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**SEDIMENTOLOGY AND PETROLOGY OF MIOCENE
COLD-SEEP CARBONATES IN SOUTHERN HAWKE'S BAY:
GEOLOGICAL EVIDENCE FOR PAST SEABED
HYDROCARBON SEEPAGE**

A thesis

submitted in partial fulfilment

of the requirements for the degree of

Master of Science in Earth Sciences

at

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by

Melissa Jane Troup



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WAIKATO
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Abstract

This study focuses on the five sites of Early Miocene aged cold seep carbonate deposits (Wanstead, Wilder Road, Haunui, Ugly Hill, and Ngawaka) in the southern East Coast Basin, North Island, New Zealand, which archive paleo-hydrocarbon seafloor seepage in a convergent margin setting. Seep deposits are hosted within calcareous slope mudstones of the Ihungia Fm and provide an important analogue to modern seep sites in the East Coast Basin. Individual fossilised seep sites have revealed, through mapping and logging, differences in outcrop extent, morphology, and lithology, while petrology has uncovered a complex array of textures, fabrics, and mineralogies within the methane derived authigenic carbonates (MDAC). Fabrics are diverse and often comprise chaotic multi-phase assemblages of various mineralogies in original and/or altered states. Enclosed within the carbonates are the fossilised remnants of chemosynthesis-based communities, particularly macro-invertebrates, which includes lucinid and vesicomid clams, modiolid mussels, corals, gastropods, and worm tubes. These fossil types, and their distribution throughout the deposit, not only reflect the variations in fluid conditions but also the maturity of the seep system. Veining and (micro)brecciation are common at a variety of scales with multiple generations of cements forming thick fill sequences representing cyclic episodes of fracturing and sealing through carbonate formation.

Detailed analysis of MDAC deposits has led to the identification of thirteen mineral fabrics, four fracturing and/or corrosion phases, and two alteration phases. Relationships between the various fabrics and phases has led to the elucidation of a generalised paragenetic sequence while appreciating that some local variation occurs. The paragenetic sequence is divided into two diagenetic stages: an early stage that includes all mineralisation and events that occurred in the (near) seafloor environment, and a late stage that includes all mineralisation and events that occurred in the burial realm.

Early diagenesis (8 events) involved precipitation of mainly aragonite phases, including clotted and peloidal microcrystalline carbonate (micarb), fibrous and radiating crystal forms (often hydrocarbon inclusion-bearing) occasionally encase

thrombolites between successive isopachous generations, and anhedral crystal masses and layers. Early destructive episodes of fracturing, (auto)brecciation, and dissolution via corrosive fluids significantly modified the deposits, ultimately increasing surface area available for further mineral growth. Late diagenesis (9 events) occurred within the burial realm and resulted in the addition of late stage pore and fracture occluding low magnesium calcite (LMC) and some minor dolomite and silica forms. Some of the early metastable aragonite forms remained pristine and unaltered, while others underwent varying degrees of fabric retentive to destructive neomorphic change generally resulting in stable LMC mineralogies. Later uplift and exhumation brought the carbonate deposits into their present-day positions.

Distinctly depleted stable $\delta^{13}\text{C}$ isotope signatures indicate carbonate carbon was largely sourced from thermogenic methane, with some of the migrating fluids likely affected by methane pool oxidation, and mixing with marine water and residual CO_2 . Stable $\delta^{18}\text{O}$ isotope signatures suggest that the ascending hydrocarbon-rich fluids experienced slight temperature fluctuations, possibly due to contact with warmer advecting fluids, and were also influenced by local gas hydrate formation and dissociation events. Preliminary lipid results importantly confirm the presence of microbes which carry out the anaerobic oxidation of methane (e.g. PMI and biphytanic diacid) and sulphate reduction (e.g. iso- and anteiso fatty acids).

The complexity revealed within these cold seep carbonates, and more particularly their cement stratigraphy, reflects the temporally and spatially dynamic nature of the fluids reaching the paleo sea floor of the East Coast Basin. Many of the features observed within these southern East Coast Basin cold seep deposits have a striking similarity with the Miocene deposits of the Italian Apennines, while others, particularly the occurrence of microbial mats (thrombolites), are an interesting feature more atypical of worldwide occurrences.

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CHAPTER 1

Introduction

1.1 OVERVIEW

Cold seeps are sites of focused fluid flow from the subsurface to the seafloor. Such sites are typically found in deep marine environments, from many geotectonic settings (Fig. 1.1) (Campbell 2006). These fluids are usually rich in hydrocarbons and are typically dominated by methane and sulphide. Due to various complex chemical processes occurring at seep sites and the presence of a suite of chemosynthetic microbes, carbonate deposits form at these sites (see Section 2.2). In the past two decades cold seep sites, both modern and ancient, have attracted immense interest from researchers and the energy industry. This is due to their unique nature and setting, and relation to hydrocarbon systems and gas hydrate formation.

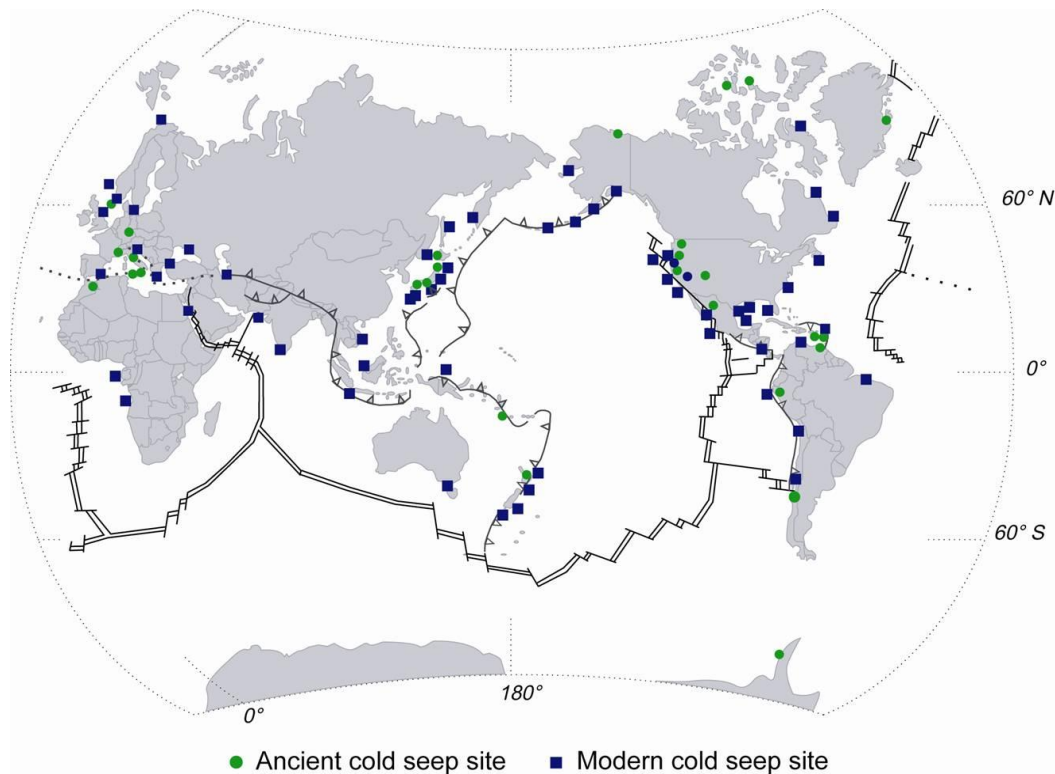


Figure 1.1 - The global distribution of modern and ancient cold seeps (modified from Campbell, 2006) .

In extreme seep environment geochemical conditions are ideal to host chemosynthetic microbes. These microbes carry out the process of anaerobic oxidation of methane (AOM), which drives carbonate precipitation (see Section 2.2) (Judd & Hovland 2007). These methane-derived authigenic carbonate (MDAC) deposits form in a variety of morphologies (lenses and nodules within the sediment, slabs, and mounds), which are typically localised on the seafloor around the seepage conduit (Conti *et al.* 2007; Judd & Hovland 2007). The microbes are the base of a food chain which supports a vast and unique community of macrofauna (see Section 2.2.3) (Sibuet & Olu 1998; Levin & Michener 2002; Boetius & Suess 2004), much of which can end up fossilised within the incrementally to continuously precipitating carbonate (see Section 2.5.2) (Campbell & Bottjer 1995; Campbell 2006; Campbell *et al.* in press). Carbonate deposits formed in seep environments eventually become buried within the surrounding host sediments, undergo various diagenetic and tectonic processes, and are often later uplifted and exhumed at the Earth's surface.

During the life cycle of cold seep carbonate systems a variety of different minerals and fabrics are precipitated. In the early diagenetic stage in the (near) seafloor environment, fibrous aragonite and high magnesium calcite fabrics typically precipitate (Peckmann *et al.* 2001b). Diagenesis in the burial realm often alters these minerals, and subsurface fluid flow can add to the suite of minerals and fabrics in a deposit (Ewen 2009). Determination of a paragenetic sequence for an ancient deposit helps to unravel the events which have occurred and processes which have affected the deposit since its initial formation, to give an idea of spatial and temporal changes within the seep system, and help to identify local pore water chemistries throughout the formation process.

Comparison of these factors from cold seep deposits within and between different sedimentary basins, and from varying tectonic settings, could highlight trends and/or anomalies in the formative processes driving these unique and dynamic systems. Patterns found throughout deposits scattered within a single basin, or even a part of a basin, could also allow for greater understanding of local hydrocarbon systems and gas migration.

This study focuses on the formation of the five known ancient seep carbonate sites in southern Hawke's Bay within the onshore East Coast Basin, North Island, New Zealand (Fig. 1.2). These five sites are laterally and temporally separated from the scattering of seep carbonate sites in the northern reaches of the basin (Fig. 1.3) and therefore may have significant variations in their formational history.



Figure 1.2 – The Ngawaka East sub-site of southern Hawke's Bay hosts one of the largest ancient seep carbonate outcrops (known as NG.A) of this study, which is hosted within Early Miocene deep-water mudstone.

1.2 PREVIOUS PROJECT RESEARCH

This MSc thesis is completed in conjunction with several other MSc and PhD studies as part of a Marsden funded research project (UOA0604; UOWV083) focused on hydrocarbon seeps and chemosynthesis in the East Coast Basin of North Island, New Zealand. The project is based at the University of Auckland and the University of Waikato, with contributions from Dave Francis of Geological Research Limited, Lower Hutt, New Zealand; IFM-GEOMAR in Kiel, Germany; Dr Crispin Little from Leeds University, UK; and from Alan Orpin at

the National Institute of Water and Atmospheric Research (NIWA) in Wellington, New Zealand.

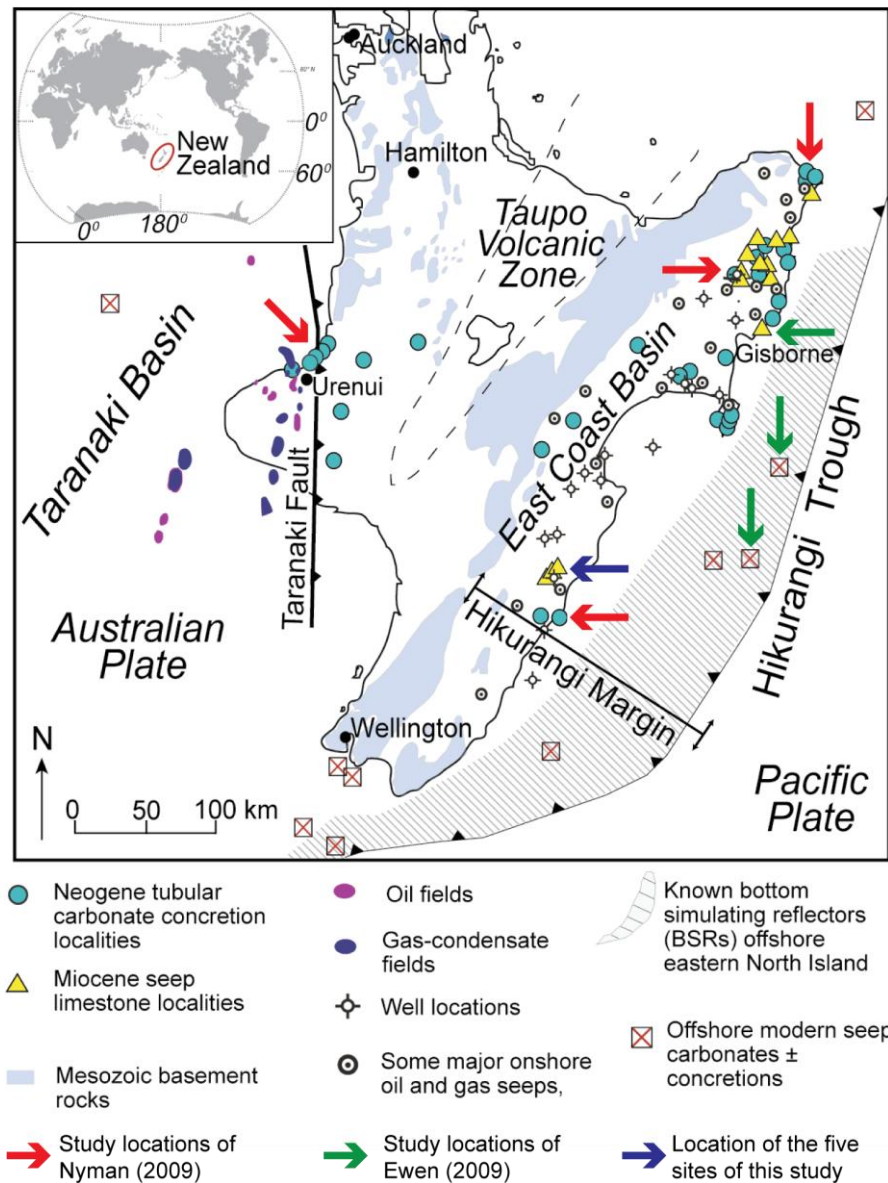


Figure 1.3 – Generalised locality map of hydrocarbon seep related features in North Island, New Zealand. The locations of the five seep carbonate sites of this study are marked by the blue arrow. Paleontological studies by Saether (in prep) are based on samples from numerous ancient seep carbonate deposits from the East Coast Basin. Modified from Nyman (2009).

In addition to the present studies, student theses, both completed and underway, that are related to the cold seeps research project are referenced below and located on Figure 1.3:

- Stephanie Nyman – PhD Thesis – University of Waikato (2009)
“*Tubular concretions from the North Island, New Zealand: Evidence for hydrocarbon migration and the subsurface plumbing of cold seeps.*”
- Kristian Saether – PhD Thesis – University of Auckland (2010)
“*Miocene hydrocarbon seep deposits in New Zealand: Taxonomy and paleobiogeography.*”
- Sarah Ewen – MSc Thesis – University of Waikato (2009)
“*Diagenetic evolution of some modern and ancient cold seep-carbonates from East Coast Basin, New Zealand.*”

1.3 OBJECTIVES OF THIS STUDY

This study is the first to focus specifically and in detail on the southern-most of the known ancient seep carbonate deposits of the onshore East Coast Basin. The results of this study will contribute to fulfilling Objective 1 of the wider Marsden funded research project to “Decipher the history of ECB seafloor hydrocarbon seeps for selected sites, concentrating efforts on pristine deposits, those with preserved fluid plumbing, and those with stratigraphic or structural significance.” It will also aid completion of Objective 4 by acting as an ancient analogue in order to “Compare and contrast the *ancient* North Island seafloor seeps, fluid plumbing features and fossils in the ECB with *modern* gas hydrates, hydrocarbon seep-carbonates and associated faunas of the offshore Hikurangi Margin.”

Specific aims of this study include:

- To document the field nature and distribution of the five known southern Hawke’s Bay ancient cold seep carbonate deposits at Wanstead, Ugly Hill, Ngawaka, Haunui, and Wilder Road (Figs. 3.4 and 3.5).
- To determine and characterise the minerals and fabrics present, and to subsequently unravel the complex evolution of the cold seep carbonates.
- To develop schematic diagrams to illustrate the diagenetic and tectonic processes and alterations which have impacted the cold seep carbonate

deposits from their initial precipitation on the sea floor, through later burial diagenesis, and subsequent uplift.

- To compare results across the five study sites of this thesis, to other cold seep carbonate occurrences in New Zealand, and to other international occurrences of cold seep carbonates.

In order to achieve these objectives, the approaches and analytical techniques adopted were tailored to the study of cold seep carbonates. These techniques include an understanding of the regional tectonic and structural development of the region, mapping (stratigraphic and facies analysis) of all outcrops at each of the five study sites with intensive sampling, detailed petrography under plane polarised light (PPL), cathodoluminescent light (CL), ultraviolet light (UV), and scanning electron microscope (SEM), stable $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotope analysis, XRD bulk mineralogy, GADDs component specific mineralogy, LECO carbonate percentage analysis, and organic carbon content analysis.

1.4 THESIS STRUCTURE

This thesis contains eight chapters followed by references and appendices. An Appendix disk, located inside the back cover, contains all field images, photomicrographs taken under PPL, CL, UV, and SEM, plus data from XRD and GADDs analyses.

Chapter 1 – Introduction: An introduction to the thesis which briefly describes cold seep carbonates, the context of the study within the wider research group, and notes the objectives of the study.

Chapter 2 - Background: Hydrocarbon Migration in Cold Seep Systems: An overview of cold seep carbonate literature, including explanations of processes operating in cold seep systems, features related to and typical of cold seep environments, and the global and local distribution of cold seep deposits.

Chapter 3 – Geologic Setting: Describes the physical setting of the southern Hawke’s Bay ancient cold seep carbonate deposits from a regional to local scale. This includes the history of the region plus modern day structure and topography.

Chapter 4 – Methodology: Describes the methods used during field work (mapping, stratigraphic logging, sampling) and the petrographic and geochemical analysis of samples in the laboratory.

Chapter 5 - Seep Carbonates in Outcrop: Results of the work carried out in the field. Includes individual field maps for each site, outcrop and sampling localities, and descriptions of sites, outcrops, lithologies, fossil content, host formations, and other seep-related features.

Chapter 6 – Laboratory Results: Presents the results for all laboratory analyses carried out on the southern Hawke’s Bay cold seep carbonate samples.

Chapter 7 – Discussion: An in-depth interpretation of the field and laboratory results, with schematic models to illustrate processes inferred to have occurred in the formation of the seep carbonate deposits. A comparison of results across sites of this study, other New Zealand cold seep carbonate sites, and international cold seep carbonate deposits is also given.

Chapter 8 – Conclusions: A synthesis of observations and conclusions of field work and laboratory results, and a summary of the main points of the discussion. Suggestions for further research in this area are also given.

Appendices are structured as follows:

Appendix 1 – Field Information: A table giving the location and brief descriptive details of many of the known ancient seep carbonate deposits of the East Coast Basin. Contact details for land owners are also given.

Appendix 2 – Sample Catalogue: A table containing details of all samples collected in the field, including source outcrops, facies codes, and brief descriptive details.

Appendix 3 – Laboratory Data: Contains the graphed GADDs data for all spots analysed plus full isotopic results.

CHAPTER 2

Background: Hydrocarbon Migration in Cold Seep Systems

2.1 INTRODUCTION

First discovered in the mid 1980s, modern cold seeps are sites of focused fluid flow from the subsurface, and the carbonate deposits formed at these sites act as a sink for hydrocarbons which have migrated from depth and that released from gas hydrates. Cold seeps are now recognised worldwide in many geotectonic settings. Similar to hydrothermal vents, cold seeps can be associated with a vibrant chemosynthetic community and with build ups of authigenic carbonate precipitates.

Cold seeps, both modern and ancient, host a range of organisms and are responsible for the precipitation of authigenic carbonate in a range of morphologies and lithologies. They typically involve a steady fluid flow, which may fluctuate at a local scale, for long periods of time that provides a sustained influx of methane and sulphide to the sea floor environment (Campbell 2006; Campbell *et al.* in press). The rock record of cold seep deposits reaches back to the Devonian, although (recognised) Palaeozoic seeps are rare (Walliser *et al.* 1999; Peckmann & Thiel 2004).

This chapter provides a brief overview of some of the research findings concerning cold seeps over the last two decades in order to elucidate the processes governing seafloor hydrocarbon seepage and its products. It covers the biological and geological processes occurring in cold seep systems, the associated features and their formation mechanisms, the distribution of cold seeps around the globe, and the key characteristics used to identify both modern and ancient cold seep environments.

2.2 COLD SEEP SYSTEMS

Hydrocarbon seeps, particularly of dissolved methane and hydrogen sulphide, are relatively common around the world's continental margins. There are many terms applied to these systems by different researchers; I will follow those defined by Campbell (2006) and used by Ewen (2009) in a companion study to mine on seep carbonate deposits elsewhere in the East Coast Basin. The hydrocarbon seep and hydrothermal vent review paper by Campbell (2006, p.384) defines cold seeps as "...fluid discharge of varying rates and temperatures generated from the accumulation and burial of organic matter, its transformation to hydrocarbons, and their migration and release from sedimentary basins". This definition allows researchers to differentiate between cold seep systems and hydrothermal systems, both modern and ancient, based on the source of the fluids; hydrothermal systems expel fluids sourced from the interactions between circulating seawater and igneous bodies. Seabed fluid flow, as the definition from Campbell (2006) implies, entails flow rates from intergranular micro-seepage to rapid seafloor mud volcano extrusions. The fluid flux varies from system to system, and this flux is often reflected in the morphological features and mineralogy of the precipitates (Conti & Fontana 2005; Conti *et al.* 2007).

On their journey from lithospheric source to the hydrosphere, these fluids can undergo many diverse biogeochemical processes; the fluids are acted upon by a suite of chemosynthetic microbes, the results of which are build-ups of methane-derived authigenic carbonate (MDAC) and a large biomass of organisms living directly off, and symbiotically with, the microbes.

2.2.1 Methane generation, migration, and seepage

The fluids exuded from cold seeps are generally of an ambient temperature and largely composed of methane and hydrogen sulphide (Sibuet & Olu 1998). They are generated at various depths in the subsurface and must migrate from their source formation or storage reservoir up to the sea floor to produce a seepage area. Methane gas is the most abundant hydrocarbon found in seabed sediments, and it can be of various origins (Judd 2003). Three types of methane are recognised in

marine sediments: thermogenic, microbial and abiogenic. The mode and depth of formation for each of these is recorded in Table 2.1.

Table 2.1 - Key information on the three types of methane present in seabed sediments. Adapted from Floodgate & Judd (1992), Judd (2003), Campbell (2006), and Judd & Hovland (2007).

Methane Type	Mode of Formation	Formation Depth	$\delta^{13}\text{C}$ Signal
Thermogenic	Traditional hydrocarbon formation method. Requires sedimentary rock containing a high proportion of organic matter; >2% TOC. Thermocatalytic degradation of the organic material produces oil and gas.	Deep burial to reach the oil temperature and pressure window; from 1 to >10 km, dependant on thermal gradient.	-50‰ to -20‰
Microbial	Methanotrophic archaeobacteria decompose organic matter. Requires: anoxic environment, adequate supply of sediment and appropriate organic matter, low temperature (35-45 °C), low sulphate concentration, adequate pore space.	From 2 m to >1 km depth - dependant on thermal gradient. Most pronounced in the upper few metres below seabed.	-110‰ to -50‰
Abiogenic	Methane is produced by the degassing of mafic magmas, cooling of mafic rocks, and serpentinisation in oceanic crust. May also be primordial gases from the mantle. Found at hot hydrothermal and volcanic emanations.	From the mantle to the crust.	-

From source, the methane migrates towards the sea floor as either free gas or methane dissolved in pore fluids. Upwards migration is achieved due to the small molecular size of methane, the low density of both the methane gas and methane-saturated pore water relative to water-saturated sediments, and any overpressure in the sediments (Judd 2003; Judd & Hovland 2007). The fluids migrate via the path of least resistance, typically along steep and dilated fault planes and through sediments characterised by, or containing lenses of, high permeability (Roberts & Aharon 1994; Lewis & Marshall 1996; Gay *et al.* 2007; Crutchley *et al.* in press). The methane must overcome any entrapments encountered on its pathway to the sea floor, such as impermeable formations or sediment lenses, structural traps, and gas hydrates (Gay *et al.* 2007; Judd & Hovland 2007).

A large proportion of the methane produced at depth does not complete the journey to the sea floor. Much of it can be utilised by microbes carrying out the anaerobic oxidation of methane or, once the methane reaches the appropriate temperature and pressure window, captured into gas hydrates (Boetius *et al.* 2000; Judd 2003; Boetius & Suess 2004). Natural seabed seeps occur where methane production rates are high and the fluid flow is concentrated. In effect, the flux rates are then high enough to account for the methane taken up by the sub-seafloor

environment and bacterial communities, with the excess methane then being able to pass through to eventually reach the sea floor.

2.2.2 Anaerobic oxidation of methane (AOM)

Upon nearing the sea floor environment, the concentrated flux of free gaseous methane is acted upon by a consortium of microbes, namely the methanogenic archaea, the sulphate reducing bacteria (SRBs), and the sulphide oxidising bacteria. The complex biogeochemical process that the methanogenic archaea undergo is key to the production of methane-derived authigenic carbonate (MDAC) found at cold seep sites globally. These archaea, often part of a structured consortium with SRBs (Boetius *et al.* 2000), thrive in the shallow subsurface in what is known as the sulphate-methane transition zone (SMTZ) - a window in which methane and sulphate concentration gradients are very sharp (Judd & Hovland 2007).

The methanogenic archaea carry out the anaerobic oxidation of methane (AOM) (Fig. 2.1) to produce energy and organic carbon. The methane is oxidised using sulphate derived from pore-water as the oxidant to produce bicarbonate and sulphur, as well as generating energy for the archaea (Judd & Hovland 2007). Carbon dioxide dissolved in sea water provides a source of carbon for the microbes to then produce organic carbon. As a small concentration of bicarbonate was initially present in the sea water it is now in excess and, promoted by the increased alkalinity due to AOM, precipitates out as calcium carbonate (Boetius & Suess 2004; Campbell 2006; Judd & Hovland 2007). If there is a supply of iron, then this combines with the sulphur to form pyrite. Any extra sulphur forms hydrogen sulphide, enriching the sediments in sulphide (Judd & Hovland 2007).

The precipitated calcium carbonate, or MDAC, occurs where the archaea are carrying out AOM, both within the shallow subsurface sediments and upon the sea floor. The carbonate precipitates in a variety of mineralogies – typically calcite, aragonite, dolomite, and rarely ankerite (also other minerals such as barite can be abundant) - and can form chimneys, tubular concretions, cemented slabs or pavements, and irregular mounds (Burton 1993; Cavagna *et al.* 1999; Stakes *et*

al. 1999; Aiello *et al.* 2001; Boetius & Suess 2004; Campbell 2006). The MDAC typically adopts the negative $\delta^{13}\text{C}$ signal of the parent methane.

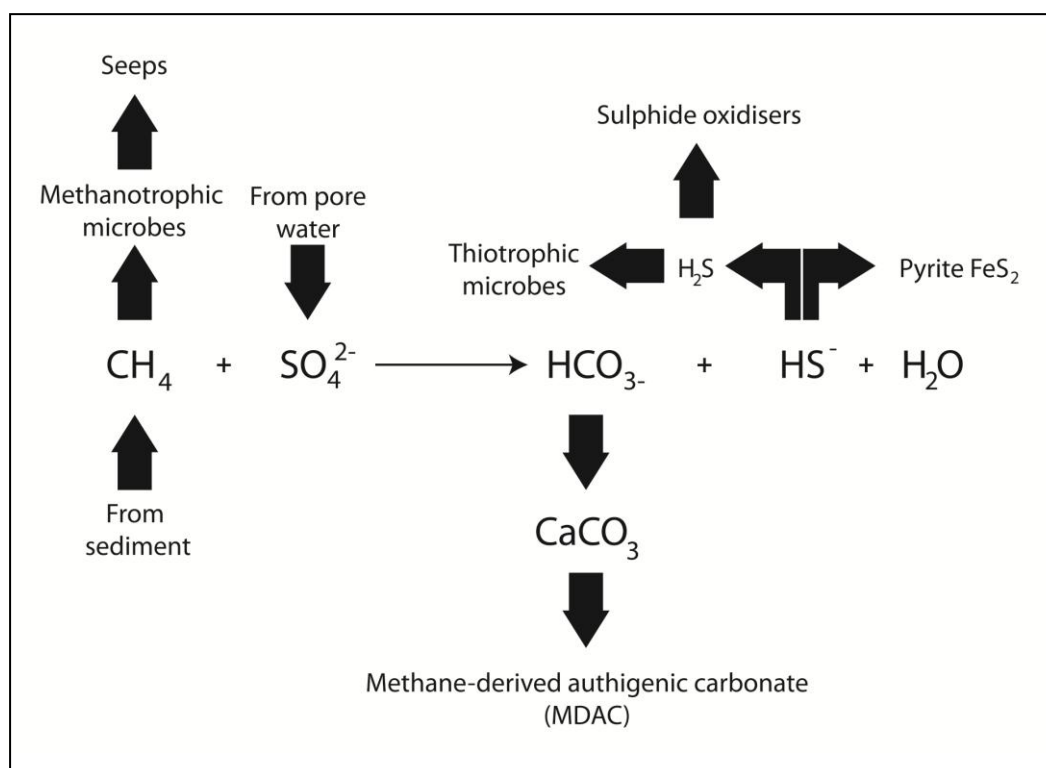


Figure 2.1 - The anaerobic oxidation of methane (AOM). Methane is oxidised by sulphate to produce hydrogen carbonate, hydrogen sulphide, and water. By-products are MDAC and pyrite. Excess methane is utilised by methanotrophs. Hydrogen sulphide reacts with iron to produce pyrite, while any excess is converted to hydrogen sulphide and utilised by sulphide-oxidising bacteria such as *Beggiatoa* sp. Adapted from Judd & Hovland (2007).

In 1999 a research expedition led by Antje Boetius (Max Planck Institute for Marine Microbiology, Bremen, Germany) discovered that the symbiotic microbial consortia consisted of about 100 archaea cells surrounded by multiple layers of SRBs beneath bacterial mats on Hydrate Ridge of the Cascadia Accretionary Wedge, western U.S.A. The average size of each consortium was 1 to 11 μm (Boetius *et al.* 2000). The SRBs surrounding the archaea were consuming the sulphate dissolved in the interstitial pore waters. This discovery provided much needed information on the relationship between SRBs and AOMs and accounted for the high sulphate reduction and methane oxidation rates in the surface sediments at seep sites (Cavagna *et al.* 1999; Boetius *et al.* 2000).

Co-operating with the archaea to utilise the methane resource are the sulphide-oxidising bacteria, or thiotrophs. Sulphide, a product of AOM, is produced at a rate almost equivalent to the concentration of sulphate being consumed (Boetius *et al.* 2000). This provides a reliable base for energy production by the thiotrophs, achieved by the oxidation of the sulphide with the use of an oxidant stored in an internal vacuole (Judd & Hovland 2007). Thiotrophic bacteria are found at the majority of cold seep sites globally, and include very common *Beggiatoa* spp., and the less abundant *Thiothrix* and *Thioplasca* spp. (Judd & Hovland 2007). Mats of the thiotrophic bacteria *Beggiatoa* are a common sight at presently active cold seep sites (Fig. 2.2), thriving at the interface between the sulphide-rich sediments and the aerated sea water. They are typically <1 cm thick, but can be up to 10 cm thick, and they range in colour from white to orange (Boetius & Suess 2004; Judd & Hovland 2007).

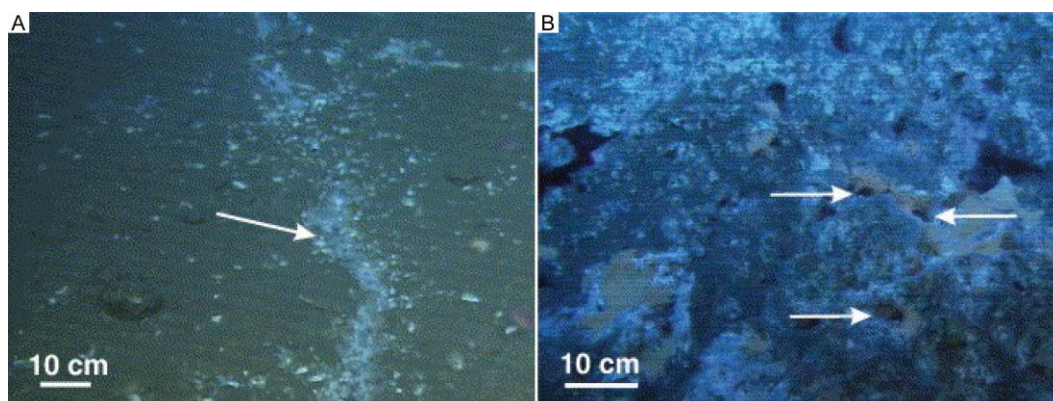


Figure 2.2 – *Beggiatoa* bacterial mats on the sea floor photographed at Hydrate Ridge by a ROV. From Teichert *et al.* (2005). **A:** A crack (arrowed) is lined by bacterial mats and *Calyptogena* clams which are best positioned to utilise the escaping fluids. **B:** Fluid channel openings (marked by arrows) on this MDAC build up are surrounded by light-coloured *Beggiatoa* mats.

2.2.3 Cold seep communities

The microbial communities thriving at cold seep environments are the basis of life around the seep system, acting as the base of the food chain for a vast and unique biota (Levin & Michener 2002). These microbes (the methanotrophic archaea, SRBs, and sulphide oxidisers) are found throughout the methane seep environment. They are present within the sea floor sediment, in the freezing conditions of gas hydrate layers, as microbial mats on the sea floor, within higher

organisms in the community, and in the water column above the seeps (Cavagna *et al.* 1999; Judd & Hovland 2007). The microbes support higher life in the cold seep environment via a symbiotic relationship with other organisms or by the more direct and typical method of predation and energy transfer through the trophic levels of the community. Many of the species are endemic to cold seeps with over 400 named species being identified over the last two decades (Campbell 2006).

The abundance of life around methane seeps would not be as prolific without symbiotic relationships, as many of the macrofauna are invertebrate species and there is simply not enough photoautotrophic organic matter to support this life. So instead, the macrofauna have evolved a symbiotic lifestyle with the chemosynthetic microbes. The macrofauna host the chemosynthetic microbes, either methanotrophs or thiotrophs, which continue to produce organic compounds from the energy gained by reactions with either methane or sulphide (Sibuet & Olu 1998; Campbell 2006). The microbes benefit from living within the macrofauna which provides them with protection, while the macrofauna benefit by utilising any excess organic compounds for growth. Macrofauna which act as a host for symbiotic microbes include members of bivalve families such as the Vesicomidae family of clams, the mussel *Bathymodiolus* of the Mytilidae family (Fig. 2.3), the deep burrowing Solemyidae and Thyasiridae families, and Lucinidae, along with Siboglinid and Pogonophora worms (Fig. 2.3), Cladorhizidae and Hymedesmiidae sponges, and certain gastropods (Campbell & Bottjer 1995; Sibuet & Olu 1998; Boetius & Suess 2004; Campbell 2006; Judd & Hovland 2007).

There is also an entire suite of species living in the methane-seep environment that feed directly on chemosynthetic microbes and their symbiont hosts (Levin & Michener 2002). Many of these species live on the hard surface provided by the MDAC. These species are opportunists; they are utilising this food source, and may be either casual guests of this environment or permanent inhabitants. These members of the community find their food using a variety of methods and include detritivore species such as limpets, gastropods, and crabs, suspension feeders such as sponges, barnacles, bivalves, and corals, and carnivorous predators including

gastropods, asteroids, ophiuroids, echinoids, crustaceans, octopus, and fish (Sibuet & Olu 1998; Levin & Michener 2002; Campbell 2006; Judd & Hovland 2007).

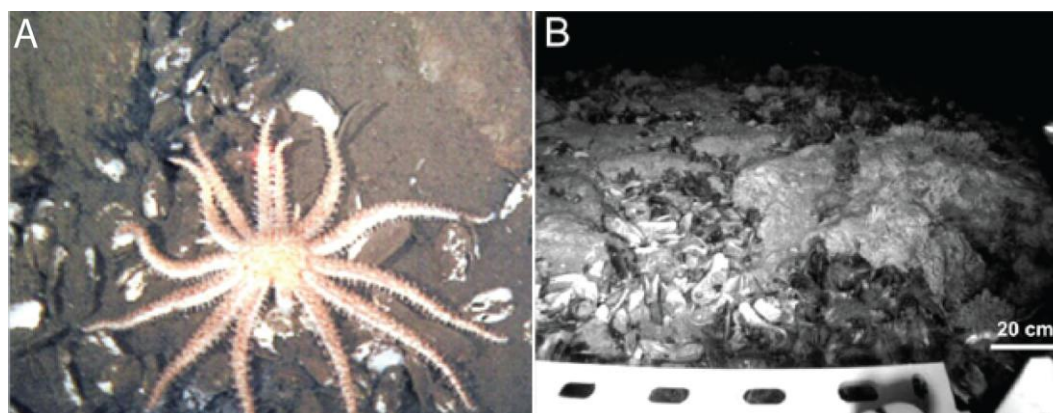


Figure 2.3 - Typical members of the community at cold seep systems. **A:** A star fish sits atop a bed of the vesicomyid clam *Calymene pacifica* at a seep in the Gulf of Alaska. From Levin & Michener (2002). **B:** *Bathymodiolus* sp. mussels on a carbonate mound at the LM-3 seep site on the Hikurangi Margin, offshore New Zealand. From Naudts *et al.* (in press).

The overall biological production and species richness (the number of species at a site) of a single cold seep site is related to environmental conditions such as the intensity and duration of the fluid flow, the flow rate, and the concentrations of methane and sulphide in the fluid being expelled. Therefore, any variations in the fluid chemistry or flux could result in dramatic changes within the community (Sibuet & Olu 1998). Cold seeps are found at a variety of maturation stages based on the communities they support. Those with a high diversity of symbiont-containing and non-symbiont-containing species, the presence of many trophic groups, and an ideal ratio of dead to living organisms are considered mature systems (Sibuet & Olu 1998). These include cold seeps found in the Gulf of Mexico, the Barbados prism, the Peru Trench, and Monterey Bay (Sibuet & Olu 1998).

The biota at each cold seep site is often spatially restricted to form a biological zonation across each site. The distribution of species around a single seep site is found to be related to (a) the spatial variation of fluid supply, (b) the concentrations of methane and especially sulphide, and (c) the substrate (Sibuet & Olu 1998; Boetius & Suess 2004). Research has shown that in areas of high fluid

flow, thiotrophic microbial mats thrive if there is an adequate level of dissolved sulphide, along with the Mytilidae (mussels) which also require a hard ground to attach to and a high concentration of either methane or sulphide (Boetius & Suess 2004). Areas with medium to slow fluid flow rates tend to be dominated by microbial-invertebrate symbiots such as the Vesicomidae clams, and epifaunal species such as Solemyidae and Lucinidae which require soft sediment and an adequate supply of sulphide (Boetius & Suess 2004; Campbell 2006). In exceptionally low fluid flow areas organisms such as the bivalve *Acharax* sp. flourish due to their ability to burrow to great depths in order to access the sulphide zone (Boetius & Suess 2004; Campbell 2006).

When the flux of methane-rich fluid from the subsurface wanes, so too does the overlying thriving community. The chemosynthetic community no longer has an energy supply, and being at the base of the food chain this causes the entire ecosystem to shut down (Cavagna *et al.* 1999). MDAC precipitation comes to a halt, and only the mounds, slabs, and tubes precipitated to date mark the location of the extinct cold seep site.

The ancient analogues of these cold-seep systems archive the once flourishing chemosynthetic-based community living at seep sites. As the organisms die, their remains become enveloped in the ongoing MDAC precipitation. Much is decomposed; however the hard shells, bones, and skeletons can become fossilised within the MDAC and preserved for study and comparison to the modern examples found on the sea floor today (see Section 2.5.2) (Campbell *et al.* in press).

2.3 COLD SEEP RELATED FEATURES

A variety of features, other than seep carbonate mounds, form in conjunction with migrating hydrocarbons through the subsurface and their expulsion at the sea floor. These include gas hydrates, tubular concretions, mud volcanoes, pockmarks, diapirs, and seabed doming. Some of these features are described in this section, along with their association with seabed fluid flow and formation mechanisms.

2.3.1 Gas hydrates

The chemical structure of a gas hydrate is known as a clathrate structure - ‘host’ water molecules are joined together with hydrogen bonding to form a crystal lattice within which is trapped methane gas (Hovland 2005). Without the support of the ‘guest’ gas within the structure, the framework would collapse.

Gas hydrate formation occurs within only a small temperature and pressure window. On and beneath the sea floor is where the highest abundance of methane hydrate on Earth is stored. In the ocean the temperature gets cooler with depth, with a minimum temperature at the sea floor. Beneath the ocean floor the temperature then increases with depth into the Earth. This geothermal gradient, coupled with the increasing lithostatic and hydrostatic pressures with depth, then provide a window in which methane hydrates can form. This window of methane hydrate stability is known as the Gas Hydrate Stability Zone, or GHSZ (Max 2003). Much of today’s deep sea environment has the pressure and low temperatures required for the formation of methane hydrate. Gas hydrates typically form in the sediments of continental margin settings, just beyond the shelf break, in water depths greater than 300 m (Max 2003). They can occur at depths ranging from the near sea floor sediments down to a few hundreds of metres beneath the sea floor (Max 2003; Gorman *et al.* 2004). Deep lakes and Arctic environments associated with permafrost (Collett & Dallimore 2003) are also capable of hosting gas hydrates within sediments (Max 2003).

Gas hydrates are characterised as “dynamic steady state systems dependant on methane flux from below” (Gorman *et al.* 2004). It is thought that due to the abundance of advecting methane-rich fluids in convergent margins, this is where up to 65% of oceanic methane hydrates are formed (Max 2003). As the rising gas enters the GHSZ, it is pulled into this carbon sink to be locked up as solid gas hydrate. A number of gas hydrate morphologies have been identified. Commonly, methane hydrate crystals will fill the pore spaces of sediments, severely reducing porosity as they act as a cement. But they can also form in secondary pore spaces such as a fill along joints and as lenticular bodies along bedding planes, as porphyraceous inclusions, as highly brecciated bodies, and as hydrate rocks (Fig. 2.4) (Hovland 2005; Judd & Hovland 2007). Any free gas able to penetrate through this zone of gas hydrate is then able to continue its journey to the sea

floor, perhaps to form a cold-seep environment. Gas hydrates have been discovered to form in association with active cold-seep systems at the sea floor (Bohrmann *et al.* 1998) and their presence has also been interpreted within ancient seep carbonate deposits (Bojanowski 2007).



Figure 2.4 - Gas hydrate at the sea floor under a sediment cap, at Blake Ridge, eastern USA. Scale bar is 5 cm. From Van Dover *et al.* (2003).

As the gas hydrates often form a highly impermeable layer within the sedimentary sequence, it is typical for a significant quantity of free gas to build up below the GHSZ. This gives rise to the most common form of indirect interpretation of gas hydrate distributions and concentrations – the bottom simulating reflector (BSR) (Fig. 2.5). The presence of this gas within the strata beneath the BSR, along with water which has a relatively low acoustic velocity of 1.5 km/s, causes it to have very low seismic velocities (Hovland 2005). Due to the contrast between the high velocity layer of gas hydrate and the low velocity underlying strata a very strong bottom simulating reflection, or BSR, is generated. As the gas hydrate zone is determined by temperatures and pressures, this causes it to be at a uniform level below the sea floor. As a result, this strong seismic reflection found at the base of the gas hydrate zone is effectively parallel to the sea floor, hence the term ‘bottom

simulating' reflector. However, by no means is the BSR a definitive indicator of the presence of gas hydrate; the two are thought to be only indirectly related.

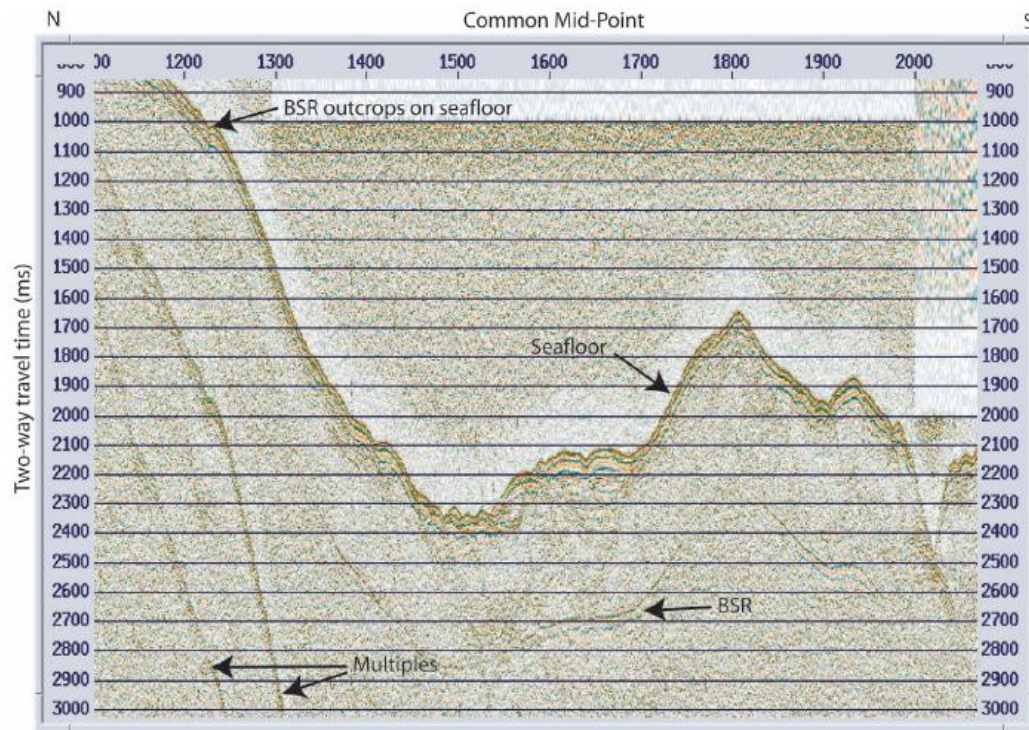


Figure 2.5 – Seismic line 61 of GeodyNZ2 along the Hikurangi Margin showing the sea floor and a strong BSR which eventually terminates on the sea floor. The BSR outcrops at approximately 1 s two-way travel time, corresponding to approximately 750 m water depth. From Gorman *et al.* (2004).

In addition, the identification of gas hydrates in the subsurface can also be aided by known zones of high methane flux through the sea floor sediments and into the water column. Gas is lost from the gas hydrate reservoir at the top of the GHSZ due to its instability in the lower temperatures and pressures at that location. This results in the need for an inbound flux of free gas in order to maintain the volume of solid gas hydrate, and also a steady supply of gas migrating up to the sediment-water interface. The link has therefore been made to focus gas hydrate investigations to regions of high methane-rich fluid flow to the sea floor (Gorman *et al.* 2004).

Studies focused in the East Coast Basin of New Zealand have aimed at assessing the size of the gas hydrate reservoir present there, and at identifying any possible

‘sweet spots’ which are regions of the sea floor which exhibit a high fluid flow and seismically show a strong BSR, indicative of a large volume of free gas (Gorman *et al.* 2004). The gas hydrate province of the Hikurangi Margin is estimated to cover approximately 50,000 km² (Henry *et al.* 2009). It is thought that up to 10% of this province could potentially house sweet spots. This volume is likely to be made up of numerous individual sweet spots, roughly 12 to 24 km² in size (Gorman *et al.* 2004).

2.3.2 Tubular concretions

Tubular concretions have been found associated with hydrocarbon seeps worldwide, with both modern and ancient analogues documented (Fig. 2.6). They are suggested to represent the subsurface plumbing system of sea floor hydrocarbon seeps, with fluids migrating through the central conduit of the cemented concretion.

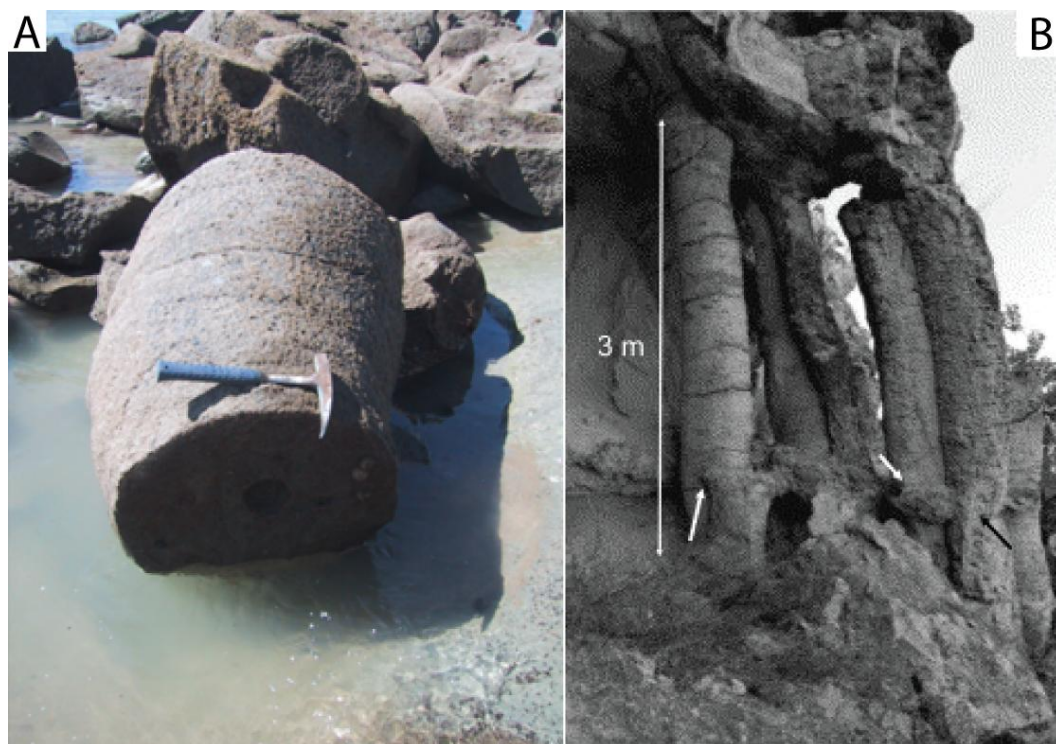


Figure 2.6 – **A:** Example of common tubular concretions littering the shore platform at Whangaehu, New Zealand. From Nyman (2009). **B:** Some of the massive columnar concretions in Varna, northeast Bulgaria. From De Boever *et al.* (2006b).

The tubular concretions can come in a range of morphologies including pipe/cylindrical, bulbous, mushroom, doughnut, corkscrew/spiral, mounded, and conical, and can have either straight or torturous inner conduits (Diaz-del-Rio *et al.* 2003; Nyman 2009). Tubes can reach exceptional lengths – they are recorded to be over 8 m in Bulgarian examples and more than 10 m in New Zealand, with their true lengths being limited by outcrop exposure (De Boever *et al.* 2006a; Nyman 2009).

Like other hydrocarbon seep phenomena, tubular concretions have been reported at modern submarine seep sites as well as ancient ones. In the “bubbling reefs” of Kattegat, Denmark, the first report of tubular concretions occurring at a modern seep site was made by Jensen *et al.* (1992). Some of the literature on the many ancient examples of tubular concretions include: (1) Diaz-del-Rio *et al.* (2003) and Leon *et al.* (2006) in the Gulf of Cadiz; (2) Orpin (1997) and Nyman (2009) in New Zealand; (3) Stakes *et al.* (1999), Aiello *et al.* (2001), and Aiello (2005) in the onshore and offshore of Monterey Bay, California; and (4) De Boever *et al.* (2006a, b) in Bulgaria.

In New Zealand, Orpin (1997) documented the presence of exhumed tubes on the upper continental slope off the Otago Shelf (Fig. 2.7). These tubes, with a maximum radiocarbon age of 33,000 yr B. P., were riddled with encrustations and borings signifying the time spent exposed on the sea floor (Orpin 1997). Nyman (2009) has compiled a study on four sites in onshore New Zealand featuring ancient (Miocene to Pliocene) tubular concretions, including at Cape Turnagain and East Cape in the East Coast Basin.

2.3.3 Mud volcanoes

As defined by Judd and Hovland (2007), a mud volcano is “a topographically expressed surface edifice from which solid material (at least mud, but generally also breccias comprising clasts of solid rock in a mud matrix) and fluid (water, brine, gas, oil) flow or erupt.” The term ‘shallow’ can be applied to mud volcanoes if they have formed specifically within near-seabed strata. Mud volcanoes are found globally, typically in tectonic compression belts and accretionary wedges, both onshore and offshore in shelf to slope/rise water

depths. However, the major characteristic of provinces supporting mud volcanoes and diapirs is a thick (several km) sedimentary sequence (Judd & Hovland 2007).

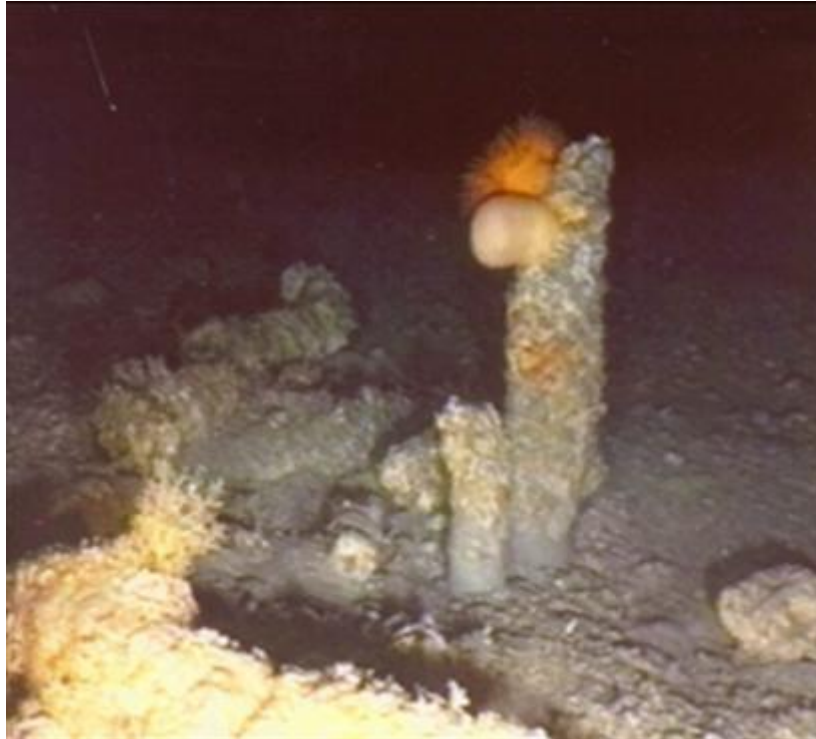


Figure 2.7 - Tubular concretions surrounded by scattered carbonate concretionary debris on the seabed off Otago, South Island, New Zealand. The taller of the two is 50 cm high. These are relict features of past seabed fluid flow, now exhumed and subject to encrusting and boring biota. From Orpin (1997).

