings samples below the TGF have little variation and are all isotopically light ranging from -27.6 to -25.1‰. Samples above the Tartan Formation (excluding the sidewall core from 2218 m) also have isotopically light values with little variation that range from -28.5 to -25.6‰. The organic matter is most likely derived from predominantly C₃ terrestrial plants.

Examination of the δ¹³C data from cuttings samples from Pakaha-1 (Fig 7.7) show that two samples from 2560 m and 2551 m have isotopically heavy δ¹³C values of -19.7 and -19.3‰ respectively. The one sidewall core sample to exhibit a positive δ¹³C shift is the sample from 2576 m, with a δ¹³C value of -20.7‰. These three samples lie within the Tartan geochemical facies (see Section 7.3). Organic matter with carbon isotopic values of approximately -20‰, such as these three Tartan Formation samples, could be derived from several sources such as C₃ marine plants derived from bacterial carboxylation and possibly some C₃ land plants. This will be discussed further in Section 7.8, combining all relevant geochemical data.
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Samples above and below the TGF in Pakaha-1 have relatively light carbon isotopic values that range from -27.9 to -25.5‰ (with the exception of the shallowest cuttings sample from 2377 m, which has a moderately heavy δ¹³C value of -23.6‰). The organic matter in these samples appears to contain significant C₃ land plant material.

Interpretations of the geochemical results for the Tartan Formation (and TGF) in Toroa-1 are complicated by the lack of available samples. As a result only one sidewall core sample lies within the TGF. This sample is from 2162 m and has the only significantly heavy carbon isotopic ratio, with a value of -21.0‰. The organic matter in this sample could have possibly been derived from C₃ marine plants, marine bacteria/algae or C₃ terrestrial plants. There is one sample from drill cuttings that may possibly represent the TGF. This sample from 2246 m has a δ¹³C value of -24.5‰ (the heaviest isotopic value of all cuttings samples examined from Toroa-1).

Samples from both sidewall cores and cuttings that are outside of the Tartan Formation interval have isotopically light δ¹³C values that range from -27.3 to -25.5‰, and are possibly derived from C₃ land plants or a combination of C₃ land plants and C₃ marine sources (This is discussed further below).

7.8 Source of organic matter in samples from the Great South Basin

Figure 7.8.1 is a plot of C/N vs. TOC for all samples that lie within the Tartan geochemical facies.
Chapter 7. Discussion

Figure 7.8.1 C/N vs. TOC for samples that lie within the Tartan geochemical facies.

C/N ratios from samples of the Tartan geochemical facies range from 20.86 to 44.33, and TOC contents range from 1.4 to 17.1% (with most samples having C/N ratios between 20-35 and TOC between 3-11%).

Figure 7.8.1 shows large increases in the TOC contents correlating positively with relatively small increases in the C/N ratios. All of the Tartan geochemical facies samples have C/N ratios above 20, indicating a primarily terrestrial source of organic matter and/or varying proportions of marine components. There is greater terrestrial influence on organic matter with increasing TOC content, possibly as a result of enhanced organic matter preservation with increasing terrestrial composition. The elevated C/N ratios likely indicate depressed organic matter degradation associated with suboxic conditions within the water column. This would have led to preferential preservation of carbon-rich organic matter over nitrogenous components (Meyers et al. 2006). Microbial degradation under suboxic conditions by denitrification preferentially utilises nitrogenous compounds, such as amino acids (van Mooy et al. 2002), and proteinaceous matter, rather than carbon-rich compounds, such as carbohydrates (Verardo and MacIntyre, 1994), and C₃ and C₄ high-cellulose plants (Meyers, 1994), leaving higher proportions of nitrogen-poor components in the sediments, and thus resulting in higher C/N ratios.
Based upon the evidence from the data recorded in this study, it would seem feasible that similar conditions and events could have influenced the organic matter contained within Tartan Formation (and TGF) sediments, resulting in the high C/N, high TOC data observed.

Figure 7.8.2 compares the C/N and TOC data from all samples analysed in this study, including the above mentioned TGF samples.

It is clear from Fig 7.8.2 that the samples from the TGF are distinct from the samples from the underlying Wickliffe and overlying Laing formations. There is much less variation in the C/N ratios of the TGF samples than from samples of adjacent formations. All but a few samples of the Wickliffe and Laing formations have TOC contents below 2%, and the trend of C/N vs. TOC is almost linear (unlike the samples from the TGF, where there is greater terrestrial influence on organic matter with increasing TOC content).