Mud volcanoes are associated with cold seeps as they too are driven by the expulsion of hydrocarbon fluids from depth, albeit with typically a much higher and spontaneous fluid flux. They are sites of active geological and geochemical processes and are also an oasis of chemosynthetic-based life, very similar to that of cold-seep environments (Milkov *et al.* 2004; Olu-Le Roy *et al.* 2004). Geochemistry, temperatures, gas hydrates, and biological processes are zoned around the vent site, controlled by the concentration of expelled fluids and sediments (Milkov *et al.* 2004; Olu-Le Roy *et al.* 2004).

As discussed by Leon *et al.* (2006), mud volcanoes can form in conjunction with other sea-floor fluid-flow features such as MDAC mounds and pockmarks. MDAC slabs and crusts are even found on top of mud volcanoes, formed during

latent fluid flow episodes (Leon *et al.* 2006). Deep water mud volcanoes can also occur in conjunction with gas hydrates due to the transportation of methane-rich fluids into the gas hydrate stability zone via the volcano conduit (Milkov 2000).

The size and morphology of a mud volcano is dependent on the volume and nature of its products (e.g. viscosity, shear strength, and grain size), the style and size of the eruptions, and extrusion mechanisms such as conduit width and reactivation period (Leon *et al.* 2006; Judd & Hovland 2007). The typical morphology of a mud volcano is the classical conical hill with summit crater; however, they also form as complex multi-coned structures, domes, flat plateau, depressions, and calderas (Leon *et al.* 2006; Judd & Hovland 2007). Larger structures can have multiple craters or multiple active vents with built-up cones/gryphons upon the summit plateau (Hovland *et al.* 1997), each producing its own flow of eruptive products (Fig. 2.7). Growth of the structures is achieved via accretion of eruptive products expelled from the vent(s), debris slides from higher up the edifice and, in the case of submarine mud volcanoes, these eruptive products are often intercalated with deep-sea sediment deposits (Olu-Le Roy *et al.* 2004; Leon *et al.* 2006).



Figure 2.8 - Five of the approximately 20 small cones (or gryphons) scattered over an area 50 m by 100 m on the summit plateau of the Dashgil mud volcano, Azerbaijan. Note backpack for scale. From Hovland *et al.* (1997).

The volume of hydrocarbon gases being emitted by mud volcanoes globally is being studied, and it is debated as to whether these fluid flow features have a significant effect on Earth's climate (Kopf 2003; Milkov & Etiope 2005). Some argue that the gas flux from mud volcanoes supplies carbon only to the oceanic carbon pool and not the atmosphere due to the high dissolution rates of methane in the water column (Milkov *et al.* 2004).

2.3.4 Pockmarks

Pockmarks are shallow depressions in the sea bed, typically only a few metres deep and several tens of metres in diameter (Judd & Hovland 2007). They are found in all oceanic settings and also lakes, and are identifiable with ROVs and through multibeam echo-sounder, side-scan sonar, and seismic imaging. Judd & Hovland (2007) give a comprehensive review of pockmark research.

Pockmarks are not necessarily just circular depressions, in soft seafloor sediments. More typically they are elongate depressions with undulating floors, and can also form with perimeters featuring lobes and indentations, as composite pockmarks, troughs, asymmetric pockmarks, amalgamated pockmarks, and in strings or chains (Fig. 2.9) (Hovland & Judd 1988; Hovland 2003; Judd & Hovland 2007). Pockmarks range in size from small “unit” pockmarks (<5 m in diameter) (Fig. 2.9) to anomalously large “giant” pockmarks up to 500 m in diameter and 20 m deep (Hovland 2003; Judd & Hovland 2007). They seldom occur singularly, but are much more commonly found in localised groups or fields of pockmarks. These fields can be of very high pockmark density – the Norwegian Sea hosts pockmark fields with up to 60 pockmarks per km², covering approximately 30% of the sea floor, although pockmark size and density varies laterally (Judd & Hovland 2007).

The origin of pockmarks remains somewhat debated, although it is widely accepted that they do indeed form due to fluid escape at the seabed and consequential erosion of seabed sediments. Evidence supporting this suggestion includes gas at depth in the sediments beneath pockmarks, indications of active gas seepage including gas plumes rising through the water column, chemosynthetic microbes, methane anomalies in the water, and the common

association of other fluid flow features with pockmarks (Judd & Hovland 2007). Pockmarks commonly feature slabs, crusts, and mounds of MDAC within the depression, for example the TASYO pockmark field in the Gulf of Cadiz also exhibits both mud volcanism and MDAC mounds (Hovland *et al.* 2005; Leon *et al.* 2006; Mazzini *et al.* 2006; Judd & Hovland 2007). Hovland *et al.* (2005) suggest a pockmark formation process based around rising gases causing initial seabed doming, micro-seepage of gasses at the sea floor, and MDAC formation in the subsurface sediments. The continual precipitation of MDAC, with time, blocks the pathway of the rising fluids resulting in a pressure build up and eventual abrupt brecciation of the MDAC to force the MDAC remains, sediment, and gasses upwards, so causing localised erosion of the sea floor and formation of a depression (Hovland *et al.* 2005).

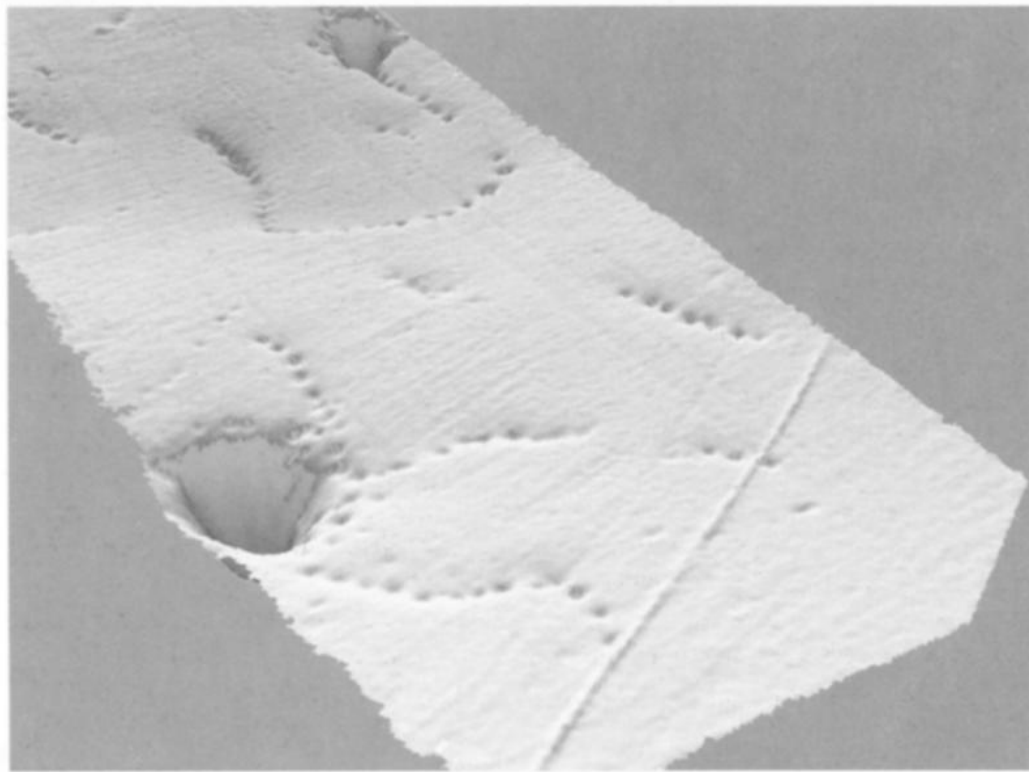


Figure 2.9 - A high-resolution bathymetry image of two types of pockmark in 320 m water depth off Norway, collected with an ROV-mounted multibeam bathymetry system. The image shows many strings of unit pockmarks, as well as two 'normal' pockmarks (the largest pockmark is approximately 5 m deep and 40 m wide). Note the 20-inch (50.8 cm) gas transport pipeline (the Haltenpipe pipeline) at the lower right. From Hovland (2003).

2.4 COLD SEEP DISTRIBUTION

2.4.1 Global occurrences

In recent years, the recognition of, and research on, cold seep systems, both modern and ancient, has intensified. They have been identified at all latitudes and in a number of geotectonic settings (Fig. 2.10). Campbell (2006) synthesised and reviewed much of this research. From this, it is evident that cold seeps most commonly form in convergent margin settings, however, they are also found at transform plate boundaries and on passive margin shelves (Suess 2010). It is the compressive tectonic regime which instigates the hydrocarbon seep system, as intensive faulting (providing fluid pathways) and over-pressuring of sediments (initiating fluid migration) are most typical in these settings.

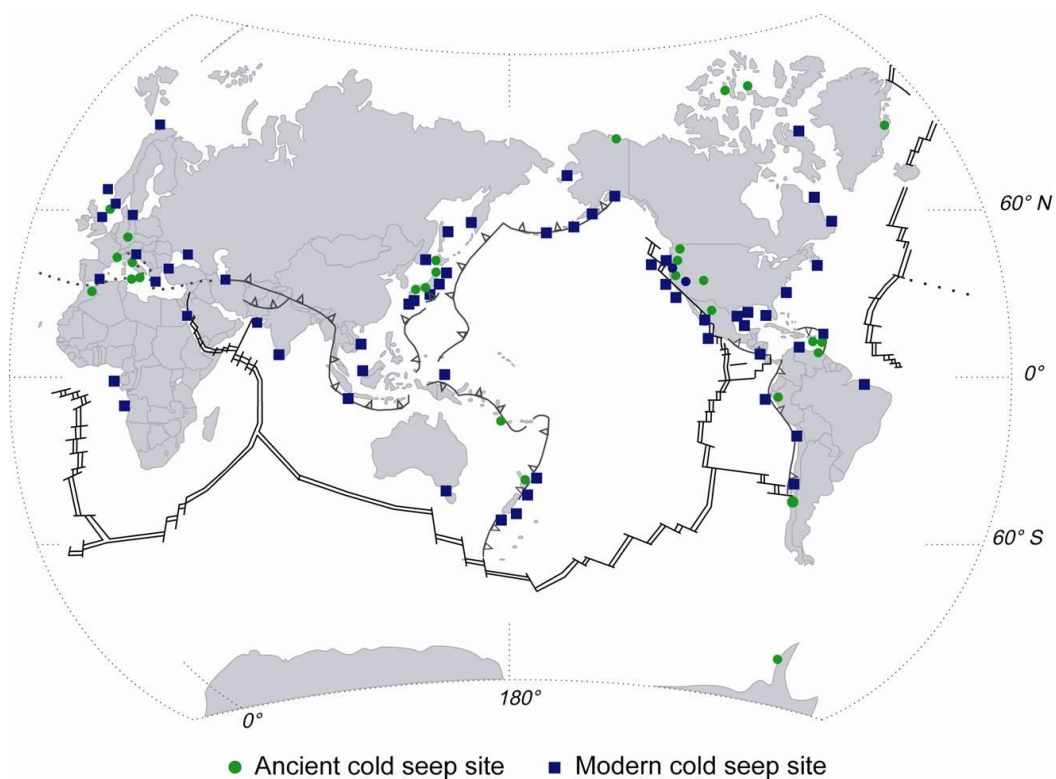


Figure 2.10 - The global distribution of modern and ancient cold seeps. Adapted from Campbell (2006).

Globally, Campbell (2006) identified 46 regional groupings of hydrocarbon seep occurrences, along with their associated chemosynthetic communities. In

comparison, only 13 hydrothermal vent regions were classified. Of these 46 seep regions, 33 are situated in convergent margin geotectonic settings. This includes the New Zealand Miocene East Coast (Campbell *et al.* 1999; Campbell 2006; Ewen 2009; Nyman 2009); western North America (Squires & Goedert 1991; Campbell 1992; Goedert & Campbell 1995; Bohrmann *et al.* 1998; Campbell *et al.* 2002; Goedert *et al.* 2003; Schwartz *et al.* 2003); Italian Apennine seeps of Miocene age (Conti & Fontana 1999, 2002, 2005; Peckmann *et al.* 1999, 2004; Conti *et al.* 2007, 2008; Terzi *et al.* 1994; Taviani 2001); and Japan's modern examples (Kanie 1996; Han *et al.* 2008).

Examples of cold seep systems in other geotectonic settings include extensional basins in Nevada (Torres *et al.* 2003) and southeast France (Gaillard *et al.* 1992; Peckmann *et al.* 1999), and passive margins in Greenland (Kelly *et al.* 2000), Germany (Peckmann *et al.* 2001a), and the Gulf of Mexico (Roberts & Aharon 1994; Orcutt *et al.* 2008).

2.4.2 New Zealand occurrences

Along the modern Hikurangi Margin, within New Zealand's offshore East Coast Basin, lies a field of cold seep carbonate deposits (Lewis & Marshall 1996; Klaucke *et al.* in press; Netzeband *et al.* in press). The locations of some of these sites are illustrated on Figure 2.11. These deposits have formed due to currently active hydrocarbon seepage at the sea floor. Other active fluid flow features are also present, including submarine pockmarks, gas plumes, mud volcanism, and many onshore oil and gas seeps (Fig. 3.6) (Ridd 1970; Nelson & Healy 1984; Barber *et al.* 1986; Pettinga 2003)

Lewis and Marshall (1996) acknowledged 13 offshore methane cold seep sites from New Zealand's East Cape south to Fiordland, all of which exhibited signs of active fluid flow, chemosynthetic fauna, carbonate chimneys and crusts, and plumes of low density fluid (Fig. 2.12). Lewis & Marshall's paper was fundamental to some of the subsequent modern seep carbonate related studies (Orpin 1997; Nyman 2009; Barnes *et al.* in press; Campbell *et al.* in press; Crutchley *et al.* in press; Netzeband *et al.* in press) due to its descriptions and discussions on the seep faunas, MDAC deposits, and other indicators of fluid

flow. Several studies in recent years have also focused on the gas hydrates and fluid flow conduits present along the margin and implications for sediment stability and sediment erosion (Gorman *et al.* 2004; Pecher *et al.* 2004, 2005; Greinert *et al.* in press).

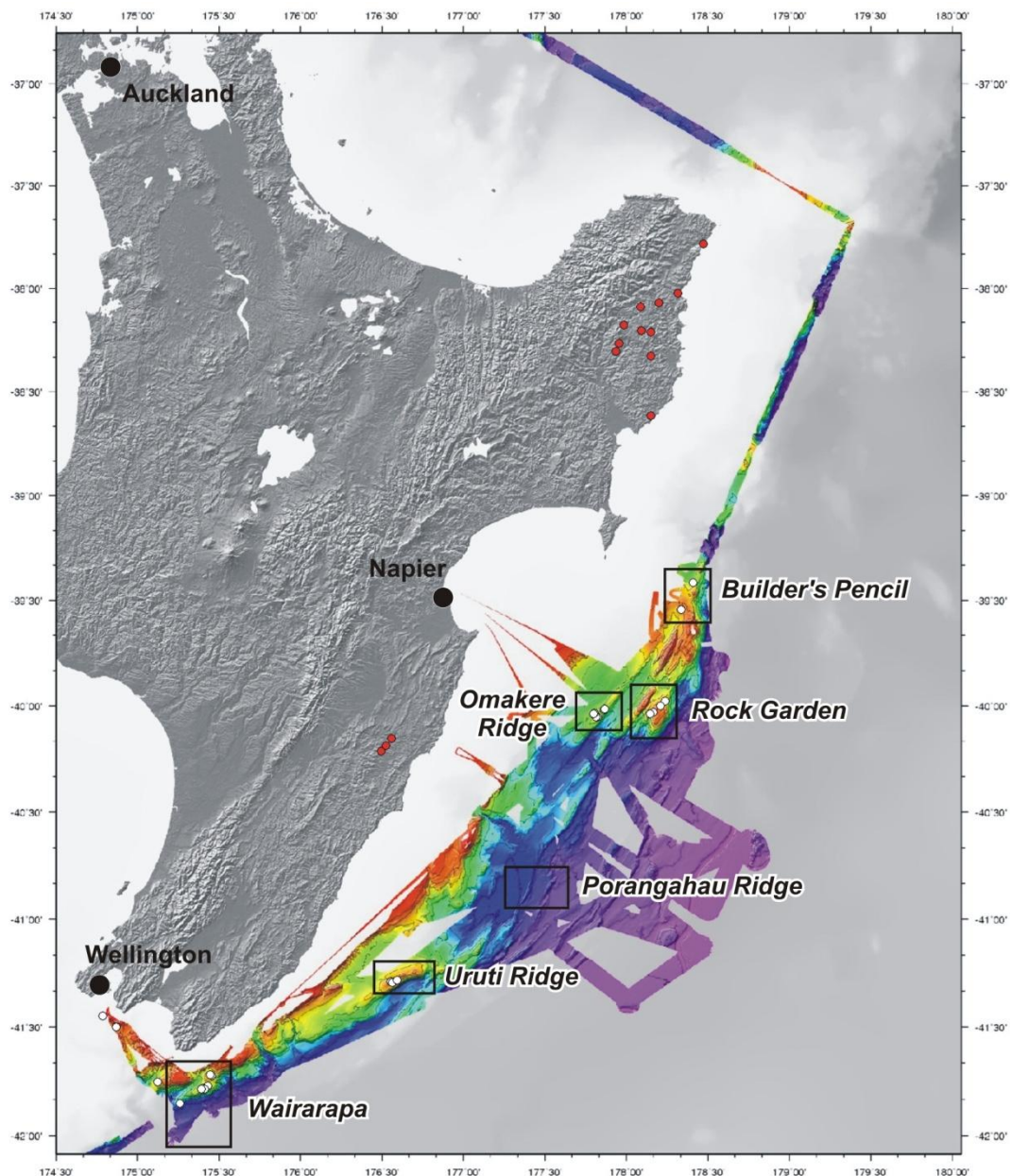


Figure 2.11 – Map of the North Island and the Hikurangi Margin bathymetry illustrating the locations of some of the modern offshore cold seep carbonate deposit sites which were investigated on the NIWA Cruise TAN0616. Red dots onshore indicate ancient seep carbonate occurrences. From Ewen (2009).

Ancient analogues to cold seep systems are found in the onshore East Coast Basin. McKay (1877a, b) was the first to record the occurrence of unusual carbonate mounds within bathyal mudstone in New Zealand, and further descriptions of these ‘unsusal’ ancient carbonates were made by Henderson & Ongley (1920) and Lillie (1953) for the Raukumara region and southern Hawke’s Bay region, respectively. Subsequently, Ongley & Macpherson (1928), Mazengarb & Francis (1985), and Kamp & Nelson (1988) also described these generally small, localised, atypical outcrops of limestones and gave them various names and suggested formation mechanisms. With the increasing knowledge about cold seep systems and their products in the last decade, it became recognised that these outcrops represented ancient analogues of cold seep carbonate systems (Lewis & Marshall 1996; Campbell *et al.* 1999, 2008).

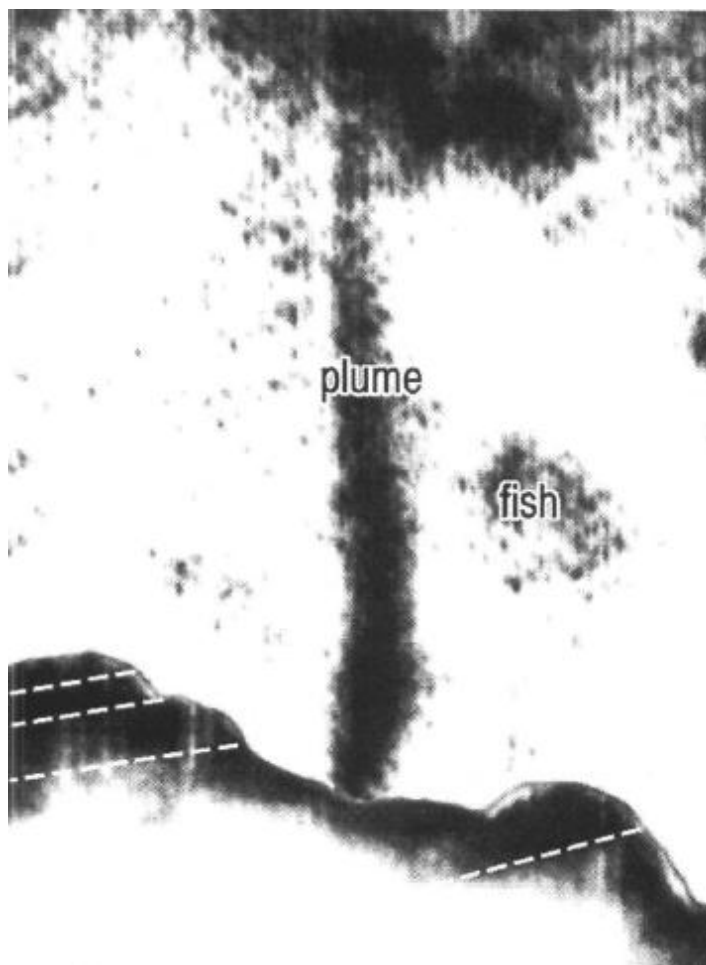


Figure 2.12 - A strongly reflective plume, thought to be methane-rich water, rising up to over 250 m from the sea floor. This image was taken from a fish-finding sonar in 900 m water depth on a slope ridge offshore Hawke’s Bay. From Lewis & Marshall (1996).

A synthesis of the research carried out on New Zealand's Miocene seep-carbonate deposits by Campbell *et al.* (2008) refers to 14 of the 16 known deposits (Table 2.2). These come in the form of carbonate buildups of varying morphology and thickness (Fig. 2.13). Each site is unique, displaying varying concentrations of fossilised cold-seep biota, intraclasts, and vein networks, and are found to exhibit multiple phases of mineral precipitation and varying degrees of brecciation (Campbell *et al.* 2008). Tubular concretions are also present at two of the seep carbonate sites (Rocky Knob and Tauwhareparae), as well as elsewhere without overlying seep deposits in the East Coast Basin (Cape Turnagain and East Cape), and represent focused fluid migration pathways through the paleo-subseafloor sediments (Nyman 2009).

Table 2.2 – Locality details for the 16 known ancient seep carbonate sites in the East Coast Basin, including the 14 sites of Campbell *et al.* (2008).

Site	Code	NZMS sheet	Grid Reference
<u>Northern sites</u>			
Bexhaven	BXH	Y16	2955810E 6333127N
Karikarihuata Stream	KKH	Y16	2965700E 6335100N
Moonlight North	MLN	Y16	2943343E 6314003N
Puketawa	PKT	Y16	2955655E 6320635N
Rocky Knob	RKN	Y16	2941200E 6310300N
Tauwhareparae	TWP	Y16	2946283E 6324166N
Totaranui	TTN	Y16	2960605E 6319160N
Turihaua	TRH	Y18	2958065E 6274500N
Waiapu	WPU	Z15	2991680E 6365369N
Waikairo	WKR	Y16	2960020E 6306500N
Waipiro Stream	WPR	Z16	2976260E 6339430N
<u>Southern sites</u>			
Haunui	HA	U23	2807264E 6104383N
Ngawaka	NG	U23	2803956E 6107494N
Ugly Hill	UH	U23	2809511E 6107680N
Wanstead	WA	U23	2813333E 6111068N
Wilder Road	W	U23	2806458E 6103321N

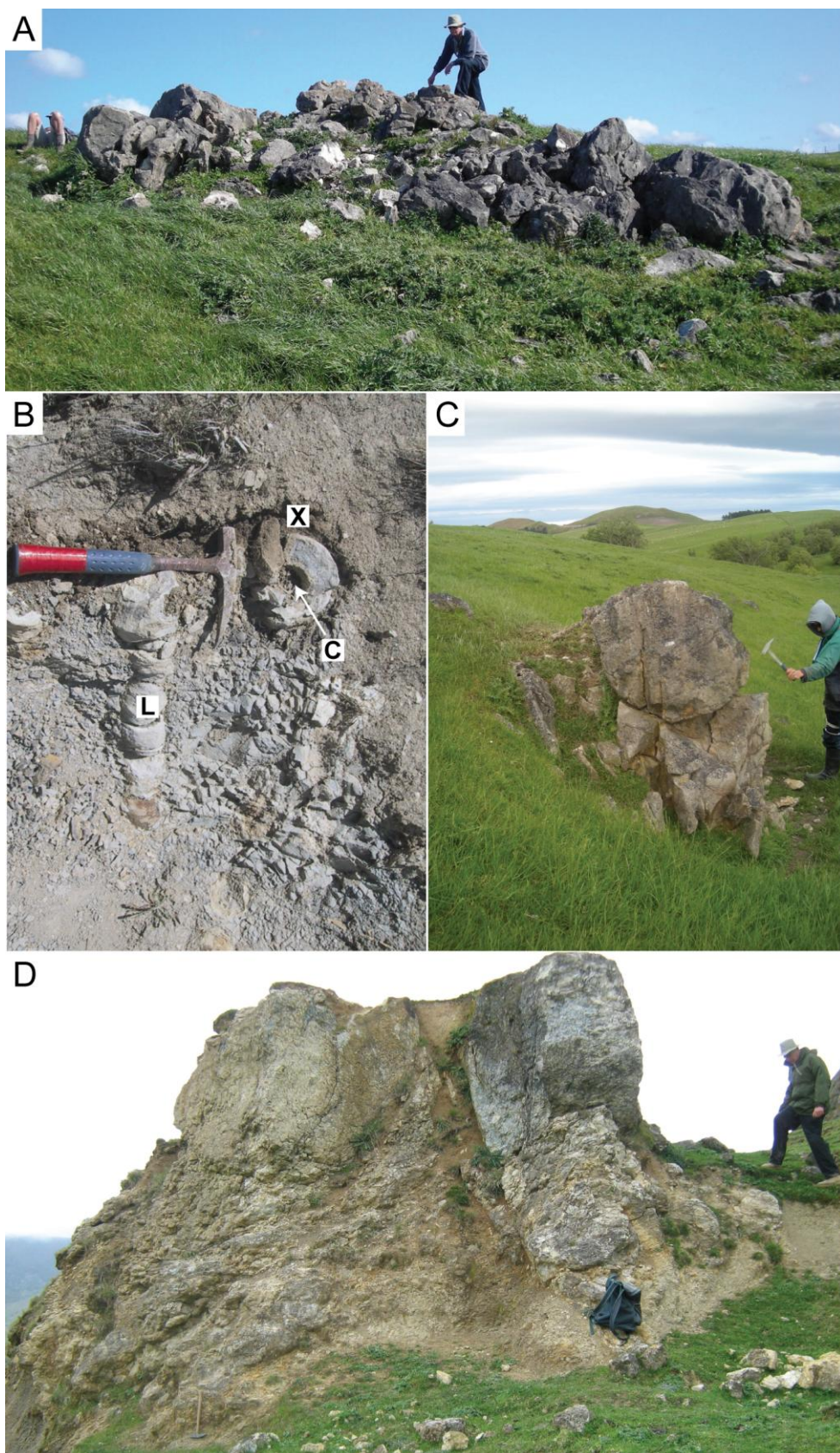


Figure 2.13 - A selection of Miocene seep carbonate outcrops in North Island, New Zealand. **A:** One of the eight outcrops at Wilder Road, southern Hawke's Bay. **B:** Tubular concretions in mudstone at Mimi, north Taranaki, seen in longitudinal section (L) and cross section (X) with a central conduit (C). **C:** One of the many small outcrops at Ngawaka East, southern Hawke's Bay. **D:** Part of the Tauwhareparae outcrop, Raukumara Peninsula.

2.5 IDENTIFYING COLD SEEP (PALEO)ENVIRONMENTS

There are many characteristics of cold seep environments that allow them to be recognised, both for modern and ancient deposits. Some of these characteristics can be visible in the field; however, others require sampling and laboratory analysis to confirm the rock as a cold seep MDAC. This section will expand on some of these characteristics and their association with cold seep identification.

2.5.1 Geometry/morphology and structure

As earlier elucidated (see Section 2.2.2), MDAC forms in a range of morphologies on and near below the sea floor due to the escape of methane-enriched fluids and the presence of chemosynthetic microbes. The MDAC deposits include irregular mounds of various sizes, slabs, pavements, and sometimes tubular concretions (Conti *et al.* 2007; Judd & Hovland 2007). In some cases, the positioning of MDAC mounds can be intimately related to faults, outcropping strata, or other structural features of the host geology (Conti & Fontana 2005).

The precipitation of MDAC is spatially restricted by the size of the seep and the fluid flux. This flux is often reflected in the morphological features and mineralogy of the precipitates, and the production of different facies (Conti & Fontana 2005; Conti *et al.* 2007). Sites with more vigorous fluid flow are often dominated by breccias, chimneys, mud volcanoes and an abundance of fibrous cements; whereas, those experiencing diffuse flow are more likely to produce lenses, slabs, and nodules with a dominance of detrital micarb (Fig. 2.14) (Campbell 2006; Peckmann *et al.* 2009). A single seep site can have an array of these features distributed along the gradient from vigorous to weak fluid flow. On larger carbonate mounds breccias can form - as the mound begins to erode, clasts of carbonate tumble down to the lower slopes to be encompassed by the host formation (talus breccias) or re-cemented back into the mound (monomictic breccias) as is commonly identified in Miocene seep carbonate deposits from the northern Apennines, Italy (Conti & Fontana 2005).

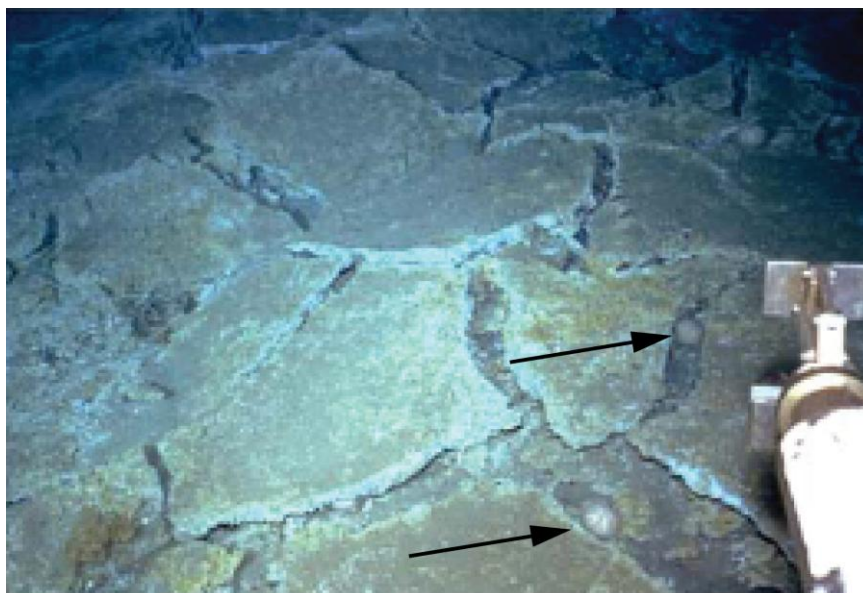


Figure 2.14 - Carbonate slabs and sea urchins (arrowed) on the sea floor near the Olimpi Mud Volcano field on the Mediterranean Ridge. From Olu-Le Roy *et al.* (2004).

Cold seeps systems, both modern and ancient, can often be found in association with other fluid flow features (see Section 2.3). These include tubular concretions, mud volcanoes and, for the modern systems, also pockmarks, gas hydrates, gas plumes and flares, diapirs, and seabed doming (Bohrmann *et al.* 1998; Leon *et al.* 2006; Mazzini *et al.* 2006; Nyman 2009). Seafloor erosion, in the form of slumps and slides, is also a common feature in the vicinity of active cold seep systems. This is suggested to be an impact of the typically present gas hydrates in the subsurface to surface sediments near cold seep sites, as their dissociation causes a loss of sediment consolidation (Pecher *et al.* 2005; Conti *et al.* 2007; Ellis *et al.* in press).

There are several features of the carbonate deposits themselves, easily visible in the field, which imply their cold seep origin. Cold seep carbonates are highly cemented and therefore resistant to weathering - they often remain as protruding mounds in an otherwise eroded landscape due to this characteristic. Talus or slope breccias are often revealed on the lower slopes of larger carbonate mounds.

Brecciation of the MDAC is a feature seen in both modern and ancient deposits. This can be either monomictic (composed of MDAC clasts) or polymictic (made up of a combination of MDAC clasts with older extra-formational clasts)

depending on the degree of disruption to the seep system (Conti & Fontana 1999). Monomictic breccias result from the explosive release of methane, often due to self-sealing of the focused flow or a rapid increase in seeping fluids owing to external instability episodes, while polymictic breccias are suggested to be related to diapiric and liquefaction processes due to overpressured sediments at depth (Conti & Fontana 1999, 2005). Brecciation structures are typically ‘healed’ by later stage calcite phases, to reconstruct an intact rock mass once again. In outcrop, these brecciation facies are typically identified without problem (Fig. 2.15A). The chaotically dispersed and typically angular clasts, combined with the calcitic inter-clast vein networks, make for a unique facies. Vein networks can range from millimetres to centimetres in width, can be extremely non-systematic, anastomosing, converging, radial, and often stand proud from the MDAC matrix due to their resistance to weathering (Fig. 2.15B) (Conti & Fontana 2005).

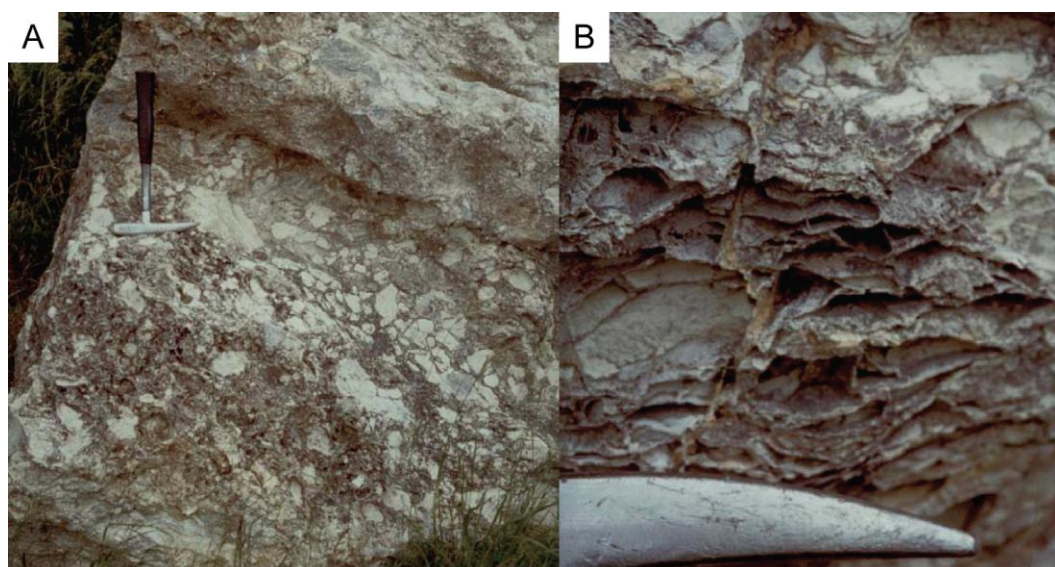


Figure 2.15 – Veined and brecciated facies in Miocene outcrops of the northern Apennines, Italy. From Conti and Fontana (2002). **A:** A large seep carbonate boulder exhibits intense and coarse brecciation. **B:** A complex network of calcitic veins stand proud from the MDAC.

2.5.2 Biotic components

Modern hydrocarbon venting sites on the sea floor have been described by Carney (1994) as deep sea oases. This analogy arises from the severe contrast in biomass between the chemosynthetic communities and the normal benthic fauna of the

Gulf of Mexico. These communities thrive on the methane and sulphide arising out of the seep (see Section 2.2.3) which provide them with energy and organic carbon for growth (Judd & Hovland 2007). The total biological production at cold seep sites is closely correlated to the intensity of the fluid flow (Sibuet & Olu 1998).

The base of the food chain is the chemosynthetic microbes. Higher organisms in the community interact symbiotically with these microbes, or consume them, to spread the energy throughout the food web. The most typical and abundant symbiotic organisms found at cold seep sites include the Siboglinidae family of tube worms, bivalve families such as Vesicomidae, Mytilidae, Solemyidae, Thyasiridae, and Lucinidae, and certain sponge and gastropod families (Campbell & Bottjer 1995; Sibuet & Olu 1998; Boetius & Suess 2004; Campbell 2006; Judd & Hovland 2007). Non-symbiotic species are also abundant in the cold seep environment. These species are opportunists, and range from detritivores and suspension feeders to carnivorous predators (Judd & Hovland 2007). Sibuet and Olu (1998) compiled the research findings of cold seep biota to collectively document a total of 211 species of ‘known or assumed symbiont-containing’ and ‘non-symbiotic’ fauna.

Many of the species common to active cold seep environments are also expressed in ancient cold seep deposits (Fig. 2.16). Through genetic studies, links can be made between the biota of the ancient and modern seep sites. Often, the fossils are key to the correct interpretation of the deposit as being of cold seep origin. Shell material is a common fossil occurrence in ancient cold seep carbonates, albeit it is typically recrystallised during diagenesis. Table 2.3 shows the original mineralogy of some taxa commonly found within cold seep carbonate deposits. This includes many species of bivalves, which can be both whole and fragmented, that typically occur in shell beds and seldom individually, and somewhat less abundant gastropod shells. The presence of fossilised corals and worm tubes is also customary in the ancient MDAC deposits, typically in dense accumulations. Burrows and borings in MDAC are a regular feature of the cold seep environment also carried through to ancient deposits, although often somewhat difficult to identify. Even microbial fabrics have a confirmed presence in ancient cold seep deposits, in the form of clotted micrite concretions, biofilms lining conduits and

cavities, complex alveolar textures, and endolithic filaments (Barbieri *et al.* 2004; Barbieri & Cavalazzi 2005). The biological zonation of seep fauna (see Section 2.2.3) can be applied to ancient cold seep deposits to allow further insight into the fluid flow regime of the paleo-seep system.

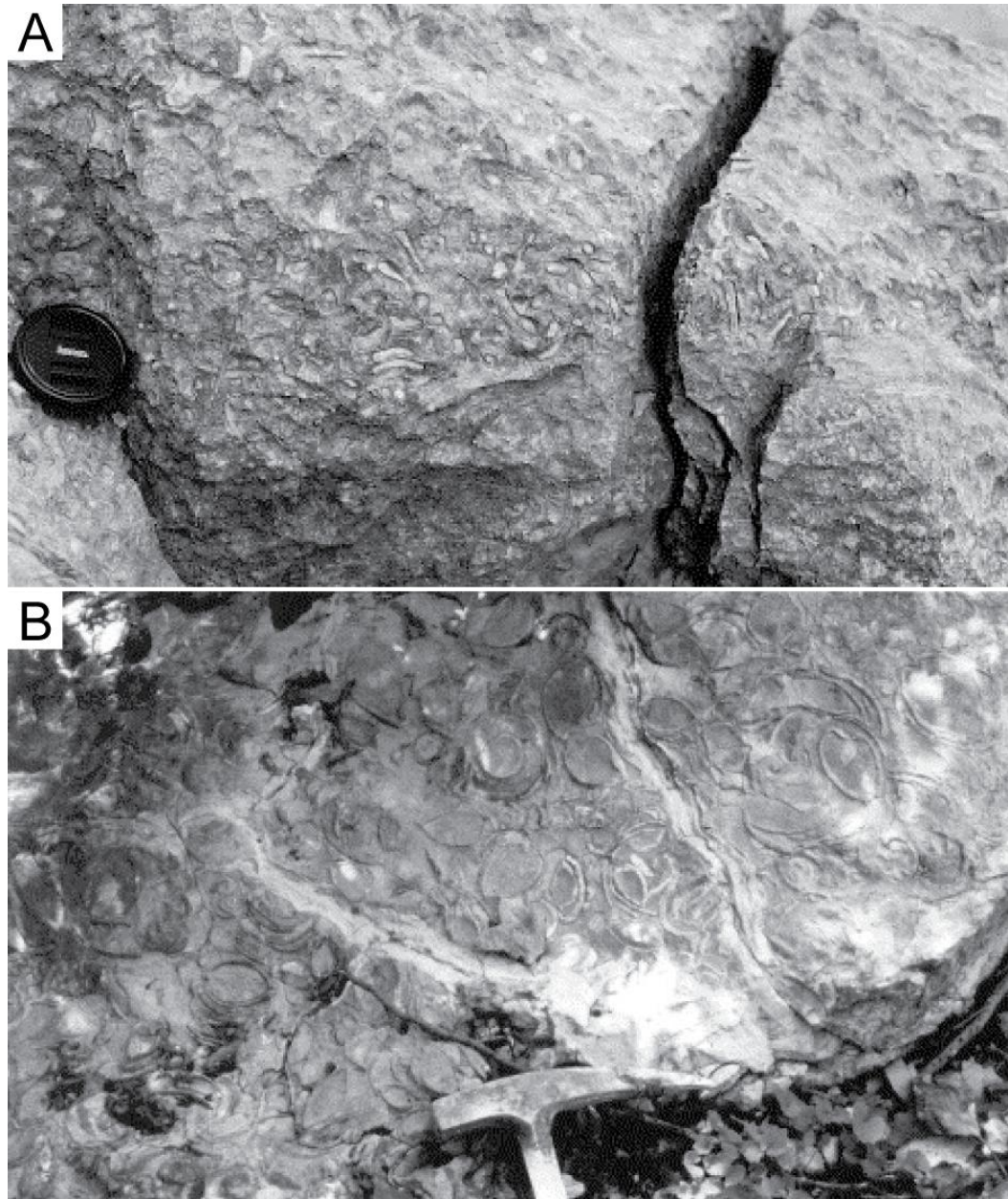


Figure 2.16 - Fossils in cold seep carbonate mounds. **A:** A field image of the “Wormtube limestone” of Holland Mound, Morocco. From Peckmann *et al.* (2005). **B:** An outcrop featuring a shell bed of infaunal bivalves. Facies 1 from Conti & Fontana (2005).

Table 2.3 – Mineralogical composition of some skeletal organisms commonly found in the cold seep environment. Open circle indicates rare occurrences, filled circle indicates common mineralogy. Adapted from Tucker & Wright (1990) and Scholle & Ulmer-Scholle (2003).

Taxon	Aragonite	Calcite			Both aragonite and calcite	Additional notes
		LMC	IMC	HMC		
Foraminifera:						
Benthic	o	•	•	•		Also tests made of silica, organic matter, and agglutinated sediment grains.
Planktic		•	•			
Molluscs:						
Bivalves	•	•			•	Some families have shells of separate aragonite and LMC (rarely exceeding 1 mole % Mg).
Gastropods	•				o	
Serpulids	•			•	•	Also tubes consisting of chitin and phosphate, and agglutinated clastic sand grains.
Corals	o	•	o			

2.5.3 MDAC mineralogy

The authigenic mineralogy of cold seep carbonates is dominated by calcite, aragonite, and/or dolomite; others include ankerite, barite, pyrite, and gypsum (Stakes *et al.* 1999; Campbell *et al.* 2002; Greinert *et al.* 2002). Also, as these minerals are precipitated on and beneath the sea floor, an often significant amount of detrital material (the sea floor sediments) is cemented and incorporated into the MDAC. Preferential precipitation of minerals is dictated by hydrological, biological, and substrate effects, depth, temperature, pore water chemistry, and the flux of hydrocarbon fluids and other trace elements into the environment (Burton 1993; Conti & Fontana 2002).

Calcite is the rhombohedral polymorph of CaCO_3 . It is the most stable mineral product precipitated at cold seep systems, and thus the most common. It can form as low magnesium calcite (LMC; <4 mole% MgCO_3), intermediate magnesium calcite (IMC; $<4 - 12$ mole% MgCO_3), or high magnesium calcite (HMC; >12 mole% MgCO_3) (Tucker & Wright 1990). Aragonite is the orthorhombic polymorph of CaCO_3 . Aragonite and HMC are both thermodynamically metastable carbonate phases, and typically recrystallise into LMC or dolomite with time and diagenesis (Burton 1993). Dolomite is a carbonate mineral, $\text{CaMg}(\text{CO}_3)_2$, with a rhombohedral structure consisting of planes of CO_3^{2-} between sheets of alternating Ca and Mg (Tucker & Wright 1990). In the presence of microbes dolomite precipitates directly, but is more commonly a replacement mineral for calcite or aragonite (Judd & Hovland 2007).

As earlier mentioned, there are a number of criteria which influence mineral precipitation. Of particular importance are the relative concentrations of sulphate and phosphate, and oxygenation of the environment. Aragonite tends to precipitate in high-sulphate/low-phosphate, oxic environments. This is reflected in a study by Aloisi *et al.* (2002) who assessed the variations in mineralogy of carbonate crusts in the Mediterranean. In the upper area of the crust, where the environment is well oxygenated and sulphate is concentrated, aragonite was dominant – up to 65% of the MDAC. Lower in the crust, primary HMC becomes dominant, despite the oxygenated conditions still ideal for aragonite formation. This change is suggested to be due to the lack of sulphate, a very important factor in the precipitation of HMC; sulphate reduction in the shallow sediments by SRBs reduces the sulphate concentration to levels low enough to allow HMC to form (Savard *et al.* 1996; Aloisi *et al.* 2002). In addition, an adequate substrate to nucleate on also plays an important role in precipitation of the acicular to spherulitic crystal morphology that aragonite typically adopts (Jorgensen 1992). Dolomite is considered to precipitate in low-sulphate/high-phosphate anoxic environments. These conditions are often achieved within the interstitial region of pillar/tubular structures in the subsurface, resulting in seep plumbing systems often containing a significant amount of dolomite (Aloisi *et al.* 2002; Nyman 2009).

2.5.4 Isotopic signatures

The isotopic composition of seep carbonates is one of the fundamental tools for the identification of an MDAC origin (Campbell 2006). Stable carbon ($\delta^{13}\text{C}$) and oxygen ($\delta^{18}\text{O}$) isotopes are used as these give indications of the methane source and water temperatures at formation, respectively. Isotopic values may vary widely over a geographic region, seep site, single outcrop, and even over adjacent precipitation phases within a vein or cavity (Greinert *et al.* 2001; Campbell *et al.* 2002; Campbell 2006).

Stable carbon ($\delta^{13}\text{C}$) isotopic values archive the source of the methane used in anaerobic oxidation of methane (AOM) to produce the MDAC, as the carbonate retains the isotopic signal. These are typically moderately to very depleted, up to -

65‰, as documented widely in the literature (Roberts *et al.* 1993; Campbell *et al.* 2002; Nyman 2009). The degree of depletion reflects the formation mechanism of the methane (see Section 2.2.1), and is related to the different precursor compounds, types and magnitudes of kinetic isotope effects, and temperatures involved at the time of methane generation (Whiticar 1999). $\delta^{13}\text{C}$ values from -90 to -50‰ imply a microbial methane source, while values from -50 to -20‰ imply a thermogenic methane source (Roberts & Aharon 1994; Whiticar 1999; Judd & Hovland 2007; Nyman 2009). Stable carbon isotopic values of MDAC vary due to a number of controlling factors such as the tapping of deep burial fluids and the mixing of carbon sources (Campbell *et al.* 2002; Campbell 2006).

Stable oxygen isotopic values of MDAC give a general indication of the water temperature and origin at the time of formation (Greinert *et al.* 2001; Judd & Hovland 2007). Variations in water origin can include meteoric water, sea water, and water derived from the destabilisation of methane hydrates, and each of these water types results in differing isotopic values for each specific mineral type, be it LMC, HMC, or dolomite (Stakes *et al.* 1999). Sea water typically has a $\delta^{18}\text{O}$ value close to 0‰ with variations according to latitude and age (Nyman 2009). Depleted values are indicative of increased water temperatures, whilst enriched values tend towards gas hydrate dissociation, decreased water temperatures, and clay mineral dehydration (Campbell 2006; Nyman 2009). However, diagenesis can substantially affect the $\delta^{18}\text{O}$ value, adding difficulty to the interpretation of isotopic results (Campbell 2006).

CHAPTER 3

Geologic Setting

3.1 INTRODUCTION

Interest in the geology and petroleum systems of the East Coast Basin (Fig. 3.1) of North Island dates back to the late 1800s. During this period several petroleum exploration companies carried out mapping in the area followed up with drilling, the earliest commencing in 1872. However, much of the information produced remained unpublished (Field *et al.* 1997). The earliest extensive geological mapping of different parts of the onshore East Coast Basin was carried out by the New Zealand Geological Survey (Lillie, 1953; Kingma 1957, 1971; Johnston 1980; Neef 1984). Of particular relevance to the present study is the bulletin published by Lillie (1953) on the geology of the Dannevirke Subdivision. Within this bulletin the “Motuotaraia” and “Porangahau” survey districts cover the area of this study. Lillie (1953) noted the presence of scattered limestone outcrops within the Miocene rocks of southern Hawke’s Bay.

Since Lillie’s bulletin, the onshore geology of southern Hawke’s Bay and the entire East Coast Basin has been extensively mapped and subsequently documented in a series of New Zealand Geologic Survey maps and Geological and Nuclear Sciences (GNS) monographs synthesising the geology of New Zealand’s sedimentary basins (Field *et al.* 1997; Mazengarb & Speden 2000; Lee & Begg 2002).

This chapter introduces the geologic setting of the sampling sites of this study. It begins with a description of the East Coast Basin, with particular reference to the Hikurangi subduction margin, and the sedimentation patterns and structural deformation associated with the development of this margin. The general geology and structure of the greater field area is then described, followed by more specific information about the geology of the southern Hawke’s Bay area, within which the five separate study sites are located. Finally, mention is made about fluid

migration history within the Basin and the possible sources of hydrocarbon-bearing fluids.

3.2 EAST COAST BASIN

The field area for this study is in southern Hawke's Bay within the East Coast Basin, North Island, New Zealand. The East Coast Basin extends along the eastern side of New Zealand's North Island into the north eastern corner of the South Island, a distance of about 500 km (Fig. 3.1A). The axial ranges of the central North Island, composed of uplifted Mesozoic basement rocks, act as the western boundary of the basin, while the Hikurangi Trough forms the offshore eastern boundary (Field *et al.* 1997).

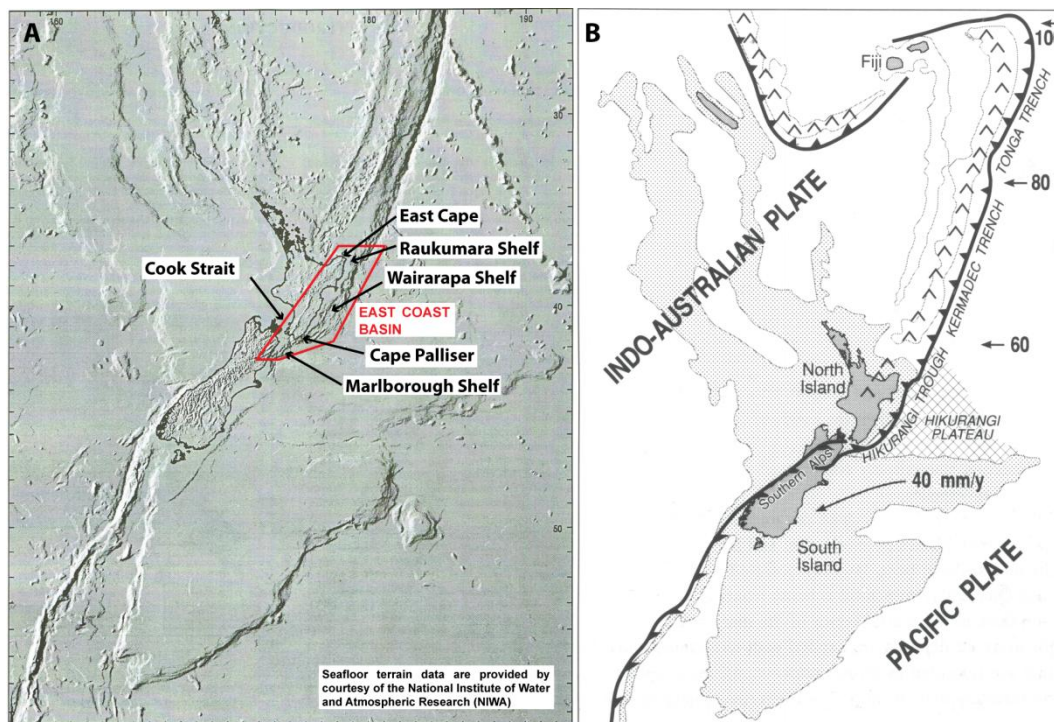


Figure 3.1 - A: New Zealand bathymetry and the location of East Coast Basin and its continental shelf sectors. Adapted from Field *et al.* (1997). **B:** Locality diagram showing the plate boundary (thick flagged line) cutting through the New Zealand continent. The numbered arrows show rates of relative convergence in mm/y. Also shown are the lines of arc volcanism and the thickened oceanic crust of the subducting Hikurangi Plateau (hatched area). From Lewis & Pettinga (1993).

The main physiographical feature of the onshore East Coast Basin is the bounding North Island axial ranges stretching from East Cape south to Cape Palliser (Fig. 3.1A). These ranges are aligned north-northeast, have an average elevation of just over 1,000 m and are generally steeper on their south-eastern side (Field *et al.* 1997). Axial range uplift is associated with a major fault belt, comprising mainly dextral strike-slip faults with a north-northeast strike (Field *et al.* 1997; Bailleul *et al.* 2007). The field area in southern Hawke's Bay is to the east of the Ruahine Ranges, a relatively narrow part of the axial ranges.

The offshore East Coast Basin bathymetry has been revealed by the work done by the National Institute of Water and Atmospheric Research (NIWA). From north to south, the continental shelf has been divided into three portions: the Raukumara, Wairarapa, and Marlborough Shelves (Fig. 3.1A). The shelf varies from 5 to 30 km wide. The continental slope is generally characterised by the presence of fault blocks and slope basins, and is incised by several canyon systems (Field *et al.* 1997). At the slope base is the Hikurangi Trough forming the eastern margin of the basin (Fig. 3.1B). The Hikurangi Trough, is the southern end of the 3,000 km long Tonga-Kermadec-Hikurangi subduction zone of the western Pacific (Field *et al.* 1997). The trough is 50 to 70 km wide in water depths of 2,000 to 3,500 m. The canyons of the continental slope feed their sediment into the Hikurangi Trough, which runs a meandering course northwards to the Kermadec Trench, where it deposits its sediment load (Field *et al.* 1997).

3.2.1 Basin evolution and structure

The East Coast Basin has a complex history due to its position on the subducting plate margin between the Pacific and Indo-Australian tectonic plates (Fig. 3.1B). The modern Hikurangi Margin is positioned at the southern end of the Tonga-Kermadec arc. Convergence along this plate margin commenced in the early Miocene (23 Ma; Waitakian – New Zealand Stage) with the onset of: (a) thrust faulting and formation of slope basins; (b) arc-related volcanism to the north and east; (c) obduction and imbrication of earlier passive margin formations; and (d) the gradual build up of a substantial accretionary wedge (Ballance 1993; Field *et al.* 1997). Further south, off southern North Island, the convergence becomes

dextral-oblique, before a halt in subduction and a change to a compressive dextral transform boundary within continental crust of South Island, south of Cook Strait.

The geologic development of the East Coast Basin occurred during three major plate tectonic regimes: rifting in the Late Cretaceous, passive margin sedimentation during the Paleogene, and active convergent margin development in the Neogene (Field *et al.* 1997). The strata of the East Coast Basin are dominated by marine siliciclastic sediments, especially deep-water sandstones, mudstones and flysch, and occasional limestones (Fig. 3.2).

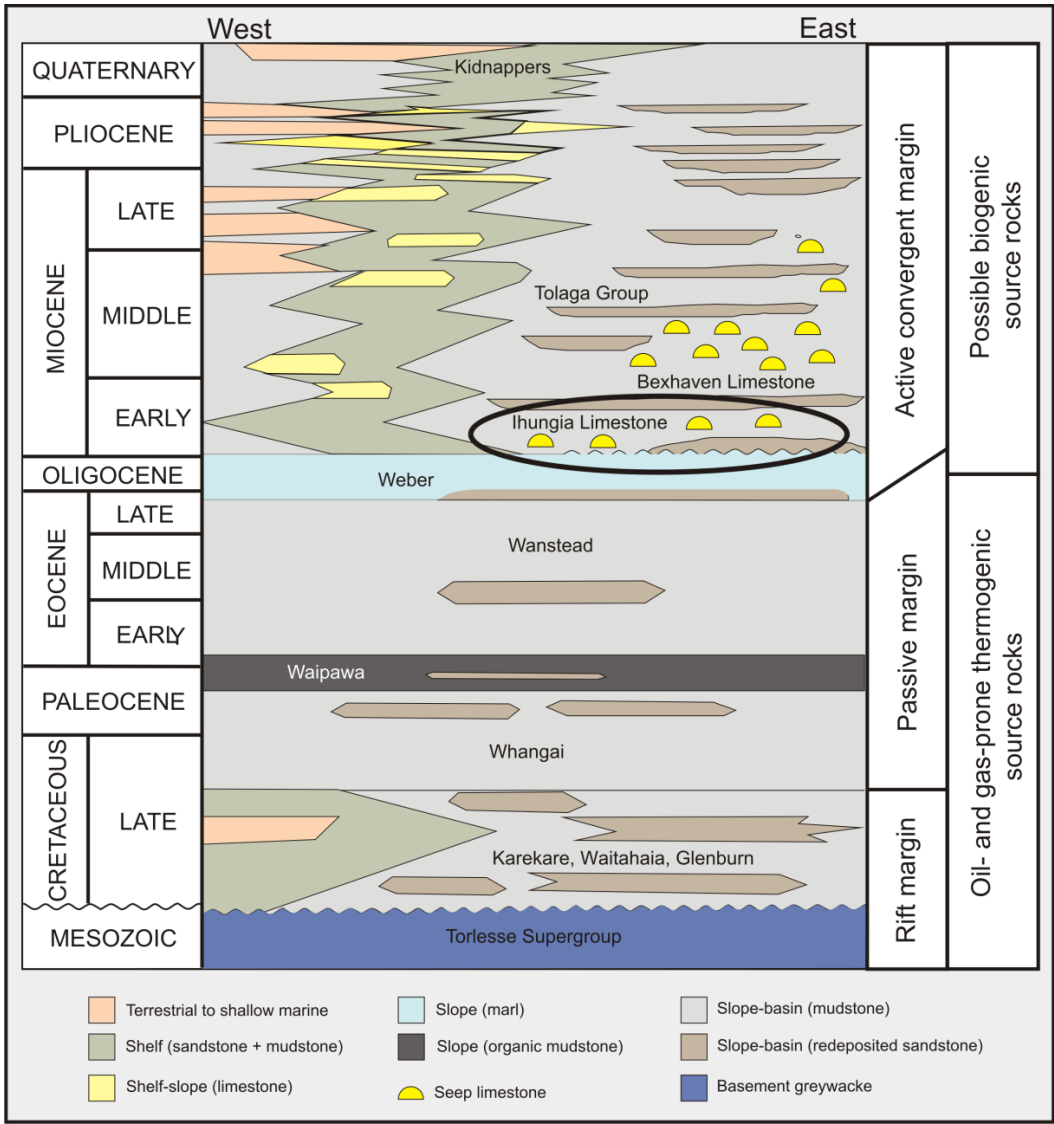


Figure 3.2 - Simplified chronostratigraphic panel of lithologies in the East Coast Basin, illustrating the general position of seep carbonates. Southern Hawke’s Bay seep carbonates are circled. Adapted from Nyman (2009).

Mesozoic stratigraphy

During the Mesozoic the paleo-East Coast Basin sat on the Pacific edge of Gondwana. It is here that the basement rocks comprising the Torlesse terrane were deposited. This terrane is also known as the Torlesse Supergroup as it encompasses various subterrane and mélange zones (Table 3.1) (Mazengarb & Speden 2000).

Crustal extension beginning in the Late Cretaceous initiated the rifting of New Zealand (Zealandia) away from the combined Australian and Antarctic continents (Field *et al.* 1997). In this setting the paleo-East Coast Basin accumulated a thick sequence of alternating shallow shelf to deep water sandstones and mudstones, with local mass flows and olistostromes (Table 3.1) (Field *et al.* 1997; Mazengarb & Speden 2000; Lee & Begg 2002).

Table 3.1 - Mesozoic to Paleogene strata of the East Coast Basin. Adapted from Field *et al.* (1997), Mazengarb & Speden (2000), and Lee & Begg (2002). Age is also given in New Zealand stages.

	Formation	Age	Description	Thickness (m)
Paleogene stratigraphy	Weber Fm	Late Eocene to Oligocene (Kaiatan to lower Waitakian)	Moderately hard, light grey, bioturbated, calcareous (40-70%), massive mudstone. Contains well-bedded sandstone.	Up to 900
	Wanstead Fm	Eocene (Teurian to lower Whaingaroan)	Poorly bedded, highly bioturbated, green-grey, calcareous mudstone. Contains beds of glauconitic sandstone and can be smectitic, siliceous, or brecciated in areas.	Up to 490
	Waipawa Fm	Mid Paleocene (Late Teurian)	Poorly bedded, dark brown, non-calcareous, micaceous siltstone. Contains localised greensand and calcareous mudstone.	Up to 80
	Whangai Fm	Late Cretaceous to Early Paleocene (Haumurian to Teurian)	Non-calcareous and calcareous shale and mudstone. Consists of 5 members varying slightly in lithology.	Up to 600
Basement cover rocks	Glenburn Fm	Late Cretaceous (Ngaterian to Haumurian)	Moderately indurated, moderately to well sorted, carbonaceous, massive to thickly bedded sandstone and alternating fossiliferous and bedded mudstone, with common conglomerate.	>1100
	Waitahaia Fm	Late Early Cretaceous to early Late Cretaceous (Motuan to Ngaterian).	Well bedded, alternating sandstone and mudstone with minor conglomerate, pebbly mudstone, and tuff beds.	Up to 1400
	Karekare Fm	Late Early Cretaceous to Late Cretaceous (Urutawan to Piripauan)	Thinly bedded, blue-grey, fossiliferous sandstone and mudstone with rare tuff beds, conglomerates, calcareous concretions, and intercalations of red and green mudstone.	Up to 2650
Basement	Torlesse Supergroup	Triassic to Early Cretaceous	Encompasses a variety of sub-terrane (Rakaia, Pahau, and Waioeka) and melange zones (Esk Head and Whakatane). Generally indurated and lithic-rich quartzofeldspathic sandstone and mudstone (greywacke and argillite).	

Paleogene stratigraphy

The Paleogene was a period of relatively little tectonic activity (Fig. 3.2). Ongoing regional subsidence and generally rising sea levels over much of New Zealand were the major events; the peak of this marine transgression was in the mid Paleocene (Field *et al.* 1997).

In this passive margin setting of the latest Cretaceous to Oligocene there was a stable pattern of increasingly fine grained sedimentation in the basin as the New Zealand continent moved away from Gondwana sediment sources and developed its own local sources (Lewis & Pettinga 1993). Continental slope and basin sediments built up, forming strata such as the Whangai, Waipawa, Wanstead, and Weber Formations (Fig. 3.2; Table 3.1) which are very widespread throughout the basin. Some of these formations (eg. the Wanstead and Weber Formations) can be significantly carbonate-influenced. Extensional faulting occurs within the Paleogene sediments of the East Coast Basin, interpreted from the geology of offshore Wairarapa and onshore Hawke's Bay (Field *et al.* 1997). This is due to the Pacific Plate's pole of rotation lying some 900 km southeast of central New Zealand during the Paleogene, resulting in gradual transtensional motion of the New Zealand continental block.

From the study of ocean floor magnetic anomalies it is thought that during the Eocene, c. 40 Ma, is when the boundary between the Australian and Pacific Plates was initially developed (Lewis & Pettinga 1993; King 2000).

Neogene stratigraphy

The onset of the Miocene (23 Ma; Waitakian – New Zealand Stage) saw active convergence along the plate boundary running through Zealandia due to another shift in the pole of rotation of the Pacific Plate to some 2,100 km south of central New Zealand, its current position (Lewis & Pettinga 1993). This new relationship between the two plates resulted in an increase in convergence with increasing dextral transcurrent motion (Lewis & Pettinga 1993). The Pacific Plate to the east began to subduct with sinistral-oblique motion at a low angle of approximately 3°

beneath the Australian Plate to the west (King 2000) (Fig. 3.2), to form the modern plate boundary known as the Hikurangi Margin (Fig. 3.1B).

During this period significant uplift and erosion of the basement rocks and cover strata ensured a rapid rise in sedimentation rates - the Miocene sequence can reach a thickness of up to 3,500 m in Hawke's Bay (Field *et al.* 1997). Sedimentation patterns moved away from being carbonate-influenced to become increasingly siliciclastic (King 2000). Early Miocene deposition was dominated by mudstones and flysch, with tuff beds also found in the basin, a record of the volcanism occurring in the Coromandel Arc to the north (Field *et al.* 1997). Generally, deposition throughout the Miocene occurred in progressively shallower environments with neritic sandstones and local shelf limestones being generated, as well as massive mudstones and turbidites (Fig. 3.2).

The inception of the subduction plate boundary in the Early Miocene also caused obduction of ocean floor to the north-northeast of New Zealand (Lewis & Pettinga 1993). This resulted in the south to southwest movement of a huge volume of Cretaceous and Paleogene sediment, encompassing passive margin sequences and oceanic crust, and its eventual emplacement in the northern reaches of the East Coast Basin (Field *et al.* 1997; King 2000). Known as the East Coast Allochthon (ECA), this remobilised rock forms a series of chaotic nappes and is often compared to the Northland Allochthon in Northland which consists of similar rocks emplaced at much the same time (Field *et al.* 1997; King 2000)

3.2.2 Basin deformation

As the East Coast Basin has sat astride an active convergent margin from the Early Miocene to the present day, a typical subduction zone cross section has developed on the over-riding Pacific Plate (Fig. 3.3). The present day structural features of this margin include the Hikurangi Trough, an accretionary frontal wedge involving also uplifted coastal ranges in the west, a forearc basin, the axial ranges bounding the East Coast Basin, and the active magmatic arc of the Taupo Volcanic Zone.

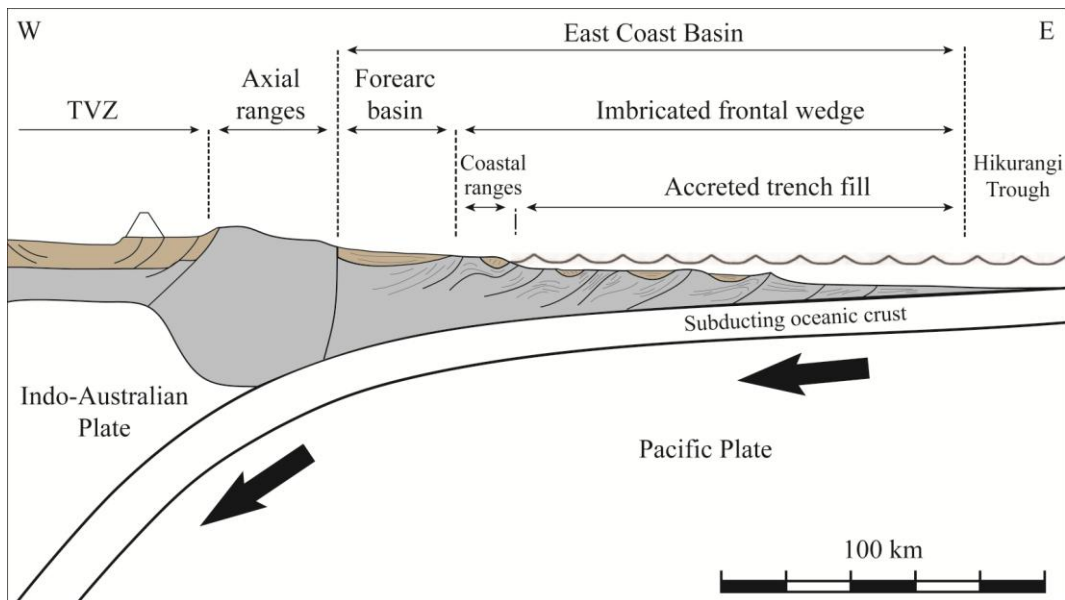


Figure 3.3 - Generalised west to east diagram of Pacific Plate subduction beneath East Coast Basin, North Island. The diagram is generalised, and is most like the mid-sector of the Hikurangi Margin, where the frontal wedge is at its widest. TVZ = Taupo Volcanic Zone. Adapted from Lewis & Pettinga (1993) and Bailleul *et al.* (2007).

The frontal wedge comprises a complex series of thrust controlled ridges and basins, which form a thick wedge of imbricated sediments thinning towards, and ultimately terminating at, the plate boundary (Lewis & Pettinga 1993). The Hikurangi Margin has been segmented into three sectors based on structure and sedimentology, with the central sector (between Hawke's Bay and Cook Strait) featuring a very wide (160 km) frontal wedge and reaching a thickness of 7 km (Lewis & Pettinga 1993; Barnes *et al.* in press). The Late Cretaceous and Paleogene rocks, which are the foundation of the wedge, became subject to the compressional forces and drag associated with subduction along the Hikurangi Margin in the Early Miocene. This brought about extensive thrusting directed both landward and seaward, resulting in major tectonic *mélange* and crush zones, thrust sheets, and ultimately the formation of ridges and basins along the length of the margin (Fig. 3.3) (Pettinga 1982; Rait *et al.* 1991). The highest of these ridges, originally at mid to upper slope depths, is represented today by the southern Hawke's Bay coastal ranges (Lewis & Pettinga 1993), while the rest of the imbricate frontal wedge currently lies beneath sea level (Fig. 3.3).

The ever-changing nature of deformation and temporal structural changes resulted in development of various types of Neogene sub-basins throughout the coastal

ranges of the modern East Coast region, such as extensional rift basins, thrust-bounded basins, and strike-slip basins (Field *et al.* 1997). In addition, during the Neogene each of the various sub-basins between the slope ridges accumulated its own, sometimes distinct, sequence of sediments dependent on the local conditions, structure, and tectonism (D. Francis *pers. comm.* 2009). The sedimentary sequence of many of these sub-basins reveals a complex evolution, including phases of tilting, faulting, folding, and basin inversion (Pettinga 1982; Paquet *et al.* 2009).

To the east of the coastal range is the modern forearc basin (Fig. 3.3) - a region of low lying plains and gently rolling hills which have been deformed by a series of major dextral strike-slip faults and mild folds (Paquet *et al.* 2009). These faults have accommodated much of the motion occurring parallel to the slope during the Neogene (Lewis & Pettinga 1993; Beanland *et al.* 1998). The forearc basin is classified into two regions; the inner foothills which are uplifting at $1 - 3 \text{ mm/yr}^{-1}$, and the 20 – 30 km wide outer region which is actively subsiding at $1 - 1.5 \text{ mm/yr}^{-1}$ (Paquet *et al.* 2009).

The Neogene and Quaternary strata covering much of the imbricated frontal wedge and forearc basin, also somewhat incorporated into the chaotic deformation of the structure, document a marine regression from outer shelf and slope mudstones through to shelf to marginal marine sandstones, limestones, and finally Pleistocene terrestrial conglomerates (Lewis & Pettinga 1993; Beanland *et al.* 1998).

The forearc basin rests against the axial ranges - a backstop composed of Mesozoic sandstone turbidites and mudstones of the Torlesse Supergroup (Lewis & Pettinga 1993). West of the axial ranges is the Taupo Volcanic Zone, which includes numerous active volcanoes which have formed in association with the subductive plate margin.

3.3 MIOCENE SEEP CARBONATES OF SOUTHERN HAWKE'S BAY

The five ancient seep-carbonate outcrops that are the focus of this study are located in southern Hawke's Bay, and represent just some of the 16 presently

known seep-carbonate deposits in the East Coast Basin (Fig. 3.4). The southern Hawke's Bay seep-carbonate outcrops are the least studied of this regional grouping of seep carbonates, and are encased within Early Miocene deep marine strata (Fig. 3.2). There are many structural complexities in the vicinity of these ancient cold-seep carbonate outcrops, as outlined below.

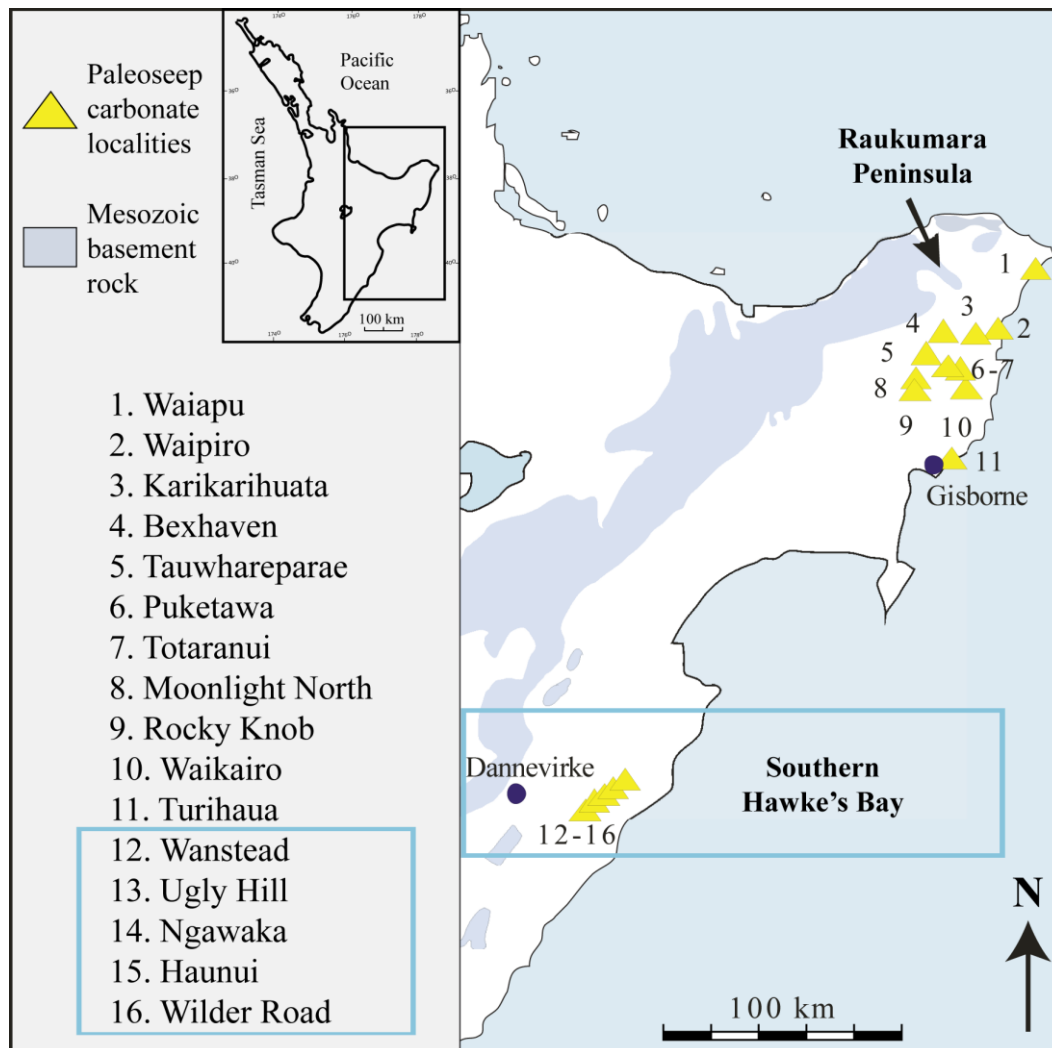


Figure 3.4 - Location of the 16 ancient seep carbonate deposits currently known in the East Coast Basin. The box outlines the five occurrences studied in this research. Adapted from Nelson *et al.* (2007).

3.3.1 Structure and deformation within the field area

Since the establishment of the modern convergent plate boundary in the Early Miocene, a number of major and minor fold structures and faults have been developed in the East Coast Basin; those relating to the study region are shown in

Figure 3.5. These include strike-slip faults at the base of the axial ranges and throughout the forearc basin due to slope parallel movement on the Hikurangi Margin, thrust faults in both the forearc basin and coastal ranges, and various contractional structures such as anticlines, synclines, and uplifted blocks. Bailleul *et al.* (2007) suggested that this complex deformation of the area occurred during three main tectonic periods rather than representing continuous and homogeneous deformation: a first regime of intense folding, thrust faulting, and reverse faulting related to the onset of subduction; a second regime of relative tectonic quiescence and erosion; and then a third period featuring folding and reverse faulting due to the renewal of compressional deformation in the Pliocene and Quaternary.

The ancient seep carbonate deposits occur within the coastal ranges, the westernmost boundary of the imbricated frontal wedge (Figs. 3.3, 3.5). It is probable that these ranges were uplifted and subsequently eroded only 0.3 my ago during the third tectonic period of Bailleul *et al.* (2007), characterised by compressional deformation (folding and thrust faulting).

In southern Hawke's Bay and northern Wairarapa, the coastal ranges contain a series of elongated synclines bordered by strips of pre-subduction Upper Cretaceous to Oligocene formations, typically reverse faulted on their eastern sides (Field *et al.* 1997; Bailleul *et al.* 2007). The synclines are composed of Miocene mudstones which, prior to the final tectonic period of compressional deformation, were the sedimentary infill sequence of the numerous sub-basins in the region. Along with the succession of major synclines, the field area is further complicated by a series of small anticline and dome structures, most of which are oriented parallel to the subduction margin.

The dominant structure of the field area is the Akitio Syncline - an elongate syncline originating inland of the coastal town of Akitio and terminating to the east of Waipukurau (Fig. 3.5). To the west the structure is bounded by the Cretaceous rocks of the Whangai Range, and to the east by the Porangahau High. All five of the ancient seep carbonate outcrops of this study lie on the western limb of this syncline structure, within 8 km of one another.

The Akitio Syncline consists of Lower to Middle Miocene sedimentary deposits (c. 24-13 Ma) which accumulated in the Tawhero trench-slope basin of Bailleul *et*

al. (2007). The syncline is structurally simple, with the synclinal axis traceable for much of its length (Lillie 1953). There are multiple small fold structures within the Akitio Syncline; of particular note is the flat-crested and symmetrical Boar Hill Anticline which is thought to be a potential oil-bearing structure (Fig. 3.5) (Lillie 1953; D. Francis *pers. comm.* 2009).

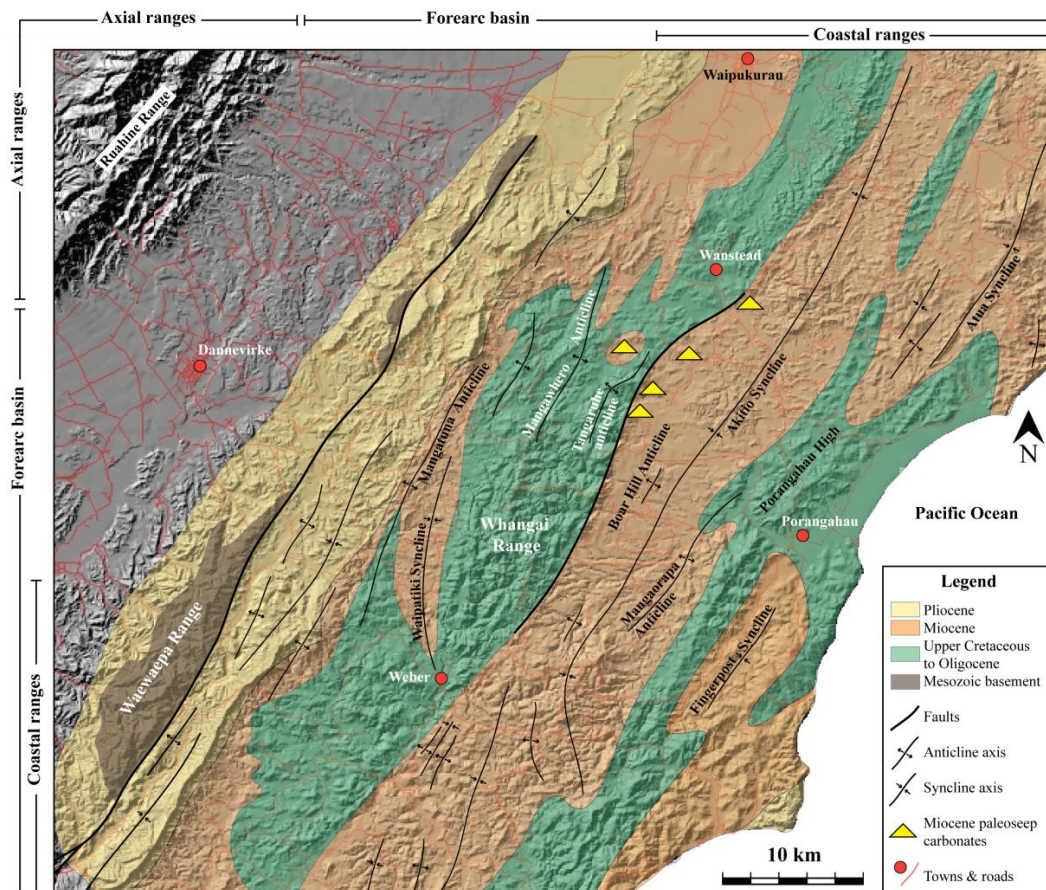


Figure 3.5 – Generalised structural map of the greater field area containing the five ancient seep carbonate deposits of this study. Adapted from Bailleul (2007) and D. Francis (*pers. comm.* 2009).

Also found within the coastal ranges is the Whangai Range, which lies to the west of the Akitio Syncline (Fig. 3.5). This is the type section of the Late Cretaceous to Paleocene Whangai Formation as described by Lillie (1953). The type sections of the Upper Calcareous and Te Uri members of the Whangai Formation are also found upon the ranges (Moore 1988). Also of note in the vicinity of the field area, and within the coastal range, are the towns of Weber and Wanstead (Fig. 3.5). Weber is located to the south of the Whangai Range at U23

(2791743E/6084571N) and is the namesake for the Oligocene Weber Formation, and the town of Wanstead lies further to the north at U23 (2811968E/6113624N) and is the namesake for the Eocene Wanstead Formation (Fig. 3.2).

To the west of the coastal range, and aligned adjacently, is the Waewaepa Range which makes up the southwest sector of the field area (Fig. 3.5). This range consists of Pliocene formations and uplifted Torlesse basement due to the Waewaipa-Oruawharo Fault (Fig. 3.5) - a major thrust fault lying on the southeast flank of the range.

3.3.2 Host strata of the southern Hawke's Bay seep carbonate sites

Exposed within the Akitio Syncline, as well as in the adjacent Waipatiki Syncline (Fig. 3.5), are the calcareous mudstones and sandstones of the Early Miocene Ihungia Formation (Reid 1998). This formation hosts the five seep carbonate sites of this study (Fig. 3.2). They are found in the lower part of the formation, typically with the basal unconformity located stratigraphically below. The five seep carbonate sites occur over a distance of 12 km, with four of the five sites positioned along roughly the same north-east strike followed by the Akitio Syncline.

This formation consists of three members, as described by Reid (1998), although previously mentioned by others dating back to Lillie (1953). The three members, from bottom to top, are the Mangapuku Mudstone (Otaian - New Zealand Stage), the Westcott Sandstone (Otaian to Altonian – New Zealand Stage), and the Tunakore Mudstone (Altonian – New Zealand Stage). These members together reach a thickness of at least 420 m (Ballance 1993; Reid 1998). The dark grey, sandy, calcareous Mangapuku Mudstone is topped with an angular unconformity and overlain by the Westcott Sandstone. This calcareous and muddy sandstone contains beds and lenses of calcite concretions, and numerous non-fossiliferous and non-calcareous turbidites (Reid 1998). The Westcott Sandstone grades up into the Tunakore Mudstone Member. This medium to dark grey mudstone, also both calcareous and feldspathic, has a matrix featuring fluctuating carbonate levels giving rise to discontinuous grey laminations throughout (Reid 1998). Reid (1998)

suggested that the Ihungia Formation was deposited in inner shelf to mid bathyal depths.

3.4 MANIFESTATIONS OF SUBSURFACE FLUID FLOW

Subsurface fluid flow in its various forms is a common phenomenon in the East Coast Basin. The migration and expulsion of fluids stems from the intense deformation occurring in the region since inception of the modern plate boundary in the Early Miocene. This deformation leads to overpressuring and subsequent fluid migration. Surface expression of the fluids is then represented by (a) active oil and gas seeps, (b) mud volcanoes, and (c) widely dispersed seep carbonate deposits, as well as a clearly defined offshore bottom simulating reflector associated with gas hydrates (Barnes *et al.* in press).

Deformation of the East Coast Basin's sediments involves lateral compression, differential uplift, and folding, thrust faulting, and rapid sedimentation, all related to active subduction of the Pacific Plate since the Early Miocene and formation of the wide accretionary wedge (Fig. 3.3). The ongoing deformation is associated with high levels of overpressurisation. Exploration wells have encountered fluid pressures >90% of lithostatic pressure at depth (pressure due to the overlying rock mass) in uplifted regions of the basin (Darby & Ellis 2003). Assessment of overpressures in the basin has shown that lithostratigraphy, disequilibrium compaction, and tectonic deformation processes such as shearing largely control the distribution of overpressure (Darby & Funnell 2001). Such overpressuring of the strata instigates the migration of any fluids present.

It is estimated that the Hikurangi Margin gains some 24 m³ of fluid per metre of strike length per year due to frontal accretion, of which >80% is later released by compaction and tectonic deformation (Barnes *et al.* in press). These migrating fluids take the easiest route from depth to the surface. According to Lewis & Marshall (1996), the expulsion of fluids at the sea floor occurs in three broad geological environments around the New Zealand subduction margin: (1) the mid to upper slope; (2) near the shelf edge and canyon heads; and (3) in areas of slope collapse. Of these, the upper slope fosters the escape of fluids from depth most effectively due to permeable formations and sediment lenses, steep faults with

minimal compression, and the relatively unstable barrier of methane clathrate (Lewis & Marshall 1996).

Throughout the East Coast Basin, both onshore and offshore, there are many indications of the prolific amount of focused fluid flow occurring in the basin. There are 16 currently known ancient seep carbonate outcrops in the onshore East Coast Basin (Fig. 3.4) which are verification of fluid flow during the Early to Late Miocene (Campbell *et al.* 2008). Modern seep carbonate deposits are also a common phenomenon along the Hikurangi Margin (Fig. 2.11) (Ewen 2009; Campbell *et al.* in press; Liebetrau *et al.* in press), along with strong bottom simulating reflectors (BSRs), pockmarks, and gas hydrates (Nelson & Healy 1984; Lewis & Marshall 1996; Townend 1997; Faure *et al.* 2006; Henrys *et al.* 2009; Barnes *et al.* in press; Crutchley *et al.* in press; Netzeband *et al.* in press).

There are abundant oil and gas seeps onshore in the East Coast Basin (Fig. 3.6). The majority, approximately 250, are gas seeps, and there are about 50 oil seeps and other impregnations of various sizes that issue from Late Cretaceous to Recent formations (Field *et al.* 1997; Rogers *et al.* 1999). Some of the larger oil seeps include the once commercial Waitangi (Fig. 3.7), Rotokautuku, and Totangi sites (Field *et al.* 1997). Many of these oil and gas seeps have been subjected to geochemical analysis in an attempt to identify a specific source for the hydrocarbons (Lillie 1953; Kvenvolden & Pettinga 1989; Field *et al.* 1997; Rogers *et al.* 1999). According to Rogers *et al.* (1999), oil seeps in the northerly reaches of the East Coast Basin (Raukumara Peninsula) and those in Marlborough are expelling oils derived from Late Cretaceous to Paleocene source rocks. Seeps in Hawke's Bay and Wairarapa contain oils generated in Paleocene marine source rocks, which are isotopically heavier than oils from Raukumara and Marlborough. Kvenvolden & Pettinga (1989) found that gasses rising from nearby seeps within the basin, although containing the same major constituents (methane, ethane, carbon dioxide, and nitrogen), are from different sources and have undergone different burial, thermal, and maturation histories.

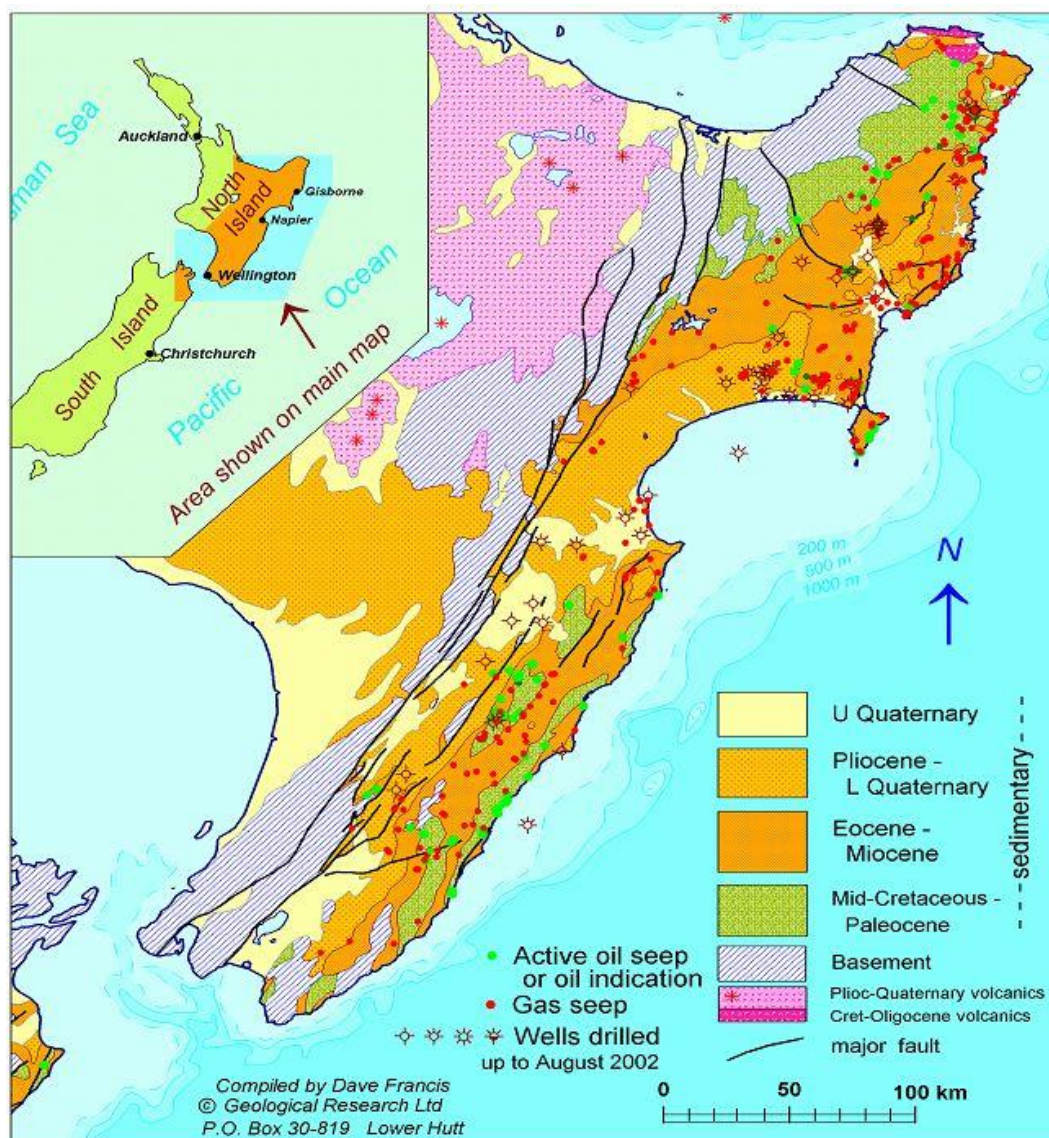


Figure 3.6 – Generalised geologic map of the eastern North Island showing oil and gas seeps, and the location of drilled wells of the East Coast Basin. From Francis *et al.* (2004).

There are also numerous mud volcanoes found both onshore and offshore within the East Coast Basin. These are thought to be a product of the interaction of rising overpressured fluids associated with diapirs (Field *et al.* 1997; Pettinga 2003). Diapirism has been occurring in the East Coast Basin since at least the Late Miocene, largely due to intense compression of the basin's strata (Neef 1992). Migrating gases accompanied by saline fluids rise through the subsurface, often through near-vertical diapir margins and faults, to produce erratic bursts of mud, which build up into generally low profile mud domes with associated splatter zones and mud flows. Pettinga (2003) carried out detailed assessment of the geological conditions and controls of the onshore Brookby Station mud volcano,

formerly a gas seep in the central East Coast Basin. Other mud volcano eruptions within the East Coast Basin include the 1908 and 1931 eruptions of the Mangaehu Stream mud volcano 21 km north of Gisborne, producing >100,000 t and >150,000 t of mud, respectively, within a short (<12 hour) period (Ridd 1970). In the vicinity of the present study area there are three large diapiric structures, Owahanga Hill, Panui, and Mt Cadmus diapirs, each with steep faults and margins but, currently, lacking any hydrocarbon seepage (Neef 1992).



Figure 3.7 – Sampling from the Waitangi oil seep, as visited in September 2008.

3.5 POTENTIAL SOURCE ROCKS

There is a long history of hydrocarbon generation and migration within the East Coast Basin, which is now further documented by the 16 Miocene seep carbonate outcrops found onshore. Of particular importance to petroleum systems in the East Coast Basin is the Whangai and Waipawa Formations, the major oil-prone source rocks in the basin (Fig. 3.2).

The Whangai Formation (Fig. 3.2) is a non-calcareous to calcareous shale containing minor sandstone, greensand, conglomerate, and breccia, of Late Cretaceous to Early Paleocene age (Haumurian to Teurian – New Zealand Stages) (Moore 1988; Field *et al.* 1997). It is typically 300 to 500 m thick, with the thickest outcrops found in central Hawke's Bay. Much of this Formation probably accumulated at bathyal depths during a major transgression, as indicated by foraminiferal assemblages (Field *et al.* 1997). The Whangai Formation has a total organic carbon (TOC) content of 0.2–1.5% (Francis *et al.* 2004).

In the East Coast Basin the Whangai Formation occurs contemporaneously with, and is conformably overlain by, the Paleocene Waipawa Formation (Fig. 3.2), also informally known since 1940 as the Waipawa Black Shale (Moore 1989). The Waipawa Formation is a poorly bedded, brownish black, moderately soft to hard, non-calcareous, micaceous siltstone with a varying thickness of up to 80 m, although an average thickness of 50 to 60 m is estimated (Moore 1989; Field *et al.* 1997). It is widely distributed around the North Island, with exposures particularly abundant in the East Cape and southern Hawke's Bay regions (Moore 1989). This formation is of particular interest as it is currently referred to as the hydrocarbon source rock in the region, with a TOC content of 4.5-12% (Francis *et al.* 2004). There are numerous accounts of oil bleeding out of this formation. Calcareous nannofossils and dinoflagellates give the formation a mid to Late Paleocene age (Late Teurian – New Zealand Stage). The Waipawa Formation has been interpreted by Leckie *et al.* (1992) to represent the peak of the marine transgression in the Paleocene. The organic material is present due to the flooding of land, with conditions possibly becoming anoxic to cause the lack of planktic foraminifera and the preservation of carbonaceous material (Field *et al.* 1997). Based on foraminiferal, paleogeographic, and geochemical studies, the depositional paleoenvironment for the Waipawa Formation is suggested to have been uppermost slope to outer shelf (Field *et al.* 1997).

CHAPTER 4

Methodology

4.1 INTRODUCTION

Due to the textural complexity of seep carbonates, the petrographic and mineralogical study of these deposits is somewhat different to that of a normal limestone or sedimentary rock. Complexity increases as one moves from field observation through to slab analysis and finally to thin section and geochemical analysis. This is related to the often dynamic paleo-fluid flux of the seep and the spatially and temporally variable physical chemical regime of the seafloor and burial environments in which the rocks have formed.

The analytical techniques applied to the seep carbonate samples collected from the five sites of this study have thus been customised to maximise the ability to unravel and understand the mineralogy (primary versus secondary) and paragenetic history of these rocks. This chapter describes the techniques used, from the broad field methods and sample preparation in the laboratory, to details on petrography and geochemical analysis.

4.2 FIELD TECHNIQUES

Field work was undertaken at the five southern Hawke's Bay seep carbonate outcrops beginning in 2006. This study, started in September 2008, began with many samples already in storage which were collected during field trips in November 2006, July 2007, and January 2008. During these preliminary field trips brief notes on each site were taken, along with brief details on the sampling location.

Upon commencement of this study a reconnaissance field trip was taken in October 2008. The aim of this field trip was to meet land owners, locate each site

and its numerous outcrops, and get a grasp on the scope of field work required. A number of samples were collected at this time.

In November 2008, the bulk of the field work was undertaken over seven days. The objectives of the field trip included mapping and profiling of the five sites and the known outcrops at each, further exploration to locate any additional outcrops or seep related features, a broad facies analysis, stratigraphic logging where applicable, and extensive sampling. Outcrops of the host formation were also sought, in order to obtain data and samples.

The mapping of each site involved obtaining GPS coordinates for each outcrop with a GARMIN E-trex hand-held GPS, noting the local geological and topographical setting of each outcrop, and details on the morphology of each outcrop and each site. Further exploration at each site revealed numerous previously unknown seep carbonate outcrops; four additional outcrops were located at the Wilder Road site, one at Ngawaka, and two at Ugly Hill. Each *in situ* outcrop was assigned a name based on the site to which it belonged. These data were later used in construction of both regional and site specific field maps.

Facies analysis of the seep carbonate deposits was often a difficult task. Variations in lithology of the outcrops occur on a small scale, with differences identified among sites, among outcrops, over individual outcrops, and even throughout a single hand sample. Lithologic descriptions were best achieved in the field by the fracturing of mounds and boulders to allow observation of a fresh surface (Fig. 4.1). Definition between *in situ* deposits and re-positioned float boulders also proved a challenge due to differential erosion between the carbonates and mudstones (largely grass-covered) at many outcrops and the typically small size of the carbonate boulders. This distinction was largely based upon outcrop exhumation, bedding indications, outcrop size, and the topographical and structural setting.

As established earlier, field and laboratory work on cold seep carbonates is somewhat unique when compared to that of a typical limestone or sedimentary formation. Stratigraphic logging becomes near-obsolete, as the typically small size (<2 m) of the outcrops makes this technique impractical. At outcrops of significant size (e.g. Ngawaka West), transects were defined and intensively

studied in an attempt to delineate any vertical variations in outcrop lithology. A composite stratigraphic log of the outcrop was then constructed from these details to illustrate any facies changes. Facies were kept broad due to both the extremely common, yet subtle, variations in lithology and the mixing of facies due to remobilisation after original deposition (c.f. Conti & Fontana, 2005).



Figure 4.1 - Field assistant accessing a fresh surface at Haunui's HA.F outcrop to enable identification of fossil specimens and a lithologic description.

Samples were collected from the five study sites using a heavy duty, long handled Estwing geological hammer, sledge hammer, and chisel (Fig. 4.1). These samples were added to the large collection of southern Hawke's Bay cold seep samples stored at the University of Waikato. Each of the five individual sites has had 30–60 samples collected since inception of this research project in 2006. A full sample catalogue is given in Appendix 2.

4.3 LABORATORY TECHNIQUES

Laboratory techniques used in this study were undertaken in 2009 and 2010 at the University of Waikato, University of Auckland, and the University of Bremen in Germany.

4.3.1 Sample preparation

All samples stored at the University of Waikato were initially cut into slab form with an Allegro Supercut Saw to thicknesses of approximately 2 cm. This enabled a more comprehensive examination of sample lithology, comparison of samples, and choice in thin section sub-samples. A representative slab from each sample collected was scanned (wet) using an A4 flatbed scanner in order to retain a digital copy of the samples.

A slab facies categorisation scheme was designed based on grain size of the dominant sediments and intraclasts, (trace) fossil components (including thrombolites), and major diagenetic and textural features (Fig. 4.2). Each sample was examined in slab form and assigned a facies code.

Major facies present at each of the five sites were identified via slab examination and classification. A sample from each facies was powdered in a ring mill, using a tungsten carbide head to prevent iron contamination, at the University of Waikato to produce powders for further analysis.

Slabs were chosen for thin sectioning based on particular features each contained. Blocks were subsequently cut from the selected slabs with the Allegro Supercut Saw. Thin sections are of a standard microscopic slide size (2.5 x 4 cm) and were prepared in accordance to standard procedures.

If porous, thin section blocks were first impregnated with Araldite resin and left overnight to harden. All block faces were then smoothed on a diamond lap wheel in preparation for mounting on glass slides. The blocks were then divided into batches ready for making into thin sections. All thin sections were made by technicians at the University of Waikato and the University of Auckland. The product is a collective 207 thin sections from the five southern Hawke's Bay cold

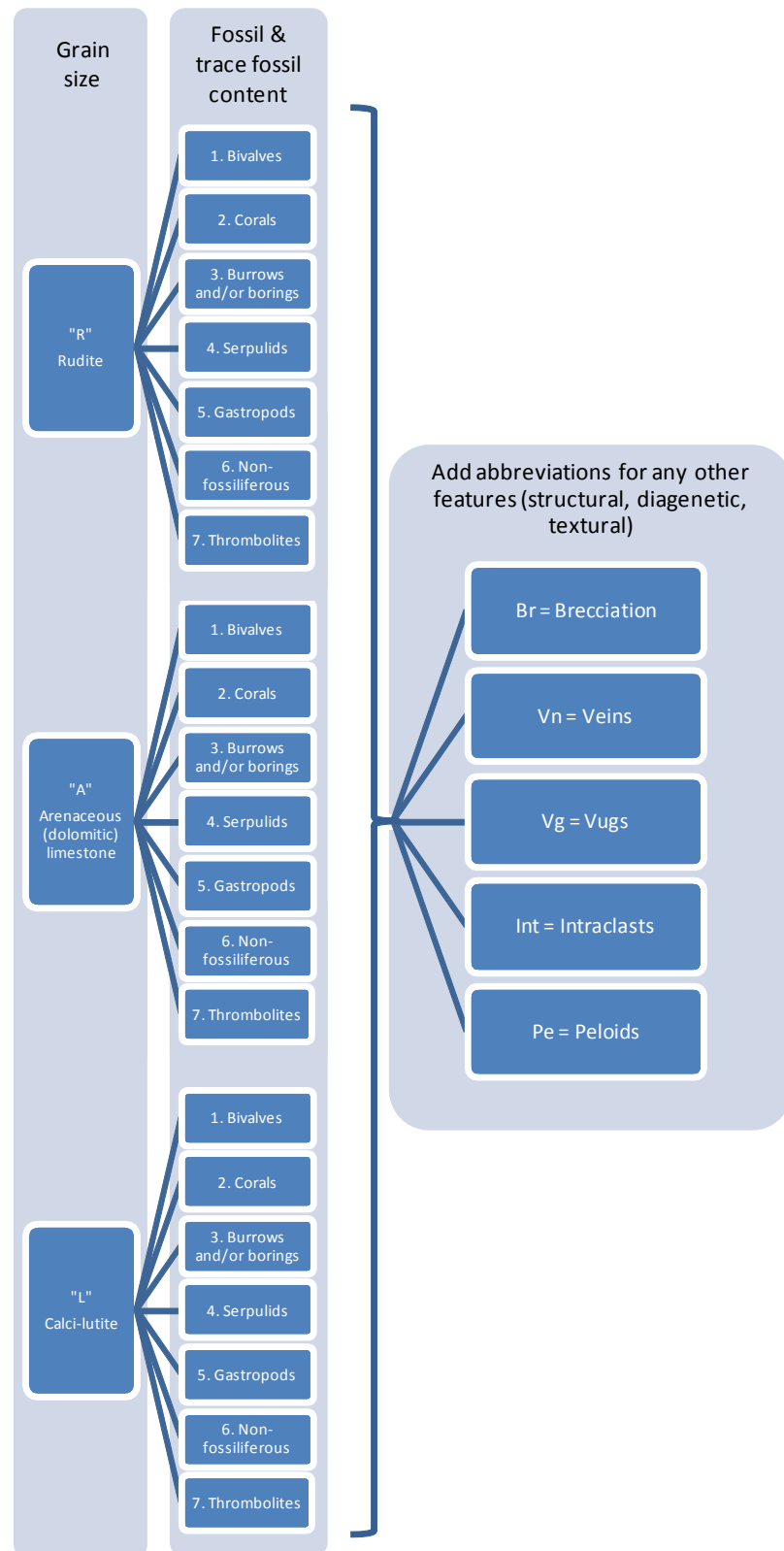


Figure 4.2 - Southern Hawke's Bay cold seep slab facies chart. The texture column refers to the dominant grain and/or intraclast size. Fossils and trace fossils include all specimens identified (in contrast to most abundant). Each sample is assigned a minimum of one 'fossil-content' number. A final prefix may be added based on structural, diagenetic, and textural features of the sample. Intraclasts (Int) range from gravel to pebble sized.

seep carbonate sites, finished to 0.03 mm thickness. Thin sections were polished on a Buehler Metaserv grinder/polisher using 0.3 μm agglomerated alpha alumina powder.

4.3.2 Plane polarised light (PPL) petrography

Standard petrography was carried out at the University of Waikato using an Olympus AX70 petrographic microscope and Nikon DXM1200 digital camera. Primary aims of plane polarised light petrography were mineral identification and descriptions of crystal morphologies, average crystal sizes, and mineral relationships. For a detailed account of the fabrics identified see Section 6.3.

4.3.3 Cathodoluminescent light (CL) petrography

Cathodoluminescence (CL) petrography was used in this study primarily to aid in the identification of minerals, variations in carbonate phases, and neomorphic phases in the thin sections of the five southern Hawke's Bay cold seep carbonate sites. Cathodoluminescent colours, textures, and fabrics can also be a useful technique in the determination of geochemical conditions of the environment of formation (Boggs & Krinsley 2006).

The CL technique is based upon bombardment of the thin section by electrons sourced from a cathode (Boggs & Krinsley 2006). This causes electrons within individual crystals to be promoted to high-energy conduction bands, before losing energy and attempting to return to their original valence bands. However, on this return journey they become trapped in a band gap. Upon vacation from this trap they release energy, the amount of which is dictated by the structure and impurities of each crystal. These defects are known as electron traps. This energy is converted into photons of light which have specific wavelengths (colours) based on the density of electron traps in the crystals, and therefore enable the viewer to identify the minerals present and any alteration products based on the intensity of luminescence (Boggs & Krinsley 2006).

For the study of calcites and dolomites under CL, the absolute concentration and ratios of trace elements present within the crystallographic structure play an important role to luminescence (Hemming *et al.* 1989). Different elements act as activators, sensitizers, and quenchers of luminescence. Mn^{2+} is the most abundant and important activator in natural calcites and dolomite (Machel *et al.* 1991; Pagel *et al.* 2000), and substitutes into the calcium site within the minerals structure (Walker & Burley 1991). The most important quencher for diagenetic calcites and dolomites is Fe^{2+} , which can begin to mask the luminescence instigated by Mn^{2+} with as little as 150 ppm present in the sample (Fig. 4.3) (Machel *et al.* 1991; Walker & Burley 1991; Pagel *et al.* 2000). Luminescent colours exhibited by some common minerals are shown in Table 4.1.