There are many samples that have C/N ratios below 20, indicating a marine plant/algal or mixed marine/terrestrial source. There are also many samples that have C/N values around or above 20, indicating higher proportions of terrestrial components in the organic matter. The change in C/N ratio without a corresponding change in the TOC amongst Wickliffe and Laing formation samples could be explained by the conditions surrounding preservation, and to what extent microbial activity degraded nitrogenous compounds of the organic matter (this is
Chapter 7. Discussion

further discussed in the C/N vs. $\delta^{13}$C discussion below). Dumitrescu and Brassell (2006) suggest that samples with uniform C/N ratios could represent organic matter derived from a uniform source. It would appear that samples from the TGF (Fig 7.8.1) have a much more uniform source of organic matter than adjacent formations (Fig 7.8.2).

The C/N ratio is plotted against the $\delta^{13}$C data for the TGF in Fig 7.8.3.

Figure 7.8.3 C/N vs. $\delta^{13}$C data for samples that lie within the Tartan geochemical facies.

The data range from 20.86 to 44.33 for the C/N ratios and from -25 to -15.8‰ for the $\delta^{13}$C data (with most of the $\delta^{13}$C data between approximately -21 to -17.5‰).

Figure 7.8.3 shows that there is a tendency for increasingly heavy $\delta^{13}$C values with increasing C/N ratios. This indicates a change in the source of the organic matter. $\delta^{13}$C ratios around -20‰ are typical of organic matter derived from C3 marine plants/algae/bacteria (White, 2001), and heavier isotopic ratios of approximately -14‰ are characteristic of C4 land plants that utilise the Hatch-Slack metabolic pathway (Meyers, 1994).

Due to the high C/N ratios of samples within the TGF, it would appear that a terrestrial source of organic matter is likely. However, conflicting data from carbon isotopes suggest that there is a marine influence that also requires some C4 land plant contribution to explain the heaviest isotopic values of -15.8‰ from Hoihoi-1C (1578 m) and -17.4 and -17.7‰ from Kawau-1A (2264 m and 2255 m). Isotopic source signals can be complicated by areas that receive or contain combinations of different types of organic matter in the sediments (Fry et al.}
Chapter 7. Discussion

1977). Figure 7.8.4 is a diagram that has been modified from Meyers (1994; Fig 1). It plots the C/N ratios against the $\delta^{13}$C values. The original diagram specified ranges for C/N and $\delta^{13}$C values for different organic matter sources. Here (Fig 7.8.4), the complete data set of all samples analysed in this study is overlain onto the diagram from Meyers (1994; Fig 1). The field containing samples from the TGF is shaded.

Figure 7.8.4 Comparison of C/N vs. $\delta^{13}$C data from all samples analysed in this study, (including the above mentioned TGF samples) overlain onto a diagram modified from Meyers (1994).

Figure 7.8.4 shows that samples of the TGF almost all lie between a marine plant/bacterial, C$_3$ land plant and C$_4$ land plant composition. From this comparison, it is likely that the organic matter of the Tartan Formation/TGF is derived from a mixture of sources, both marine and terrestrial, differences are likely produced by variations in the relative proportion of each type of source material. Figure 7.8.4 also displays samples from the Wickliffe and Laing formations. There is a distinct difference between the Tartan Formation (and TGF) samples and those of the enclosing formations. These samples generally lie within the -28 to -25‰ $\delta^{13}$C range, with large C/N variations. This suggests that there was a consistent source of deposited organic matter, with varying degrees of preservation. On the basis of the data presented in Fig 7.8.4, it
is probable that the organic matter of the enclosing formations of the Tartan Formation was derived from a combination of C₃ land plants and marine components.

Variation of TOC contents and δ¹³C ratios across Great South Basin exploration wells investigated in this study are shown in Fig 7.8.5. The figure compares wells with increasing water depth (and distance from the paleo-shoreline). Enclosure 1, map 6 from Cook et al. (1999) shows that the relative proximity of each well to the paleo-shoreline, which at present is similar to positions during the Paleocene.