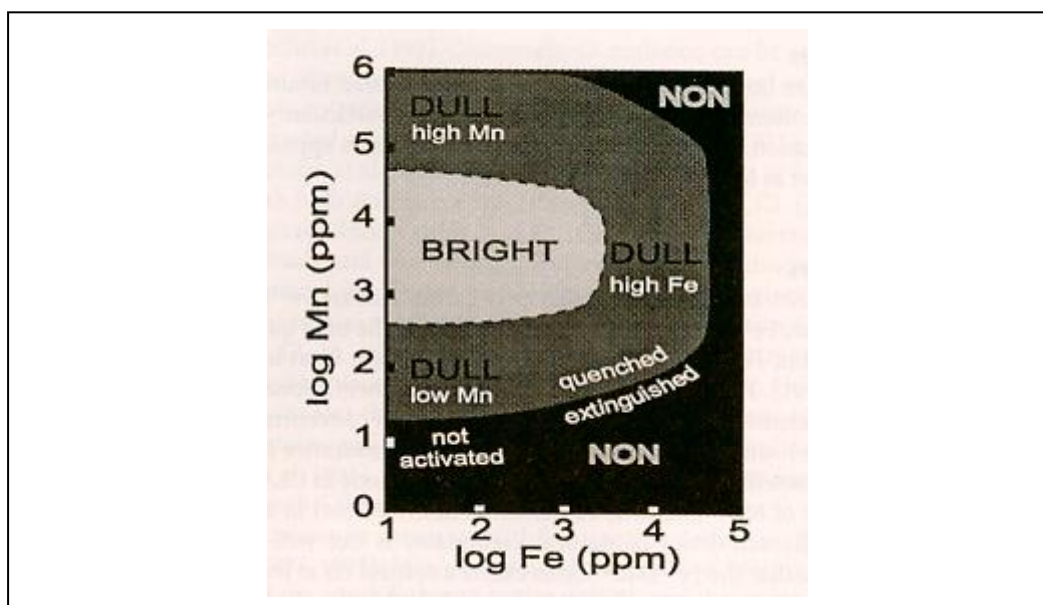


Figure 4.3 – Luminescence intensity with various Mn and Fe concentrations. Dull luminescence is due to low Mn (activator element) concentrations (*lower left*), and extinction is due to Fe-quenching (*lower right*) as well as self-quenching by Mn (*right and upper right*). From Pagel *et al.* (2000).

Cathodoluminescence petrography was undertaken in the Department of Earth and Ocean Sciences at the University of Waikato on selected polished thin sections. The instrument used was the CITL MK5-1 Cathodoluminescence Chamber attached to a Nikon Eclipse E400 POL petrographic microscope. Electron gun voltage was set to 16–18 kV with a current of 350–450 μA . Images were captured with the use of a Nikon Digital Sight DS-U2 camera and NIS-

Elements F software. For a detailed account of the fabrics identified under CL see Section 6.3.

Table 4.1 - Some common minerals and their typical CL luminescence colours. Adapted from Boggs & Krinsley (2006) and Pagel *et al.* (2000).

Mineral	CL luminescence
Aragonite	Dark blue to purple (dull luminescence)
Calcite	Orange to yellow (dull to brightly luminescent)
Dolomite	Pink to red
Feldspars	Commonly bright blue (potassium feldspar), however varies through red (typically orthoclase), green (anorthite), and yellow
Quartz	Varies from bright blues, violets, and reds (volcanic quartz) to brown (metamorphosed quartz) and very dull, almost indistinguishable colouration (authigenic quartz)

4.3.4 X-ray diffraction

4.3.4.1 Bulk mineralogy

Bulk mineralogy analysis was undertaken by means of X-ray diffraction (XRD). The bulk powders generated from each major facies present over the field area were analysed using a Philips PW1130 generator and PW1050/25 goniometer in the Department of Geography and Geology, University of Auckland. Two batches of samples were run at two different scan speeds; all samples were run at a normal scan speed from 3-40° 2 θ , and 6 samples were run a second time at a slow scan speed from 25-35° 2 θ . All samples were mounted in an aluminium sample holder and run with a step size of 0.02°, a speed of 0.5°/min, and operating conditions of 40 kV and 20 mA.

Mineralogy of the samples was then determined by the peak positions. The intensity of each peak is related to the relative abundance of each mineral present in the sample. This allows for a semi-quantitative estimate of the abundance of the minerals present in each sample, which is then comparable to other outcrops and sites. For bulk mineralogy results see Section 6.6.

4.3.4.2 Component mineralogy

In order to identify the mineralogies of the various fabrics identified with petrographic techniques and changes in mineralogy across various features present in thin sections, the SIEMENS General Area Detector Diffraction system (GADDs) at the University of Auckland was utilized. This technique uses an X-ray beam to scan small points (down to 0.5 mm) on a thin section allowing an interpretation of mineralogy on a very small area of the sample, in comparison to bulk XRD analysis, which typically is not precise enough to accurately analyse an individual fabric in an average cold seep carbonate sample. The machine was run with the following specifications:

Generator – 40kV, 30mA

$^{\circ}2\theta$ (detector) - 40

Omega (stage) - 20

Scan range ($^{\circ}2\theta$) – 23-58

Collimator – 0.5 mm

Count – 120 seconds

Once the desired part of the thin section was positioned under the beam (Fig. 4.4), the X-ray gun was run for 120 seconds. The reflected rays were detected and processed into an image consisting of a scattering of points of various sizes, brightness, and alignment. These factors are dictated by the reflected beam, which is influenced by crystal size and orientation(s). The brightness and size of the points relates to crystal sizes, with well-developed bands of points indicating well-oriented crystal faces, and scattered points indicating poorly-oriented crystal faces. The position of the points along the x-axis of the image is based on crystal mineralogy.

Similar to XRD analysis, Chi analysis identifies peaks in the data and produces a graph to illustrate these peaks, and EVA software matches the peaks with mineral types. For component specific mineralogical results see Section 6.7.

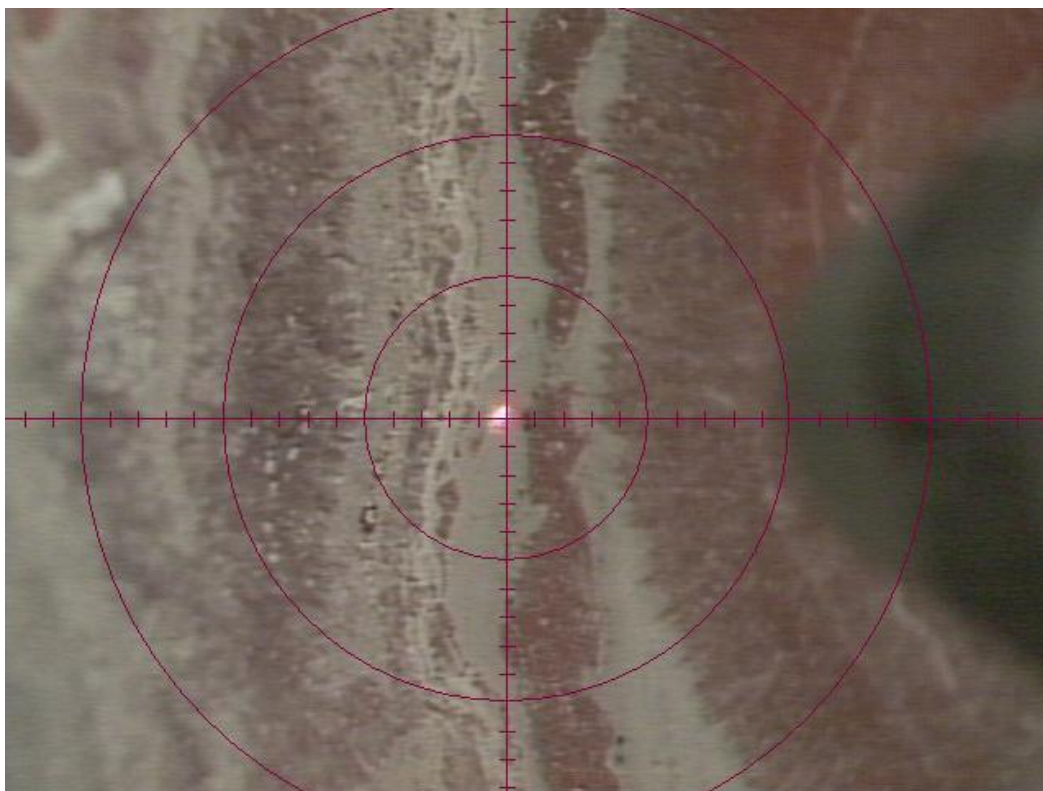


Figure 4.4 – GADDs analysis on thin section W.2.1.1B, spot 2. The red laser point lines up fabric M2 for scanning by the X-ray beam.

4.3.5 Stable isotopic analysis

Stable $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ isotopic analysis was undertaken for the five study sites in the Department of Earth and Ocean Sciences at University of Waikato. The bulk powders generated from the major facies of each site were used, with the addition of a suite of powders drilled for component-specific analysis.

After the plane polarised light petrography was carried out, the thin section blocks were micro-drilled for powders to be used for isotopic analysis. Areas suitable for drilling were defined during petrographic analysis, which attempted to cover the major fabrics of each site (micarb, sparry calcite, aragonite, and bioclasts) and any unique features such as thrombolites. A MultiPro 395VX Dremel drill and a selection of drill tips were used to extract the powders.

Powdered samples were reacted in a Europa Carbonate Automatic Preparation System (CAPS) with 105% orthophosphoric acid at 70°C while the evolving CO_2 was frozen onto a dedicated cold finger. This reaction was left to complete for 10

minutes, during which time water was removed by passing the CO₂ through a loop maintained at -90°C. The CO₂ (g) was then introduced to the Europa Geo 20-20 mass spectrometer, calibrated against internal standard NBS-19 and cross-checked against NBS-20.

Isotopic values are expressed in delta (δ) notation per mille (‰) deviation of the ¹⁸O/¹⁶O or ¹³C/¹²C ratio of the sample relative to Vienna Peedee belemnite (VPDB) standard. Instrument precision is better than ±0.05‰ for both oxygen and carbon.

4.3.6 Carbonate percentage analysis

Carbonate percentages were determined for 31 bulk powdered samples, with a minimum of 5 samples per site. This was carried out by the LECO TruSpec CN Carbon/Nitrogen Determinator in the Department of Biological Sciences, University of Waikato. The machine's carbon detection method is based on optimised, low noise, non-dispersive infrared absorption.

The bulk powders were each weighed to 0.25 g, purged of atmospheric gases, burnt off at 950°C in a resistance furnace and flushed with oxygen, and finally put through a secondary furnace. The gaseous combustion products were then analysed for CO₂ content by the infrared detector. Results were given in the form of % carbon which was then calibrated against a suite of standards consisting of known percentages of quartz and calcite. For results see Section 6.8.

4.3.7 Ultraviolet (UV) light microscopy

Petrography of seep carbonates under ultraviolet light aids the interpretation of small, dark inclusions identified in calcite and aragonite crystals during plane polarised light petrography. These inclusions are inferred as trapped hydrocarbons (c.f. Campbell *et al.* 2002; Ewen 2009). Under ultraviolet light the liptinite macerals found in oil and coal fluoresce a bright blue to yellow colour (Hutton 1991). Therefore, similar fluorescence patterns exhibited by these dark fluid

inclusions suggests there is an abundance of remnant hydrocarbons in some of the the authigenic phases of the cold seep carbonates.

Ultraviolet light microscopy was carried out in the Department of Biological Sciences at the University of Waikato. An ultraviolet attachment on the LEICA DMRE microscope provided the UV excitation, which operated under the following conditions:

Excitation type – Ultraviolet

Excitation/emission filter – BP 340-380 nm

Dichroic mirror – 400 nm

Supression filter – LP 425

Images were viewed via DP Manager and DP controller software and captured by an Olympus DP70 camera. For images taken under ultraviolet light see Section 6.4.

4.3.8 Scanning electron microscopy

A scanning electron microscope (SEM) was used in this study to gain insight into crystal morphologies, microfacies, and microbial textures. Microscopy was carried out in the Department of Earth and Ocean Sciences at the University of Waikato using the Hitachi S-4700 Field Emission Scanning Electron Microscope running at 20 kV. Samples included chips of seep carbonate <5 mm in length and thin sections. Samples were coated in platinum prior to microscopy by the Hitachi E1030 IonSputter Coater. For images taken under the scanning electron microscope see Section 6.5.

The technique of X-ray micro-analysis (elemental mapping) was employed in addition to the still images produced by SEM. This technique involves analysing the electrons removed from the sample by the microscope's electron beam to identify the elements present. Results are in the form of a map for each element present in the microscope's field of view (see Section 6.5, Figs. 6.14 and 6.15).

4.3.9 Total organic carbon (TOC)

Total organic carbon and total carbon content of 20 samples representative of the major facies of the five sites of this study were analysed at GEOMAR (Kiel, Germany). 10-20 mg samples were combusted at 1050°C and the resultant CO₂ analysed by a Carlo Erba NA 1500 elemental analyser. Two runs of each sample were undertaken to allow for any discrepancies associated with the method.

4.3.10 Lipid analysis

Analysis of lipid biomarkers within the southern Hawke's Bay seep carbonate samples was carried out at the University of Bremen, Germany. The decalcification of the microbialite samples and the extraction protocol are described in detail in Birgel et al. (2006, 2008a). The extracts were separated using column chromatography into four fractions of increasing polarity: (i) hydrocarbons, (ii) ketones/esters, (iii) alcohols, and (iv) fatty acids. Alcohols were analysed as trimethylsilyl ethers by adding 100 µl BSTFA and 100 µl pyridine (TMS derivatives). Fatty acid methyl esters (MEs) were prepared from free fatty acids liberated after saponification by adding 1 ml boron trifluoride (BF₃) in a screw cap vial (1 h, 70°C) to the polar fraction. All fractions were measured with a gas chromatograph-mass spectrometer (GC-MS) using a Thermo Electron Trace MS equipped with a 30 m RTX-5MS fused silica column (0.32 mm i.d., 0.25 µm film thickness). The carrier gas was He. The GC temperature program was 60 °C (1 min) to 150 °C at 15 °C min⁻¹, to 330 °C at 4 °C min⁻¹ (hold 60 min). Identification of individual compounds was based on GC retention times and published mass spectral data.

CHAPTER 5

Seep Carbonates in Outcrop

5.1 INTRODUCTION

This chapter outlines the field characteristics of each of the five southern Hawke's Bay Miocene seep carbonate outcrops in detail. For each site a description provides information on the local setting, the number and locations of outcrops, the morphology of the outcrops, the main field facies and their fossil content, and any other special lithological features. For a complete list of samples collected, see Appendix 2.

The five sites are located within 12 km of one another. Four of the sites (Wanstead, Ugly Hill, Haunui, and Wilder Road) are positioned along a northeast-southwest strike, with the fifth site (Ngawaka) lying slightly to the west (Figs. 5.1, 5.2). Details of the location of each outcrop are given using the NZMS 260 Map Grid 1:50,000 U23.

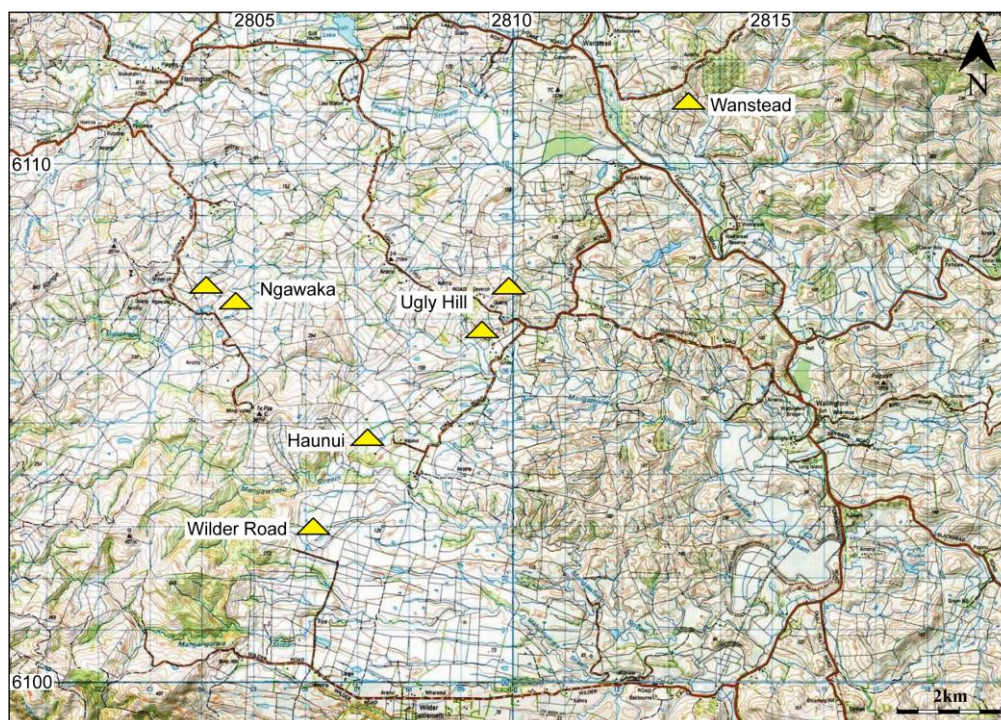


Figure 5.1 - Location of the five Miocene seep carbonate sites in southern Hawke's Bay in relation to one another.

Each site differs in morphology, ranging from hilltops composed of seep carbonates to a series of small outcrops almost hidden in the vegetation. In the following site descriptions the term ‘small’ is applied to deposits/boulders which are less than 1 m in size, ‘medium-sized’ applied to boulders 1-3 m in size, and intact deposits/boulders larger than 3 m are termed ‘large’.

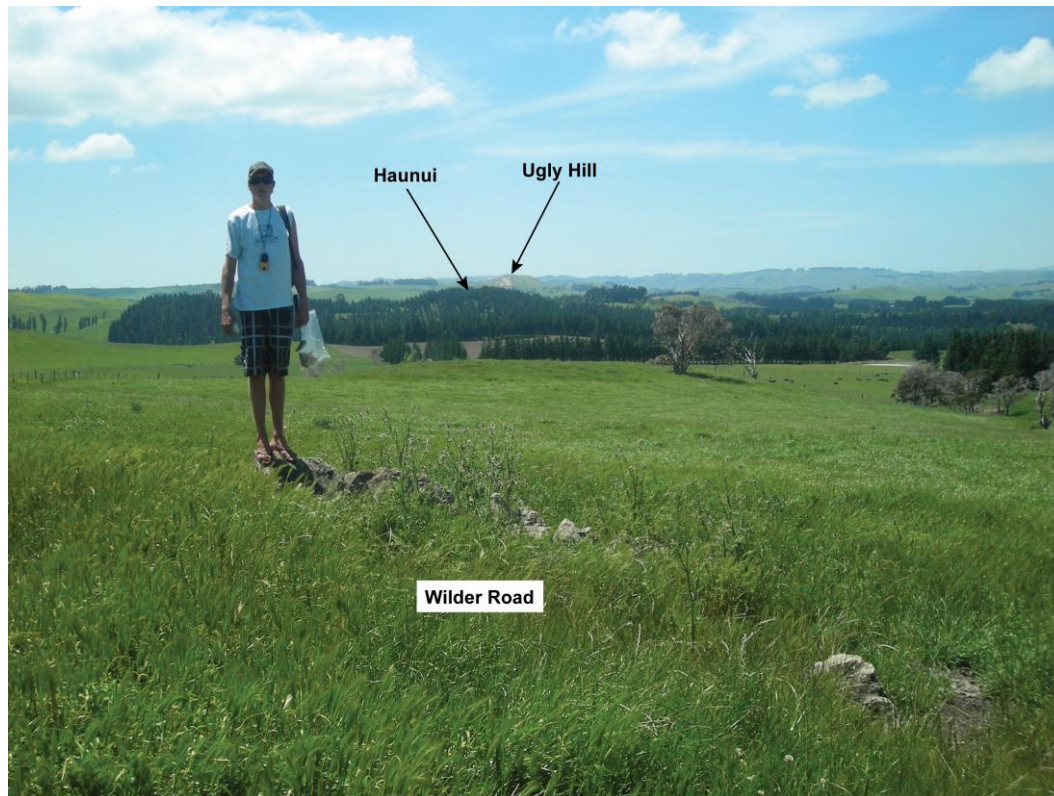


Figure 5.2 - This photograph, taken from the W.C outcrop at Wilder Road, illustrates the linear positioning of three of the seep carbonate sites. The pine tree covered Haunui site is visible in the centre of the image, and in the centre distance is Ugly Hill.

5.2 WANSTEAD

The Wanstead site is the northernmost of the five southern Hawke’s Bay seep carbonate sites of this study. It comprises six small outcrops, some of which contain a number of seep carbonate boulders. There is an abundance of float material at this site, due to the position of the boulders on a steep hillslope. Access to the site is gained off Hiranui Road, with permission from the land owner (see Appendix 1).

5.2.1 Site description

All six outcrops at the Wanstead site are situated on a steep, northeast-facing, pastoral slope (Figs. 5.3, 5.4A). Each of the outcrops has a designated code, beginning with the abbreviation “WA” for Wanstead and followed by a capital letter for an *in situ* outcrop or a lowercase letter for float material (Fig. 5.3). A summary of the outcrop morphologies, field characteristics, GPS co-ordinates, and sampling is given in Table 5.1. Specific facies found throughout the site are given codes WA.F1 through to WA.F3.

Table 5.1 – Summary of the field characteristics of the seep carbonate outcrops at Wanstead (WA).

Site	Outcrop name	Outcrop size and morphology	Outcrop lithology & characteristic features	NZMG Easting	NZMG Northing	Samples collected
Wanstead	WA.A	The largest outcrop of the site; many windows of seep carbonate in the soil/grass of a small ridge; covers 15 m downslope and 10 m horizontally; group of three medium-sized boulders 40 m to the south.	Very coarse grained - light to medium brown micarb contains abundant yellow-brown, moderately sorted, rounded to sub-angular intraclasts; an abundance of spar-filled cavities and anastomosing veins; bivalves, corals, worm tubes, and burrows; associated float zones.	2813326	6111126	WA.1 WA.2 WA.3 WA.13.5 WA.13.6
	WA.b	Single boulder; 1x 0.5 m in size; partially buried.	Coarse grain size; rich in small, medium to dark coloured, foreign grains and small intraclasts; blue-grey micarb in central areas; bivalves, corals.	2813484	6111120	W.8
	WA.C	Smallest outcrop of site; window in grass reveals 0.3 x 0.35 m boulder top.	Very coarse grained - brown micarb contains abundant yellow-brown, moderately sorted, sub-rounded intraclasts and dark foreign grains; spar-filled veins;	2813472	6111103	WA.M1
	WA.D	Two large boulders together covering 1.9 x 2 m down slope; partially to mostly buried; likely to be in situ.	Brown to blue-grey micarb; many small, dark grains; thin spar-filled veins and cavities.	2813537	6111077	
	WA.E	Single boulder; length of 1.1 m, width of 0.9 m, and height of 1.2 m; positioned high on slope, with base buried in soil.	Abundant fossilised branching coral, average diameter of branches is 9 mm; light brown, fine grained micarb; few dark foreign grains; abundant thin, spar-	2813549	6111068	WA.13.1 WA.13.2 WA.M2
	WA.F	Two boulders separated by ~1 m on steep grassy slope; 0.9 x 1.3 m and 0.9 x 0.77 m; partially buried.	Brown micarb with abundant sand sized, dark, foreign grains and numerous spar-filled cavities; occasional patches of a purer, pale brown micarb; vague	2813555	6111070	WA.13.4 WA.M3

Size and morphology

The outcrops at Wanstead are typically scattered accumulations of small (<1 m) seep carbonate boulders protruding through the grass or soil (e.g. outcrops WA.A and WA.C) (Fig. 5.4B). These outcrops can be difficult to locate if the vegetation is overgrown. It is possible that outcrop WA.A was quarried in the past. Currently it constitutes a gentle ridge in the hillside over which many 'windows' of seep carbonate are revealed by soil slippage over an area of 15 m vertically/down-slope and 10 m horizontally. Quarrying may have accentuated the ridge, but removed much of the bulk of the deposit.

Other outcrops comprise larger boulders, with only their base remaining buried in the slope (e.g. outcrops WA.D, WA.E, and WA.F). As this is pastoral land the sheep and cattle often rub against the more sizable boulders, and consequently remove the surrounding grass so that they stand out prominently on the slope (Fig. 5.4C).

In addition to the outcrops located on the slope, there are also countless smaller float boulders distributed down the slope and resting on the valley floor (Fig. 5.3). This abundance of float boulders is due to the weathering of the steep slope on which this site is situated, and also due to possible quarrying activities. There are three float zones associated with the WA.A outcrop, distributed around the ridge on or close to the valley floor (Figs. 5.3, 5.4A). Two of these included seep carbonate boulders sizable enough to be studied, and they were therefore given the codes WA.a1 and WA.a2. Float zone WA.a1 consists of five medium-sized seep carbonate boulders and numerous smaller ones; WA.a2 comprises a single, medium-sized, float boulder only.

Lithology and other features

The seep carbonate lithology at Wanstead is typically very coarse grained, with the light to medium brown micarb matrix containing abundant intraclasts and dark foreign grains (facies WA.F1) (Fig. 5.4D). Intraclasts range in colour from light to medium yellow-brown, are poorly to moderately sorted, and are rounded to sub-angular in shape. In some boulders these intraclasts reach up to 8 mm, but in other

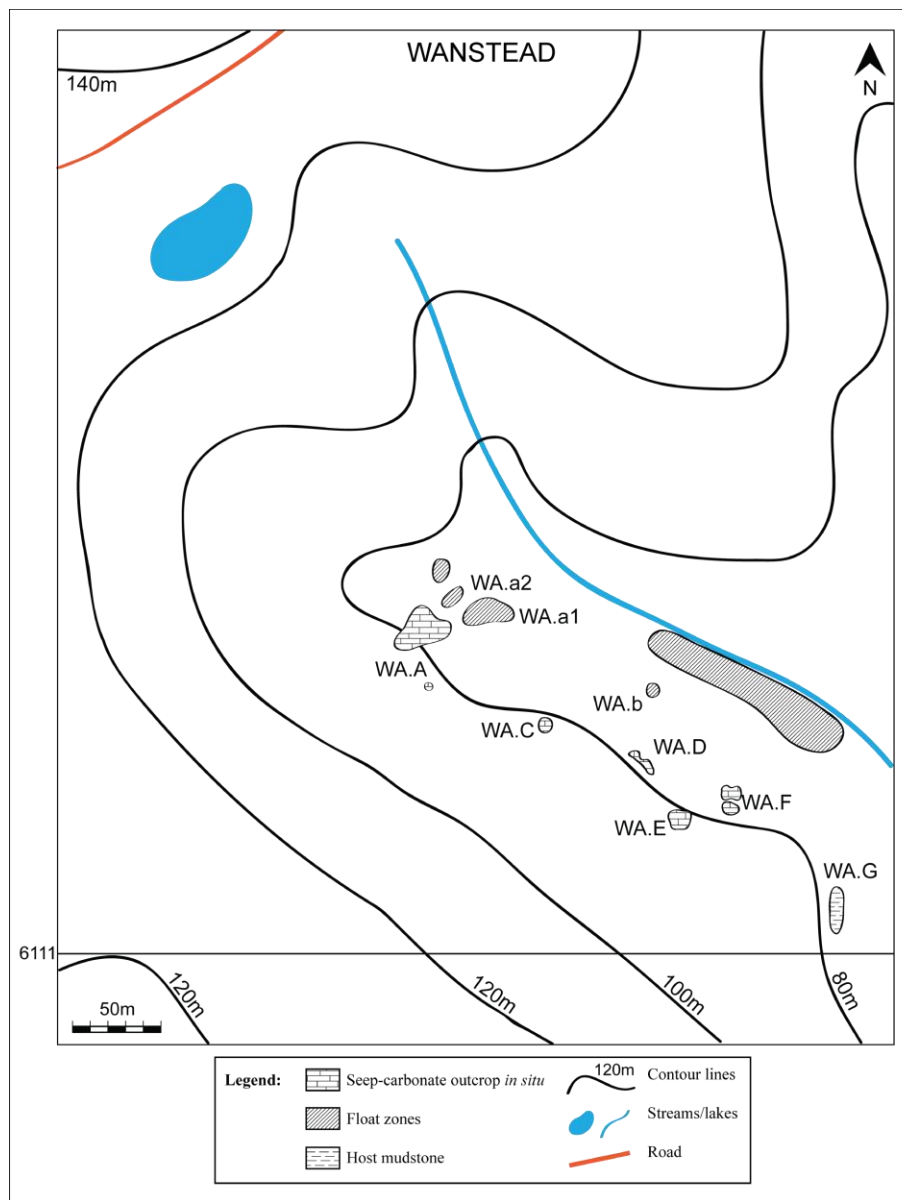


Figure 5.3 - Wanstead field map illustrating the size and location of the six seep carbonate outcrops and the host mudstone. The vertical gridline 2813 lies 125 m to the west of the map edge.

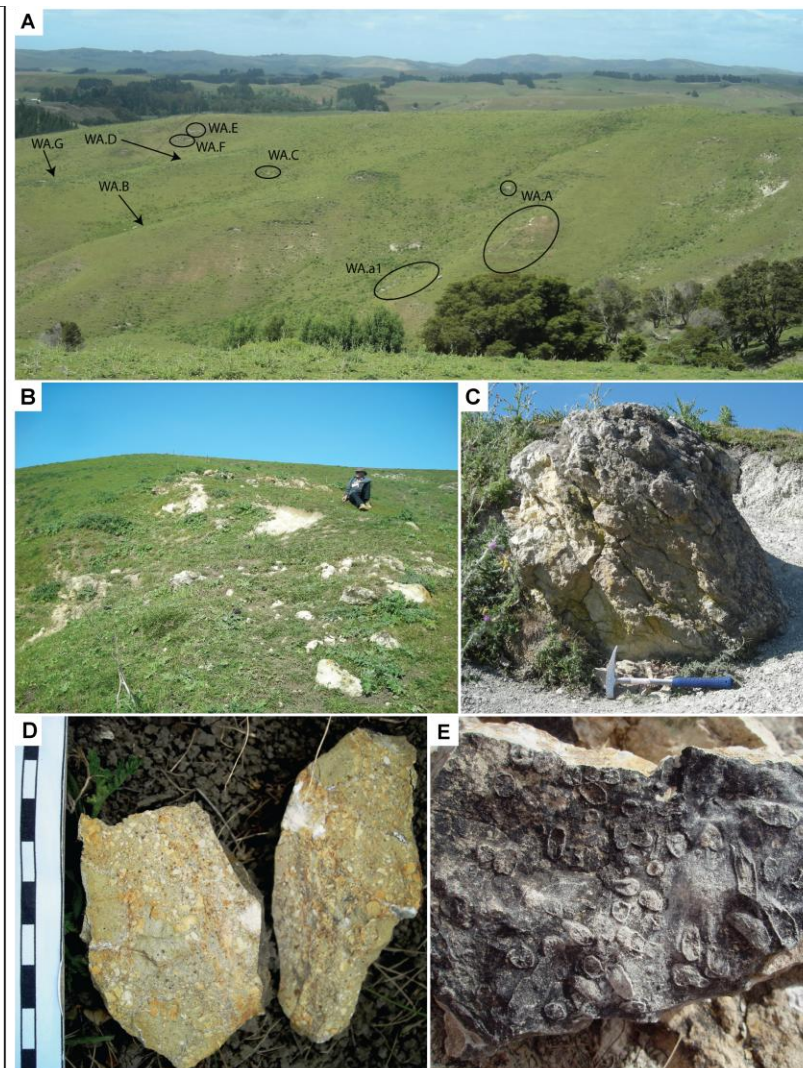


Figure 5.4 - Images of various outcrops at the Wanstead site. **Image A:** The hillside containing the six seep carbonate outcrops at the Wanstead site. Note that outcrops WA.b, WA.D, and WA.G are all situated on the southern flank of small ridges and are therefore not in the field of view. Arrows denote the ridges which these outcrops are hidden behind. View is looking south from Hiranui Road. **Image B:** The WA.A outcrop is composed of many small windows of seep carbonate spread down the axis of a small ridge on the hill slope. **Image C:** The WA.E outcrop stands in bare soil on the steep slope. **Image D:** A sample from WA.C features very large yellow-brown intraclasts scattered throughout a dull brown micarb matrix. **Image E:** Coral fossils, both in cross section and lengthwise, in a piece of the WA.E outcrop.

areas they are significantly smaller. Nonetheless, their size and abundance, in addition to the concentration of dark foreign grains, classify the facies overall as coarse grained. Commonly, patches of a similar facies (WA.F2) with only few small intraclasts and dark grains occur intermingled with the major coarse-grained WA.F1 facies.

Spar-filled cavities and veins are also abundant. Veins are typically <3 mm in width. Many boulders feature these thin sparry veins which have formed between large clasts of brecciated micarb. Within some boulders the veins are in such concentration as to show anastomosing vein networks over the weathered outer boulder surfaces.

Within the two intermingled facies (WA.F1 and WA.F2) there is a wide range of fossils. Bivalves are the most common and are evident on both weathered boulder surfaces and in freshly broken samples. The bivalves range in size from 20–80 mm long, but are typically of a similar size in any one sample. Coral fossils are sporadic, and the boulders in which they are found typically contain multiple specimens. Burrows are common in samples, and one specimen in particular (sample WA.M1) has been infilled by an extremely complex sequence of mineral precipitates (see Fig. 7.18). Worm tubes are rare, and are seen in both cross section and length-wise views.

Outcrop WA.E is particularly interesting for both its lithology and fossil content (facies WA.F3; samples WA.13.1, WA.13.2, WA.M2). The dominant feature of this outcrop is the abundance of branching coral. This seep carbonate deposit precipitated around a dense coral thicket which had grown off a previously cemented hardground. The specimens visible on the boulder surface (Fig. 5.4E) are both in cross section and length-wise, giving little indication of the original orientation of the boulder. The void within each coral branch, between the septa, is infilled with a sparry mineral (see Section 6.3.1; Fig. 6.3F). The coral branches have an average diameter of 9 mm, with a minimum of 5 mm and maximum of 14 mm recorded. The host micarb is beige/light brown in colour and very fine grained; rare, dark, foreign, silt-sized grains occur within the micarb, identifiable only with a hand lens. There also are numerous thin, 2-mm-wide, sparry veins running in various directions throughout the micarb, along with some thicker

sparry veins, reaching 7 mm in width, which stand proud on the weathered boulder surface.

Some boulders appear to have vague bedding structures. These are gently undulating planes in the boulders. Outcrop WA.E contains bedding with an average strike and dip of 170/30 W to 170/58 W. The boulders of outcrop WA.F also display bedding, however at a somewhat different orientation from one another. The bedding of the upper boulder has a strike and dip of 075/40 NW, and the lower boulder has a strike and dip of 055/56 S.

Host formation outcrop

The formation hosting the seep carbonate boulders at the Wanstead site is labelled WA.G (Fig. 5.3) and crops out at U23 (2813561E/6111054N). This is located directly over the ridge and in the adjacent paddock from the WA.F outcrop. At this locality the hill slope is very steep, causing the overlying vegetation and soil to slip away to reveal a scarp of the underlying geology.

This host formation is the Ihungia Formation - a pale brown mudstone which is poorly lithified, and therefore a very weak and friable rock. This mudstone was sampled in November 2006 and January 2008.

5.2.2 Site summary

The lithology of the Wanstead outcrops is dominated by a micarbit containing abundant intraclasts in various shades of brown as well as dark, foreign grains assumed to be from the host sediment. These clasts within the micarbit categorise it as coarse grained. There is a wide range of fossilised biota preserved within the seep carbonate boulders including worm tubes, burrows, a thicket of branching coral, and bivalves reaching 80 mm in length and often in dense clusters.

5.3 UGLY HILL

Ugly Hill is a large and centrally located seep carbonate site named after the nearby small, rounded Ugly Hill. It is located at U23 (2807145E/6104264N). The site has been divided into three sub-sites: Ugly Hill North, Ugly Hill South, and Ugly Hill Valley (Fig. 5.5). The northern and southern sub-sites are separated by Ugly Hill itself, which has a large bare scarp on its southern side due to quarrying of the Whangai Formation (see Section 3.2.1). The valley sub-site is located some 500 m to the southeast. A summary of the outcrop locations, field characteristics, and sampling is shown in Table 5.2. All outcrops are situated on private farm land. Access to the north and south sub-sites is gained off Ugly Hill Road, with permission from the two land owners (see Appendix 1). The valley sub-site can be reached via Epae Road, and is located on the same farm as the southern sub-site.

5.3.1 Site description

The Ugly Hill site has 12 seep carbonate outcrops; two at the north sub-site, six at the south sub-site, and four at the valley sub-site, plus an outcrop of the host rock (Fig. 5.5). The outcrops at Ugly Hill have designated outcrop codes fronted by the abbreviation “UH” for the Ugly Hill site followed by a capital letter or lowercase letter for *in situ* and float zones, respectively. Specific facies found throughout the site are given codes UH.F1 through UH.F3.

Size and morphology

The majority of the outcrops at Ugly Hill are small groups of small to medium sized boulders (generally covering $<3\text{ m}^2$ of land) with associated float debris. Some outcrops are much smaller windows (typically $<0.7\text{ m}$ across) of seep carbonate in the pasture (UH.C, UH.D, UH.F, UH.L, UH.M), barely able to be located when there is ample vegetation. Other outcrops are much larger, such as the quarried outcrop at Ugly Hill South which forms the base of a ridge some 15 m long. Many of the larger groups of boulders are very well exposed from the vegetation due to trampling by stock.

Table 5.2 – Summary of the field characteristics of the seep carbonate outcrops at Ugly Hill (UH).

Site	Outcrop name	Outcrop size and morphology	Outcrop lithology & characteristic features	NZMG Easting	NZMG Northing	Samples collected
Ugly Hill	UH.A	Main outcrop of the Ugly Hill North sub-site; three partially buried boulders situated half way down a moderately sloping, north facing hill, all ≤ 3 m in length; UH.A float zone is a large accumulation of scrappy boulders sitting atop the grass; extends down the slope to the north; most boulders are < 1 m in size, largest ~ 1.5 m.	Two major facies; a) patchy blue-grey and beige micarb micarb is of a moderate grain size; common veins with pink-grey to white spar infill, 4-15 mm wide; b) beige, blue-grey, and dark brown micarb intermingle; common spar-filled cavities and extensive veining, $\pm$ peloids; bivalves, mussels, tube worms, gastropods, scaphopods.	2809511	6107680	UH.6 UH.10.1 to UH.10.5 UH.100.8 to UH.100.11 UH.M1 UH.M5
	UH.B	A scattering of small seep carbonate scraps, used as gravel on a farm track; less than 0.4 m in width.	Samples of well preserved fossil specimen were taken from this site.	2809530	6107625	UH.100.4 UH.100.5
	UH.C	A single, half buried seep carbonate boulder in pasture; 0.6 m in length, width of 0.5 m.	Light brown micarb; abundant spar-filled veins and cavities, infill white to pink-grey, which stand proud on boulder surface; common small bivalves typically partially infilled with white spar with a central empty void.	2809406	6107235	UH.4A
	UH.D	Two small seep carbonate boulders both less than 1.5 m in length.	Light to medium brown micarb with abundant sand-sized dark grains intermingled with patches of a red-brown micarb lacking any foreign grains; one boulder also features abundant bivalve fragments and burrows infilled with micarb, spar, and peloids.	2809401	6107219	UH.4B UH.11.6
	UH.E	A quarried outcrop consisting of a steep ridge protruding from the moderately sloping, southwest-facing hill side which exposes many windows of the seep carbonate beneath the grass; there are many float boulders scattered around the base of the ridge; ridge is ~ 15 m long, and the height from its base to the top is 6 m.	Dominant lithology is a light beige to white micarb containing ≤ 1 mm light to dark brown inclusions; abundant cavities in some areas, typically with many infill layers of micarb and spar; 1–2 mm thick, spar-filled veins are common; fossils occur in patches, burrows and bivalves; a minor facies has a light brown micarb rich in mussel and worm tube fossils.	2809292	6107071	UH.11.1 UH.11.2 UH.11.3 UH.11.4 UH.11.5 UH.102 UH.104.1 UH.M9
	UH.F	A series of small outcrops stretching up a hill side; eight boulders, 0.3-1 m in length, are revealed in a sequence along ~ 20 m of the slope, each separated by 1 – 12 m of grass; mostly to partially buried.	Light to medium brown, fine grained micarb with few small dark grains within; central patches of blue-grey micarb; 1-2 mm wide, white to grey, spar-filled veins; largest boulder exhibits bedding.	2809330	6106822	UH.M8 UH.M17
	UH.G	A small boulder with its upper surface exposed from the pasture; length of 1.1 m, width of 0.65 m.	Light brown to grey micarb; vein network with an average thickness of 4 mm; bivalve shell hash.	2809346	6107016	UH.5
	UH.H	A cluster of three large seep carbonate boulders, covering 2.2 x 1.9 m; numerous smaller boulders scattered around the central three.	Fine grained micarb with few to no foreign grains; patchy dark brown to blue-grey colour; common spar-filled veins, 2 – 6 mm wide; abundant large bivalves, articulated and hash; gastropods; strong hydrocarbon smell.	2809409	6107006	UH.M6 UH.M7
	UH.I	A group of outcrops on the eastern arm of the valley spread horizontally over ~ 15 m of the slope near the hill summit; four boulders > 1 m in size plus many smaller.	Light beige, dark brown, and blue-grey micarb, featuring dark foreign grains, are intermingled; common spar-filled cavities; bivalves, burrows; large, 15 cm thick, bifurcated vein with layers of pink-grey to white spar.	2809629	6106691	UH.3A
	UH.J	A group of 12 small boulders, all < 1 m in size, scattered along 15 m from the base to 5 m up the eastern valley arm; partially buried; likely to be float boulders.	Light brown, fine grained micarb with dark blue-grey central patches; many cavities and burrows with infills of a siliciclastic rich brown micarb; inconsistent lithology, changes to a dull, medium brown micarb with abundant thin, spar-filled veins.	2809574	6106662	UH.2 UH.M16
	UH.L	A scattering of small boulders on the western arm of the valley; largest reaches 0.75 m in size; mostly buried in the slope.	Homogeneous dark brown micarb with patches of blue-grey; common thick veins, white to grey spar infill; bivalve fragments in small but dense patches; strong hydrocarbon smell when fractured.	2809540	6106608	UH.1 UH.1.5
	UH.M	A single boulder situated in gently sloping pasture; 1 x 0.4 m in size; mostly buried with only a single, irregular face revealed.	Light brown micarb with orange to brown foreign grains; extensive spar-filled vein network is visible on the weathered boulder surface.	2809686	6106650	



Figure 5.6 - Ugly Hill North. In the foreground is the largest boulder of the UH.A outcrop. The small scrappy boulders of the UH.a float zone can be seen scattered down the hill below.



Figure 5.7 - The quarried UH.E outcrop at Ugly Hill South. This image looks up the southwest facing ridge, upon which many 'windows' of seep carbonate are revealed.



Figure 5.8 - The dominant lithology at UH.E outcrop is a light beige micarb containing many dark, foreign, sand-sized grains and a few thin, spar-filled veins.

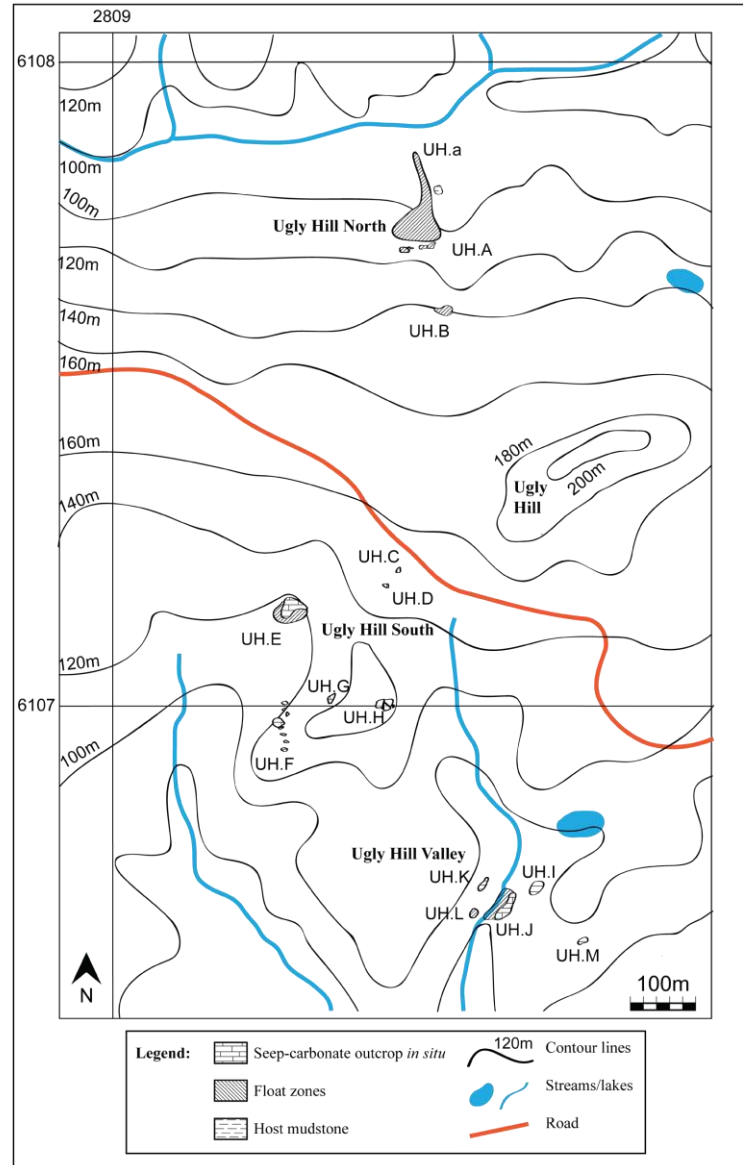


Figure 5.5 - Ugly Hill field map illustrating the three sub-sites of the Ugly Hill site, the size and location of the 12 seep carbonate outcrops and the location of the two host formation outcrops.



Figure 5.9 - Most of the 12 small boulders of the UH.J outcrop of Ugly Hill Valley. These boulders may be related to UH.I above, since tumbled to the valley floor due to erosion of the slope.



Figure 5.10 - The 15 cm thick vein found in a boulder at UH.I. The fresh surface reveals an infill of many layers of white to pink-grey minerals, which become discoloured in the weathered boulder surface.



Figure 5.11 - A rare gastropod fossil is present on the weathered surface of a boulder at UH.H.

The Ugly Hill North sub-site comprises only one main *in situ* outcrop constituting three angular boulders situated approximately half way down a moderately sloping, north-facing hill. Below this is a large float zone, UH.a, which extends for some 200 m down the slope to the north (Fig. 5.6). This area of seep carbonate float comprises mainly small, scrappy boulders ≤ 1 m in size, although the largest boulder, found near the base of the slope, reaches 1.5 m across. It appears that much of this material has tumbled from the slopes above, as most of the UH.a boulders extend down to the base of the slope directly below and to the west of the *in situ* UH.A boulders. This indicates that the UH.A boulders may previously have been a much larger deposit of cold seep carbonate, which has gradually tumbled down slope due to erosion of the hillside.

The Ugly Hill South sub-site contains five outcrops which are only small clusters of seep carbonate boulders, typically weathered and well rounded. The exception is the UH.E outcrop - a quarried outcrop consisting of a steep ridge protruding out from the moderately sloping hillside in a southwest direction, which exposes many windows of the seep carbonate protruding from the soil and vegetation. The ridge has been made more prominent by quarrying activities, and there are many float boulders to be found scattered around the base of the ridge. It is also possible that some of these float boulders have been transported to this outcrop location by slips moving down the valley (Francis *pers. comm.* 2009). The ridge is approximately 15 m long, and the height from its base to the top is 6 m. The best seep carbonate exposures are on the southeast side of the ridge, from the base to the ridge top (Fig. 5.7), and continuing around to the east of the ridge. There are many float boulders hidden within the long grass and pine tree off-cuts in the amphitheatre-shaped space between the ridge and the hillslope.

The outcrops of the Ugly Hill Valley sub-site occur on both arms of a small, northeast-southwest orientated valley. Valley walls are steep, and there is a small stream at its base. On the eastern arm there are many scattered boulders of various sizes, which have been divided into two broad outcrop groups (UH.I and UH.J). The 12 small seep carbonate boulders of UH.J are scattered along 15 m of the lower section of the slope (Fig. 5.9), and combined with their shallow burial this implies that they are likely to be float material - perhaps genetically related to the UH.I outcrop higher on the slope, and which since have slumped down off the

major capping carbonate mound to their present location. The western arm of the valley hosts one group of small, mostly buried boulders and the eroded slope reveals a scarp of the host formation.

Lithology and other features

The seep carbonate lithology across the Ugly Hill site varies considerably. Micarbs are typically medium to dark brown in colour, in places exhibiting patches of blue-grey (fresh) in more central portions of samples (facies UH.F1). In some boulders there is an intermingling of brown, light beige, and orange-brown micarbs. Only at the UH.E outcrop is there an extremely pale beige micarb (facies UH.F2; Fig. 5.8), which may be the result of intense weathering. The micarbs contain from nil to common dark, sand-sized, foreign grains and intraclasts which can reach 4 mm in size. Boulders at outcrops UH.E, UH.H, and UH.L emitted a very strong hydrocarbon smell upon fracturing to reveal a fresh rock face.

Spar-filled veins and cavities are a common feature, with infill minerals ranging from white to pink-grey to brown micarbs. Rarely, there are accumulations of peloids cemented within these voids. Veins are typically thin, most <10 mm wide and in places these appear to have caused some alteration in the surrounding fabric, hinted by a colour change in the adjacent micarb area. However, an exceptionally large vein, 15 cm wide, occurs at the UH.I outcrop (facies UH.F3), where it bifurcates near the centre of the boulder (Fig. 5.10). This particular boulder was extensively sampled (sample UH.3A). The vein itself is made up of many alternating layers of pink-grey and white spar, colours which appear only on fresh surfaces and not on the weathered boulder surface. The indurated, sparry infill mineralisation of the veins and cavities causes them to stand out as ridges and knobs on the weathered boulder surfaces. Samples taken from the UH.F outcrop feature pockmarked bands on their outer surface, due to the weathering away of large intraclasts from within thick spar-filled cavities and veins. Multiple phases of brecciation and subsequent healing are implied by complex vein networks and associated large micarb clasts which are, in places, found throughout the boulders.

Fossils are abundant throughout the site. Large bivalves (clams and mussels) are widespread, although they tend to be found in localised yet dense accumulations. The best examples of these are at outcrops UH.A and UH.H. Beds of whole shells (Fig. 5.12A), often still articulated, or shell hash (Fig. 5.12B) are found at all the three sub-sites. The bivalves reach 6 cm in length but typically occur in groups of a similar size/maturity. Shell interiors can be filled with the same matrix material as their surroundings, be partially infilled with sparry mineralisation and later phases of micarb precipitation, or have a central empty void.

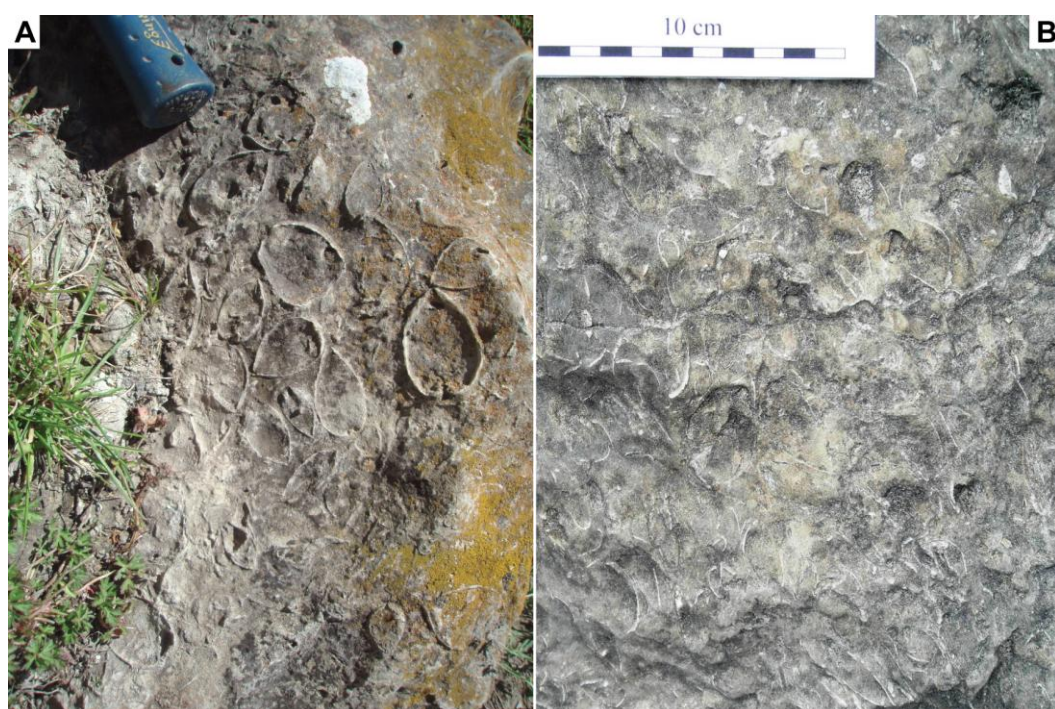


Figure 5.12 - Fossilised lucinid bivalves in the UH.A outcrop. **A:** A bed of well preserved, articulated bivalves stands proud of the weathered micarb boulder surface. **B:** A shell hash bed composed of highly fragmented bivalve shells with occasional intact and articulated specimens.

Accumulations of preserved worm tubes are also identified on these boulders, typically seen in cross section. Often associated with worm tube clusters are small, asymmetrical fossilised mussels (Saether in review) – the best examples of these species and their relationships is at the UH.E outcrop. Many of the mussels remain articulated, their asymmetrical shells hosting a variety of infill materials - white sparry precipitation, a dull pink-grey mineral, cream to light brown micarb, a green-grey micarb, or a combination of any of these. Numerous specimens

exhibit a geopetal infill of micarb and spar, indicating the orientation of the sea floor during carbonate precipitation. The articulated mussel shells are typically small, with an average length of 1.5 cm, and in addition there are many disarticulated and fragmented shells.

In addition to bivalves and worm tubes, there are some gastropod fossils scattered throughout the site with an average diameter of 3.5 cm (Fig. 5.11). A single scaphopod specimen (Fig. 5.13) was found on the central boulder of the UH.A outcrop, and burrows are common, from 1.0 – 2.5 cm in diameter.



Figure 5.13 - A scaphopod, or tusk shell, on the surface of the central boulder at the UH.A outcrop. Note the bivalve fragments in the surrounding micarb.

Ugly Hill Valley host formation outcrop

The host formation encompassing the Ugly Hill Valley and the Ugly Hill South outcrops was sampled on the western arm of the valley at U23 (2809562E/6106673N). The over-steepened slope in this location has fallen away to reveal the underlying geology. It is a massive, dark grey mudstone containing

scarce tiny bivalve macrofossils. It has weathered to yield a weak and frittery surface.

5.3.2 Site summary

Ugly Hill consists of a vast amount of float/repositioned seep carbonate boulders. This includes the majority of Ugly Hill North and many of the Ugly Hill Valley boulders. It can be inferred that the topographically low UH.J outcrops are likely to be genetically related to the UH.I outcrops, and have slumped down to their present location post-formation.

There are a number of lithologies displayed in the 12 separate seep carbonate outcrops of Ugly Hill. These vary from carbonate cemented facies containing fine to medium grained siliciclastics, various amounts of spar-filled cavities, a variety of fossilised biota (numerous bivalves, tube worms, gastropods, scaphopods), and veins ranging from thin, <1 mm, white, stringer-veins to extensive anastomosing vein networks and extremely thick veins (up to 15 cm wide) displaying a multitude of mineralisation phases.

5.4 NGAWAKA

Ngawaka is the westernmost of the five seep carbonate sites in this study, and is displaced some 4 km from the general northeast-southwest strike line along which the other four outcrops lie (Fig. 5.1). The site is divided into two sub-sites; Ngawaka East and Ngawaka West. The sub-sites are located on two separate farms, but are only some 500 m apart. Access to both outcrops is down Ngawaka Road, with permission from the two land owners (see Appendix 1). A summary of the field characteristics, data and sampling is included in Table 5.3.

Table 5.3 – Summary of the field characteristics of the seep carbonate outcrops at Ngawaka (NG).

Site	Outcrop name	Outcrop size and morphology	Outcrop lithology & characteristic features	NZMG Easting	NZMG Northing	Samples collected
Ngawaka	NG.A	Largest un-interrupted outcrop of the study; 15 m long, 8 m high; steep, weathered; float extends down slope to the northwest.	Four vertical transects reveal lithological variations up the outcrop; base micarb is light beige, and contains coarsely brecciated, orange-brown clasts, spar-filled veins, and bivalves; mid-section has light to medium brown micarb with abundant dark foreign grains, thick spar-filled veins, and common burrows and bivalves; uppermost micarb is very pale grey to beige, has abundant brown foreign grains and intraclasts, zones of brecciation, and vague bedding.	2803956	6107494	NG.2 NG.A-F NG.M7 NG.M1 NG.M2
	NG.B	A group of three large and numerous smaller, irregularly shaped seep carbonate boulders; half exposed from the soil; largest boulder is 2.4 x 1.5 m, however average size is ~0.4 m by 0.7 m.	Light to medium brown micarb containing foreign brown, orange, and black grains up to 3 mm in size; many spar-filled vugs and extensive vein networks; burrows.	2804027	6107510	NG.1 NG.M6
	NG.C	A small group of small boulders covering an area of 4.3 m ² , with an average boulder size of 0.3.	Brown micarb hosts an abundance of orange-brown and grey grains and intraclasts; numerous iron stained areas; spar-filled veins and brecciation are common.	2804376	6107585	NG.8
	NG.D	A quarried outcrop, with the major seep carbonate body removed to leave a horse-shoe shaped ridge of dirt and scrappy seep carbonate boulders; largest boulder present is 0.3 m in size.	Homogeneous brown micarb, containing few dark, foreign grains, and thin spar-filled veins; many burrows; rough bedding.	2804473	6107366	NG.M5
	NG.E	A large seep carbonate outcrop composed of a large number of boulders stacked up on top of a large intact seep carbonate mound; covers 10 x 8 m; upper section appears <i>in situ</i> , float on slope beneath.	Light to medium brown micarb with few brown foreign grains; common thin veins in-filled with a white to grey mineral, <2 mm wide; accumulations of bivalves.	2804430	6107266	NG.5A
	NG.F	A scattering of small boulders at the hill top; average boulder size is 0.7 m; irregularly shaped; remain half buried in the soil.	Medium brown micarb containing silt to sand sized dark foreign grains; very thin, ≤1 mm, veins infilled with white-grey spar; the few cavities are infilled with a pure looking, dark grey-brown micarb; bivalves; strong hydrocarbon smell.	2804383	6107259	NG.6
	NG.G	Two irregularly shaped, partially buried boulders on the western side of the hill just below the summit.	Light to medium brown, pure looking micarb with few fine, brown, foreign grains. Most veins are <2 mm in width, occasional thicker veins with many layers of infill - white to grey-pink spar and dull	2804371	6107251	
	NG.H	Largest grouping of boulders on the hillside; a large number of boulders, positioned either individually and scattered down the south-facing slope or in accumulations of boulders; boulder size varies from 0.4 - >2 m in width.	Typical homogeneous light to medium brown micarb with tiny, dark, foreign grains; lower boulders feature abundant bivalves and some corals, and complex and anastomosing vein networks which stand proud of boulder surfaces; upper section has few bivalves, numerous burrows, large spar-lined cavities, and some 1 mm wide spar-filled veins.	2804378	6107236	NG.M3
	NG.I	Soil has slipped down the steep slope to reveal this large, intact, carbonate mound and surrounding scrappy boulders; 2.3 x 1.5 m in size.	Light to medium brown micarb with an abundance of fine grained, brown, foreign grains and common thin veins and cavities; bivalves, whole and shell hash; vague bedding.	2804364	6107215	
	NG.J	A long zone of boulders near the base of the slope; generally small, <0.8 m in width; likely to be repositioned float boulders.	Light to medium brown micarb, with abundant fine brown grains, white to grey spar-filled veins and cavities; rare thick veins, 8-12 mm wide, infilled by a cream to pink spar and pale, pure looking micarb; bivalves, whole and shell hash.	2804365	6107214	NG.3 NG.7 NG.M4
	NG.K	Six seep carbonate boulders ≤1 m in width; clustered together near slope base, likely to be float material.	Micarb is light to medium brown with plentiful fine, brown grains; spar-filled veins from 1-8 mm wide; areas of a pure, inclusion free micarb ranging from a pale beige to blue-grey, often in irregular layers reaching 20 mm thick; bivalves, coral; vague bedding.	2804307	6107197	NG.M8

5.4.1 Site description

The Ngawaka site has 11 outcrop groups; three at Ngawaka East and eight at Ngawaka West (Fig. 5.14). The largest, continually exposed seep carbonate outcrop is at Ngawaka East, in addition to two much smaller outcrops and an outcrop of the host formation. The outcrops at Ngawaka West can also be of a significant size, whether they are a single intact mound or accumulations of boulders. These outcrops are spread over the southern and western slopes and summit of a hillside.

The outcrops at Ngawaka have designated outcrop names fronted by the abbreviation “NG” for the Ngawaka site followed by a capital letter for presumed *in situ* outcrops or a lowercase letter for float zones below outcrops (Fig. 5.14). Specific facies found throughout the site are given codes NG.F1 through NG.F3.

Size and morphology

As at the other sites in this study, the majority of the outcrops at Ngawaka are composed of small groupings of boulders. These boulders can range in size from <0.4–2.5 m across, and be free-standing on the grass/soil or in large accumulations (Fig. 5.15A), partially buried, or almost totally buried so as only to have the upper surface exposed. Individual boulders are typically very weathered and well rounded. There are many such outcrops at the eastern sub-site, which is dispersed over a gently sloping hill to the southeast of the Ngawaka West sub-site (Fig. 5.19). Seep carbonate boulders are found over the southern and eastern flanks of the hill, up on the hill summit, and further along the ridge to the northeast (Figs. 5.14, 5.15B). These outcrops are all assumed to be *in situ*, or only slightly locally displaced. The typically widely scattered groups of seep carbonate boulders have all been designated an outcrop code, with a total of eight outcrop groups.

At the Ngawaka West sub-site there are two outcrops composed of small boulder groups (NG.B, NG.C); however, the NG.A outcrop is somewhat distinctive. This is the largest uninterrupted outcrop of the five southern Hawke’s Bay seep carbonate sites. It is situated on a steep, northwest-facing slope used for grazing.

The outcrop is partially exposed on three sides, constituting the large and very steep northwest-facing outcrop front, approximately 15 m in length and 8 m high (Fig. 5.20), and the two sides of the outcrop, as well as the outcrop top. It is unknown how far back into the hillside the deposit sits. The centre of the outcrop is at U23 (2803956E/6107494N).

Lithology and other features

Lithologically, many of the boulders at Ngawaka are very similar. The major facies (NG.F1) is a light to medium brown coloured micarb which contains few to abundant silt to sand sized foreign grains in shades of brown, orange, and black, and small (≤ 3 mm) intraclasts (Fig. 5.15C). It is common for central areas of boulders to show micarb with a blue-grey shade, indicating freshness.

The micarb often features large cavities and veins, with the infill cement varying from spar in shades of white, pink-grey and orange-brown, to pure-looking micarbs (Fig. 5.15D). Spar-filled veins are typically thin, ≤ 5 mm; however, larger veins, up to 12 mm in width, occur within some boulders. The vein networks commonly dissect the boulders, surrounding brecciated clasts of micarb. Spar-filled veins and cavities are an apparent feature on the weathered outer surfaces of boulders due to their resistant mineralogy (Fig. 5.15E). Iron staining affects exposed areas of the boulders – typically this rusty orange-brown stain is found around the edges of cavities and veins, and less commonly covering patches of micarb.

Localised variations of this dominant facies include patches of a very pure looking, inclusion free micarb, ranging in colour from pale beige to blue-grey (facies NG.F2). This fabric occurs sporadically in the NG.K outcrop, and in few boulders of the NG.J outcrop as irregular layers reaching 20 mm thick, perhaps infilling large voids in the primary micarb, and often associated with a cream to pink sparry mineral. Small peloids also are seen re-cemented by later phases of spar. Irregular and sporadic bedding planes were identified on boulders at outcrops NG.D, NG.I, and NG.K (Fig. 5.16). The main boulder found at outcrop NG.D consists of a micarb containing relatively large foreign grains and

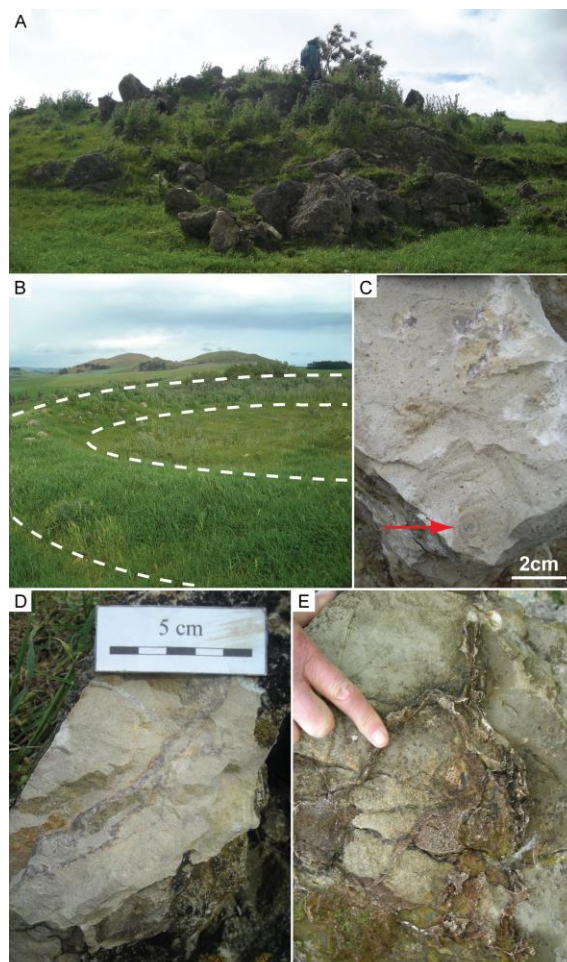


Figure 5.15 - Various images of Ngawaka outcrops, features, and facies. **Image A:** The NG.E outcrop is a large group of both *in situ* and float boulders. **Image B:** The quarried NG.D outcrop has had the bulk of the micarb removed to leave a small, rounded ridge of soil containing many small, scrappy, seep carbonate boulders (between dashed lines). **Image C:** A fresh exposure on the NG.B outcrop. These boulders are composed of a light grey-brown micarb containing abundant dark grains, spar- and micarb-filled veins and cavities, and burrows (arrowed). **Image D:** A fresh surface on the NG.G outcrop reveals the typical brown micarb containing dark, foreign grains, thin spar-filled veins, and cavities. Of note is the larger vein infilled with a grey-pink mineral and a pure-looking, dull green-grey micarb. **Image E:** An extremely resistant vein network stands proud of the weathered surface of a boulder at the NG.H outcrop.

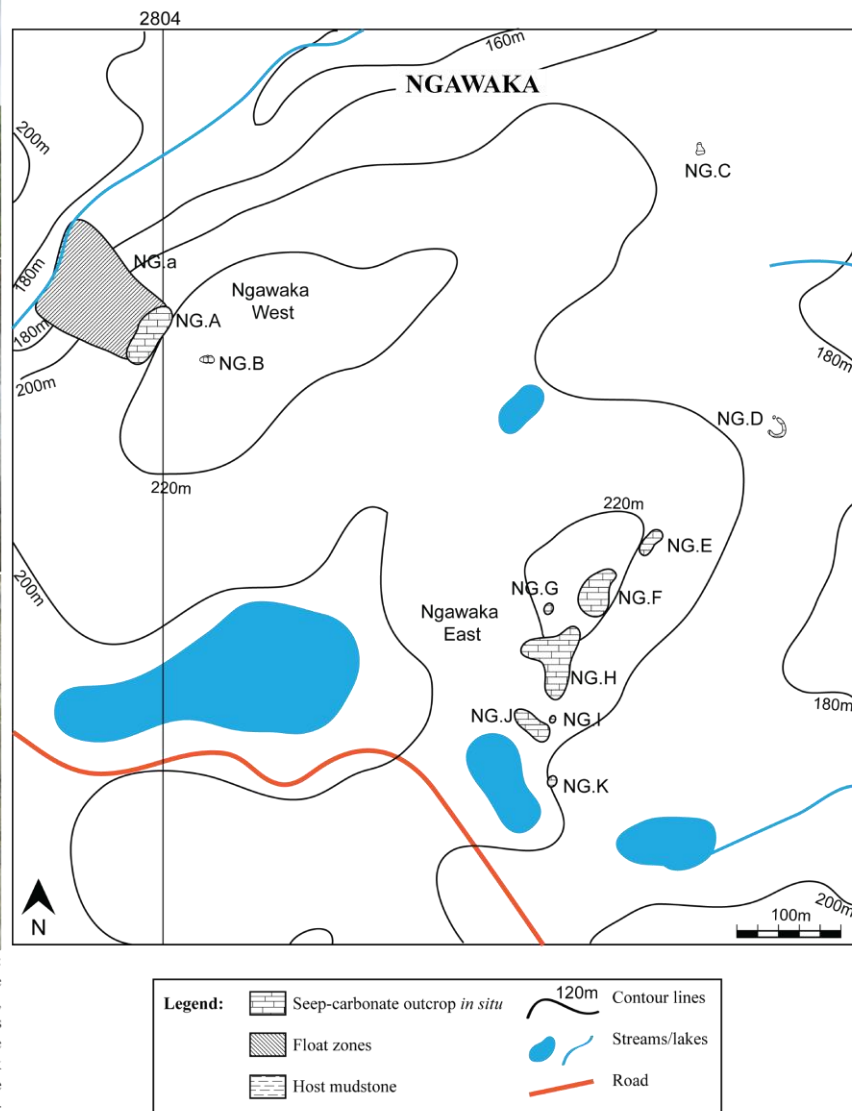


Figure 5.14 - Ngawaka field map illustrating the size and location of the two sub-sites and the combined 11 seep carbonate outcrops.



Figure 5.16 - Horizontal bedding exhibited by a float boulder at NG.D.

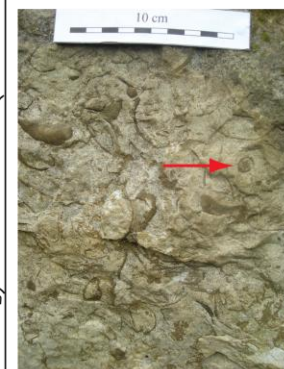


Figure 5.17 - A shell bed in a NG.K boulder also features fossilised branching corals (arrowed).

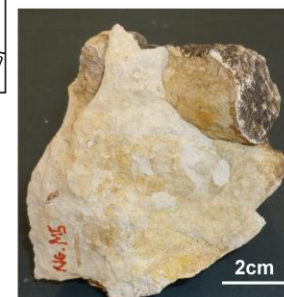


Figure 5.18 - A large burrow, 27 mm in width, from outcrop NG.D.

intraclasts. Bedding at NG.K is exhibited by most of the boulders at this outcrop; however, these are oriented in a range of directions and dips, supporting the idea that they are in fact repositioned float boulders.

Fossil content over the site includes an abundance of bivalves, both whole specimens and shell hash (Fig. 5.17). Whole specimens are relatively small in comparison to those at other sites, reaching a maximum of only 5 cm in length. These are commonly seen standing proud of boulder surfaces due to unequal rates of weathering. Corals are rare, seen only at outcrops NG.I and NH.K. Burrows (reaching 27 mm in diameter) are a common feature present throughout boulders of both sub-sites (Fig. 5.18), with infill fabrics including spar and micarb in shades of brown to grey.



Figure 5.19 - Some of the outcrops of the Ngawaka East sub-site. Photo taken facing north east. The outcrops of this site are generally groups of seep carbonate boulders. Outcrops NG.E and NG.F are found just over the hill; outcrop NG.D is some distance behind the hill.

Over the wide scattering of boulders which make up outcrop NG.H there are a number of lithological variances. The bulk of the outcrop is facies NG.F1 - a light to medium brown colour with an abundance of sand-sized, dark, siliciclastic grains. However, some major lithological characteristics vary vertically through the scattered outcrop boulders. Lower in the hillside are dense accumulations of fossilised bivalves and corals. Bivalves are found both articulated and disarticulated. The vein network here is complex and anastamosing; the mineral infill is extremely resistant to weathering, causing it to stand up to 5 mm proud from the micarb on boulder surfaces (Fig. 5.15E). Higher up the hillside bivalve

fossils can still be identified in the NG.H boulders, although these are not as common nor in such densely packed groupings. Here, numerous burrow structures occur, along with some large crystal-lined cavities. The vein network also reduces substantially, although rare, thick veins still occur amongst the typical 1-mm-thick spar-filled veins.

Outcrop NG.A

A different approach to studying the lithology of outcrop NG.A was undertaken in order to gain some insight about the broad facies changes that occur vertically down the exposure. Four vertical transects of the outcrop were studied in detail during the course of the field work. These columns are distributed along the face of the outcrop (Fig. 5.21).

The base of the outcrop is dominated by a coarsely brecciated facies (facies NG.F3; Fig. 5.22). This facies features an abundance of micarb clasts with an average size of 40 mm. The micarb clasts are light brown, although they usually appear peach-coloured due to weathering. The individual clasts are closely packed and healed together into an intact rock mass by sparry veins ranging from >1 to 8 mm wide and later micarb fabric. This later micarb phase, intermingled with the brecciated NG.F4 facies is a more homogeneous light brown to cream coloured micarb featuring common bivalve remnants and crystalline vugs.

In the central horizon of the NG.A outcrop NG.F3 grades out. Here, the outcrop is dominated by facies NG.F1 - light to medium brown micarb containing abundant dark brown to black siliciclastic grains and localised iron staining (Fig. 5.22). There are abundant mineralised veins throughout this facies, ranging in colour from white sparry infill to pink-grey infill and reaching 20 mm in thickness. These vein networks are extensive and often chaotic. Burrows are also a common feature of this section of the outcrop, the largest found reaching 29 mm in diameter. Bivalves are abundant, occurring sporadically in small accumulations. They have an average length of 40 mm.

The uppermost region of the outcrop features relatively sparse crystalline veins and patchy zones of the brecciated facies NG.F3 of the lowermost section (Fig.



Figure 5.20 - The entire *in situ* part of the NG.A outcrop and the top of the associated float zone. View facing east. Backpack in foreground for scale.

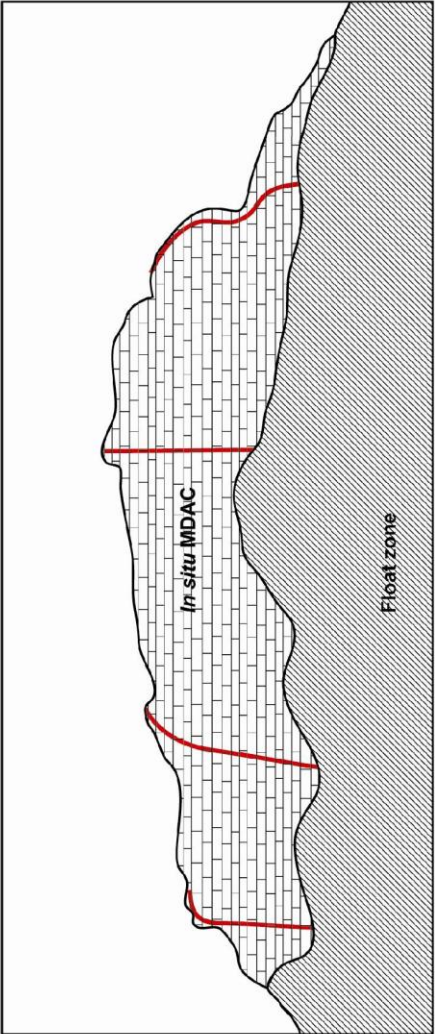


Figure 5.21 - A sketch of the NG.A outcrop illustrating the *in situ* and float zones, and locations of studied transects (in red).

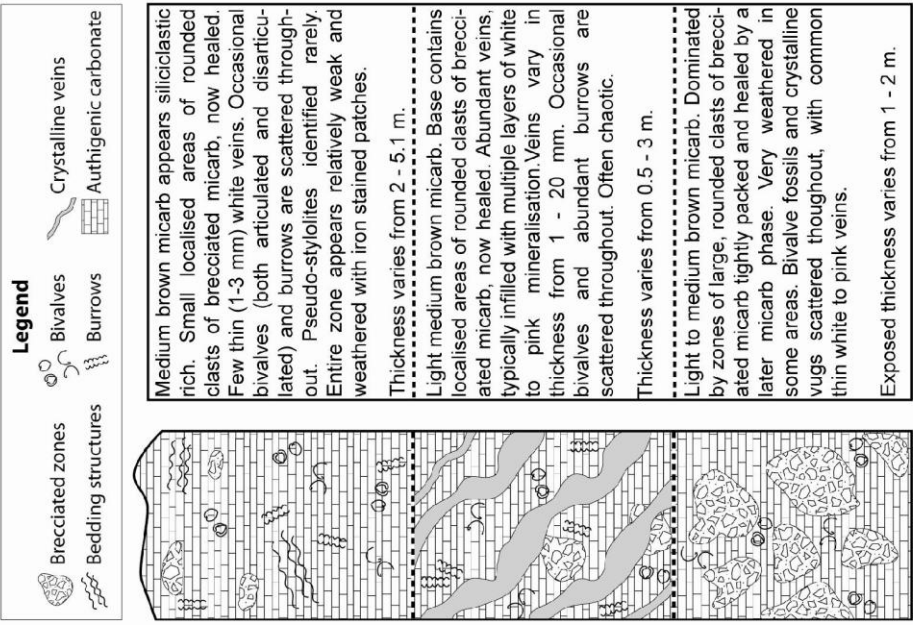


Figure 5.22 - A composite, schematic stratigraphic column for NG.A illustrates the three major variations in lithology over the outcrop.

5.22). The veins present are typically very thin (<3 mm wide). The micarb varies from pale grey to light brown in colour, and contains abundant medium brown clasts and silt to sand sized dark siliciclastic grains. In this upper sector bedding can be identified. These structures are undulating along their length as well as showing variable dips (100/28° ESE to 150/62° SE).

5.4.2 Site summary

Over the many scattered groups of boulders of the Ngawaka East sub-site there is little change in lithology; the main facies is a light to medium brown micarb with a varying abundance of foreign, dark grains of coarse silt to sand size, common thin veins and cavities with infill varying from white and pink-grey spar to pure-looking, dull coloured micarbs (facies NG.F1). However, variations do occur:

- The uppermost outcrop, NG.D, contains brown foreign grains of a much larger size.
- Bivalve fossils have been identified continuously throughout the scattered outcrop groups; however, only in the upper reaches of the hillside are burrows typically found, and corals are scattered amid the bivalves of the lower outcrop boulders.
- In the lowest extent of this sub-site there is also the addition of a minor micarb facies (NG.F2); a very pure looking, pale brown to blue-grey micarb often coupled with the cream to pink mineralisation.

At the main outcrop of Ngawaka West, there are some variations in the 8 m high exposed face. These variations are based on the abundances of fossils and burrowing structures, zones of brecciation, and the concentration and intensity of veins.

5.5 HAUNUI

Haunui is one of the largest cold seep carbonate outcrops in southern Hawke's Bay. A summary of the outcrop morphologies, field characteristics, GPS coordinates, and sampling is included in Table 5.4. The site is on private land off Epae Road, with access to the site gained by permission from the land owner (see Appendix 1).

5.5.1 Site description

Seep carbonate outcrops at Haunui are distributed over an entire hill, which is some 250 m in length (Fig. 5.23). The hill has been planted with pine trees and, depending on the season, is also covered in long grass. As a result, the locating of new and previously visited outcrops is often a complex task. Outcrops are scattered about all sides of the hill, as well as in a large outcrop at the summit which has been quarried in previous years.

The outcrops all have a designated code name; each begins with the abbreviation "HA" for the Haunui site, followed by a capital letter for an *in situ* outcrop or a lower-case letter for float zones (Fig. 5.24). Specific facies found throughout the site are given codes HA.F1 through HA.F3.

Size and morphology

Summit outcrops

At the summit of Haunui Hill is an extensive amount of seep carbonate boulders and rubble ridges occupying two separate, flat tiers. This area of the hill has been quarried by past farmers to utilize the store of hard rock, which has resulted in the current unusual morphology. Three channels (approximately 1 m deep) have been dug down into the upper tier of the summit, leaving two ridges comprising scrappy clasts of seep carbonate hosted in mudstone (Fig. 5.25A). The channels are surrounded by numerous large repositioned seep carbonate boulders and piles of boulders, which extend down onto the lower of the two summit tiers. The

strewn float boulders and ridges of the lower and upper tiers are collectively known as outcrop HA.G (Fig. 5.24).



Figure 5.23 - The pine-tree covered hill which makes up the Haunui site, viewed towards the southwest.

To the northeast of the upper tier of the summit is the highest point of the entire hill. This is a small area containing numerous large seep carbonate boulders, many over 1 m in length, which are positioned partially exhumed from the soil. This is labelled as the HA.H outcrop (Fig. 5.24). It is presumed that most of these boulders are *in situ*, with just a rim of small float boulders plus a larger zone to the north of float boulders tumbled from above.

Flank outcrops

Associated with the summit outcrops are float zones HA.I and HA.J (Fig. 5.24). These are composed of generally small seep carbonate boulders which have

tumbled from the uppermost outcrops due to erosion of the hill top and quarrying activities. Outcrop HA.I is to the southeast of the uppermost outcrops. It is a small zone primarily composed of one medium-sized seep carbonate boulder exposed vertically due to the steep incline of the hillside. It is likely that this boulder is *in situ*; however it is surrounded by abundant small clasts and boulders, all repositioned float which has fallen from above. HA.J is a large zone of float boulders, 0.3 - >1.5 m in size, which have been scattered down the northeast slope of the hill. Some of the large, upper boulders could potentially be *in situ*; however, the lack of evidence for their original orientation makes tumbling an equally likely option.

On the flanks of the hill are many outcrops of multiple small seep carbonate boulders. On the south and west slopes of the hill the outcrops become increasingly rare down slope, and they are also more difficult to find as the vegetation gets denser. There are five outcrops (UH.B, UH.C, UH.D, UH.E, UH.F) mapped on these slopes, plus many small float boulders derived from outcrops above, and possibly also during the extraction of the quarried material.

Outcrop HA.D is the largest of the flank outcrops (Fig. 5.24). It is an elongated outcrop stretching some 40 m down slope on a small ridge on the southern side of the hill (Fig. 5.25B). It consists of a central *in situ* outcrop which protrudes from the soil to a maximum of only 1 m, surrounded by a zone of small float boulders. All other flank outcrops are groups of small to medium sized boulders spread over <10 m of the slope (Fig. 5.25C). It is difficult to distinguish between *in situ* and float boulders, in particular the small boulders, however it is likely that the bulk of this material has tumbled from higher outcrops.

Lithology and other features

The most abundant facies at Haunui is a micarb containing abundant silt- and sand-sized, green-brown to black foreign grains which reach 2 mm in size and, less commonly, grains which appear to be intraclasts (HA.F1). Thin, spar-filled veins are common, with few boulders exhibiting complex vein networks. There

Table 5.4 – Summary of the field characteristics of the seep carbonate outcrops at Haunui (HA).

Site	Outcrop name	Outcrop size and morphology	Outcrop lithology & characteristic features	NZMG Easting	NZMG Northing	Samples collected
Haunui	HA.B	20 m of gentle slope containing numerous seep carbonate boulders ranging in size from 0.3-2 m in length.	Most boulders are a fine grained beige micarb with central areas of blue-grey micarb and an abundance of thin sparry veins; few coarser grained boulders; burrows, bivalves.	2807145	6104264	
	HA.C	A linear series of only partially exhumed boulders exposed down approximately 10 m of the northwestern slope.	An intermingling of fine and coarse grained micarb, with areas of beige and blue-grey micarb; coarser grained fabric contains many brown to black foreign grains; abundant spar-filled cavities.	2807085	6104289	HA.M1
	HA.D	Elongated outcrop stretching ~40 m down slope on a small ridge in the southern hillside; a central <i>in situ</i> outcrop surrounded by a zone of small float boulders, dense below the <i>in situ</i> outcrop.	A combination of a) dull, fine grained facies with light coloured lamina, spar-filled cavities and thin veins, peloids, and areas of blue-grey micarb, with b) beige micarb with many brown to black foreign clasts plus spar-filled veins.	2807179	6104248	HA.4 HA.12
	HA.E	Two large, partially exhumed seep carbonate boulders plus numerous smaller, scrappy boulders; the largest of the boulders has approximately 4 m of its length exposed by the slope.	Coarse grained facies containing abundant dark brown to black grains, cavities, vein networks, and patches of the much finer grained, beige facies; many thick, spar-filled veins run vertically up the largest boulder; burrows, bivalves, corals.	2807202	6104301	
	HA.F	Three large boulders exposed up the steep incline of the western facing slope; each boulder is >1 m in length, with the lowest nearing 2 m in length; the uppermost boulder is situated just below the lower tier of the hill summit.	Coarse grained facies containing abundant dark brown to black grains, cavities, vein networks, and patches of the much finer grained facies; many thick, spar-filled veins; abundant bivalves.	2807200	6104339	HA.13.3 HA.M2
	HA.G	A large number of seep carbonate boulders and rubble ridges upon two flat tiers.	Sandy, coarse grained facies with abundant green-brown to black grains; patches of a finer grained facies; common thin sparry veins; bivalves, burrows.	2807264	6104383	HA.3 HA.5 HA.11 HA.13
	HA.H	A small area containing numerous large seep carbonate boulders, many over 1 m in length, which are positioned partially exhumed from the soil.	Similar to HA.G - a coarse grained micarb with dark grains; a series of near-vertical sparry veins cuts through micarb.	2807296	6104395	HA.13.8
	HA.I	Float zone associated with the summit outcrops; a small zone composed of one large boulder exposed vertically, surrounded by abundant small clasts and boulders.	Very coarse, sandy facies; common burrows; bedding visible with a strike and dip of 035/60 SE.			
	HA.J	Float zone associated with the summit outcrops; large zone of float boulders, 0.3 - >1.5 m in length; scattered down the northeast slope of the hill.	The same coarse, sandy micarb facies common at the upper outcrops; few boulders comprised of a finer grained, blue-grey facies; abundant cavities; bivalves.	2807284	6104438	HA.1 HA.2

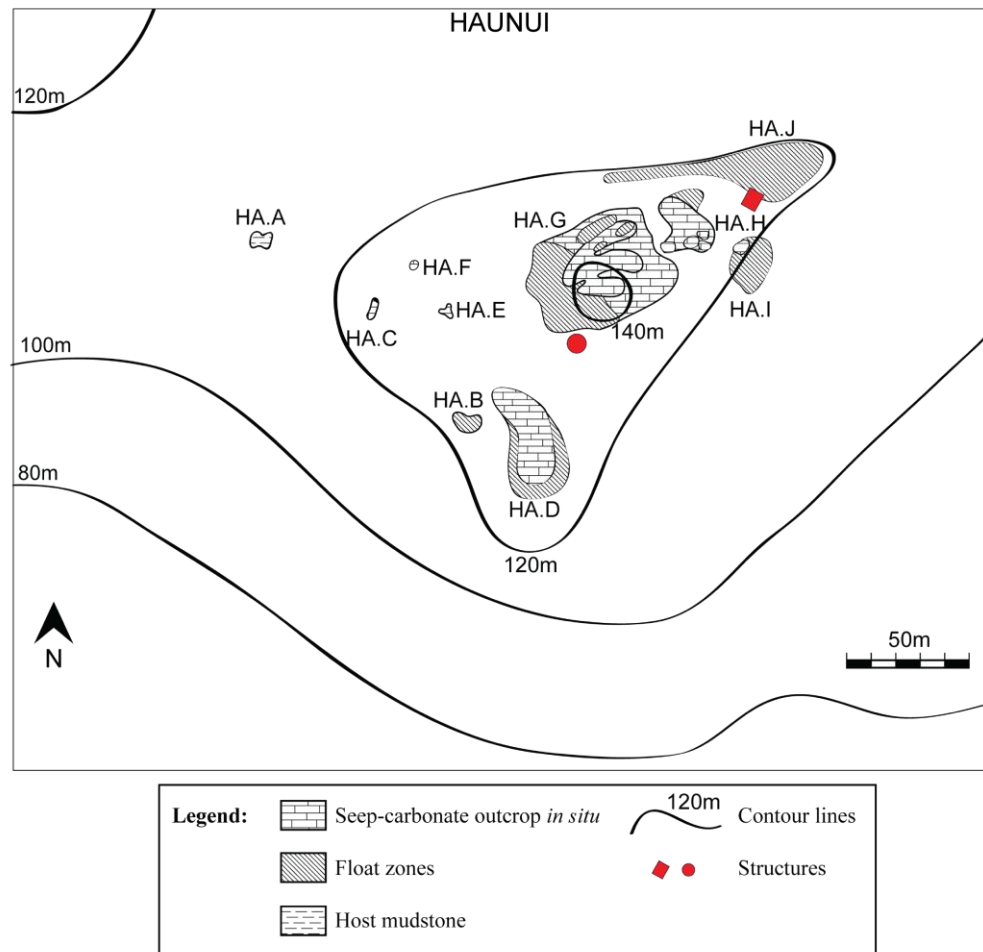


Figure 5.24 - Field map for the Haunui site illustrating the spread of outcrops exposed around the hill.

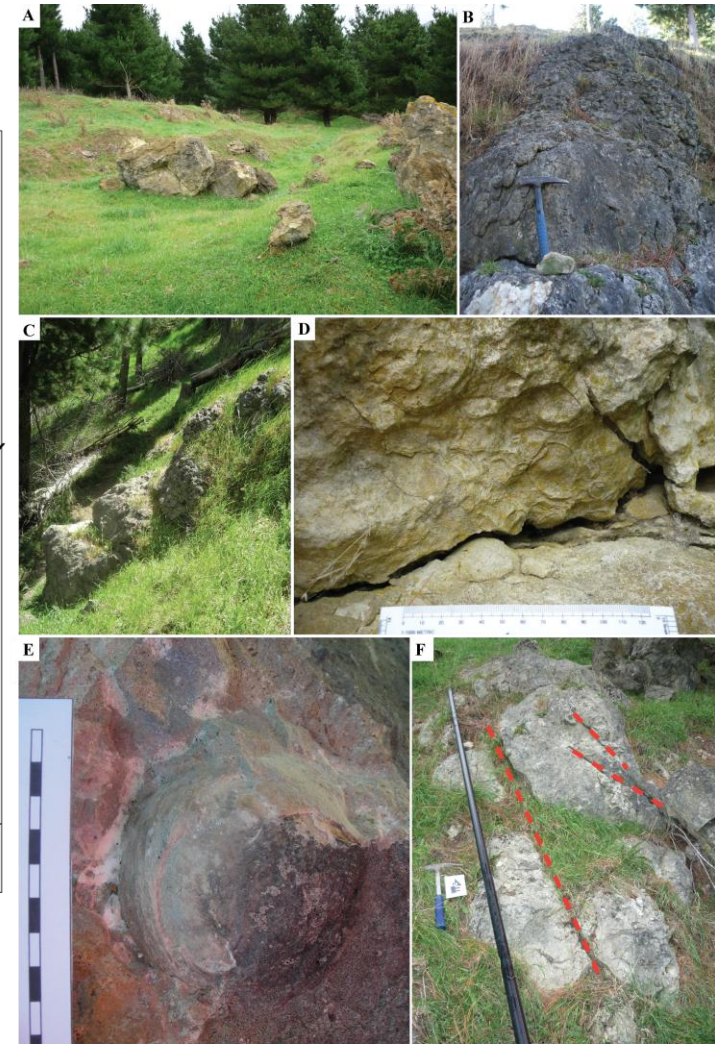


Figure 5.25 - Images of various outcrops at the Haunui site. **Image A:** The upper tier of the hill summit (HA.G). Note the central channel dug during quarrying of the site, leaving the two ridges in the foreground and centre left, and the number of large, loose seep carbonate boulders. **Image B:** The large, central, *in situ* section of the HA.D. Verticle changes in outcrop lithology are subtle. **Image C:** The HA.E outcrop is composed of a number of large and irregular boulders aligned down slope, their outer surface exposed by the steep slope of the southeast flank of the hill. **Image D:** A shell bed of articulated bivalves in the base of a float boulder at HA.G outcrop. **Image E:** A large, articulated bivalve within the HA.E outcrop. Scale bar divisions are in cm. **Image F:** Bedding in the mid-section of the HA.D outcrop (red dashed lines).

are many spar-filled cavities, generally less than 30 mm across, which are evident even on the highly weathered outer surface of the boulders.

A much finer-grained facies (HA.F2) occurs as patches interspersed within the coarser HA.F1 facies, and also makes up entire boulders. This finer grained facies is a dull medium brown colour with a scant amount of dark brown to black grains. It features occasional light coloured laminae. It commonly contains central areas of an unoxidised blue-grey micarb, small crystallised cavities, areas containing micarb peloids, and extremely thin sparry veins.

Boulders are typically well weathered on the outside – well rounded, stained, and leached of colour. Moreover, internally both facies (HA.F1 and HA.F2) can be considerably weathered in some areas - rust coloured iron staining is often visible along veins, lamina and on cavity edges. Also of interest at the Haunui site is the presence of vague, slightly undulating bedding. At outcrop HA.I the medium-sized, *in situ* boulder had bedding planes with a strike and dip of 035/60 SE. Approximately half way up the HA.D outcrop, bedding is also evident (Fig. 5.25F), with a strike and dip of 032/65 SE. In addition to these features, many of the boulders exhibit a strong hydrocarbon smell upon fracturing.

The boulders of the Haunui site host significant fossilised biota. Most common are bivalves, typically occurring in localised yet concentrated shell beds of either whole (Fig. 5.25D) or highly fragmented specimens; articulated valves occur sporadically. The bivalves are from 20-70 mm long. Bivalves are particularly common within the upper most boulder of outcrop HA.F (Fig. 5.25E). Many of these have been preserved articulated, and they reach a length of 90 mm. Burrows, 3-35 mm in diameter and of various lengths, are common throughout the site. Outcrop HA.E hosts a significant amount of fossilised branching coral.

Close inspection of the HA.D outcrop (Fig. 5.25B) reveals subtle variations in lithology from its base to its top. The bulk of the outcrop comprises an intermingling of the two major facies (HA.F1 and HA.F2). At the base of the outcrop fossils are few, limited to rare burrows and bivalves <50 mm in length. In this zone there are also extensive spar-filled veins, which are collectively lying at a right angle to bedding. The top of the outcrop is distinguished by an abundance of bivalve fossils that reach a length of 70 mm, and the presence of a third facies.

This final facies is a highly brecciated version of the fine grained micarb facies, with the inter-clast voids filled with a darker, late micarb (HA.F3).

5.5.2 Site summary

Haunui seep carbonate boulders are characterised by a combination of two main facies: (a) a coarse grained fabric containing abundant clasts ranging in colour from green to brown-black and containing a varying abundance of spar-filled veins and cavities, and (b) a finer grained facies of a medium brown colour and often containing lamina or streaks of beige micarb and very thin spar-filled veins. Bedding within boulders is present but uncommon. Fossilised remnants of biota are abundant at this site, dominated by bivalves, and also include common burrows and corals.

5.6 WILDER ROAD

The Wilder Road site is the southernmost site of the study (Fig. 5.1). It comprises eight small outcrops dispersed over <1 km² of farmland. It is divided into northern and southern sub-sites, which are located on different farms and separated by some 500 m. Access to the site is gained by four wheel drive vehicle along a farm track, with permission from the two land owners (see Appendix 1), and some easy walking is required to access the northern outcrops.

5.6.1 Site description

The Wilder Road site consists of four outcrops in the north and four in the south (Fig. 5.26). Each of the outcrops has been designated code name, starting with the abbreviation “W” for the Wilder Road site, followed by a capital letter for *in situ* outcrops and a lower-case letter for float zones. All of the outcrops are found in gently rolling pastoral hills. In addition, there is a currently active gas seep found locally (grid reference - U23E2806510/N6102926). A summary of the outcrop morphologies, field characteristics, GPS co-ordinates, and sampling is given in

Table 5.5. Specific facies found throughout the site are given codes W.F1 and W.F2.

Table 5.5 – Summary of the field characteristics of the seep carbonate outcrops at Wilder Road (W).

Site	Outcrop name	Outcrop size and morphology	Outcrop lithology & characteristic features	NZMG Easting	NZMG Northing	Samples collected
Wilder Road	W.A	Two clusters of boulders 10 m apart; northern most set contains 5 large boulders covering an area of 5 x 6.2 m; southern set contains 1 large boulder plus rubble, covering 5.6 x 6.9 m.	Beige & blue-grey, fine grained micarb; mild fluting; anastomosing vein networks, often standing proud of boulder surfaces; extensive brecciation.	2806458	6103321	W.M1
	W.B	A group of small boulders covering 10 x 8.6 m; individual boulders range from 0.3 - 1.0 m in diameter.	Two facies; a) homogeneous beige & blue-grey, fine grained micarb with few silt-sized dark-coloured grains; b) angular clasts of brecciated facies-a, re-cemented by micarb; spar-filled veins and cavities ± peloids.	2806423	6103266	W.M2 W.M7
	W.C	Small cluster of boulders covering 2 x 2 m; possibly with a much larger boulder buried beneath with irregular upper surface partially exposed; individual boulders range from 0.5 - 1.2 m in diameter.	Fine grained homogeneous micarb with spar-filled veins and cavities.	2806357	6103167	W.M3 W.M6
	W.D	Smallest outcrop of the site; a tiny window of boulders with only uppermost segments exposed by soil; covers 1.6 x 2 m.	Finely brecciated beige to blue-grey micarb re-cemented by micarb and spar-filled vein networks.	2806339	6103121	W.M4 W.M5
	W.E	Small group of boulders dominated by a 1 large boulder plus many smaller, scrappy boulders distributed around and downslope of the main boulder; covers 3 x 3 m on a moderate slope.	Fine grained, homogeneous, beige to brown micarb; contains spar-filled cavities, extensive vein networks, and brecciation.	2806278	6102718	W.M11
	W.F	Small group of tiny boulders which barely rise out of the grass; covers 2 x 2 m.	Fine grained blue-grey to beige micarb; contains abundant thick pink-grey to white spar-filled veins and brecciated clasts.	2806270	6102692	W.1
	W.G	Small group of boulders which barely rise out of the grass; boulders reach 0.9 m across, average of 0.5 m.	Fine grained blue-grey to beige micarb; contains abundant thick pink-grey to white spar-filled veins, many partially-filled cavities, and brecciated clasts.	2806268	6102668	W.2
	W.H	A large cluster of boulders, covering 5 x 5.5 m, on top of a ridge; float boulders scattered down slope to the east; boulders reach 2.2 m across, but average size is 1.2 m.	Two intermingled facies; a) homogeneous beige & blue-grey, fine grained micarb with few silt-sized dark-coloured grains; b) angular clasts of brecciated facies a, re-cemented by micarb; spar-filled veins and cavities ± peloids.	2806384	6102733	W.3.1, W.3.2, W.4.1, W.7.2, W.8.2, W.8.7, W.8.8, W.M8, W.M9

Size and morphology

Seep carbonate outcrops at Wilder Road range from very small boulders, which remain mostly buried and only show one face protruding out of a small ‘window’ in the grass or soil, to groups of small to medium sized boulders often in prominent accumulations in the pasture.

Many of the small, mostly buried outcrops barely rise out of the soil (e.g. outcrops W.C, W.D, W.F and W.G) (Fig. 5.27). The numerous loose boulders of these outcrops (typically <0.5 m in size) often appear to be sitting atop a much larger and mostly buried ‘boulder’ with an irregular upper surface. Perhaps what we are seeing is the uppermost surface of a much larger buried seep carbonate deposit revealed by erosion of the surrounding mudstone host formation. These extremely low-lying sub-crops are easily overlooked because they can be obscured by vegetation. Samples collected from these outcrops were taken from the exposed boulder-tops.

Boulders of the larger accumulations are typically <1.2 m across, and these groups of boulders can cover up to $\sim 10 \times 9 \text{ m}^2$ (Fig. 5.28). The largest outcrop (W.H) is a concentration of boulders at the top of a ridge with various *in situ* and float boulders scattered down the slope to the east to the small stream at its base (see Fig 5.3 for location). These boulders are assigned the code W.h to distinguish them from the *in situ* outcrop (W.H) at the hilltop. The biggest of the down-slope boulders is some 2.2 m long, 1.9 m wide, and 2 m high, although the average size of the float boulders is considerably smaller (0.5 m across). For many of the boulders, their small size and only partial exhumation makes it difficult to determine if they are currently *in situ* or if they are tumbled float material. It is likely that some of the upper boulders along with the hilltop exposure are *in situ*, with the lower boulders having fallen to their present position due to erosion of the hillside. Therefore, estimates of the true stratigraphic thickness of this outcrop are difficult to make, and could lie anywhere between 2 m and 15 m.



Figure 5.27 - The tiny outcrop of W.F. is composed of many small boulders which barely protrude from the surrounding soil and grass.

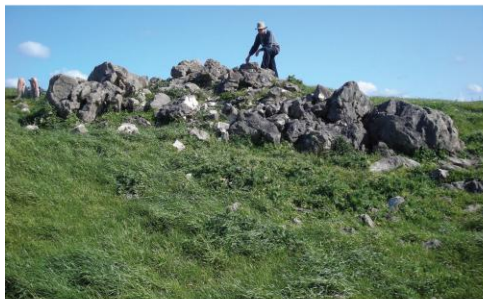


Figure 5.28 - A large group of small to medium sized boulders makes up the W.B. outcrop.



Figure 5.29 - The brecciated facies of the W.D. outcrop.

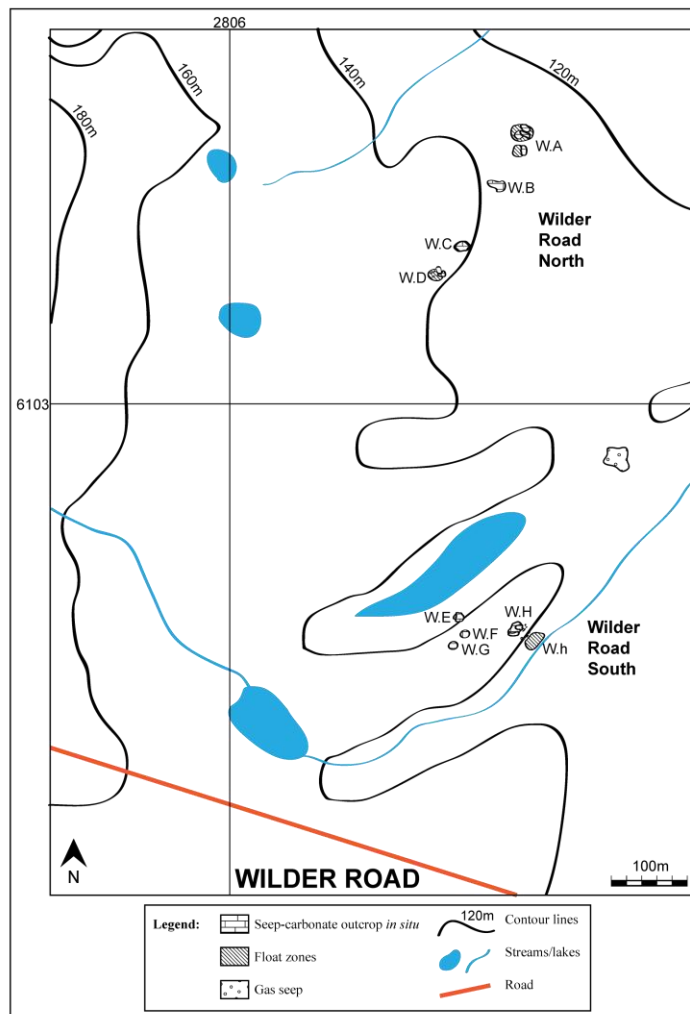


Figure 5.26 - Wilder Road field map showing the location of the 8 individual outcrops and the gas seep.



Figure 5.30 - A complicated mosaic of crystalline cavities and veins within a homogenous beige micarb fabric. Outcrop W.E.



Figure 5.31 - Anastomosing veins stand proud of the micarb background on a boulder at the northern W.A. outcrop.



Figure 5.32 - The gas seep at Wilder Road. View looking northeast.

Lithology and other features

Two major facies were identified at this site during fieldwork. Both facies exhibit a pure-looking micarb fabric as it contains only sparse, fine grained, dark inclusions, which are often difficult to discern. Facies W.F1 comprises the fine micarb with a massive, homogeneous texture with areas of beige (oxidised?) and blue-grey (fresh?) (e.g. samples W.3.2, W.M8; Fig. 5.33A). It contains few veins and cavities. Facies W.F2 consists of small, angular clasts of the fine grained micarb cemented together into an intact mass by a later micarb phase and/or an extensive, spar-filled vein network (e.g. sample W.M5; Figs. 5.29, 5.33B). The angular clasts show both a beige and blue-grey colouration, and range in maximum size from 2-20 mm. Large crystal-lined cavities and peloidal infills are also common in this facies. It appears that Facies B is a result of the (micro)brecciation of Facies A followed by subsequent micarb and/or spar precipitation to ‘heal’ the brecciated clasts back into an intact mass once again.

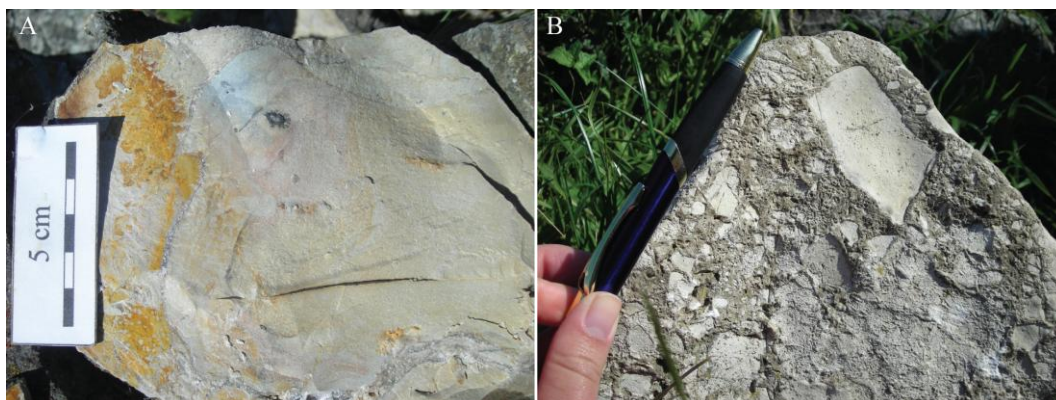


Figure 5.33 – Field images of the W.B outcrop at Wilder Road showing the variation in lithology across a single outcrop. **Image A:** Generally homogeneous fine grained micarb fabric of facies W.F1. **Image B:** Highly brecciated facies W.F2 containing angular clasts of facies W.F1.

Other minor facies include: (1) zoned, swirled micarb textures in an otherwise homogeneous fabric; (2) some extremely thick (>7 cm), pink-grey veins; and (3) fabrics featuring a mosaic of cavity and vein networks composed of multiple phases of mineral precipitation (Fig. 5.30). It is common to observe extensive, anastomosing, crystalline vein networks standing proud of boulder surfaces due to their greater resistance to weathering (Fig. 5.31).

A defining characteristic of the Wilder Road localities is their complete lack of macro-fossils. Not a single fossil or trace fossil has been found, which is in marked contrast to the other four sites in this study, all of which contain abundant fossilised remains of species typical of seep environments. This lack of fossils may aid in the interpretation of outcrop proximity to the main seepage conduit or have implications related to carbonate formation in relation to the paleo-seafloor.

Weathering is a common feature of the Wilder Road outcrops. In addition to the well rounded, smooth boulder surfaces, there are also long but shallow flutes down the sides of many boulders (e.g. outcrop W.A). Vague bedding structures were also noted on boulders at the W.A outcrop.