![Figure 7.8.5 TOC and δ¹³C variations with increasing water depth across Great South Basin based on peak TOC and δ¹³C values for each well. (Data are in Appendix 3).](image)

Figure 7.8.5 TOC and δ¹³C variations with increasing water depth across Great South Basin based on peak TOC and δ¹³C values for each well. (Data are in Appendix 3).

It is evident from Fig 7.8.5 that, as the TOC content increases gradually through the progression of wells, δ¹³C values become isotopically heavier. A basic trend observed from Fig 7.8.5 is that the further away from the paleo-shoreline a well is located, the heavier the carbon isotopic ratio becomes, and there is a corresponding TOC increase. Comparison of Fig 7.8.5 with the specific data points plotted on Fig 7.8.4 indicates that the contribution of C₃ land plants is greatest in wells located closest to the shoreline (e.g. Takapu-1A). As the distance from the paleo-shoreline increases, the C₃ land plant contribution within the TGF decreases and a mixed marine and terrestrial composition predominates (e.g. Toroa-1 and Pakaha-1). Kawau-1A appears to be dominated by heavier δ¹³C values, indicating a greater marine influence, with some C₄ land plant contribution (explaining the high C/N ratios observed), and some C₃ land plant contribution, explaining the heaviest δ¹³C values. A sample from 1578 m in Hoiho-1C appears to have a high C₄ land plant composition; however other samples from this well appear to have a combination of marine plant, C₃ land plant and C₄ land plant...
components. A possible explanation for the above mentioned trend could be due to transport currents moving large quantities of terrestrial debris away from the coast (Rogers, Pers comm. 2008).

Further data comparing the TOC and δ\textsuperscript{13}C increases are presented in Fig 7.8.6. In this plot Rock-Eval TOC data are compared to the mass spectrometry δ\textsuperscript{13}C data. Again, there is a clear distinction between samples from the Tartan Formation/TGF (shaded) and the vertically adjacent formations.

![Graph showing Rock-Eval TOC data vs. mass spectrometry δ\textsuperscript{13}C data. Shaded areas are samples from the TGF.](image)

**Figure 7.8.6** Rock-Eval TOC data vs. mass spectrometry δ\textsuperscript{13}C data. Shaded areas are samples from the TGF.

Fig 7.8.6 also demonstrates that there are significant variations in δ\textsuperscript{13}C values within TGF samples, indicating a change in the source of organic matter, whereas samples from the Wickliffe and Laing formations generally have similar isotopic values (also see Fig 7.8.4 and corresponding discussion).

### 7.9 Correlation of the Tartan Formation to the Waipawa Formation

The enrichment of \textsuperscript{13}C and the high TOC contents within the Tartan Formation/TGF are consistent with that of the mid to Late Teurian Waipawa Formation. However, samples from
Chapter 7. Discussion

Hoiho-1C (1554 m; -15.8‰) and Kawau-1A (2264 m; -17.4‰) have δ13C values that exceed those previously reported for the Waipawa Formation (Hollis et al. 2006).

The Tartan and Waipawa formations are defined by lithology. The Tartan Formation is of Late Teurian age (Cook et al. 1999) and the Waipawa Formation is of mid-Late Teurian age (Moore 1988b). It is possible that the oceanographic environmental events that produced the geochemical changes associated with the deposition of the Tartan and Waipawa formations were synchronous. Isotopic evidence presented by Killops et al. (2000) from East Coast Basin outcrops show that the start of the geochemical changes correspond to the lithological base of the Waipawa Formation. Rogers et al. (2001) give geochemical data for two East Coast Basin outcrops: Tawanui and Angora Stream. The Tawanui outcrop has no Waipawa Formation present; however, the Te Uri Member is present and is proposed as a Waipawa Formation equivalent. The Angora Stream section has Waipawa Formation present and no Te Uri Member is identified. In other outcrops, the Te Uri Member is overlain by Waipawa Formation (Moore 1988b, 1989). Rogers et al. (2001) concluded that the upper part of the Te Uri Member is a correlative to the Waipawa Formation. Geochemical data from some wells in the Great South Basin demonstrate changes that appear below the recognised base of the Tartan Formation, in the upper Wickliffe Formation. It is possible that the geochemical change observed prior to the base of the Tartan Formation in some wells is caused by a similar geochemical change below the Waipawa Formation as documented in the East Coast Basin. This could indicate that the Tartan Formation (which is characterised by gamma ray response) is only equivalent to the middle and upper parts of the Waipawa Formation, whereas the Tartan geochemical facies (characterised by TOC and δ13C values) is equivalent to the entire Waipawa Formation.
CHAPTER 8
CONCLUSIONS

• There is no geochemical evidence for the presence of the Tartan Formation in the Takapu-1A well.

• Geochemical studies of the four other wells show that, in general, the Tartan Formation can be recognised by enrichments in TOC and $^{13}$C, with C/N ratios above 20. These changes agree with the top of the formation, as defined by its lithology.

• However, in some wells the geochemical changes appear below the recognised base of the formation, in the upper part of the underlying Wickliffe Formation. This is likely due to oceanographic environmental changes beginning prior to changes in the depositional processes. A geochemical facies, Tartan geochemical facies (TGF) is proposed for this interval.

• The high organic richness of the Tartan Formation (and TGF) with respect to the relatively low organic richness of adjacent formations establishes that there was a profound change in the conditions under which the Tartan Formation was deposited.

• TOC data from Kawau-1A (the most comprehensively sampled well) provide evidence for more favorable preservation and/or accumulation of organic matter during the mid stages of deposition of the Tartan Formation than during the initial and final stages. Further, TOC data for the Wickliffe and Laing formations (especially in Kawau-1A) suggest that conditions for the preservation and accumulation of organic matter were more favorable prior to the deposition of the Tartan Formation than following it.

• C/N ratios appear to increase with the proximity of the well site to the inferred paleo-shoreline. All samples within the Tartan geochemical facies have C/N ratios above 20, with little variation. There appears to be a greater terrestrial influence on organic matter with increasing TOC content, possibly as the result of enhanced organic matter preservation with increasing terrestrial composition, and depressed organic matter degradation associated with suboxic conditions in the water column.
Chapter 8. Conclusions

- Samples from the Wickliffe and Laing formations show a wide range of C/N values. Many samples have C/N ratios below 20, indicating a marine bacterial/plant/algal or mixed marine bacterial/plant/algal and terrestrial source. Many others that have C/N ratios of 20 and above indicate a significant terrestrial composition. There is little variation in the TOC contents within these formations, with most samples having values below 2%. This indicates that there were varying degrees of preservation of organic matter within the Wickliffe and Laing formations.

- C/N ratios for samples from within the Tartan geochemical facies increase with increasingly heavy $\delta^{13}C$ ratios. These samples also have C/N ratios that indicate a predominantly terrestrial source of organic matter (C/N >20), however heavy $\delta^{13}C$ values for corresponding samples suggest a marine source of organic matter.

- It is probable that samples within the Tartan geochemical facies are composed of a mixture of C$_3$ land plant, marine bacterial/plant/algal, and C$_4$ land plant material. The organic matter within the Wickliffe and Laing formations appear to have been derived primarily from C$_3$ land and marine sources.

- The composition of C$_3$ land plant material appears to be greatest in wells located closest to the paleo-shoreline (e.g. Takapu-1A). There appears to be a decreasing C$_3$ land plant contribution as the distance from the paleo-shoreline increases (e.g. Toroa-1 and Pakaha-1). The more distal Kawau-1A seems to have a higher marine influence with some C$_4$ land plant material. Geochemical data from the most distal well from the paleo-shoreline, Hoiho-1C, has the highest marine and C$_4$ land plant contribution, with varying degrees of C$_3$ land plant material incorporated.

- If the oceanographic environmental changes that produced the geochemical changes associated with the Waipawa and Tartan formations were synchronous, this suggests that the Tartan Formation is equivalent to the middle and upper parts of the Waipawa Formation, whereas the Tartan geochemical facies is equivalent to the entire Waipawa Formation.
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## Appendix 1. Full list of geochemical data from GNS analyses

### Takapu-1A

**Cuttings**

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<th>Depth (m)</th>
<th>Ave sample depth (m)</th>
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<th>%N</th>
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### Hoiho-1

**Sidewall Cores**

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<th>%N</th>
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### Kawau-1A

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### Kawau-1A

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### Pakaha-1

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### Toroa-1

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### Toroa-1

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## Appendix 2. Comparison of Rock-Eval TOC and GNS TOC data

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## Appendix 4. TOC Data from APT and GSC Rock-Eval, with GNS mass spectrometry results as a comparison

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