In relation to outcrop W.H, there appeared to be no systematic patterns in the distribution of lithologies in sampling stratigraphically downwards through the hillside boulders; rather the two major facies (W.F1 and W.F2) were intermingled. This lack of trend could be a natural characteristic of the paleo-seep system, or any original pattern previously present could be masked by the subsequent down-slope repositioning of the boulder material.

Host Formation Outcrop

The formation hosting the Wilder Road seep carbonate outcrops was sampled at a road cutting on the farm track leading to the southern outcrops, found at U23 (2806447E/6101794N). This site is undesirably far from the outcrops themselves, approximately 1.5 km directly to the south; however, there are no exposures of this host rock located any closer to the seep carbonate outcrops.

The host rock is a flysch that is well exposed by the road cutting (Fig. 5.34). The brown sandstone layers are typically better lithified than the alternating friable mudstone layers, making the former stand proud. The brown colouration of the sandstone is a weathering feature which commonly extends down into the grey mudstone as long fingers, typically along major fractures. Due to the extremely weak and friable nature of the mudstone layers, no distinct bedding could be identified.



Figure 5.34 – A road cutting on route to the Wilder Road outcrops exposes the host flysch; it is composed of alternating layers of a friable, grey mudstone with a poorly lithified brown sandstone.

5.6.2 Wilder Road Gas Seep

Between the northern and southern seep carbonate outcrops at Wilder Road is a currently active gas seep (Fig. 5.32). This seep was visited during March-April 2009 and is located at U23 (2806510E/6102926N). It occupies an area of 40-50 m², comprising both wet and dry mud with a small amount of overlying water.

Gases, presumably dominated by methane but also likely to contain other light hydrocarbons, rise up to the surface accompanied by significant amounts of water. During its journey to the surface the water has entrained silt and clay along the way, essentially forming mud. The water also contains dissolved salts. As this

water is discharging in a paddock, naturally the cattle are drawn to the source of water and salt. Therefore, at the time of visiting the gas seep was relatively unremarkable due to extensive pugging of the ground underfoot caused by the cattle, followed by evaporation of much of the water during the dry weather experienced over the summer period. The high salinity of the water prevents any vegetation from growing on the site.

What was observed in April 2009 was small areas of pugged wet mud and overlying water within a larger area of dry, hardened mud (Fig. 5.32). During cooler conditions the entire area would remain wet due to the upwelling fluid supply; however the late summer heat dries up all but the lowest lying areas. Upon closer inspection, one could see occasional bubbles emanating from the wet mud and rising up through the overlying water to finally escape into the atmosphere at the water-air interface. Venturing into the mud causes gas to be forced out of the mud and bubble up through the water (Fig. 5.35).



Figure 5.35 – The pugged and muddy ground of the Wilder Road gas seep. Note the oily film on the top of the water, and the gas bubbles rising due to compression of the mud by the person's weight.

5.6.3 Site summary

The Wilder Road seep carbonate facies throughout the eight outcrops are dominated by both beige and blue-grey micarb featuring some very thick crystalline veins with many successive layers of infill, spar-filled vugs, and a few foreign, dark, siliciclastic grains. Often, this fabric is highly brecciated, with the clasts cemented by networks of spar-filled veins or later micarb phases. The Wilder Road occurrences are unique in their absence of marcofossils.

5.7 AGE OF THE SOUTHERN HAWKE'S BAY SEEP CARBONATE DEPOSITS

Verification of the ages of the southern Hawke's Bay cold seep carbonate deposits is based upon paleo-foraminiferal ages from host mudstones at the Haunui site. This host mudstone is located at a stream-cut exposure along the northern bank of the Mangawhero Stream, directly to the south of the Haunui hill.

Samples collected by Dave Francis (Geological Research Ltd) in the 1980s gave maximum ages of 25 Ma, or Lower Waitakian New Zealand Stage. However, subsequent field work in this region has revealed the presence of an angular unconformity (Dave Francis, *pers. comm.* 2009), upon which are positioned at least four of the southern Hawke's Bay seep carbonate sites (Haunui, Ugly Hill, Wanstead, and Wilder Road). The early samples were collected from beneath this unconformity and the overlying section has not been dated. It is therefore concluded that, until confirmation by dating of this upper section, the southern Hawke's Bay seep carbonate sites likely have a maximum age of 25 Ma, or Lower Waitakian.

As all five of the ancient seep carbonate sites are found within the inner shelf to mid bathyal Ihungia Formation, this gives them a minimum age constraint of 15 Ma, as this formation is suggested to have formed no later than the Altonian New Zealand Stage (Reid 1998).

In conclusion, the southern Hawke's Bay seep carbonate deposits formed during any of the Waitakian, Otaian, or Altonian New Zealand stages.

CHAPTER 6

Laboratory Results

6.1 INTRODUCTION

The study of cold seep carbonate deposits is somewhat unique in comparison to that of other sedimentary formations. Transition from field outcrop through to slabbed-sample and finally to thin section reveals complexity increasing in orders of magnitude. Research on the origin of the seep carbonate deposits relies heavily on petrographic analysis. For this research on southern Hawke's Bay seep carbonate deposits, microscopy has been undertaken with plane polarised light (PPL), cathodoluminescent light (CL), ultra-violet (UV) light, and with a scanning electron microscope (SEM). In addition to these petrographic techniques, other laboratory methods such as X-ray diffraction (XRD), General Area Detector Diffraction (GADDs), stable carbon and oxygen isotopic analysis, carbonate percentage analysis, and total organic carbon analysis have been carried out (for methodologies refer to Chapter 4). The fundamental aims of these analytical techniques are:

- To classify broad componentry (i.e. identify key fabrics plus any variations and patterns in these fabrics).
- To determine mineralogy (i.e. relative mineral abundances, crystal textures and habits, mineral relationships) and subsequently relate this to the componentry classifications.
- To determine if any diagenetic processes have lead to alteration of minerals and/or fabrics, and to identify alteration products.
- To identify temporal mineralogical variations during formation of the seep carbonate deposits.

The fulfilment of the above aims will make it possible to produce a paragenetic sequence of the formational events for the southern Hawke's Bay cold seep

carbonate deposits, based mainly upon mineral relationships, alteration of minerals, and basic geologic principles such as cross-cutting relationships.

For full results of XRD, GADDs, and isotopic results see Appendix 3 and the Appendix DVD.

6.2 SLAB FACIES

Samples collected in the field were cut into slabs approximately 2 cm thick and these were analysed and assigned a code from the facies categorisation scheme (Fig. 4.2). This scheme is based upon the grain size of the sediments and intraclasts, (trace) fossil components, and major structural/tectonic, diagenetic and textural features, and is not related to the broad facies noted in the field (see Chapter 5). The dominant facies categories and examples of some of these categories are shown in Table 6.1 and Figure 6.1, respectively. Based on the modified limestone classification scheme of Dunham (1962) these carbonate deposits fall under the titles floatstone (the coarser grained samples), mudstone (the ‘purest’ samples containing few silt and sand sized siliciclastic grains), and wackestone (the bulk of the samples which contain few intraclasts and common to abundant siliciclastic grains).

Figure 6.1 – Various slabbed samples from the southern Hawke’s Bay seep carbonate deposits. **A:** A sample from a shell bed at Ugly Hill reveals whole and fragmented *Lucinoma taylori* clams within a homogeneous micarb matrix. Sample UH.M7, facies L1/Vn. **B:** A thicket of caryophyllidae coral at Wanstead is encased within a homogeneous micarb. Sample WA.13.1.2, facies L2/Vn. **C:** A sample from Ugly Hill South reveals an abundance of *Bathymodiolus* mussels (red arrows) and siboglinidae tubeworms (blue arrows). Note that the interior fill of the mussel shells is significantly different to that of the matrix fabric. Sample UH.11.4.1, facies A1,4/Vg,Vn. **D:** A thick vein at Ugly Hill is comprised of many layers of pink-grey spar and white microbial mats. Drawn rectangles indicate location of thin sections. Sample UH.3A.1A, facies A1/Vn. **E:** Sample WA.M1 of Wanstead is coarse grained due to the abundance of dark, foreign grains and intraclasts. A burrow/boring near centre shows several generations of infill. Facies A3/Int. **F:** The coarse-grained HA.13.6.1B sample of Haunui features a thick vein infilled with white spar and a late phase of beige micarb. Facies A1/Vn,Int. **G:** Sample W.8.9.2 is a typical siliciclastic-poor, nonfossiliferous micarb from Wilder Road. This sample also features a very thick, multiphase vein. Facies L6/Vn. **H:** A highly brecciated slab with areas of both beige and blue-grey micarb. Sample W.M5 from Wilder Road, facies L6/Br,Vn.

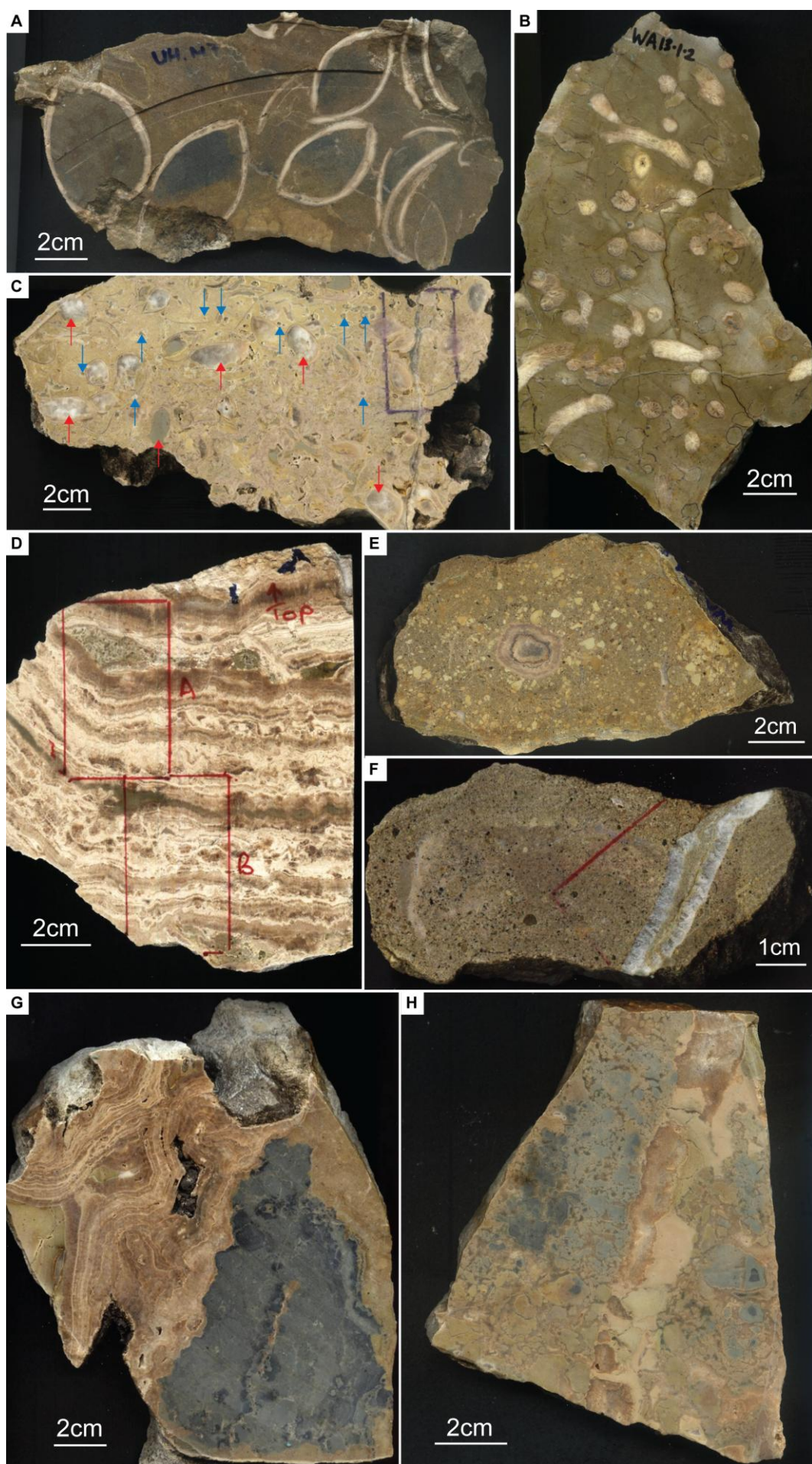


Table 6.1 - The dominant facies categories from each of the five southern Hawke's Bay seep carbonate sites, as revealed by slabbed samples. The most common facies are shown in bold. Refer to Figure 4.2 for facies code definitions, eg. A1/Int,Vg,Vn refers to an arenaceous limestone containing bivalve fossils, and featuring intraclasts, vugs, and veins.

Site	Facies present	Site	Facies present
<i>Haunui</i>	A1/Int,Vg,Vn A6/Vg,Vn,Int L6/Vn A5/Vn,Int A1,2/Vg,Vn	<i>Wanstead</i>	A1,2/Vn A1/Int,Vg,Vn R1/Int,Vg A6/Int,Vg L2/Vn A3/Vn,Vg,Br
<i>Ngawaka</i>	A3/Vg,Vn A1/Vg,Vn A6/Vg,Vn,Int A1/Vg,Int A2	<i>Ugly Hill</i>	A1/Vn,Int A6,7/Vn A4/Vg,Vn L1/Vn A6/Vn,Int A3/Pe,Vg
<i>Wilder Road</i>	L6/Vg,Vn L6/Vn,Br A6 L6/Vn,Pe		

Attention was also given to the fossil and trace fossil content of the slabs and fossils noted in the field. All sites, with the exception of Wilder Road, hosted fossils. The (trace) fossils identified at each of the five study sites are shown in Table 6.2. These taxa, or the families to which they belong, have all been identified at modern or ancient seep sites worldwide (cf. Goedert & Peckmann 2005).

The most abundant fossil taxa are assemblages of bivalves. These are found at four fossil-bearing sites. Moreover, throughout the Ugly Hill and Haunui sites, multiple shell beds are readily identified in outcrop. These ranged from beds of intact shells, both articulated and disarticulated, to zones of fine- to coarsely-fractured shell hash. The shell beds are composed of either lucinid clams, vesicomid clams, or *Bathymodiolus* mussel shells (Fig. 6.1C), which are packed into small/localised, yet often dense, patches. The accumulations of lucinids are

similar to those described by Cavagna et al. (1999) in Monferrato, Italy. *Bathymodiolus* mussels are a common occurrence in modern seep systems throughout the southern and western Pacific Ocean. Vesicomysids are known to have exceptional migrating capabilities which have allowed the family to flourish at ancient and modern seep sites in many of the world's oceans. The total percentage of shell material within a slabbed sample is estimated to reach a maximum of 15% (Fig. 6.1A) - a relatively low percentage in a global perspective as shell material can be the volumetrically dominant component of a cold seep deposit, reaching >40% in samples from the Gulf of Mexico (Feng et al. 2009).

Table 6.2 - The fossils and trace fossils found at the five southern Hawke's Bay seep carbonate deposit sites (HA = Haunui, NG = Ngawaka, UH = Ugly Hill, WA = Wanstead, W = Wilder Road). Adapted from K. Saether (*pers. comm.* 2009) and Sibuet & Olu (1998).

	Species	Abundance	Species details and/or niche	Sites				
				HA	NG	UH	WA	W
Bivalves	Lucinid (indet. sp.)	Common	Diffuse seepage or marginal to fluid escape site. Low pore water sulphide concentrations. Infaunal.	•	•	•	•	•
	<i>Lucinoma taylori</i>	Common	Diffuse seepage or marginal to fluid escape site. Semi-infaunal/epifaunal.	•		•	•	
	Vesicomysid	Common	Epifaunal, require a hardground to attach to. Thrive in high fluid flux environments near vent sites.			•	•	
	<i>Bathymodiolus</i> sp.	Common	Require a hardground to anchor to. Thrive in high fluid flux environments near vent sites.	•		•		
Tube-worms	Siboglinid (indet. sp.)	Common	Cold-water, reef building corals requiring a hardground to anchor to.	•	•		•	
Corals	Caryophyllid (indet. sp.)	Some		•	•		•	
	<i>Goniocorella dumosa</i>	Some					•	
Gastropods	<i>Cirsotrema kuriense</i>	Rare	Predate on chemosynthetic microbes and other symbiont-containing macrofauna in the seep environment. Opportunists. No preferred niche within seep environment.	•				
	Turrid (indet. sp.)	Rare				•		
	Buccinid (indet. sp.)	Rare					•	
	Naticid (indet. sp.)	Rare				•	•	
	<i>Naticidae</i> indet	Rare		•				
	<i>Provanna</i> (indet. sp.)	Rare				•		
	<i>Homalopoma</i> sp.	Rare				•		
Trace fossils	<i>Teredolites</i>	Rare	A boring made by the Pholad bivalve <i>Teredo</i> .	•	•	•	•	
	<i>Thalassinoides</i>	Common	A burrow made by Thalassinideans - an infraorder of decapod crustaceans - in sandy to semi-consolidated substrates.	•		•		
Other	Shark teeth	Rare	Not seep related.	•	•			

Other common fossils are siboglinid tubeworms (Fig. 6.1C), *Bathymodiolus* mussels, and the trace fossil *Thalassinoides*. Corals (Fig. 6.1B), different species of gastropods, and sharks teeth are relatively rare throughout the sites. In slabs it appears that the majority of the fossil specimens are well preserved – only a few slabs expose corroded bioclasts.

6.3 PETROGRAPHIC COMPONENTS

This section outlines the major fabrics identified in thin section under plane polarised light (PPL), including crossed polarised light (XPL), and cathodoluminescent light (CL). Thirteen fabrics are defined based on factors such as mineralogy, crystal size and morphology, degree of alteration, luminescence colours under CL, and relationships with other fabrics. Table 6.3 provides a summary of all 13 fabrics. This section, along with Table 6.3, orders the fabrics based on the interpreted paragenetic sequence constructed at the end of the petrographic studies and further elaborated on in Section 7.1.

6.3.1 Microcrystalline carbonate (micarb) 1 – M1

The term micarb has been coined to incorporate both fine grained calcitic and aragonitic cements, in contrast to the term micrite which is a contraction of microcrystalline calcite cement (Folk 1959, 1962; Reid *et al.* 1990).

Micarb 1 is a brown to grey-black microcrystalline carbonate cement (Fig. 6.2A, B) which constitutes the bulk of cold seep deposits (i.e. it is the background/matrix fabric). This micarb is the first stage of authigenic carbonate precipitation at or near the seafloor. It originally precipitates as aragonite (as confirmed via GADDs and CL) (Fig. 6.2C, D); however, with later burial this typically alters to calcite and is then termed pseudo-micarb (see Section 6.3.8).

Individual crystals are anhedral and are less than 4 μm in size. The micarb has precipitated as highly irregular micro-peloids, up to 70 μm in size, with a varying density or degree of compaction to give a range of appearances from very dense micarb through to clotted/mottled micarb distributed within blocky cement (Fig. 6.2B). The latter is similar to structure grumeleuse, which Bathurst (1971) described as many little clots of extremely fine grained crystalline calcite which are irregular in shape, have diffusive boundaries, lack any internal differentiation, and are found within a 'matrix' of colourless calcitic spar. These larger spar crystals have formed contemporaneously with the finer grained micarb globules (Bathurst 1971). The irregular shape of the clots may be attributed to

microenvironments caused by microbial metabolism (Peckmann *et al.* 2002). Primary (micarb 1) and secondary micarb (pseudo-micarb) are indistinguishable under PPL, however, under CL microscopy micarb 1 shows a dull dark blue to purple luminescence, whereas pseudo-micarb is pink to orange.

Within micarb 1 there is typically an array of bioclastic and detrital grains, as described below. These include siliciclastic grains such as quartz and feldspar, disseminated pyrite, glauconite, micarb peloids and intraclasts, mega-invertebrate benthos, foraminifera, and trace fossils (Fig. 6.2A). The concentration and variety of such grains differs among the five sites.

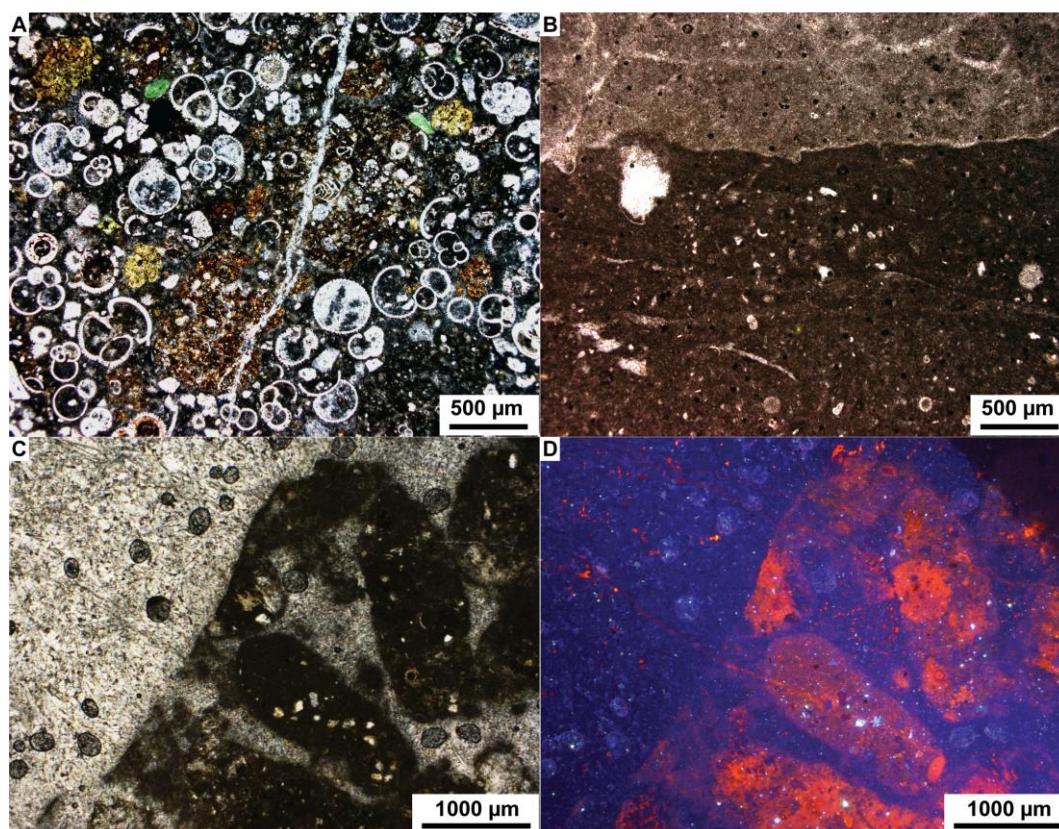


Figure 6.2 – Photomicrographs of micarb 1 (M1). **A:** Micarb in thin section HA.13.8.1B from Haunui is siliciclastic- and foraminifera-rich and also features iron-stained glauconite, both fresh (bright green) and limonitised (brown rimmed), and a thin, spar-filled vein. **B:** Two phases of siliciclastic poor micarb. Micarb of the upper third contains less siliciclastic grains than the micarb in the lower two thirds of the image, which is significantly denser in appearance. Sample W.1.4.1 from Wilder Road. **C and D:** PPL and CL photomicrograph pair of thin section UH.3A.1A from Ugly Hill shows micritic peloids encased within white to grey spar. The blue-purple coloured patches within the peloids in Image D are aragonite, and indicate that the peloids were originally aragonite however now are partially neomorphosed into calcite.

Mineral-forming phase	Code	Petrographic character	Crystal morphology	Crystal size	Cathodoluminescent (CL) character	Figure
Early diagenetic stage	M1	Brown to grey-black microcrystalline carbonate cement ± structure grumeleuse, fenestral (Sp2), siliciclastic grains, disseminated pyrite framboids, glauconite, iron oxide staining, intracasts, peloids, mega-invertebrate benthos, and bioturbation structures.	Anhedral	<4 µm	Dark blue to purple. Detrital grains give pinpricks of bright green, blue, purple, dull brown, and pink.	6.2 6.3
	C1	Yellow-brown crystals forming a patchy/mottled fabric; can be inclusion-rich; typically forms as layers in veins and vugs.	Anhedral	10-80 µm	Mottled pink to peach.	6.4A,B,C
	C2	White to light grey needles orientated perpendicular to the growth surface; typically forms off micarh or bioclasts; an infill cement in voids; ± dark hydrocarbon inclusions.	Fibrous	300-2000 µm	Dull luminescence, dark blue to purple.	6.3F 6.4D
		Partial rosettes of elongate crystals radiating out from a point; can form as crude isopachous layers of adjacent splays; splays are orientated (near) perpendicular to the growth surface; typically an infill cement in voids; undulose extinction; ± dark hydrocarbon inclusions within needles or as bands throughout isopachous layers.		1000 µm thick		6.4E,F
		Grey to brown, mammillated crystal splays; can be individual or in crudely isopachous layers; an infill cement in cavities and veins; undulose extinction; ± bands of light to dark inclusions.		Av. layer thickness 500 µm		6.4G,H
	Th	Masses of dense micrite clots; individual clots are anhedral with boundaries ranging from diffuse to distinct and varying in colour from light to dark brown; a very mottled, 'oatmeal-like' fabric; forms on earlier cements (C1 and C2), and typically occurs within sequences of vein and cavity infill.	Anhedral	<4 µm	Mottled purple.	6.5
	M2	Brown to grey-black microcrystalline carbonate cement; often forms as thin, irregular layers alternating with C1 and C2, infilling veins, cavities, and biocavities.	Anhedral	<4 µm	Dark blue to purple. If altered, pink to peach.	6.5A 6.6A,B
	Si1	White to cream crystals in PPL; form in dense but localised accumulations; act as vein and cavity fill; have a bright array of interference colours under XP and is both microcrystalline and polycrystalline.	Euhedral	<50 µm	Dull pink to purple.	6.6C-F 6.10
	Si2	Cream/light yellow, comprised of crystals with no definable boundaries under PPL; mammillated outer surface; can be highly fractured; undulose extinction; a vein and cavity fill precipitate.	Anhedral	Layers reach 125 µm thick	Dull pink to purple.	6.6C-F
	PM	Neomorphic product of M1 and M2; brown to grey-black microcrystalline calcite cement ± structure grumeleuse, fenestral (Sp2), siliciclastic grains, disseminated pyrite framboids, glauconite, iron oxide staining, intracasts, peloids, fossil metazoa, and bioturbation structures.	Anhedral	<4 µm	Pink to bright orange.	6.7
Late diagenetic stage	PC	Neomorphic product of earlier cements (M1, M2, C1, C2) to produce spar with a variety of crystal morphologies; ± traces of original crystal morphology and dark inclusions.	Anhedral to euhedral/blocky. Rarely fibrous.	Up to 1000 µm	Maroon to bright orange.	6.8
	Sp1	Translucent/white tightly packed crystals; well developed to poor cleavage; infills cavities, veins, and bio-cavities, often drusy; ± twinning, light to dark inclusions, and iron staining.	Blocky/euhedral, also dentate and rhombohedral	Up to 875 µm	From maroon to orange; concentric to oscillatory zonation is common.	6.8A,B 6.9 6.10
	Si3	Translucent/white, polycrystalline crystals in dense but localised accumulations; typically act as the latest vein and cavity fill; bright array of interference colours.	Euhedral	<700 µm	Dull pink to purple.	6.10
	Sp2	Translucent/white crystals; occurs in cavities, pre-corroded cracks along weaknesses, and fenestrae in earlier fabrics; often indistinguishable from surrounding fabrics under PPL	Blocky/euhedral	<875 µm	Bright yellow.	6.9C,D
	Sp3	Translucent/white, clean crystals infilling cavities and fractures; ± twinning; often the final infill stage of cavities; can be drusy.	Blocky/euhedral	Up to 875 µm	Maroon to orange.	6.9

Table 6.3 – Details on the petrographic and cathodoluminescent characteristics of the thirteen identified fabrics in thin sections from the five seep carbonate sites of this study.

Bioclasts

The fossilised remains of organisms identifiable in thin section include bivalves (clams and mussels), worm tubes, corals, gastropods, and both planktic and benthic foraminifera. Trace fossils/bioturbation structures are also seen in slabbed samples and occasionally in thin section, such as burrows and borings. For a species list see Table 6.2. Under plane polarised light fossil fragments/bioclasts range from well preserved to neomorphosed. Those with well preserved shell structure show clear original textures. Those which have been neomorphosed to more stable calcite forms indicate that two processes have been at work. First, the dissolution-precipitation process of calcitization allowed ghosts of the original bioclast texture to be preserved. In contrast, the process of solution-deposition where the original bioclast was dissolved out, leaving a void which was later infilled by calcite often results in bioclasts comprising a drusy spar and surrounded by a micritic envelope (Horowitz & Potter 1971; Tucker & Wright 1990).

The shell beds common at Ugly Hill and Haunui contain a range of very well preserved and articulated bivalve specimens, forming localised coquinas (Fig. 6.3B) to beds of shell hash – small fragments of shell material down to 200 μm in size – (Fig. 6.3A). In thin section these bivalve shells range from well preserved to neomorphosed. Well-preserved specimens generally exhibit multiple layers of shell microstructure, typically of prismatic crystals involving a range of sizes. Altered specimens show no original fabrics or textures, and are composed of light-brown, blocky, pseudo-spar crystals under PPL and show homogeneous calcite colours under CL (intermediate maroon, pink, peach to fully neomorphosed orange calcite).

Due to the concave nature of bivalve shells they commonly contain infill sequences of mineral fabrics, and sometimes geopetal infills and umbrella voids. General infill material includes micarbs 1 and 2, fibrous cements, and neomorphosed blocky spars. In places geopetal infills were recognised, which indicate the orientation of the sample during formation with respect to the seafloor (Scholle & Ulmer-Scholle 2003). Siliciclastic-rich micarb precipitation in the bottom of the shell void was followed by a later phase of fibrous or blocky cements that infilled the remaining upper region of the void. Umbrella voids were

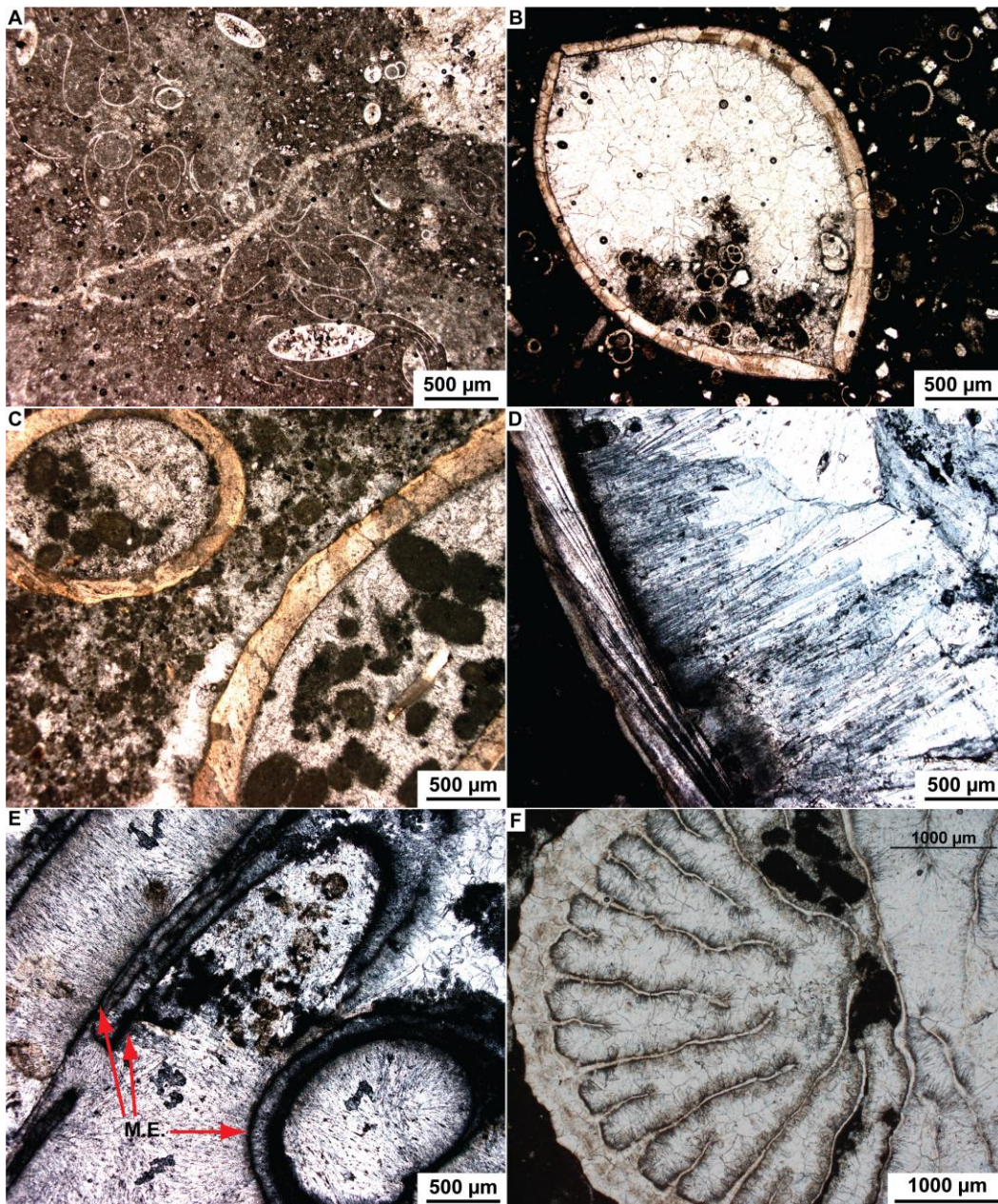


Figure 6.3 – Photomicrographs of bioclasts present in micarb 1 (M1) and fibrous cements (C2). **A:** Thin section W.8.2.1 from Wilder Road features an abundance of small lucinid or calyptogena bivalves, both fragmented and whole. **B:** A very dense micarb houses a well-preserved, articulated *Bathymodiolus* mussel shell which has an infill of spar and micarb peloids. Thin section WA.3F.1B from Wanstead. **C:** Two worm tubes in thin section UH.5A.1A from Ugly Hill. Tube walls comprise altered blocky calcite, and infill is fibrous cement and micritic peloids. **D:** A close up of a worm tube wall shows a striated, fibrous structure. The tube is lined with a thin layer of micarb followed by fibrous cement (C2) and a blocky spar. Thin section UH.11.4.2B from Ugly Hill. **E:** The micritic envelopes (M.E.) are all that remain of worm tubes after they are dissolved out. Thin section UH.10.1.1C from Ugly Hill. **F:** Thin section WA.13.1.1A from Wanstead houses many coral specimens, all of which are very well preserved and contain infill of fibrous cement (C2) and a blocky spar.

found in the inner curve of shells, where the bioclast sheltered an area from precipitation to create a void beneath the shell that later infilled with blocky

cement (Scholle & Ulmer-Scholle 2003). In addition, it is common to observe fibrous and blocky spar crystals forming directly upon bivalve fragments within micarb.

Worm tubes are a common fossil identified in thin section and are generally found in small clusters of tubes (Fig. 6.3C). The worm tubes have diameters ranging from 1-6 mm, which is similar to those found in Californian, Canadian, and Moroccan fossil seep deposits (Beauchamp & Savard 1992; Campbell *et al.* 2002; Peckmann *et al.* 2005). Tube walls, originally comprising bundles of chitinous microfibrils and a proteinaceous material (Fig. 6.3D) (Campbell *et al.* 2002; Peckmann *et al.* 2005), are typically altered to a dark, yellow-brown, blocky pseudo-spar (Fig. 6.3C). Commonly, both the inner and outer surface of tubes are coated with a thin micarb envelope (Fig. 6.3D). Some tubes have been partially to fully dissolved, with a fibrous or blocky replacement mineral having filled the void, leaving only a micarb envelope to allow recognition of the feature (Fig. 6.3E). This type of fossil is particularly useful in the construction of a paragenetic sequence as the tube acts as a secondary fluid pathway once the original depositional porosity is gone, so that the precipitants within the tube reflect the sequence of mineral-forming diagenetic events (Campbell *et al.* 2002). Most commonly in this study, worm tube infill began with a thin layer of micarb followed by fibrous spar, pseudo-spar, blocky spar, or micarb peloids (Fig. 6.3D).

Fossilised branching corals are most common at the Wanstead site (Fig. 6.3F), but are sporadically seen in thin section in other sites of this study. As is typical for branching corals, the preserved exoskeleton constituting a circular outer wall and a series of well-developed vertical plates (septa), radially-perpendicular to the outer wall (Horowitz & Potter 1971). The outer wall and the septa of the coral have altered from their original mineralogy (aragonite) to a light-brown blocky pseudo-spar. The hollow central area is typically infilled with acicular aragonite, an inclusion rich blocky spar, and finally a clear blocky spar (Fig. 6.3F).

Foraminiferal tests enclosed within micarb 1 and pseudo-micarb range from scattered to extremely abundant (Fig. 6.2A). Planktic foraminifera are much more abundant than benthic foraminifera, of which only a few different forms were noted.

Siliciclastic grains

Throughout the micarb, varying amounts of scattered siliciclastic grains may occur (Fig. 6.2A). These are dominantly quartz and feldspar, of silt to fine sand size, and are sourced from the enclosing host sediment. Under CL these grains have a great range of colours, including light blues, purples, green, dull brown, and pink.

Glaucinite

Glaucinite is very common and forms as rounded pellets and lobed globules (Fig. 6.2A). These are typically bright green; however, weathering caused pellets to become altered to a red-brown limonite from the outside in. These rusted glauconitic globules occur from sporadic to significant amounts throughout micarb.

Pyrite

Pyrite typically is preserved as very dark red-brown to black disseminated framboids distributed sporadically within micarb, in small, localised accumulations, and also commonly infilling foraminiferal tests. SEM analysis of pyrite framboids in seep carbonate mounds from the Gulf of Mexico by Feng *et al.* (2009) found that the framboids (from 5-10µm in diameter) comprise groupings of smaller pyrite crystals (approximately 0.5 µm in diameter) typically of cubic and pentagonal dodecahedron crystal habit. Pyrite can also form in the samples of this study as single euhedral to subhedral crystals, reaching a maximum size of 140 µm.

6.3.2 Anhedral yellow-brown cement – C1

Under PPL, this cement is yellow-brown in colour and varies in brightness within and between crystals to result in an extremely patchy or mottled appearing fabric (Fig 6.4A, C). The individual crystals are anhedral, between 10 and 80 µm in size,

and are typically rich in dark inclusions to give a dirty or cloudy appearance in PPL. Under CL, this fabric is typically a mottled dark-pink to peach colour (Fig. 6.4A,B). It is similar to the yellow calcite of Beauchamp & Savard (1992) and Campbell *et al.* (2002); however, with a more dull colouration in PPL

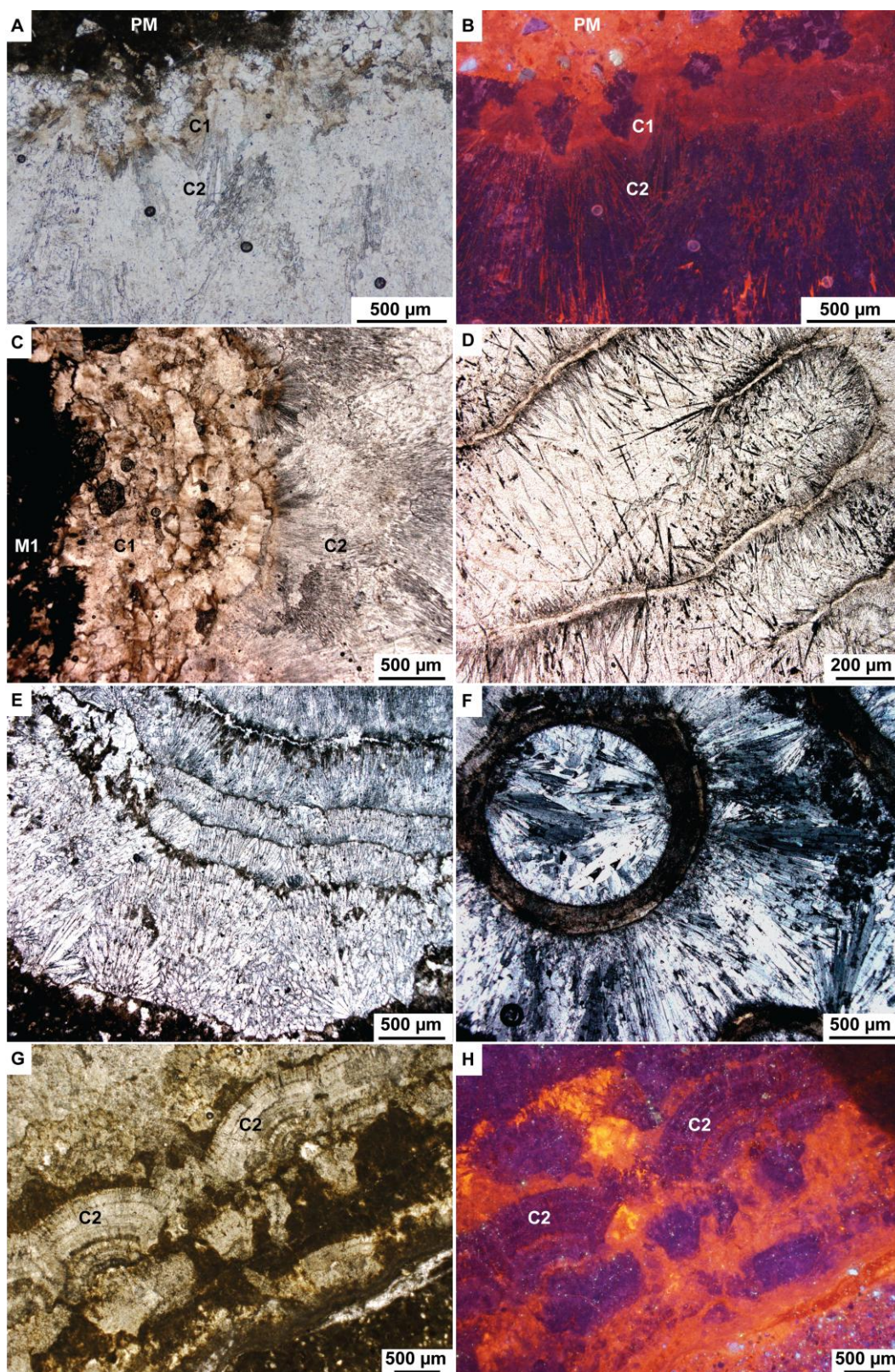
This fabric always acts as a cement which lines cavities and veins. It is typically the first infill precipitate, forming on corroded or fractured micarb surfaces (Fig. 6.4C), but also forms in successions of irregular layers alternating with fibrous cements and thrombolites, much like the yellow calcite of Beauchamp & Savard (1992) and Campbell *et al.* (2002). It is unknown if this fabric initially precipitated as aragonite or calcite; however, CL colours indicate a possible aragonitic heritage and GADDs analysis confirms that the fabric is currently calcitic in composition (see Section 6.6.2). Campbell *et al.* (2002) found the anhedral yellow calcites of Mesozoic seep carbonates in California to be easily altered by late diagenetic neomorphism.

6.3.3 Fibrous cements – C2

Pervasive fibrous cements are common throughout the five study sites. These cements are the dominant ones to fill cavities and line corrosion surfaces in the micarb fabrics. The fibrous crystals grew (near)-perpendicular to the growth surface, which is typically either micarb or a bioclast (e.g. bivalves and worm tubes).

These fibrous cements can be divided into three categories: acicular, splayed, and botryoidal (see Table 6.3). As shown by the dark blue to purple CL colours, all these fibrous spar cements originally formed as aragonite in the (near) seafloor environment. However, during later burial some of these fibrous cements may have undergone diagenetic alteration, which alters the crystal morphology and/or crystal mineralogy to calcite. We commonly observe these fibrous fabrics neomorphosed into a calcitic form whilst retaining the fibrous habit (see Section 6.3.9, pseudo-cement).

It appears that these fibrous forms of spar could precipitate (near) contemporaneously with one another. This is suggested by the common layered sequences involving chaotic alternations of the three fibrous forms.



6.3.3.1 Acicular cement

Acicular cement constitutes needle-like crystals which nucleate off an earlier-formed surface in a perpendicular orientation (Figs. 6.3F, 6.4D). Individual crystals have a high length to width ratio, reaching up to 300–2000 μm (0.3 – 2 mm) in length. Under PPL these needles appear white to light grey, and can often contain dark fluid (hydrocarbon-bearing) inclusions.

Acicular needles typically grow directly off a corroded/fractured micarb surface or bioclasts, rather than off other fibrous forms. Therefore, we characteristically observed acicular cements around cavity and vein margins, in contrast to other fibrous forms which were typically more centrally positioned within cavities.

6.3.3.2 Splayed cement

This fibrous cement is similar to acicular cement but features splays of elongate crystals radiating out from a point (Figs. 6.4E, 6.4F). The elongate crystals comprising the splays reach approximately 1000 μm in length. Splays are orientated perpendicular to an earlier-formed surface and, because of the plane of the thin section, only a part (up to two-thirds) of the overlapping rosettes are visible.

Splays can occur sporadically along micarb surfaces or as many adjacent splays, which can be overlapping along a surface to form an isopachous layer of splayed

Figure 6.4 – Photomicrographs of yellow-brown cement (C1) and fibrous cements (C2). **A and B:** A photomicrographic pair of images under PPL and CL, respectively, show the yellow-brown cement (C1) appearing as mottled dark-pink to purple under CL, indicating that it originally precipitated as aragonite which later altered to calcite. This cement has formed off the micarb (PM), and is covered by a thick layer of splayed cement (C2) which appears dark purple under CL. Thin section HA.13.1.1B from Haunui. **C:** A thick layer of yellow-brown cement (C1) is the first to form off a corroded micarb surface (M1) in thin section W-2-1-1B from Wilder Road. This fabric is later covered by layers of splayed cement (C2). **D:** Acicular needles grow off the inner septa of a coral in thin section WA.13.1.1A from Wanstead. **E:** Many layers of splayed cement, some separated from one another by thin layers of micarb (M2). Thin section UH.100.9 from Ugly Hill. **F:** Splayed cement grows off bioclasts (tube worms) to result in a mass of sparry cement. Under XPL splays show undulose extinction. Thin section UH.10.3.1C from Ugly Hill. **G and H:** A photomicrographic pair of images under PPL and CL, respectively, from thin section UH.100.8.1B from Ugly Hill, show a discontinuous layer of large botryoids (C2) within layers of micarb and other fibrous aragonite cements. Botryoids are aragonitic, as indicated by the dark purple colour under CL.

cement (Fig. 6.4E). Commonly multiple generations of crudely isopachous splayed cement layers which collectively acted as thick infill cement within cavities and veins. Individual layers can alternate with layers of other fibrous cements, thin layers of micarb, or layers of thrombolites.

Under PPL the rosettes and individual elongate crystals appear as white to light grey spar, often containing dark hydrocarbon-bearing inclusions within individual crystals and in discrete bands across isopachous layers. With cross-polarised light the fans exhibit undulose extinction (Fig. 6.4F).

6.3.3.3 Botryoidal cement

Botryoidal cement occurs as individual horizons or layers of botryoids consisting of radiating needles (Fig. 6.4G). Individual botryoids are similar to the botryoidal calcite of Beauchamp & Savard (1992). Botryoids can be densely packed adjacent to one another, so as to appear as mammilated crystal splays which form crudely isopachous layers. Layers reach 1000 μm in thickness but are typically <500 μm thick. This cement differs from the splayed cement variety by its finer needle size and darker colour under PPL. The botryoidal cement initially nucleated off corroded micarb surfaces and other early cements, and largely acted as an early cavity and vein lining precipitate.

Under PPL, botryoids are light grey to a patchy light yellow-brown colour. Throughout individual botryoids and layers of botryoids, there can be bands of inclusions ranging from streaks of white and cream through to dark brown/black. These are likely to be growth lines, illustrating the staggered growth of the botryoids. Under cross-polarised light the botryoids exhibit undulose extinction, and under CL they appear dark purple (Fig. 6.4H).

6.3.4 Thrombolites - Th

Thrombolites are masses of dense micrite which are the result of the calcification of bacterial cells, sheaths, and biofilms (Riding 2000). The clotted texture of thrombolites sets them apart from their laminar stromatolite cousins. In this study,

the clotted texture is macroscopic (layers of white clotted fabric up to 3 mm thick in hand specimen), and petrographically individual clots are anhedral with boundaries ranging from diffuse to distinct and varying in colour from light to dark brown (Fig. 6.5A, B). Overall, this gives a very mottled, blotchy fabric which can be described as oatmeal-like. Riding (2000) gives descriptions of multiple varieties of thrombolites, and by these definitions the thrombolites present in seep carbonates from southern Hawke's Bay are classified as 'calcified microbial thrombolites'.

Irregular layers of thrombolites are found in thin sections from Wilder Road and Ugly Hill. This fabric forms on earlier cements (C1 and C2), and typically occurs within sequences of vein and cavity infill (Fig. 6.5B).

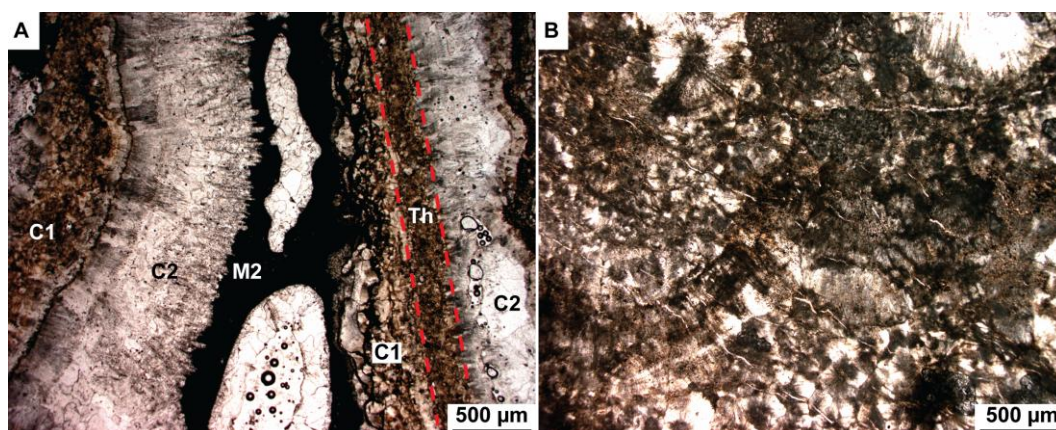


Figure 6.5 – Photomicrographs of thrombolites. **A:** Under PPL thrombolites appear as layers of light to dark brown, oatmeal-like precipitates occurring on early cements and micarb (between dashed lines). This is in contrast to slabbed samples, in which thrombolites appear as thin white layers. Thin section W.2.1.1B from Wilder Road. **B:** A very thick layer of thrombolites in thin section UH.3A.1A from Ugly Hill covers much of this image, which has been cut from a thick vein sequence of alternating fibrous cements and thrombolites.

6.3.5 Microcrystalline carbonate (micarb) 2 – M2

Micarb 2 is a brown to grey-black microcrystalline carbonate cement. The individual crystals are anhedral, less than 4 µm in size, and are densely packed giving an overall dark appearance. It is very similar to micarb 1, but lacks significant amounts of detrital grains. Also in contrast to micarb 1 is the tendency for this fabric to form as thin irregular layers upon, and alternating with, early blocky and fibrous cements (e.g. C1, C2) infilling veins and cavities (Figs. 6.5A,

6.6A). This micarb fabric infills bioclasts such as bivalves (Fig. 6.3B) and worm tubes (Figs. 6.3B, 6.3C), and rarely acts as a geopetal fill material.

This fabric, like micarb 1, originally precipitated as aragonite in the (near) seafloor environment, giving a dull dark blue to purple colour under CL (Fig. 6.6B). However, with later burial, micarb 2 typically alters to calcite, and is then termed pseudo-micarb (see Section 6.3.8). This latter cement exhibits intermediate shades of pink and peach, to bright orange typical of the neomorphosed calcitic micarb cement under CL.

6.3.6 Authigenic silica 1 – Si1

This fabric consists of tightly packed, translucent/white, blocky siliceous crystals (Fig. 6.6C). It varies from being monocrystalline to polycrystalline (in which each crystal, up to 50 μm , is composed of many equant subcrystals). Under cross-polarised light the crystals have a bright array of interference colours, changing from white/brown/blue to white/grey/yellow as the stage is rotated through 90° (Fig. 6.6D, E). Under CL the fabric is a patchy dull pink to purple colour (Fig. 6.6F). These crystals form in dense but localised accumulations at a number of sites, and act as vein and cavity fill precipitates typically associated with anhedral yellow-brown (C1) and fibrous (C2) cements.

6.3.7 Authigenic silica 2 – Si2

This cream coloured mineral comprises crystals with no definable boundaries identifiable under PPL (Fig. 6.6C). However, the crystals, which have precipitated free of physical constraint, have grown to produce a rounded and undulating, or mammillated, outer surface (Fig. 6.6C). The fabric appears to be highly fractured - very fine fracture planes can be seen throughout the crystal mass. However, this may be an artefact of the thin sectioning processes. This mineral phase acts as a fill precipitated within veins and cavities at only two of the five study sites, and is usually associated with the blocky authigenic silica 1 (Si1).

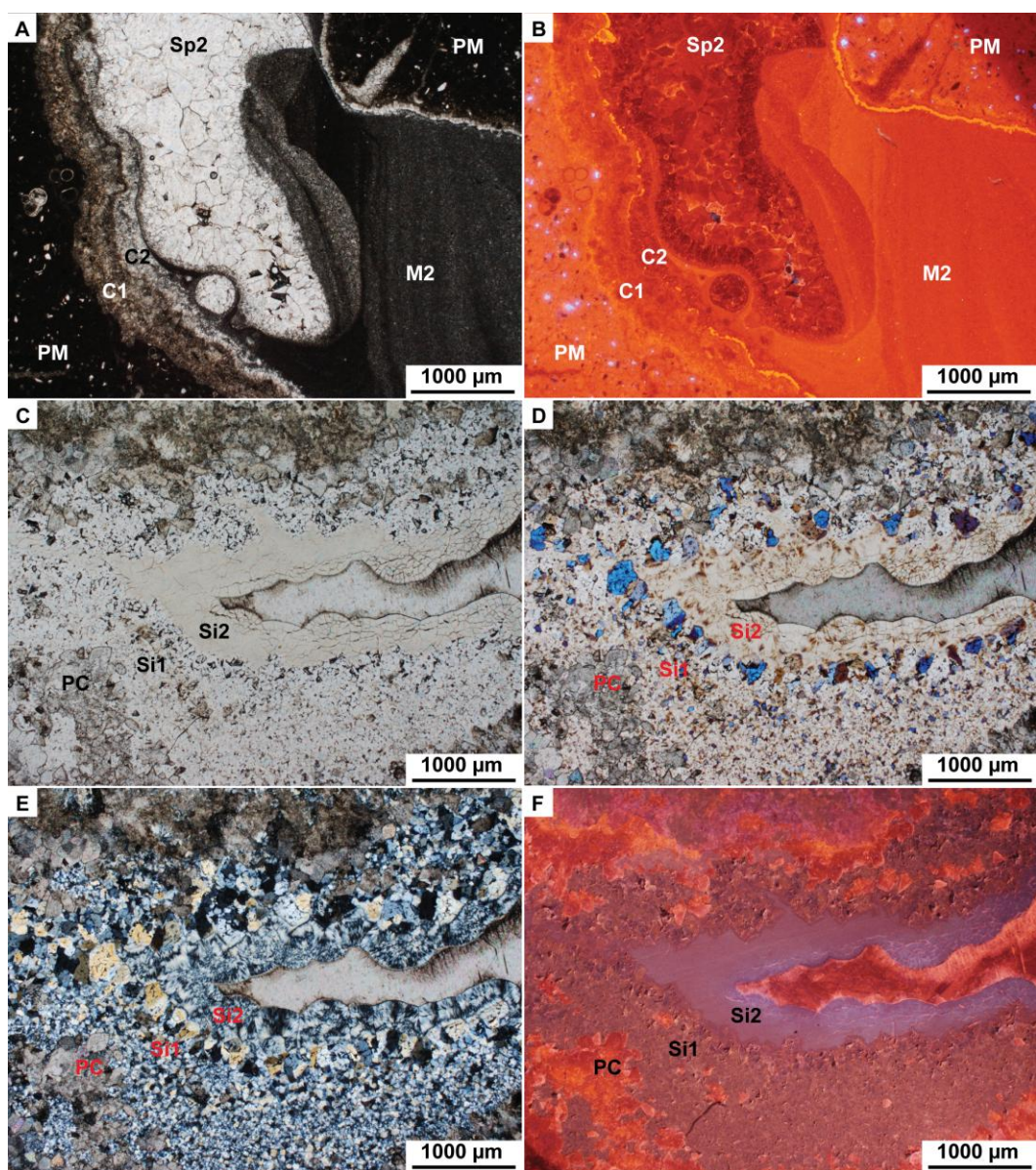


Figure 6.6 – Photomicrographs of micarb 2 (M2) and the two early silica fabrics (Si1 and Si2). **A and B:** Photomicrographic pair of images of thin section W.M8 from Wilder Road under PPL and CL, respectively. A large cavity in the pseudo-micarb (PM) contains a series of infill precipitates – yellow-brown cement (C1), fibrous cement (C2), and large areas of late micarb (M2) and blocky cement. The CL image shows that both micarbs have been neomorphosed from aragonite to calcite. **C:** Within a large, early vein cut through micarb (M1) is layers of yellow-brown cement (C1) and an altered blocky spar, before the large central fill of two silica phases (Si1 and Si2). Viewed under PPL. The first silica fabric (Si1) is composed of tightly packed, translucent/white, blocky crystals. Si2 is a smooth mass of white to cream coloured crystals which appear finely fractured in some areas and have a mammillated outer surface. Thin section NG.F5 from Ngawaka. **D and E:** Same view as Image C under XPL. Images have been taken with stage rotated through 90° to illustrate the wide range of interference colours of the two silica phases. XPL reveals that Si1 is both monocrystalline and polycrystalline. With crossed nicols the individual crystals of Si2 remain indistinguishable, but appear as a feathery, radiating mass. **F:** Under CL Si1 is dull purple with evident topography, whereas Si2 is a blue-purple, smooth mass.

Under cross-polarised light the individual crystals can be identified by contrasting interference colours that reveal a texture of radiating splays. The crystals have

undulose extinction and their interference colours vary from white/light-brown to white/dark-grey as the stage is rotated through 90° (Fig. 6.6D,E). Under CL light this fabric luminesces dull purple-blue colour (Fig. 6.6F).

6.3.8 Pseudo-micarb - PM

This is a secondary/late stage micarb which is the neomorphic product of micarb 1 and micarb 2, and therefore the term ‘pseudo’ is applied to its name. The term “neomorphism” was coined by Folk (1965) to incorporate the two *in situ* processes of (a) polymorphic transformation and (b) recrystallisation. The term covers all transformations where the primary mineral is broken down and simultaneously replaced with secondary crystals of the same mineral type or a polymorph (Bathurst 1971).

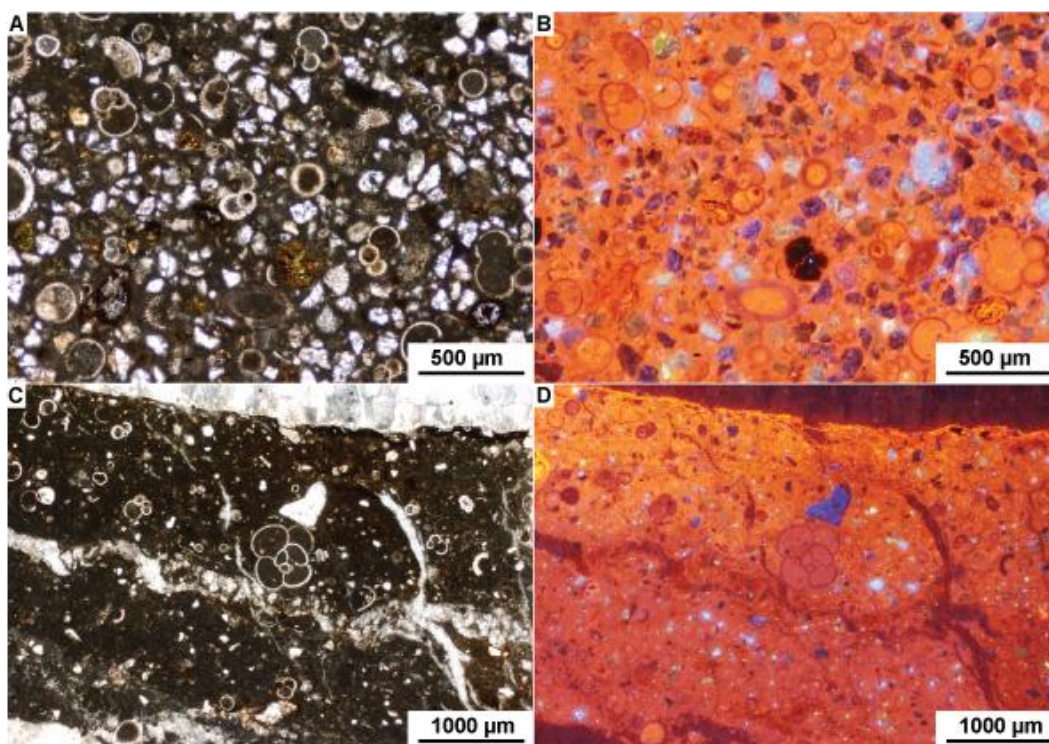


Figure 6.7 – Photomicrographic pairs of images illustrating pseudo-micarb (PM) under PPL (images A and C) and CL (images B and D). **A and B:** A typical siliciclastic- and foraminifera-rich micarb from Haunui contains iron-stained foraminifera and glauconite. The bright orange colour of the micarb under CL indicates that it has undergone neomorphism from its original aragonite and is now calcitic. Thin section HA.13.1.1A. **C and D:** Micarb of thin section WA.7B.2 from Wanstead shows partial neomorphism under CL - the upper, orange area has progressed through the neomorphic process more than the lower, pinkish area.

In this instance, the primary aragonite of micarb 1 and micarb 2, which formed in the (near) seafloor environment, became altered into calcite. Under PPL the fabric looks identical to its original phase – it is still brown to grey-black in colour and all detrital and bioclastic material remains (Fig. 6.7A). CL is a useful tool for identifying neomorphic fabrics as it reveals specific colour changes and patterns which are indicative of alteration. Under CL, pseudo-micarb commonly exhibits the orange colour typical of calcite (Fig. 6.7B), and also a range of maroons, pinks, and peach colours which appear to represent phases in the transition between aragonite to calcite (i.e. still in the process of undergoing neomorphism) (Fig. 6.7C,D). This neomorphosed pseudo-micarb (PM) is much more common than primary micarb (micarb 1 and micarb 2) in most samples, making up the bulk of their matrix.

6.3.9 Pseudo-cement - PC

Pseudo-cement is also a neomorphosed fabric (see Section 6.3.8 for definition). The calcitization of aragonite is known to be a texturally disruptive alteration process (Sandberg 1985). According to Bathurst (1971) the process of neomorphism may result in the new mineral structure having a larger or smaller crystal size, and it may be of a different morphology/shape and texture than that of the original mineral. This phase covers a wide range of fabrics, all of which are alteration products. It includes cements with anhedral, euhedral, and fibrous crystal morphologies which have been recrystallised from any of the earlier precipitates (e.g. micarbs, anhedral cements, and fibrous cements).

These fabrics can be identified and classified as products of neomorphism or calcitization due to a number of traits, including: (a) an irregular mosaic of coarse calcite crystals whose crystal boundaries cross-cut relict features associated with the original aragonite cement (e.g. rows of dark fluid inclusions or ‘ghosts’ of a fibrous crystal morphology; Figs. 6.8C, E, F); and (b) the CL colours of these fabrics are no longer the dark purple-blues of aragonite but consist of oranges typical of calcite crystals or an intermediate maroon to peach colour (Figs. 6.8B, 6.8D) (Sandberg 1985; Pagel *et al.* 2000).

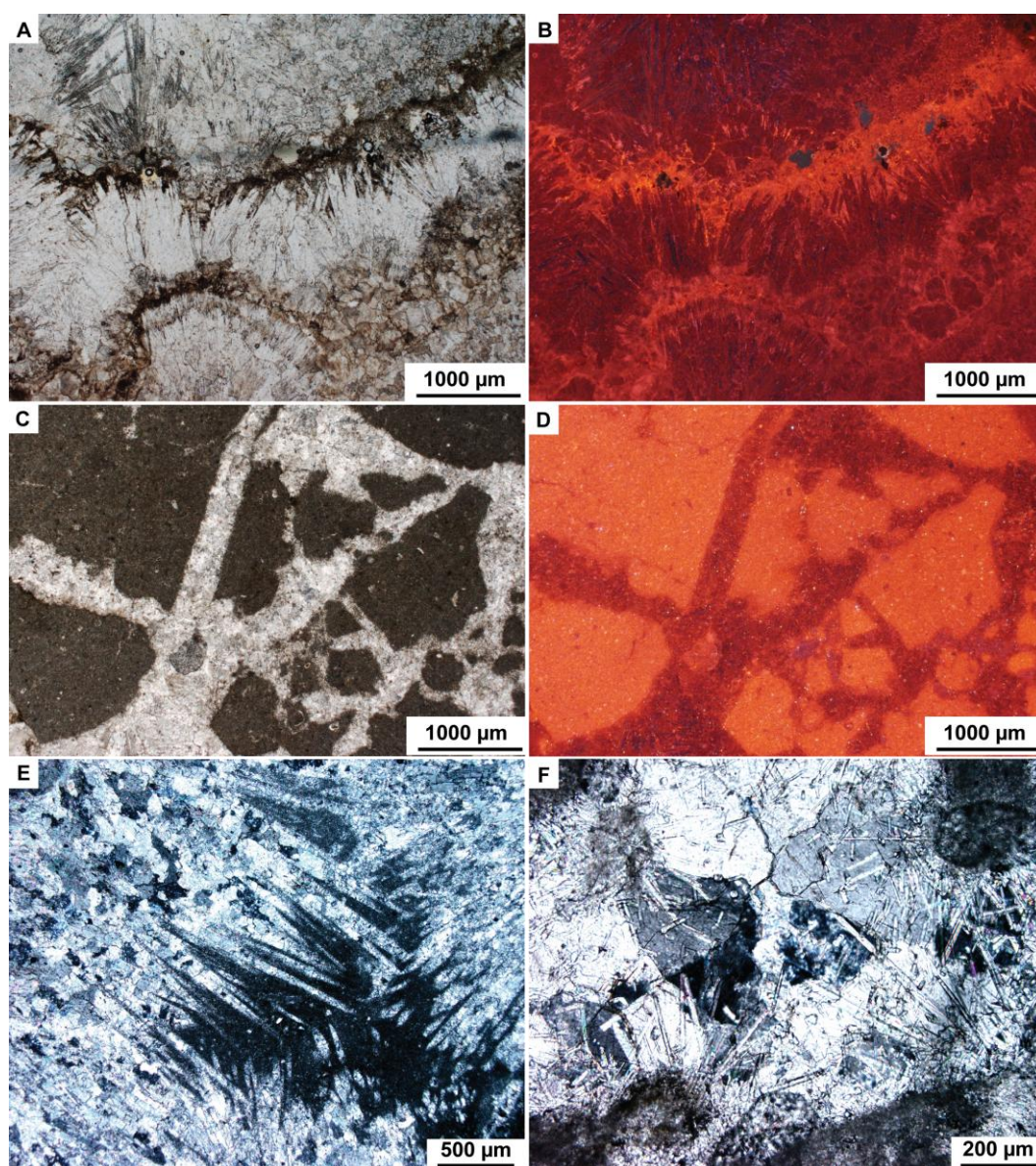


Figure 6.8 – Photomicrographs illustrating pseudo-cement (PC). **A and B:** Photomicrographic pair in PPL (A) and CL (B) of a succession of layers of formerly aragonitic acicular to splayed cement in thin section WA.M1 from Wanstead. Most of the individual crystals have retained their needle-like shape, however the CL image shows that this fabric is no longer aragonite (purple-blue) but has undergone partial neomorphism into calcite. Much of the fabric is now an intermediate maroon colour, with hints of purple aragonite still showing. **C and D:** Brecciated pseudo-micarb (PM) is re-cemented by dense fibrous cement. This cement, originally aragonitic, is has undergone partial neomorphism to calcite resulting in CL colours ranging from purple to dark orange. Thin section W.8.5.1 from Wilder Road. **E:** The outline of large acicular needles is still very evident in the surrounding micarb, however the now-blocky crystal morphology is obvious under XPL. Thin section HA.M1 from Haunui. **F:** A close up of blocky pseudo-cement crystals in which the original fine, acicular needles are still very evident under XPL. Thin section UH.10.1.1B from Ugly Hill.

Neomorphism appears to have preferentially affected fabrics consisting of fine, loosely packed crystals over fabrics with large and tightly packed crystals. This tendency is suggested by the common occurrence of neomorphosed pseudo-

micarbs positioned adjacent to primary, unaltered cements, and the orientation and direction of neomorphic fronts – the microcrystalline carbonate cement (micarb) is neomorphosed before fibrous and blocky cements (Figs. 6.7C,D).

6.3.10 Blocky spar 1 – Sp1

Blocky spar 1 is a late secondary cement (i.e. it is not an alteration product of an earlier precipitant). Under PPL it appears as tightly packed translucent/white crystals (Figs. 6.6A, 6.9A, 6.10A) that may contain variable amounts of light brown to dark inclusions which give the crystals a ‘cloudy’ or ‘dirty’ look. These inclusions can be scattered throughout the crystals, zoned within the crystals, or concentrated along crystal boundaries – likely to be growth zoning, a feature which is revealed in crystals due to variations in the density of inclusions (Schneidermann & Harris 1985). Zoning within crystals can be either concentric or oscillatory (Fig. 6.10B). Crystals often exhibit twinning, which is visible in both PPL and XPL. Morphology varies somewhat with equant, dentate, and rhombohedral varieties seen, reaching a maximum crystal size of 875 µm. Under cross-polarised light, the crystals exhibit the typical first order pastel colours of calcite. Under CL this fabric is typically bright orange, however can exhibit colours anywhere from maroon to orange (Figs. 6.6B, 6.9B, 6.9F). Similar late cements were observed in Mesozoic seep carbonates of California by Campbell *et al.* (2002).

This fabric precipitates relatively late as it is typically seen as infill cement within cavities, veins, and bio-cavities after layers of fibrous cements. These infills are often drusy, with a smaller crystal size around the edge grading to larger crystals in the centre of the void.

6.3.11 Authigenic silica 3 – Si3

This siliceous fabric is very similar to Si1, being a fabric of tightly packed translucent/white crystals; however, it is only found to post-date blocky spar crystals (Sp1). Si3 crystals are euhedral, polycrystalline, and reach sizes of 500

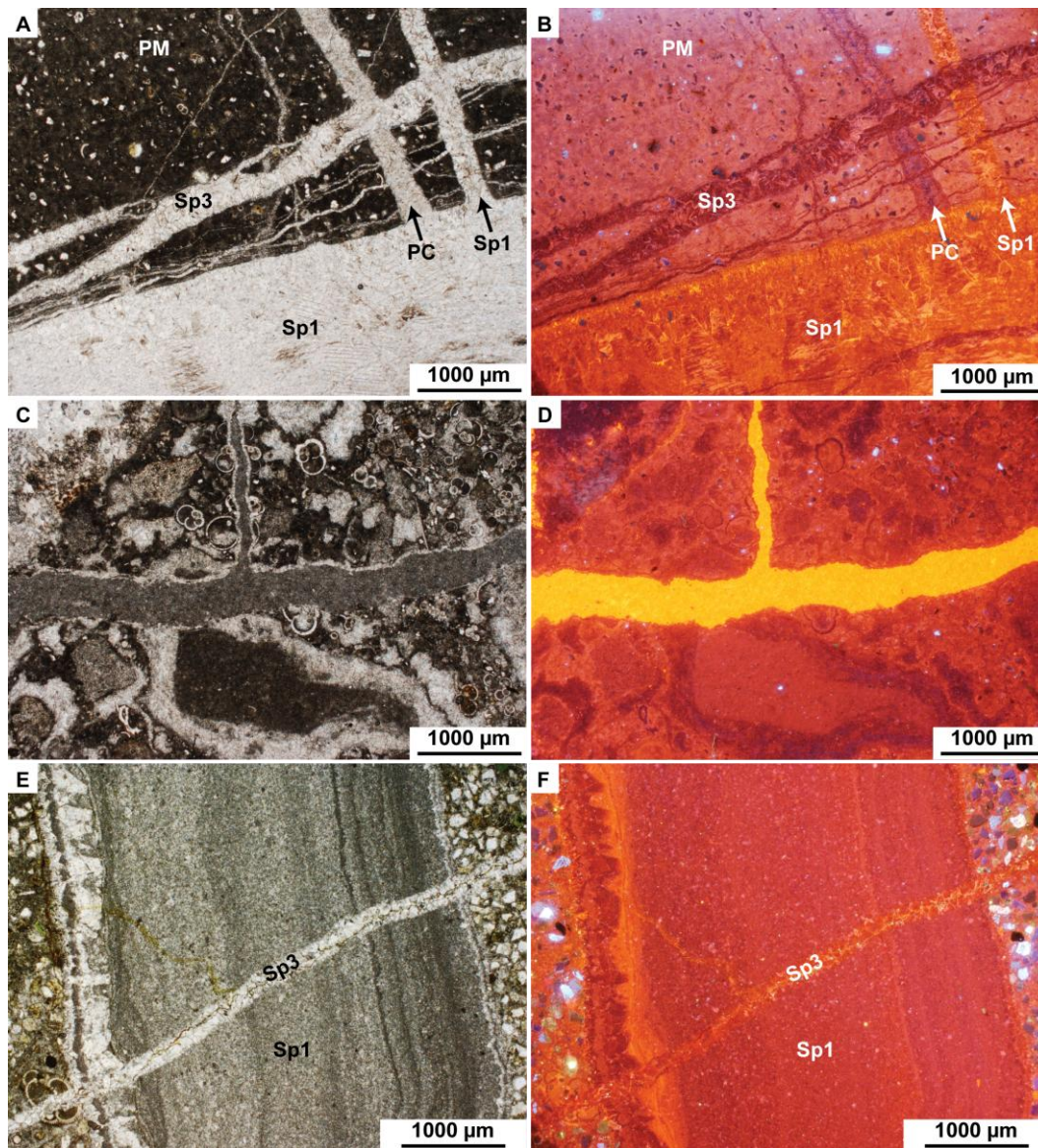


Figure 6.9 – Photomicrographic pairs of images illustrating blocky spars 1, 2, and 3 (Sp1, Sp2, and Sp3) under PPL (images A, C, and E) and CL (images B, D, and F). **A and B:** A series of veins cuts through the micarb of thin section NG.M7 from Ngawaka. Earliest veins are infilled with blocky spar 1 (Sp1) having maroon to orange CL colour, which are later cross-cut by veins infilled with blocky spar 3 (Sp3) with a maroon CL colour. **C and D:** A thin, branching vein cuts through a mosaic of early fabrics in thin section W.M6 from Wilder Road. It is infilled with blocky spar 2 (Sp2) as shown by its bright yellow CL colour. **E and F:** A thick vein infilled with many layers of a fine-grained blocky spar 1 (Sp1) cuts through a siliciclastic-rich pseudo-micarb in thin section UH.2D.1 from Ugly Hill. The zonation of infill layers is also evident under CL. Both pseudo-micarb and vein are later cross cut by a vein infilled with blocky spar 3 (Sp3).

μm. Under cross-polarised light the crystals have a very bright array of interference colours, changing from white/brown/blue to white/grey/yellow as the stage is rotated through 90°. Under CL the fabric is a patchy dull pink to purple colour. This fabric occurs only at Ngawaka where it acts as the final vein and cavity fill.

6.3.12 Blocky spar 2 – Sp2

Blocky spar 2 is also a late, secondary fabric (Figs. 6.9C, 6.9D). It occurs in generally small abundances as a cavity fill fabric but more commonly within pre-corroded cracks and fenestrae in earlier fabrics which typically form in zones of weakness such as along the borders of bioclasts (e.g. bivalves, corals, worm tubes), around peloids, along fabric boundaries, and within previously infilled veins. Crystals are equant and range in size from microspar to 875 μm .

Under PPL this spar is often indistinguishable from the surrounding fabrics as it appears simply as another translucent/white to grey infill precipitate (Fig 6.9C). Under XPL the crystals exhibit the typical first order pastel colours of calcite. Under CL, blocky spar 2 is readily identifiable by its very bright yellow colour (Fig. 6.9D).

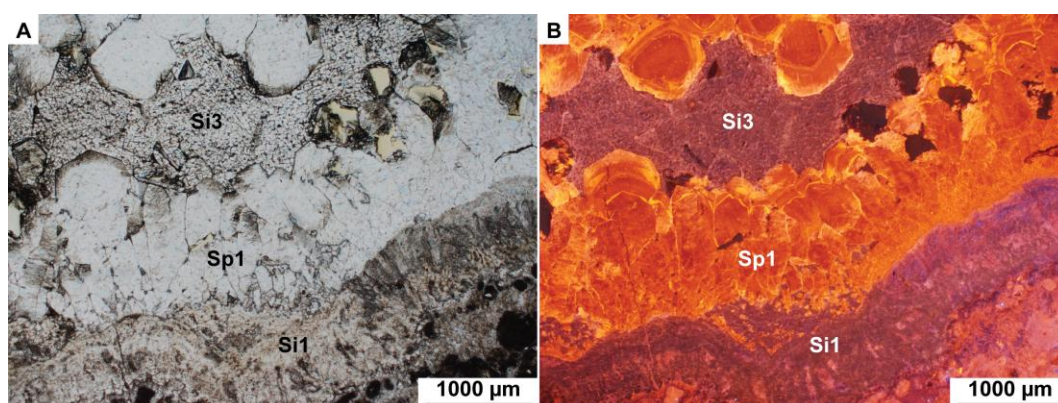


Figure 6.10 – Photomicrographic pair of images illustrating the layered infill of authigenic silica 1 (Si1), blocky spar 1 (Sp1), and authigenic silica 3 (Si3) in a cavity within pseudo-micarb (PM) (seen in the lower right corner). Thin section NG.2B.B from Ngawaka. **A:** Under PPL Si3 appears as tightly packed translucent/white crystals, which post-date late blocky spars (e.g. Sp1). **B:** Same view under CL shows authigenic silica luminescing purple. The blocky spar 1 crystals show growth zonation, and an earlier silica phase also appears purple.

6.3.13 Blocky spar 3 – Sp3

Again this is a late, secondary cement. Under PPL it appears as tightly packed, clean looking, translucent/white euhedral crystals (Figs. 6.9A, 6.9E). Under XPL light the crystals exhibit the typical first order pastel colours of calcite. Twinning is common, visible in both PPL and XPL. Under CL this fabric typically exhibits

a maroon colour (Fig. 6.9B), but grades to orange in a few samples (Fig. 6.9F). Some crystals have zoned CL colours, which are typically concentric or oscillatory.

6.4 ULTRAVIOLET LIGHT PETROGRAPHY

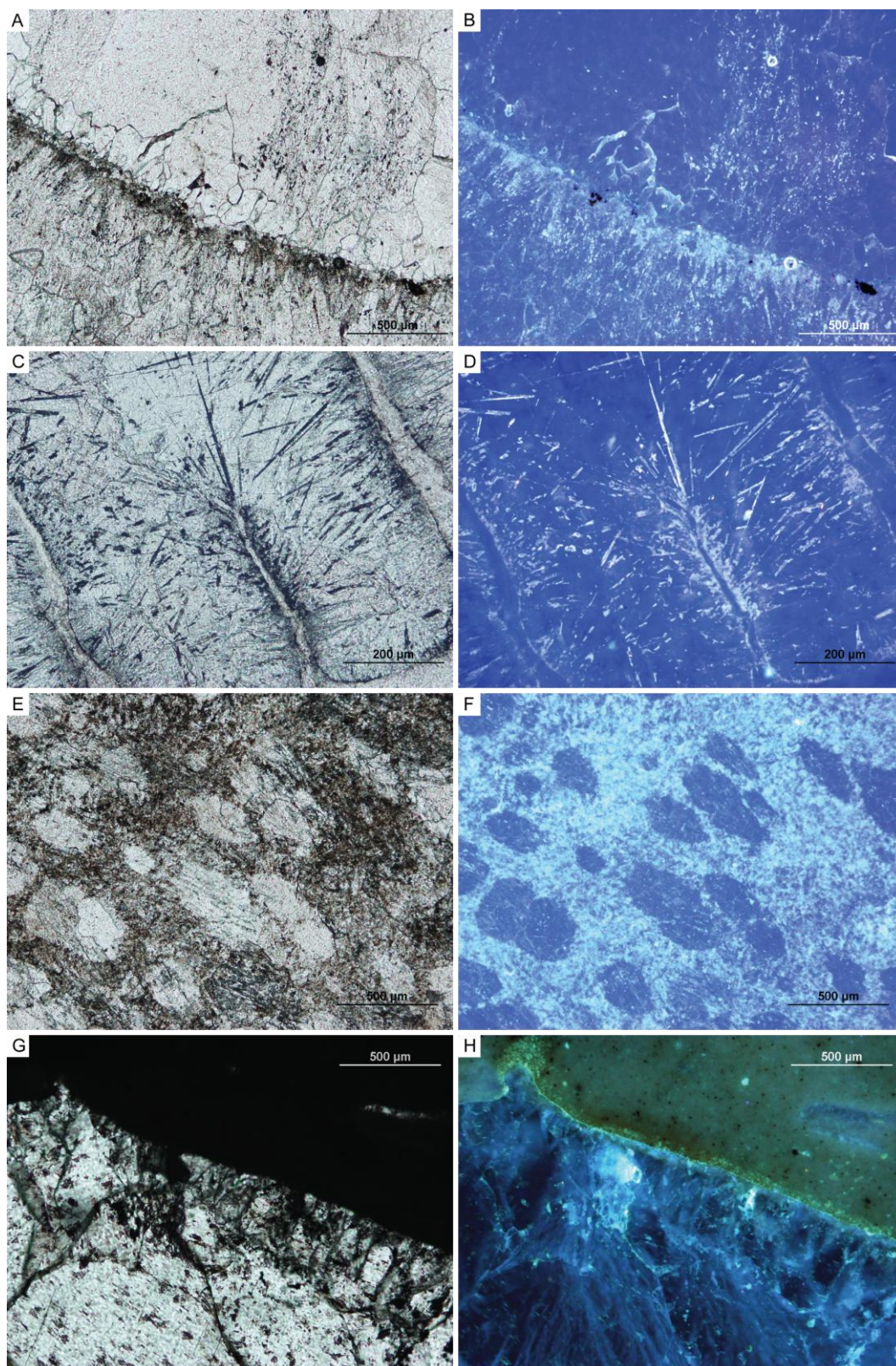
A suite of thin sections was analysed under ultraviolet (UV) light to aid in the interpretation of small, dark inclusions within minerals identified during PPL petrography. Figure 6.11 illustrates the typically white to bright blue and green fluorescence exhibited by the inclusions under UV light in the southern Hawke's Bay ancient seep carbonate deposits. The dark fluid inclusions as seen in PPL are associated with fibrous and blocky crystals of various petrographic fabrics. They are present throughout individual crystals, around the terminus of crystals, and are typically concentrated about the borders of these petrographic fabrics. Other petrographic fabrics viewed under UV light usually failed to show any fluorescence.

6.5 SCANNING ELECTRON MICROSCOPY

The scanning electron microscope (SEM) was used in this study to gain insight on crystal morphologies, microfacies, and microbial textures. Still images of samples from the Ugly Hill, Wilder Road, and Ngawaka sites were captured along with X-ray micro-analysis of a Ngawaka thin section to produce elemental maps.

Figure 6.11 - Photomicrographs of southern Hawke's Bay ancient seep carbonate thin sections under PPL (images A, C, E and G) and UV light (images B, D, F, and H). Where present organic hydrocarbons fluoresce bright blue/green. **A and B:** Thin section HA.13.5.1A from Haunui exhibits hydrocarbon inclusions within blocky spar crystals (upper fabric) and concentrated along the border of a phase of micro-equant to dentate, neomorphosed early cement. **C and D:** Thin section WA.13.1.1A from Wanstead exhibits hydrocarbon inclusions, often in dense accumulations, within acicular aragonite which has nucleated off neomorphosed coral. Note the coral bioclast itself does not fluoresce. **E and F:** Thin section WA.M1 from Wanstead exhibits peloids (which have been neomorphosed from micarb to spar) cemented by an inclusion-rich blocky spar. The peloids contain no fluid inclusions, while the blocky spar is rich in hydrocarbon inclusions that fluoresce brightly. **G and H:** Thin section W.8.9.3A from Wilder Road exhibits hydrocarbon inclusions within blocky spar crystals. The dark coloured micarb is inclusion-free.

Figure 6.12 shows high magnification images of some of the fabrics described in Section 6.3. These images suggest that acicular and splayed cements were



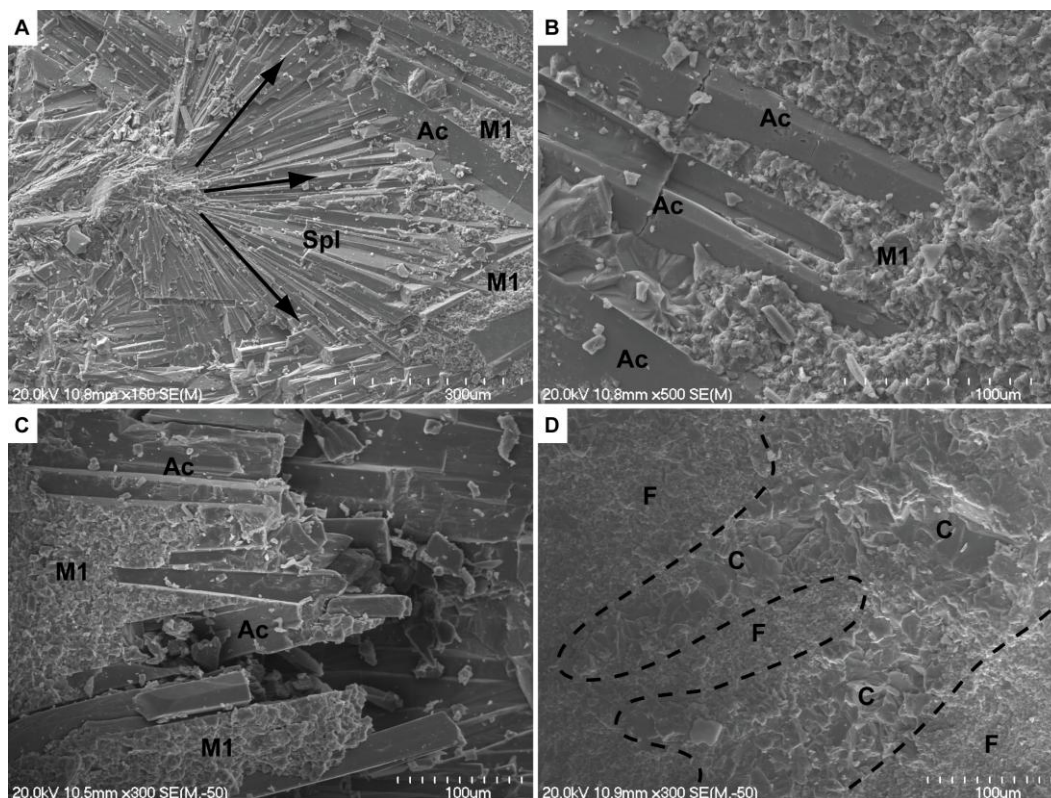
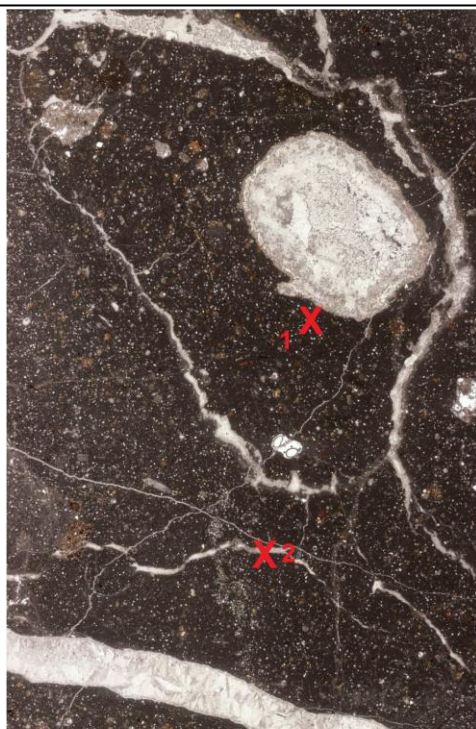


Figure 6.12 – SEM images of some seep carbonate fabrics. **A:** A large splay of needles (Spl) has formed amongst larger acicular needles (Ac) and micarb (M1). Arrows indicate the direction of splay growth. **B and C:** Close-ups of the interaction/relationship between acicular needles (Ac) and micarb (M1). By the way the micarb wraps around the individual needles it is inferred that the micarb formed after and around the needles. **D:** Micarb is a very fine grained fabric with a very irregular crystal habit. An area of a coarser grained micarb (between dashed lines, denoted with ‘C’) appears to interfinger with the finer-grained fabric (F).

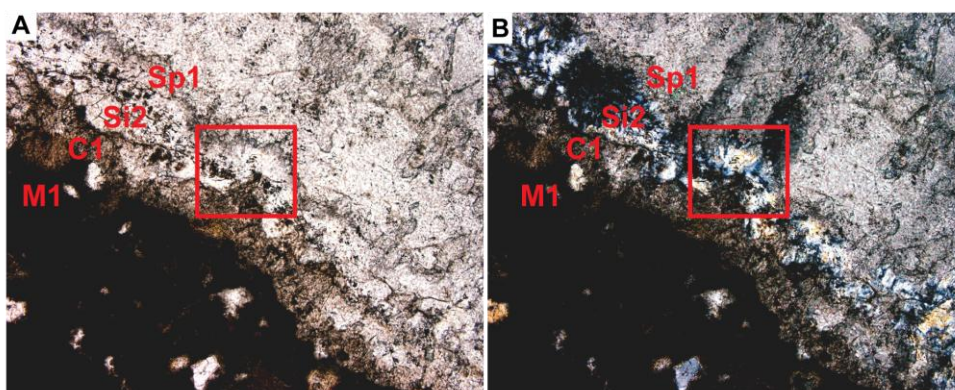
forming at much the same time, as well as contemporaneously precipitating micro-crystalline carbonate (micarb).

Elemental mapping was carried out on two portions of the Ngawaka thin section NG.B1 (Fig. 6.13). An electron beam was used to identify the minerals present in the field of view, with output in the form of multiple maps illustrating element intensities and a graph showing relative counts of each element present (Fig. 6.14, Fig. 6.15). The two localities were selected based on the array of fabrics present and the need for mineralogical confirmation.

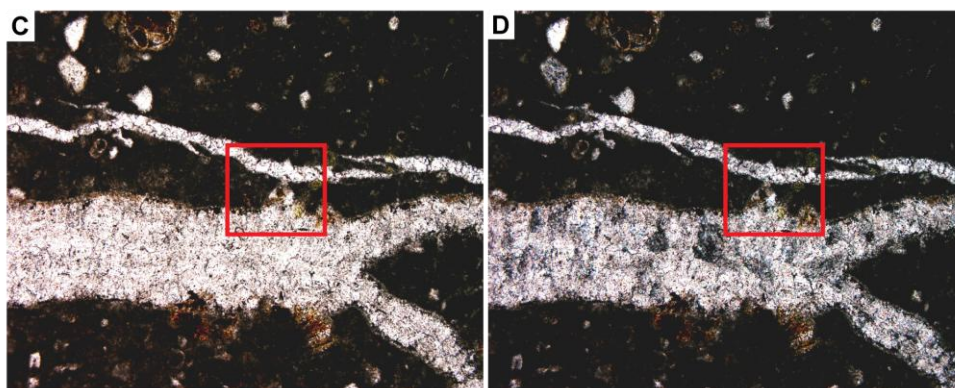
Elemental mapping for locality 1 (Fig. 6.14) reveals that the layer of authigenic silica is indeed very rich in silicon and also oxygen when related to the other



Entire NG.B1 thin section (2.5 x 4 cm). Red crosses mark elemental map localities.



Photomicrographs of locality 1, in PPL (A) and XPL (B). This field of view includes the early layered fill of a cavity within micarb (M1). A yellow-brown cement (C1) is followed by a layer of authigenic silica (Si2) and finally blocky spar. Red box shows the view of the elemental map (Fig. 6.14).



Photomicrographs of locality 2, in PPL (C) and XPL (D). This field of view includes a micarb background (M1) interrupted by two spar-filled veins. Red box shows the view of the elemental map (Fig. 6.15).

Figure 6.13 – Thin section image and photomicrographs to illustrate the location of, and fabrics included in, SEM elemental maps 1 and 2 of thin section NG.B1 from Ngawaka.

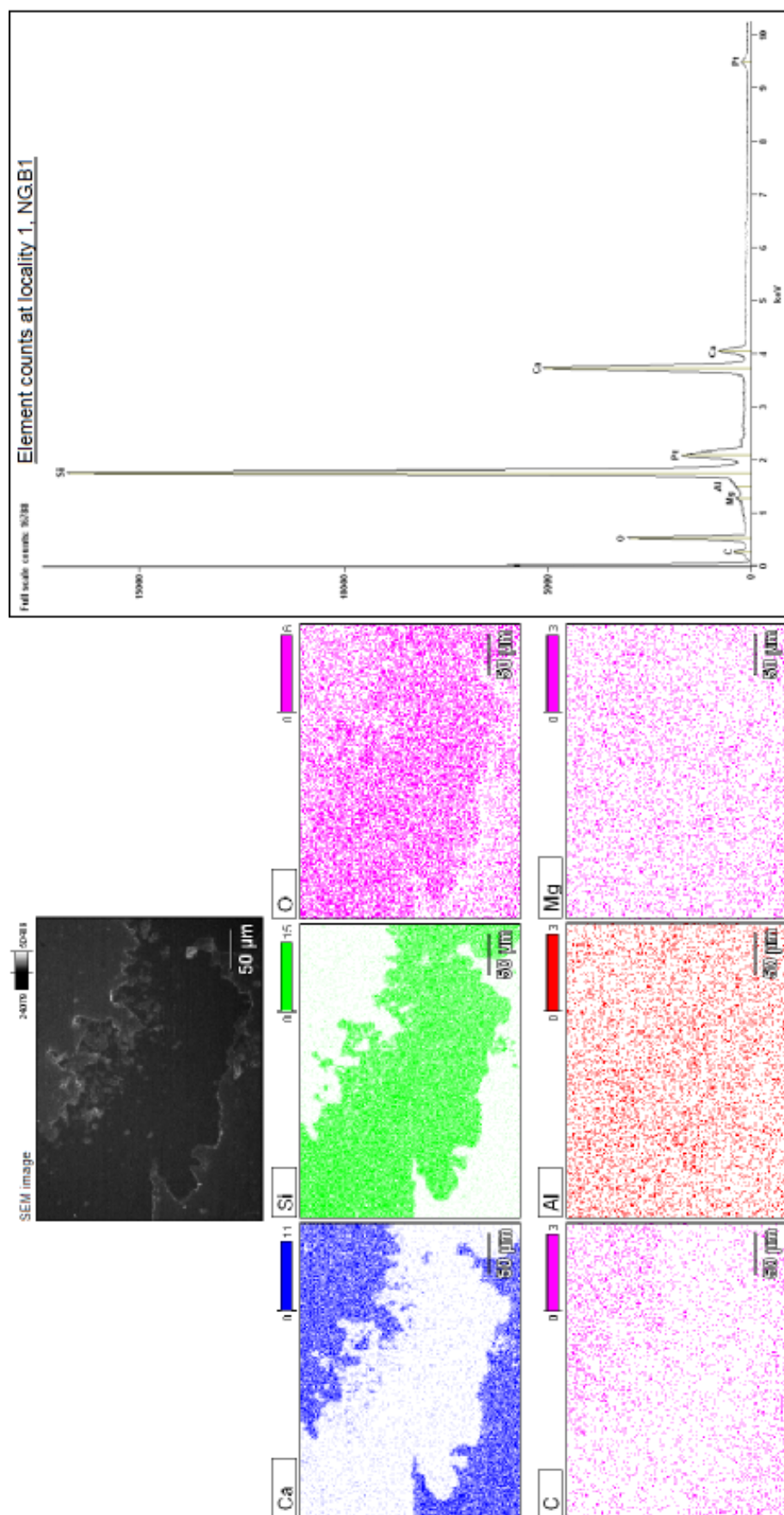


Figure 6.14 – Elemental map images of locality 1 on thin section NGB1 (see Fig. 6.13A,B). SEM image shows the outer portion of the first mineral layer (yellow-brown cement C1), the entire second mineral layer (authigenic silica Si1), and part of the third layer (SP1) of the cavity infill. Coloured images relate to elements noted at the top left corner of each image. Colour intensity reflects element abundance. The graph shows the relative abundance of each of the six main elements present. Note that Pt is the platinum coating on the thin section.

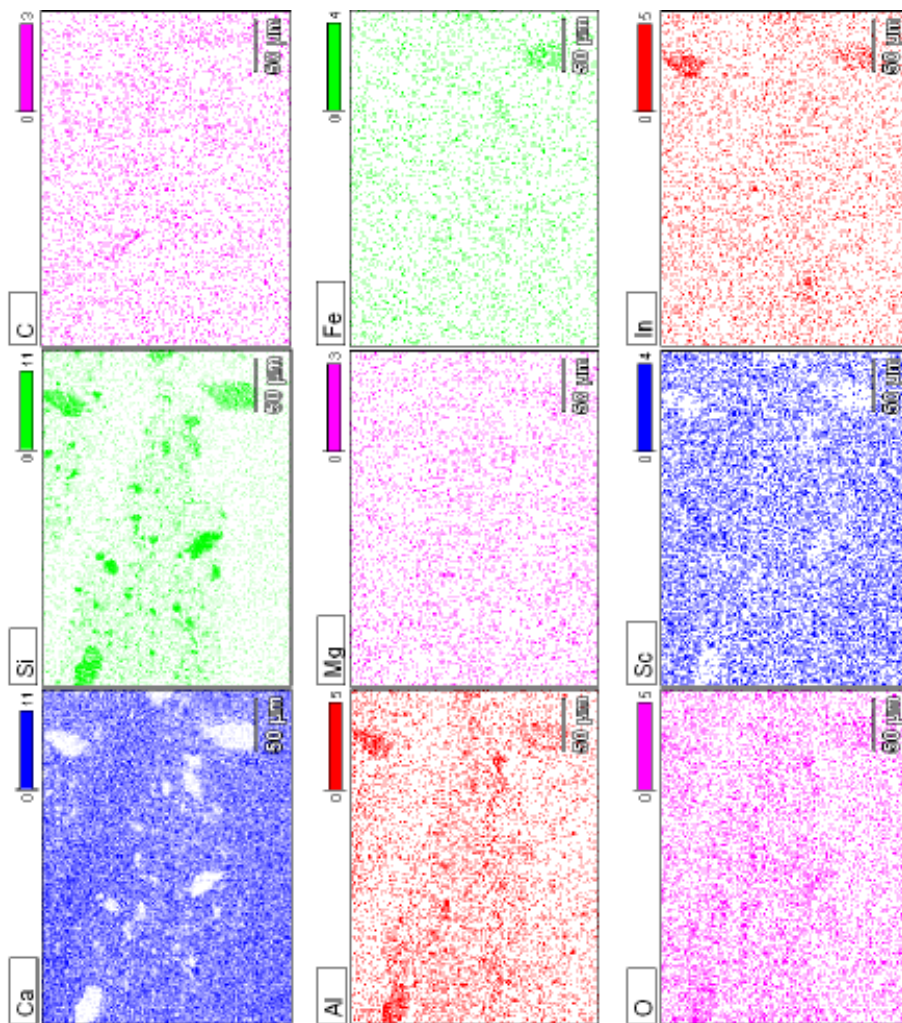
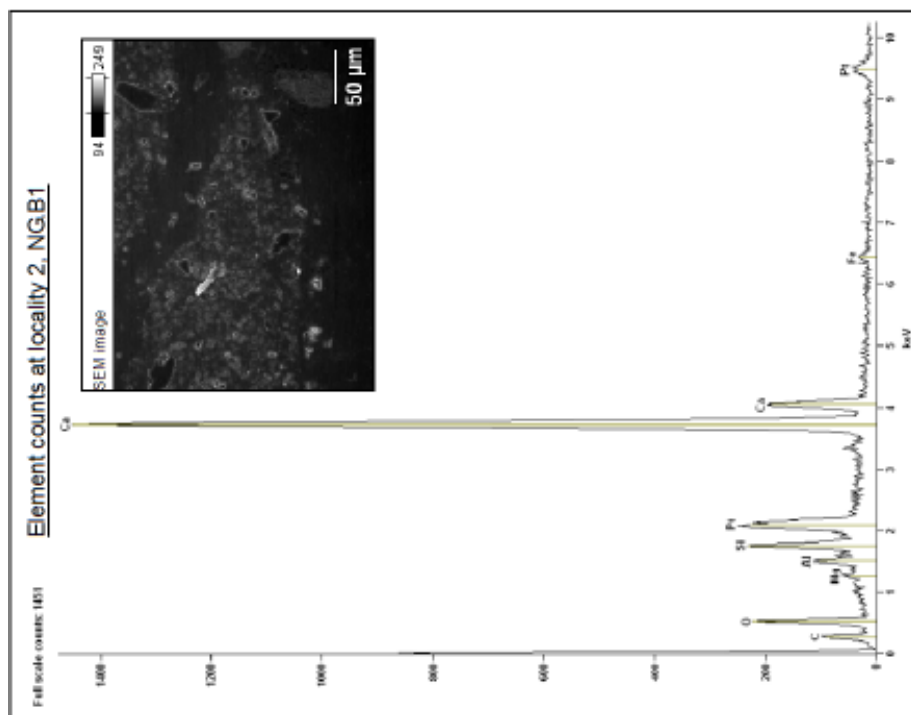


Figure 6.15 – Elemental map images of locality 2 on thin section NG.B1 (see Fig. 6.13C,D). SEM image shows the micarb rich in siliciclastic grains and intraclasts, and the two veins cutting through the micarb. Coloured images relate to elements noted at the top left corner of each image. Colour intensity reflects element abundance. The graph shows the relative abundances of seven of the nine main elements present. Indium and scandium are in too low an abundance to be observed on the graph. Note that Pt is the platinum coating on the thin section.

layers, implying that it is a silicon dioxide, probably quartz. The surrounding layers (yellow-brown cement and blocky cement) are rich in calcium and oxygen, and slightly enriched in carbon when compared to the silica-rich layer. This implies a calcium carbonate mineralogy. All layers have a roughly uniform abundance of aluminium and magnesium.

Elemental mapping for locality 2 (Fig. 6.15) reveals differences in mineralogy of the micarb, the cross-cutting veins, and the intraclasts within the micarb. Carbon, oxygen, and magnesium appear to be of uniform abundance throughout the area. The micarb appears to be particularly rich in calcium, and contain more aluminium and silicon than the veins. The veins are very rich in calcium. Many of the crystals within the micarb appear to be enriched in silicon, depleted in calcium, and some feature significant abundances or depletions in aluminium, iron, scandium, and indium.

6.6 X-RAY DIFFRACTION

Bulk mineralogical analysis was undertaken by means of X-ray diffraction (XRD). For methods, see Section 4.3.4.1. A summary of the bulk mineralogy is shown in Table 6.4, with all raw data present in the Appendix CD. The dominant minerals are the calcium carbonate polymorphs, calcite and aragonite. Calcite is present in all samples at either an abundant (A) or common (C) amount. Aragonite is present in 10 of the 38 samples and dolomite in 5 of the 38 samples, both with amounts ranging from abundant (A) to rare (R). Siliciclastic grains were present in nearly all samples (35 of 38) and include quartz, potassium feldspar, plagioclase feldspar, and clays. Clays are likely under-represented in samples because of the use of unorientated bulk powder XRD sample mounts.

In order to differentiate between high (>12 wt % MgCO_3), intermediate (4-12 wt % MgCO_3), and low (<4 wt% MgCO_3) magnesium calcite (HMC, IMC, and LMC, respectively) the exact position of the calcite 100 peak needed to be determined. Slight shifts in the position of this peak can occur due to instrumentation error, and this needs to be corrected by checking for any off-set in the halite or quartz peak and applying this off-set to the calcite 100 peak. Thus, halite was added to all samples to provide a strong internal standard peak, with

quartz occurring naturally in most samples. However, the small concentration of halite added to samples remained dwarfed by the overwhelming dominance of calcite in the samples, to the point where the halite peak is not even recognisable in three of the samples. This made interpretation of the position of the halite peak difficult, and thus corrections to the calcite 100 peak based on the halite and quartz peaks probably have a degree of inaccuracy.

Table 6.4 – Mineral abundances in 38 bulk samples from the five southern Hawke’s Bay cold seep carbonate sites. Sample names with (*) are those run for a second time at a slow scan speed. Abundances are relative to the other minerals found in the sample (see legend below). The two column sets for the calcite type are based on corrections relative to the position of the halite and quartz peaks, respectively (see text for details). Numbers next to calcite concentrations refer to the inferred percentage of magnesium in samples. For all XRD graphs refer to the Appendix disk.

Run #	Sample	Aragonite	Dolomite	Quartz	Feldspar	Clays	Calcite based on halite peak			Calcite based on quartz peak		
							LMC	IMC	HMC	LMC	IMC	HMC
HA.1	HA.13.1.1	-	-	C	C	-	-	A 8%	-	A 1%	-	-
HA.2	HA.11.1.1	-	-	C	R	R	-	A 7%	-	A 1%	-	-
HA.3	HA.M1	-	C	C	R	R	-	A 7%	-	A 1%	-	-
HA.4	HA.1F.1A	-	-	C	R	-	-	A 8%	-	A 1%	-	-
HA.5	HA.12.6.1	-	-	C	C	R	-	A 7%	-	A 2%	-	-
HA.5*	HA.12.6.1	-	-	C	R	-	-	A 6%	-	A 2%	-	-
NG.15	NG.E3	-	-	C	-	-	-	A 7%	-	A 1%	-	-
NG.16	NG.2B	-	-	C	R	-	-	A 5%	-	A 1%	-	-
NG.17	NG.2G.2	-	-	R	R	-	-	N/A	-	C 0%	-	-
NG.18	NG.F4	-	-	R	-	-	-	N/A	-	C 1%	-	-
NG.18*	NG.F4	-	-	C	R	-	-	C 7%	-	C 1%	-	-
NG.19	NG.5A	-	-	C	R	-	-	A 8%	-	A 3%	-	-
NG.19*	NG.5A	-	-	C	R	-	-	A 9%	-	A 0%	-	-
UH.1	UH.3A.1	A	R	-	R	-	C 3%	-	-	-	N/A	-
UH.1*	UH.3A.1	C	-	-	-	-	-	C 8%	-	-	N/A	-
UH.2	UH.3A.2	A	R	R	-	-	-	N/A	-	C 2%	-	-
UH.3	UH.104.1	-	-	C	C	R	-	A 5%	-	A 0%	-	-
UH.4	UH.11.3	R	-	C	R	-	A 1%	-	-	A 1%	-	-
UH.4*	UH.11.3	-	-	C	C	-	-	A 8%	-	A 0%	-	-
UH.5	UH.5C.1	-	-	C	C	-	A 3%	-	-	A 0%	-	-
UH.6	UH.11.4.2	R	-	-	-	-	-	A 6%	-	-	N/A	-
UH.7	UH.10.1.3	C	C	C	R	-	-	N/A	-	A 1%	-	-
UH.8	UH.100.8.1	C	A	C	R	-	-	N/A	-	A 1%	-	-
WA.1	WA.1A.1	-	-	C	R	R	A 3%	-	-	A 1%	-	-
WA.2	WA.M1	-	-	C	C	-	-	A 9%	-	A 2%	-	-
WA.3	WA.2B.1	-	-	C	R	-	-	A 8%	-	A 1%	-	-
WA.4	WA.7F.1	-	-	C	R	-	-	A 9%	-	A 0%	-	-
WA.5	WA.13.1	-	-	C	R	-	-	A 10%	-	A 1%	-	-
WA.6	WA.M2	R	-	C	-	-	-	A 8%	-	A 2%	-	-
WA.22	WA.13.4.1B	R	-	C	R	-	-	A 7%	-	A 2%	-	-
W.1	W.1.2	-	-	C	-	-	A 3%	-	-	A 0%	-	-
W.20	W.3.2	-	-	C	-	-	-	A 7%	-	A 2%	-	-
W.21	W.8.2	-	-	C	-	-	A 3%	-	-	A 1%	-	-
W.22	W.8.7	-	-	R	-	-	-	A 7%	-	A 0%	-	-
W.23	W.M10	-	-	C	-	-	A 3%	-	-	A 1%	-	-
W.24	W.2.1	C	-	-	-	-	-	A 8%	-	-	N/A	-
W.25	W.8.9.4	-	-	R	R	-	-	A 8%	-	A 0%	-	-

-	None	0 counts
R	Rare	1-200 counts
C	Common	201-999 counts
A	Abundant	>1000 counts

LMC	<4% Mg
IMC	4-12% Mg
HMC	>12% Mg

* = slow scan speed from
25-35 degrees 2 θ

In order to overcome this discrepancy, five samples were re-run at a slow scan speed from 25-35° 2 θ to derive an accurate position of the calcite, halite, and quartz peaks. However, again the halite peak was dwarfed, despite an increase in the amount added to samples.

Consequently, two separate corrections were made to the calcite 100 peak of each sample run in order to make an interpretation of the magnesium content of the calcite – one value with a correction based on the position of the halite peak at 31.72 °2 θ , where applicable, and a second value based on a correction gained from the position of the quartz peak at 26.6 °2 θ , also where applicable, as not all samples contained quartz. Both values are presented in Table 6.4, which shows the percentage of magnesium derived from published graphs (Chave 1952; Goldsmith *et al.* 1961) and the corresponding type of calcite (i.e. HMC, IMC, or LMC). Note that IMC dominates based on the halite internal standard, but LCM is the dominant mineralogy in relation to the position of the quartz peak.

6.7 GENERAL AREA DETECTOR DIFFRACTION (GADDs)

Component mineralogical analysis was undertaken on 20 areas from seven thin sections from the five southern Hawke's Bay cold seep carbonate sites using the General Area Detector Diffraction (GADDs) technique. The technique allows mineralogical identification of individual fabrics identified during petrographic analysis.

Raw data are in the form of an image consisting of a scattering of points of various sizes, brightness, and alignment which are influenced by crystal size and orientation(s). Chi analysis produces a graph to illustrate mineral peaks, and EVA software matches the peaks with mineral types. Examples of the resultant graphs are shown in Figures 6.16 and 6.17.

The mineralogical results of the 20 spots analysed are shown in Table 6.5. For all raw data see Appendix CD, and for a complete set of the graphed results for each spot analysed see Appendix 3.1 All thirteen fabrics identified in petrographic analysis (Table 6.3) were run through GADDs, and the results confirm that all fabrics are aragonite, calcite, quartz, or some combination of these minerals. In

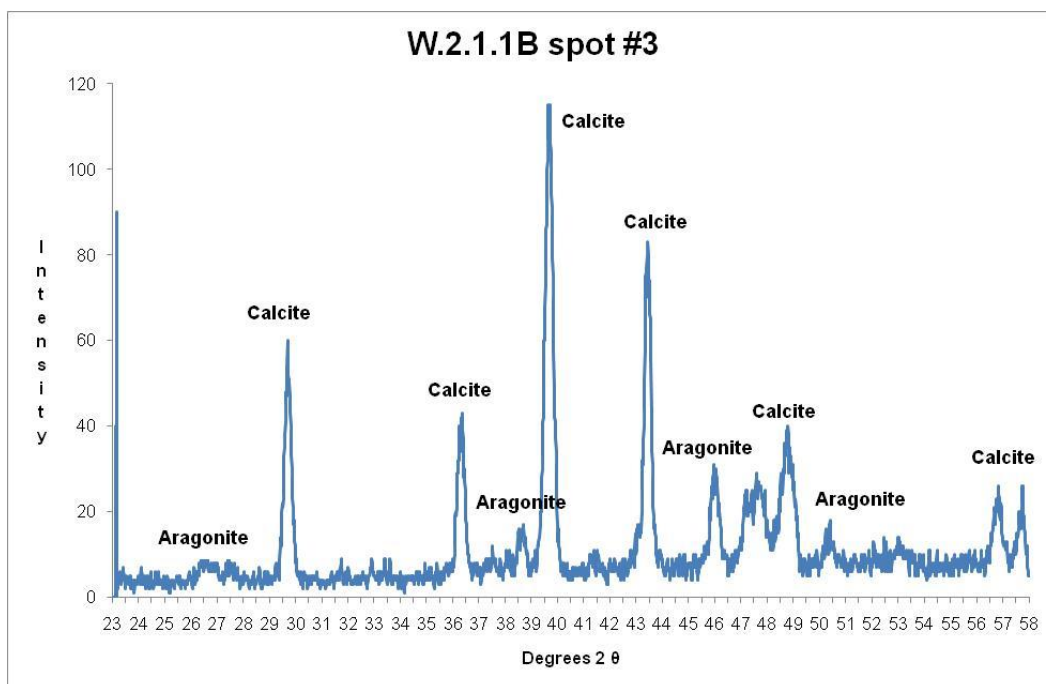


Figure 6.16 – GADDs analysis on spot 3 of thin section W.2.1.1B from Wilder Road targeted yellow-brown cement (C1). The graph indicates that calcite is the main component of this fabric, along with minor aragonite.

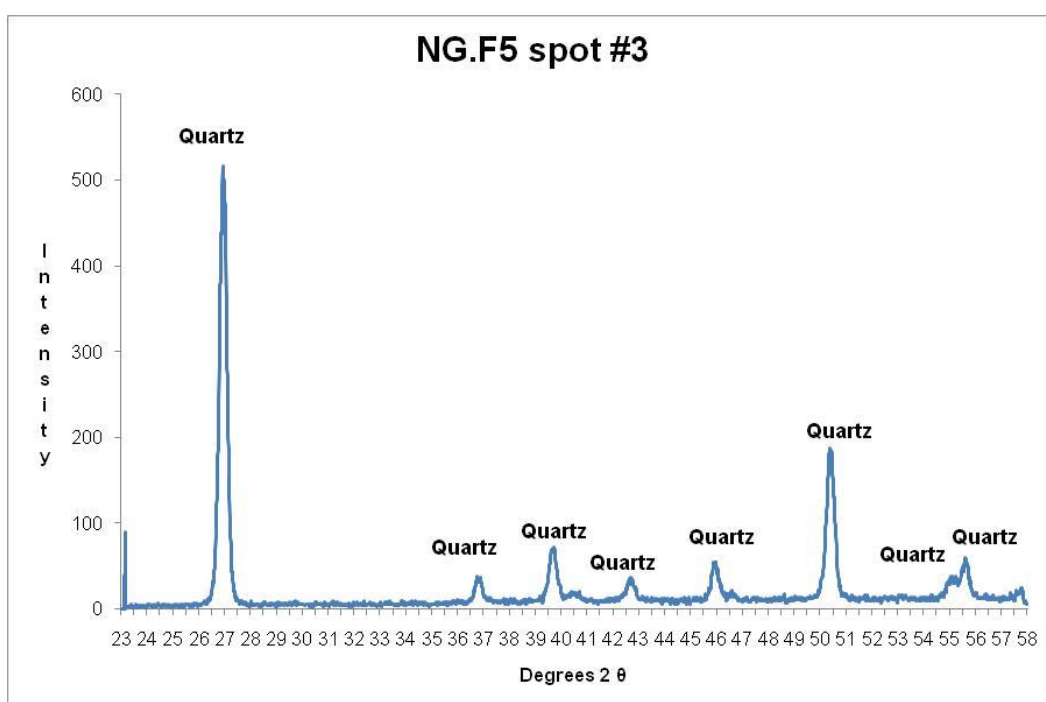


Figure 6.17 – GADDs analysis on spot 3 of thin section NG.F5 from Ngawaka targeted authigenic silica 1 (Si1). The graph shows that quartz is the only mineral present in this fabric.

some cases neomorphosed fabrics still contained remnant aragonite, which was indicated by minor aragonite peaks (e.g. neomorphosed fibrous cement (C2) of sample UH.10.1.2A from Ugly Hill). The mineralogy of siliciclastic grains within micarb fabrics is also reflected in these results.

Table 6.5 – Mineralogical summary based on GADDs analysis of 20 fabrics from seven thin sections from southern Hawke’s Bay seep carbonate sites. Codes for target fabrics defined in Table 6.3.

Thin section / spot	Target fabric	Mineralogy, morphology
NG.2B.B_1	Si3	Quartz, large crystal size
NG.2B.B_2	Sp1	Calcite, large crystal size
NG.2B.B_3	PM	Calcite. Quartz. Possibly feldspar or clay
NG.F5_2	Si2	Quartz, small crystal size, randomly orientated
NG.F5_3	Si1	Quartz, a range of crystal sizes
NG.M7_1	Sp1	Calcite, perhaps enriched in Mg, large crystal size
NG.M7_2	Sp1	Calcite
NG.M7_3	Sp3	Calcite
NG.M7_4	Sp1	Calcite, well orientated crystals
NG.M7_5	PC	Calcite
UH.3A.1A_1	M1	Calcite, enriched in Mg. Quartz
UH.3A.1A_2	C2	Aragonite
UH.3A.1A_3	Th	Calcite, large crystals. Aragonite, many small crystals
UH.10.1.2A_1	C2	Aragonite. Minor calcite
UH.10.1.2A_2	Sp1	Calcite
W.2.1.1B_1	Sp1	Calcite
W.2.1.1B_2	M2	Calcite
W.2.1.1B_3	C1	Calcite, moderately orientated crystals. Minor aragonite
W.2.1.1B_4	Th	Calcite, moderately orientated crystals. Aragonite
W.M6	Sp2	Calcite

6.8 CARBONATE PERCENTAGE ANALYSIS

Carbonate percentage analysis was carried out on a minimum of five bulk powder samples from each of the five sites in this study using the LECO method. The carbonate percentages of the Miocene southern Hawke’s Bay seep carbonate deposits vary from 58-86% (Table 6.6). As anticipated, the carbonate values reflect the purity of the micarb and dominant fabrics of each sample. For example, micarbs from Ugly Hill and Haunui sites typically contain a relatively high proportion of siliciclastic components giving a lowered carbonate percentage, while Wilder Road samples, which typically have few siliciclastic grains, have the highest carbonate percentages.

Table 6.6 - Carbonate content (%) of representative samples from the five ancient seep carbonates sites in southern Hawke's Bay, plus the range and average of carbonate content over each site.

Site	Sample	Carbonate %	Site range	Site average
Ugly Hill	UH1	65.8		
	UH2	58.2		
	UH3	65.0		
	UH4	63.2		
	UH5	68.5		
	UH6	65.9		
	UH7	64.8		
	UH8	76.3		
			58 - 76	66
Wanstead	WA1	76.3		
	WA2	81.2		
	WA3	72.0		
	WA4	80.2		
	WA5	81.1		
	WA6	83.0		
	WA22	78.1		
			72 - 83	79
Wilder Road	W1	84.2		
	W20	79.4		
	W21	85.5		
	W22	80.9		
	W23	79.3		
	W24	76.2		
	W25	85.4		
			76 - 86	82
Haunui	HA1	69.6		
	HA2	69.3		
	HA3	77.6		
	HA4	75.5		
	HA5	83.1		
			69 - 83	75
Ngawaka	NG15	79.6		
	NG16	76.8		
	NG17	77.8		
	NG18	76.1		
	NG19	77.8		
			76 - 80	78

6.9 STABLE ISOTOPE ANALYSIS

Stable oxygen and carbon isotopic analysis was undertaken on multiple samples from the five study sites. The bulk powders generated from the major facies at each site were used, with the addition of a suite of powders drilled for component-specific analysis. The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values for all samples analysed (107 in total) are plotted on Figures 6.18 – 6.23. For raw data see Appendix 3.2.

Stable $\delta^{13}\text{C}$ values reflect carbon sources (Roberts *et al.* 1993; Campbell *et al.* 2002; Nyman 2009). The southern Hawke's Bay seep carbonate samples exhibit $\delta^{13}\text{C}$ values ranging from -30.16‰ to +9.82‰, although most of these lie below -20‰.

Stable $\delta^{18}\text{O}$ values indicate the water temperature and isotopic composition during precipitation, fractionation of carbonate phases, the presence of gas hydrates, and clay mineral dehydration (Greinert *et al.* 2001; Campbell 2006; Judd & Hovland 2007; Nyman 2009). The southern Hawke's Bay seep carbonate samples have $\delta^{18}\text{O}$ values ranging from -6.54‰ to +3.04‰.

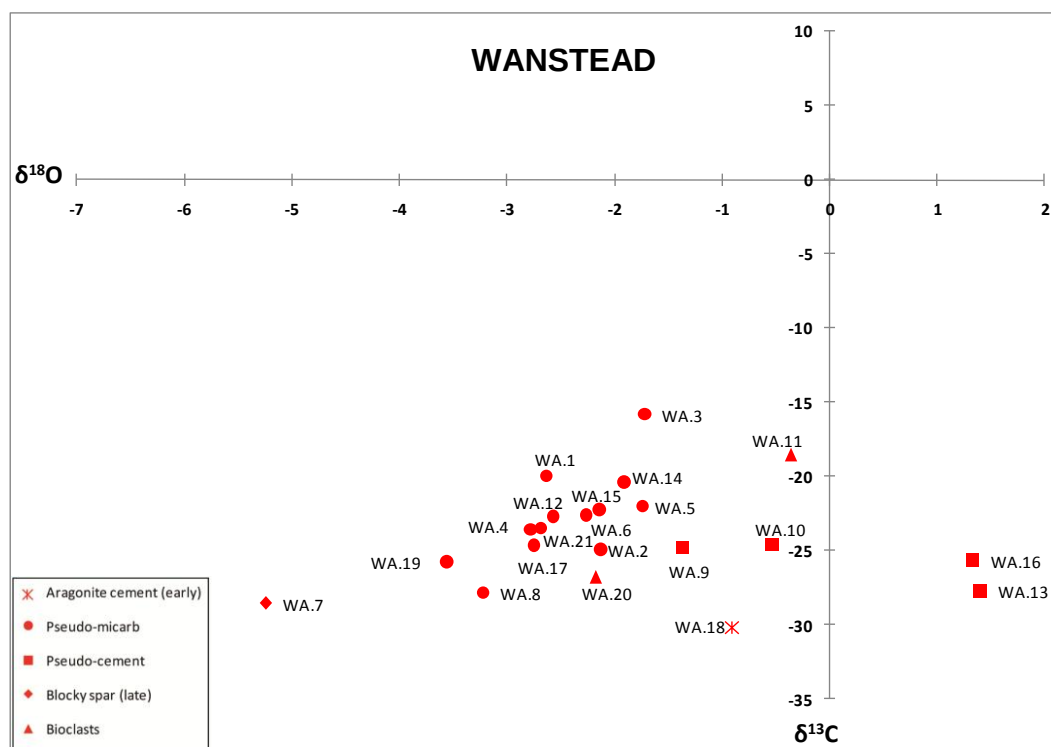


Figure 6.18 – Stable $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ cross plot showing the values of the 21 bulk and component-specific powders from Wanstead samples.

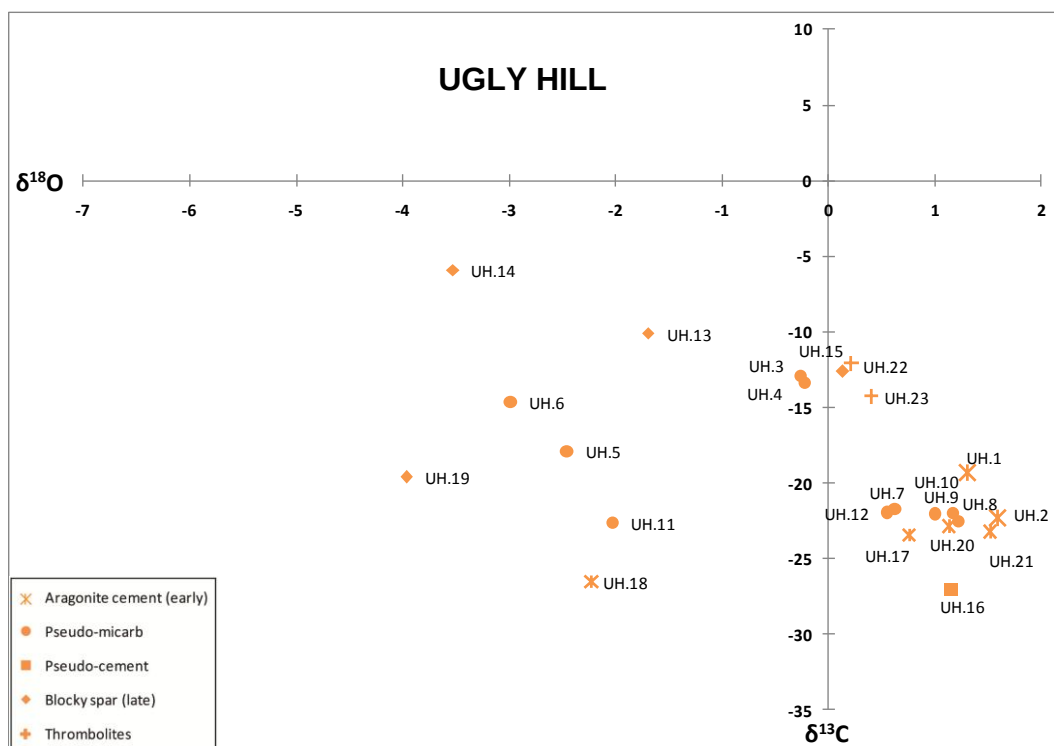


Figure 6.19 – Stable $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ cross plot showing the values of the 23 bulk and component-specific powders from Ugly Hill samples.

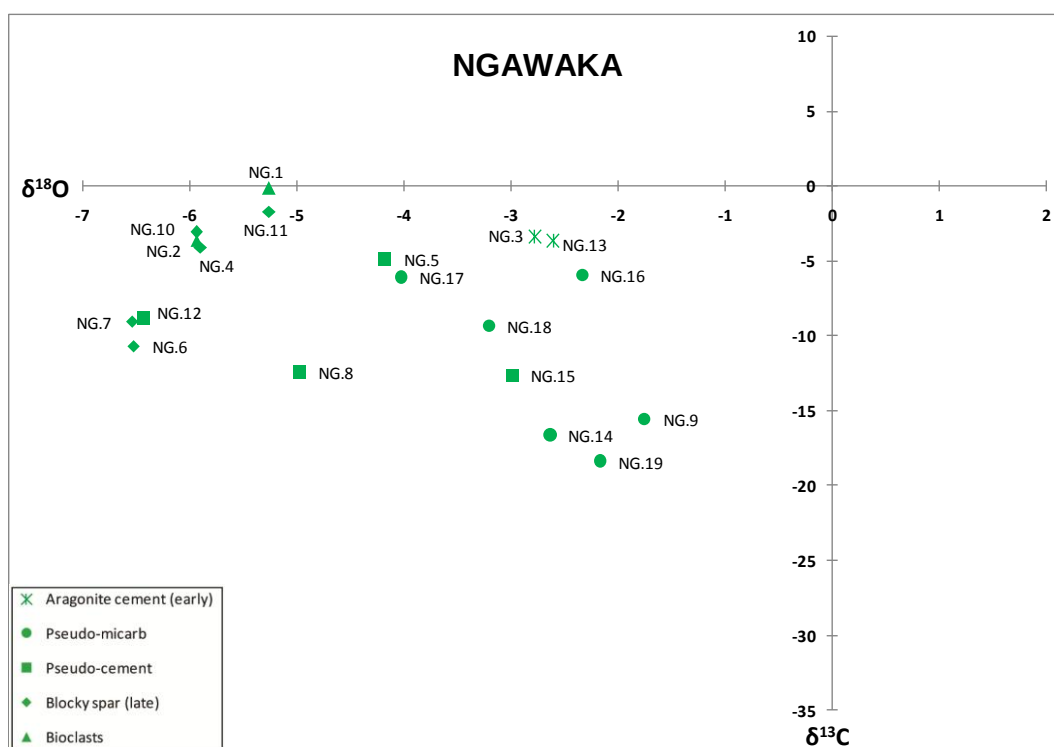


Figure 6.20 – Stable $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ cross plot showing the values of the 19 bulk and component-specific powders from Ngawaka samples.

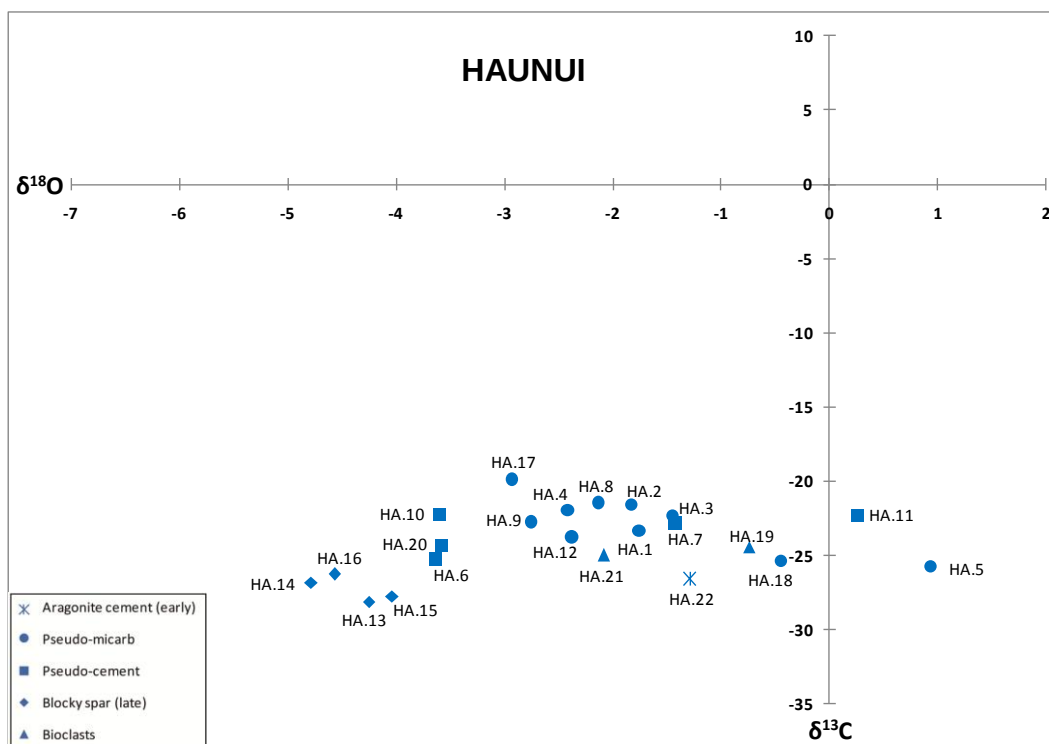


Figure 6.21 – Stable $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ cross plot showing the values of the 22 bulk and component-specific powders from Haunui samples.

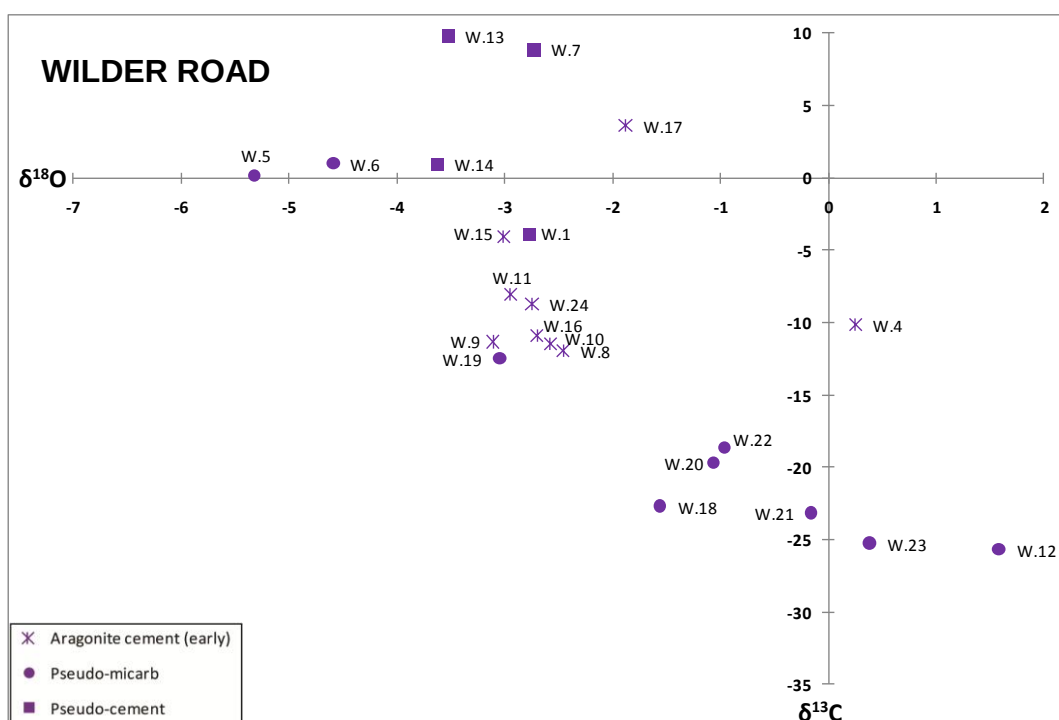


Figure 6.22 – Stable $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ cross plot showing the values of the 22 bulk and component-specific powders from Wilder Road samples.

Some general isotopic trends can be seen across the five study sites. Wanstead and Haunui have relatively light $\delta^{13}\text{C}$, with data points clustered below -15‰. Ugly Hill and Wilder Road show a trend of increasing $\delta^{13}\text{C}$ and decreasing $\delta^{18}\text{O}$. Ugly Hill also has a clustering of data points towards the right side of the plot, illustrating that many of these samples have a relatively heavy $\delta^{18}\text{O}$ signal. In contrast, the Ngawaka samples have relatively light $\delta^{18}\text{O}$ values, and also $\delta^{13}\text{C}$ values are all above -20‰ which is relatively heavy.

6.10 ORGANIC CARBON PERCENTAGES

Organic carbon content (C-org) for the major facies at each of the five study sites vary from 0.060% to 0.133% (Table 6.7). There does not appear to be any trends evident across the sites.

Total carbon values (C-org plus TC) for each of the samples were also measured (Tables 6.7, 6.8). These values appear to be consistently higher than those generated by LECO analysis (Table 6.6), an issue that is further discussed in Chapter 7.

6.11 LIPID BIOMARKER ANALYSIS

Lipid biomarker analysis was carried just prior to completion of this thesis, therefore allowing only some of the sample results to be included. Lipid analysis of southern Hawke's Bay seep carbonate samples continues in Bremen, Germany, under the supervision of Joern Peckmann and Daniel Birgel.

Each biomarker listed is indicative of microbes at the paleo-seep environment which carry out various chemical reactions. Of these biomarkers, the most important relevant to this study are the compounds which indicate anaerobic oxidation of methane and sulphate reduction, as these processes drive carbonate precipitation at the seep site and ultimately give rise to the formation of the MDAC deposits. A brief description of the biomarkers found within the samples is given in Table 6.9. Preliminary results are listed in Table 6.10.

Table 6.7 – Total organic carbon and total carbonate percentages for representative samples from each of the five study sites. Each sample was run twice to gauge reproducibility. TC = total carbon; C-org = organic carbon.

Sample	TC %	TC %	Average TC%	C-org %	C-org %	Average C-org %	Carbonate %
HA1	8.26	8.28	8.27	0.128	0.088	0.108	68
HA2	8.22	8.28	8.25	0.142	0.090	0.116	68
HA3	9.89	10.00	9.94	0.070	0.081	0.076	82
HA4	9.00	8.84	8.92	0.082	0.077	0.080	74
NG15	9.67	9.66	9.67	0.109	0.125	0.117	80
NG16	10.16	10.24	10.20	0.090	0.096	0.093	84
NG17	10.00	10.17	10.08	0.084	0.082	0.083	83
NG19	10.71	10.84	10.77	0.055	0.065	0.060	89
UH1	12.11	12.15	12.13	0.098	0.143	0.121	100
UH2	12.24	12.01	12.12	0.128	0.137	0.133	100
UH3	9.70	9.74	9.72	0.105	0.100	0.103	80
UH5	11.52	11.59	11.56	0.086	0.075	0.081	96
UH7	10.74	10.78	10.76	0.123	0.110	0.117	89
WA1	10.56	10.59	10.58	0.090	0.115	0.103	87
WA3	10.42	10.34	10.38	0.065	0.075	0.070	86
WA6	11.14	11.33	11.23	0.090	0.106	0.098	93
W1	11.94	12.01	11.97	0.062	0.063	0.063	99
W20	11.33	11.35	11.34	0.142	0.118	0.130	93
W22	11.82	11.79	11.80	0.081	0.056	0.069	98
W24	12.01	12.02	12.01	0.095	0.066	0.081	99

Table 6.8 – The range and average of total carbon percentages (C-org plus TC) for each of the five seep carbonate study sites in southern Hawke’s Bay.

Site	Range (%)	Site Average (%)
Haunui	68-82	73
Ngawaka	80-89	84
Ugly Hill	80-100	93
Wanstead	86-93	89
Wilder Road	93-99	97

Table 6.9 – Brief descriptions of biomarkers found within some of the southern Hawke’s Bay seep carbonate samples and the geochemical processes that they are suggestive of (Daniel Birgel *pers comm.* 2010).

Compound	
Croctetane/phytane	An archaeal compound only found in association with AOM.
PMI	The most reliable marker indicating AOM.
Squalane	Indicates presence of methanotrophic archaea.
Biphytane	Biphytane might point to the former presence of tetraether-bound biphytane chains and methanotrophic archaea.
Nor-lanostane	Chiefly derived from aerobic methanotrophs.
Bisnor-hopane	Likely to indicate the presence of thiotrophic bacteria (see Peckmann <i>et al.</i> 2004).
Hop17(-21)-ene	Chiefly derived from aerobic methanotrophs.
<i>i</i> -15 fatty acid	Sulphate reducing bacteria marker.
<i>ai</i> -15 fatty acid	
<i>i</i> -17 fatty acid	
<i>ai</i> -17 fatty acid	
Phytanic acid	An archaeal compound indicating methanogenic archaea and/or methanotrophic archaea.
<i>Bishomo</i> -32-hopanoic acid	Probably derived from aerobic methanotrophs.
Acyclic biphytanic diacid	Excellent biomarkers indicating methanotrophic archaea and the anaerobic oxidation of methane (see Birgel & Peckmann, 2008)
Monocyclic biphytanic diacid	
Bicyclic biphytanic diacid	
DAGE C30 (ld, le, lf)	Sulphate reducing bacteria marker.
DAGE C31/C32 (lia & lib)	
Archaeol	Chiefly associated with methanotrophic archaea and the anaerobic oxidation of methane.

Table 6.10 – Lipid biomarkers present within the southern Hawke’s Bay seep carbonate samples analysed to date. tr = trace amounts; n.m. = not measured.

Compound	HA.M.1	W.M.10	NG.E.1	UH.10.1.3	UH.3.A.1	W.8.9.2
Croctetane/phytane	30/70% (-74)	0/100% (-49)	0/100% (-62)	20/80% (-78)	(50/50%) (n.m.)	(40/60%) (n.m.)
PMI	yes (-88)	yes (-49)	yes (-85)	yes (-91)	yes (n.m.)	yes (n.m.)
Squalane	tr (n.m.)	no	yes (-81)	yes (-78)	tr	tr
Biphytane	no	no	yes (-87)	no	no	no
Nor-lanostane	no	no	no	no	yes (n.m.)	no
Bisnor-hopane	no	no	no	yes (-63)	no	yes (n.m.)
Hop17(-21)-ene	no	no	no	no	yes (n.m.)	tr
<i>i</i> -15 fatty acid	yes (-66)	yes (-56)	yes (-59)	yes (-53)	yes (n.m.)	yes (n.m.)
<i>ai</i> -15 fatty acid	yes (-70)	yes (-56)	yes (-62)	yes (-59)	yes (n.m.)	yes (n.m.)
<i>i</i> -17 fatty acid	yes (-65)	tr (n.m.)	yes (-71)	yes (-63)	yes (n.m.)	yes (n.m.)
<i>ai</i> -17 fatty acid	yes (-64)	tr (n.m.)	yes (-66)	yes (-60)	yes (n.m.)	yes (n.m.)
Phytanic acid	yes (-86)	yes (-40)	yes (-58)	yes (-78)	yes (n.m.)	tr
<i>Bishomo</i> -32-hopanoic acid	yes (-52)	no	yes (-56)	yes (-57)	yes (n.m.)	yes (n.m.)
Acyclic biphytanic diacid	yes (-82)	no	tr (n.m.)	yes (-73)	yes (n.m.)	yes (n.m.)
Monocyclic biphytanic diacid	tr (n.m.)	no	tr (n.m.)	yes (-81)	yes (n.m.)	yes (n.m.)
Bicyclic biphytanic diacid	yes (-89)	no	tr (n.m.)	yes (-82)	yes (n.m.)	yes (n.m.)
DAGE C30 (ld, le, lf)	no	no	no	no	yes (n.m.)	no
DAGE C31/C32 (lia & lib)	no	no	no	no	yes (n.m.)	no
Archaeol	no	no	no	no	yes (n.m.)	no

CHAPTER 7

Discussion

7.1 OVERVIEW

This study focused on five sites of Miocene-aged cold seep deposits in southern Hawke's Bay, North Island, New Zealand. These are ancient carbonate deposits which have formed in conjunction with focused fluid escape on the paleo-seafloor of the East Coast Basin. The deposits are analogues of modern cold seep sites within the East Coast Basin today, situated along the convergent Hikurangi Margin (Faure *et al.* 2006; Barnes *et al.* in press; Campbell *et al.* in press; Crutchley *et al.* in press).

Field work was carried out to determine the nature and distribution of the outcrops and sites (Chapter 5). Samples collected from these ancient cold seep carbonate deposits have undergone thorough petrographic analysis (PPL, CL, UV, SEM), as well as X-ray diffraction (XRD), General Area Detector Diffraction (GADD), stable carbon and oxygen isotopic analysis, carbonate percentage analysis, total organic carbon analysis, and lipid analysis (Chapter 6).

This chapter synthesises all field work and lab analyses carried out for the five study sites. It provides interpretations for patterns in the data, insights to the processes likely responsible for carbonate formation, suggestions on the processes which may have resulted in spatial and temporal variations in the deposits, compares characteristics across outcrops and sites, and relates these ancient seep carbonate deposits of the Miocene to the modern deposits forming at seep sites in the East Coast Basin and in other deposits around the world. Finally, a generalised paragenetic sequence has been constructed to give order to the various formational processes and to elucidate between early and late diagenetic events.

7.2 FIELD ASPECTS

7.2.1 Outcrop distribution

The five study sites are dispersed over approximately 12 km, with four of these situated in a north-northeast lineament along the western limb of the Akitio Syncline (see Section 3.3). The migration of fluids in this region during the Miocene was a result of compression and deformation along the convergent Hikurangi Margin (Lewis & Pettinga 1993; Field *et al.* 1997). The fluids ascended through pre-Miocene strata via paths of least resistance, typically along steep and dilated fault planes or through sediments characterised by, or containing lenses of, high permeability (Roberts & Aharon 1994; Lewis & Marshall 1996; Gay *et al.* 2007; Campbell *et al.* 2008; Crutchley *et al.* in press). Such paths of least resistance dictated the lateral position and distribution of the seeps on the paleo-seafloor. However, while there are several large strike-slip and thrust faults in the field region (see Section 3.3.1; Fig. 3.5) no direct evidence of an ascending pathway via faults has been identified in close proximity to each of the ancient seep carbonate outcrop occurrences. Broadly, these seep carbonate sites overlie a relatively thin Miocene section as they occur at or near to the basal unconformity of the Ihungia Formation (D. Francis, *pers. comm.* 2009). The unconformity itself could have acted as a fluid migration pathway, directing fluids towards the East Coast Basin paleo-seafloor.

7.2.2 Outcrop morphology

Morphologically, there are differences across the five study sites. Small (<2 m in size), isolated, irregular shaped mounds are the most common morphology of the southern Hawke's Bay paleo-seep carbonates (Fig. 7.1A). Some (sub)sites, such as Wanstead, Wilder Road, Ugly Hill, and Ngawaka East, are completely composed of these small solitary boulders. In contrast are the larger-scale Ngawaka West and Haunui (sub)sites. Ngawaka West is an intact deposit much larger than those typically seen in southern Hawke's Bay (15 m long by 8 m high), but still stands as a relatively solitary feature. Haunui is a large hill comprising many individual outcrops, likely to be (partially) linked in the subsurface.

The “mound” morphology relates to differential erosion between the relatively weak host formation and the resistant carbonate mounds (Beauchamp & Savard 1992). As the mudstone topography is subjected to weathering and slowly erodes away, the tops of the resistant MDAC outcrops are gradually revealed. Depending on their stratigraphic position and the local topography (and therefore degree of weathering endured to date), there are southern Hawke’s Bay outcrops of which only the uppermost surface is exposed (Fig. 7.1B). Many of these have been steadily unearthed to the point where the mound tops are eroded yet the bases remain concealed (Fig. 7.1A), while complete exhumation can form boulder fields (many of these become float boulders as they are prone to re-positioning). In places it can be difficult to determine whether boulders positioned near the base of a slope are in their original position or have tumbled down from topographically higher locations (e.g. outcrop UH.J at Ugly Hill Valley).

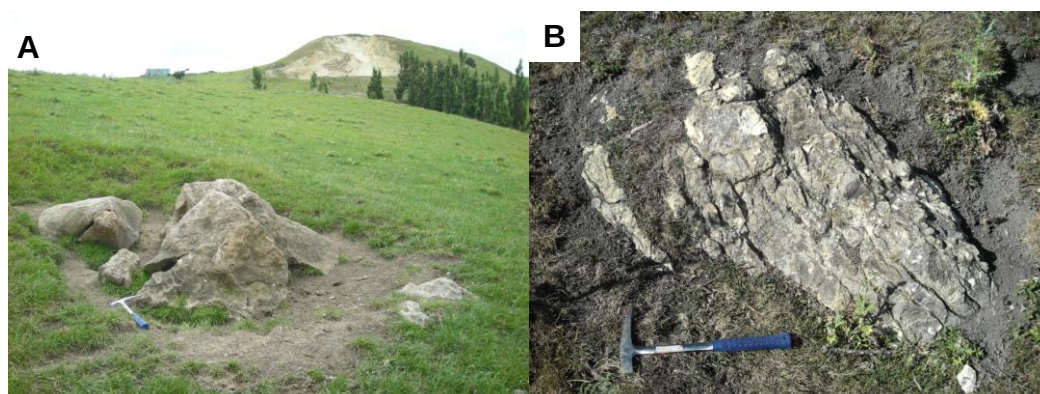


Figure 7.1 – Examples of very localised southern Hawke’s Bay seep carbonate outcrops. **A:** Outcrop UH.H at Ugly Hill comprises multiple small, irregular seep carbonate boulders (as in foreground here) which are isolated from other outcrops, a typical situation for the southern Hawke’s Bay seep carbonate outcrops. These boulders have been partially exhumed due to erosion of the softer mudstone host. **B:** Outcrop WA.F at Wanstead presently only has its upper surface exposed, due to erosion of the mudstone slope in which it sits.

The ratio of float material to *in situ* seep carbonate deposits is largely based upon the structural development of the region since formation of the seep carbonates. In topographically steep areas (due to folding and tilting) the seep carbonate outcrops present are likely to be subject to erosion and have slumped or tumbled down the slope. Often there are remnant boulders upslope, marking the original location of the repositioned material. This occurs at each of the five sites, in

particular Ugly Hill North, the W.H outcrop of Wilder Road, and along the length of the Wanstead site – in particular outcrop WA.A. Talus breccias (carbonate clasts within the host formation that formed about the seep carbonate mounds) were not identified at any of the southern Hawke's Bay ancient seep carbonate sites. This may be due to the general lack of host exposures, as they have been noted at the Rocky Knob seep carbonate site in the northern part of the East Coast Basin (Collins 1999; Campbell *et al.* 2008).

7.2.3 Outcrop lithology

As mentioned earlier (Section 6.2) these seep carbonate deposits can be classified as floatstone, mudstone, and wackestone based on the modified limestone classification scheme of Dunham (1962) and contain the fossils of a variety of species from the associated chemosynthesis-based community which the seep supported. The zonation of fabrics across seep carbonate deposits and sites allows inferences on fluid fluxes to be made (cf. Sahling *et al.* 2002). These features are typically easily identified at outcrop scale.

Thick sequences of alternating bands of pink-grey and light grey fabrics are commonly recognised in the field (Fig. 5.10) and in slabbed hand specimen (Fig. 6.1D). From petrographic and mineralogical analysis, these were confirmed to be layers of early yellow-brown cements (C1), fibrous cements (C2), thrombolites (Th), and minor micarb (M2). Advective fluid flow tends to precipitate such thick, layered fabrics (Conti & Fontana 2002; Campbell *et al.* 2008). Sequences of such fills are likely to form within and very close to the conduits through which the methane-charged fluids are escaping, with brecciation occurring due to explosive release of fluids (Conti & Fontana 2002). The present day locations of these conduits over the field area should give some idea of the density and distribution of concentrated advective fluid flow on the seafloor during the Miocene. As illustrated in Fig. 7.2, several major conduits are identified at Ugly Hill, Haunui, and Wilder Road.

The presence of intraclasts and signs of brecciation within outcrops indicates that the deposits were physically disturbed on the seafloor. Brecciation can occur due to a sudden increase in fluid flux or by plugging of the fluid conduits. Violent

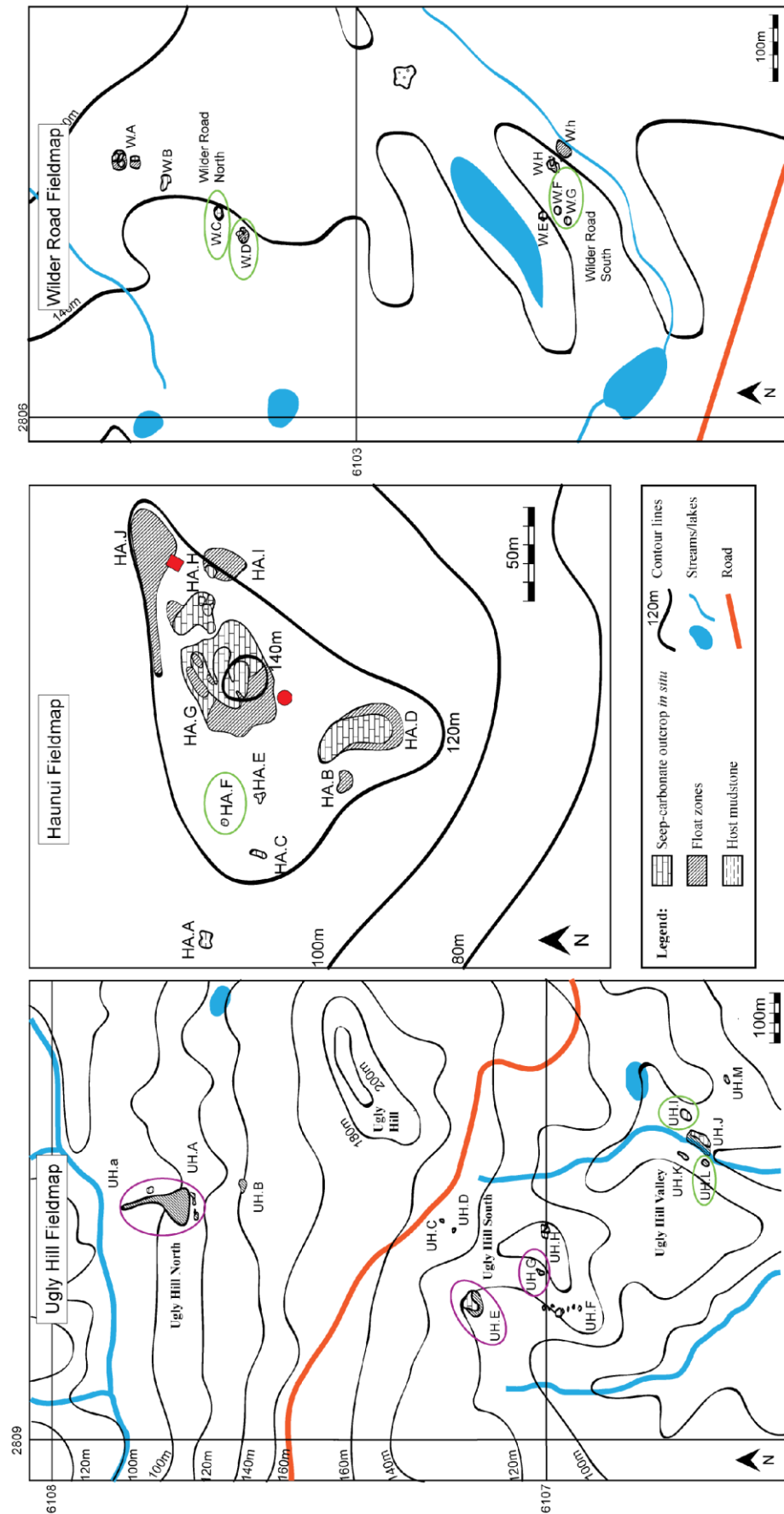


Figure 7.2 - Field maps from sites Ugly Hill, Haunui, and Wilder Road - all study sites which exhibit thick, multiphase sequences of early cements (circled in green) and fossilised colonies of *Bathymodiolus* mussels and Siboglinid worm tubes (circled in purple). The multiphase cements typically form within, or in very close proximity to, paleo-fluid conduits, while the biota mentioned are known to inhabit areas with high concentrations of methane and sulphides. Therefore, the circled outcrops are inferred to be locations of major paleo-fluid conduits constraining a high fluid flux.

expulsion of the fluids results in fracturing of the MDAC: (1) with clasts being incorporated into host sediments to form talus breccias; (2) clasts recemented by micarb back into the main mound as intraclasts; and (3) the smallest clasts winnowed, eroded, rounded, and incorporated back into the main carbonate mound by cementation to form peloids. Intraclasts are found in abundance throughout Haunui and Wanstead, and in some outcrops at Ngawaka and Ugly Hill (see Table 6.1). Brecciation is mainly noted in Wilder Road outcrops where large, angular, micarb clasts are cemented by early cements.

Bedding was identified at a number of outcrops, albeit typically irregular and often quite vague (Fig. 5.25F). It appears to be a form of stylolitic bedding, formed as a result of compression and pressure solution during burial diagenesis (Tucker & Wright 1990). This process results in roughly horizontal bedding planes due to the downward-acting force. The pseudo-stylolitic bedding (stylo-bedding) exhibited in the field dips at angles anywhere between horizontal and vertical. It can be assumed that those boulders and mounds displaying horizontal bedding are likely to be *in situ* as this is the orientation in which such stylo-bedding is formed. Those with stylo-bedding at a high angle are likely to be either repositioned float boulders, or are *in situ* boulders which have been subject to local structural tilting, or possibly formed from tectonic rather than burial forces.

7.2.4 Biota distribution

The presence of particular taxa and biotic relationships throughout a deposit or site is also reflective of the fluid flux and geochemical gradients across the seep environment (Sahling *et al.* 2002; Jenkins *et al.* 2007). Areas where fluid flow is rapid and advective are those in close proximity to the locus of focused fluid escape from the paleo-sea floor. This includes within the fluid conduit itself, and the area immediately surrounding it - which is often well cemented/lithified by MDAC cement due to the high rate of AOM. Thiotrophic (sulphide oxidising) bacteria, such as *Beggiatoa* spp., are commonly present in this zone. Their remains often become fossilised into the MDAC deposits (Campbell *et al.* 2008), and frequently form layers within the multiphase cement sequences. *Bathymodiolus* mussels thrive in this zone of high fluid flux, with the epifaunal

species anchoring to the hardgrounds provided by the abundant MDAC. It is thought that the rate of AOM restricts the dispersal of *Bathymodiolus* mussels - they require high levels of sulphide (a by-product of AOM) which is found in high concentration in the fluids close to the vent due to the high rate of AOM here (Campbell *et al.* in press). The presence of fossilised *Bathymodiolus* mussels around the southern Hawke's Bay ancient seep sites would thus likely mark areas of high fluid flux and sulphide concentration (Fig. 7.2). The absence of *Bathymodiolus* mussels at some sites is likely to be indicative of an extremely diffuse seep system (Barry *et al.* 1997). Siboglinid tube worms typically, but not exclusively, occur in conjunction with mussels (Fig. 6.1C). This is a trend seen in both the fossil record and at modern seep sites (Campbell *et al.* in press) and indicates that the tube worms also prefer zones of high fluid flux (Jenkins *et al.* 2007; Campbell *et al.* 2008).

Diffuse fluid flow occurs at distal areas of the seep environment, when the fluid flux is waning, and at seep systems which are fed off only a slowly ascending fluid supply, perhaps a result of a long and torturous pathway to the sea floor. Lucinid and vesicomyid bivalves are the most prolific colonisers of these areas. Vesicomyid clams are semi-infaunal to epifaunal, and lucinids are infaunal (burrowing) clams which require low pore-water sulphide concentrations (Boetius & Suess 2004). These taxa are common to both modern and ancient seep sites (Fig. 7.3) (Cavagna *et al.* 1999; Campbell *et al.* 2008; Campbell *et al.* in press). Bivalves such as lucinids also are commonly seen in the talus breccias on the flanks of carbonate mounds (e.g. at the Rocky Knob site to the north; Collins 1999, Campbell *et al.* 2008), but no talus breccias were identified in the five sites of this study. Dramatic fluctuations in fluid flux can cause massive die-offs in chemosynthesis based communities, which are marked in the ancient deposits by large accumulations of bivalve shells, both whole (coquinas) and fragmented (shell hash). This is a possible origin of some of the shell beds at Ugly Hill and Haunui (e.g. outcrop UH.A, see Fig. 5.12).

In addition to biotic zones associated with different fluid flux rates are taxa whose presence indicates a degree of lithification of the host sediment by MDAC. Unconsolidated sea floor sediments are often burrowed, with trace fossils dominated by *Thalassinoides* scattered throughout the four fossil-bearing sites in

southern Hawke's Bay. Infaunal taxa (e.g. lucinids) also require softgrounds to burrow within. Well cemented/lithified MDAC deposits can be subject to borings, and they are also a requirement for the colonisation by branching corals such as caryophylliids and by *Bathymodiolus* mussels. Additionally, the formation of micarb on the inner and outer surface of siboglinid worm tubes implies that they were free-standing in the water column (Peckmann *et al.* 2005), likely to be anchored onto the micarb hardground.

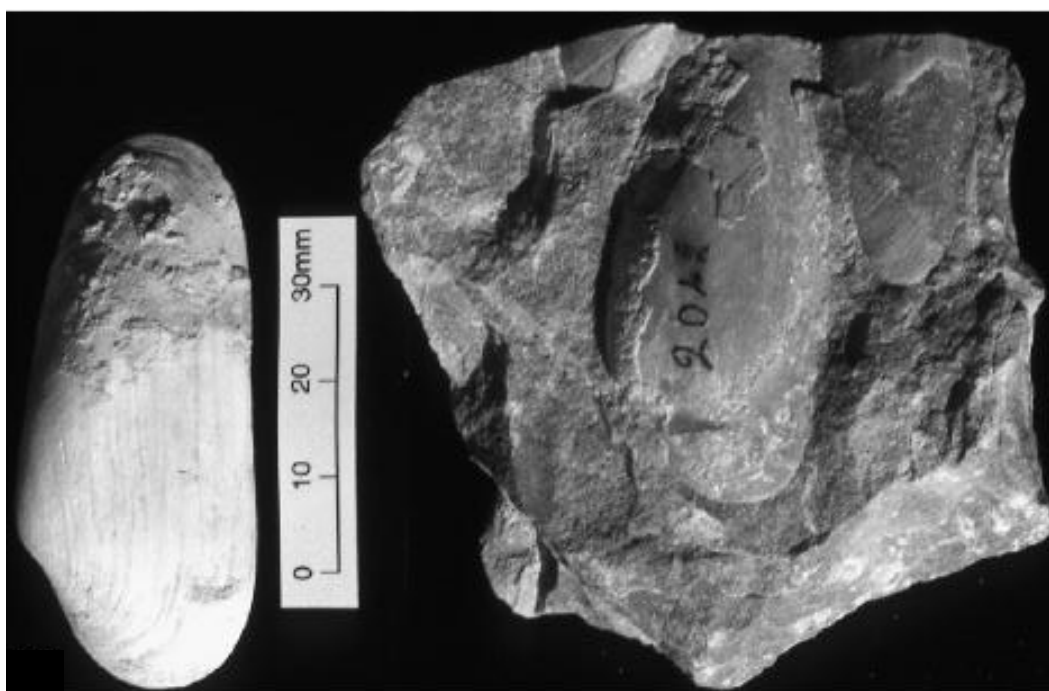


Figure 7.3 – The mould of a vesicomid clam (right) from the Wanstead site appears very similar to clams found at Ritchie Ridge on the modern Hikurangi Margin cold seep sites. From Campbell *et al.* (2008).

On several occasions in field study, fossils (particularly bivalves) were commonly seen standing proud of the micarb on the surface of weathered boulders (Fig. 5.12). This reflects both the shell fabric and their mineralogy; during diagenesis those fossils comprising unstable aragonite and high magnesium calcite (HMC) undergo neomorphism to the more stable low magnesium calcite (LMC). The calcitic fossils or replacement spar tend to better resist weathering, compared to the encasing aragonitic MDAC, resulting in pronounced shell beds and other fossilised biota on the surface of weathered outcrops. This is also the case for

many of the vein systems seen in the field. These veins generally came in two categories: white crystalline veins typically standing proud on boulder surfaces, and pink to grey veins level with the MDAC. It was inferred in the field, and confirmed in the laboratory via petrography and GADDs, that the white veins constitute sparry calcite, its stable form enabling resistance to weathering, while the grey-pink veins are aragonitic in composition.

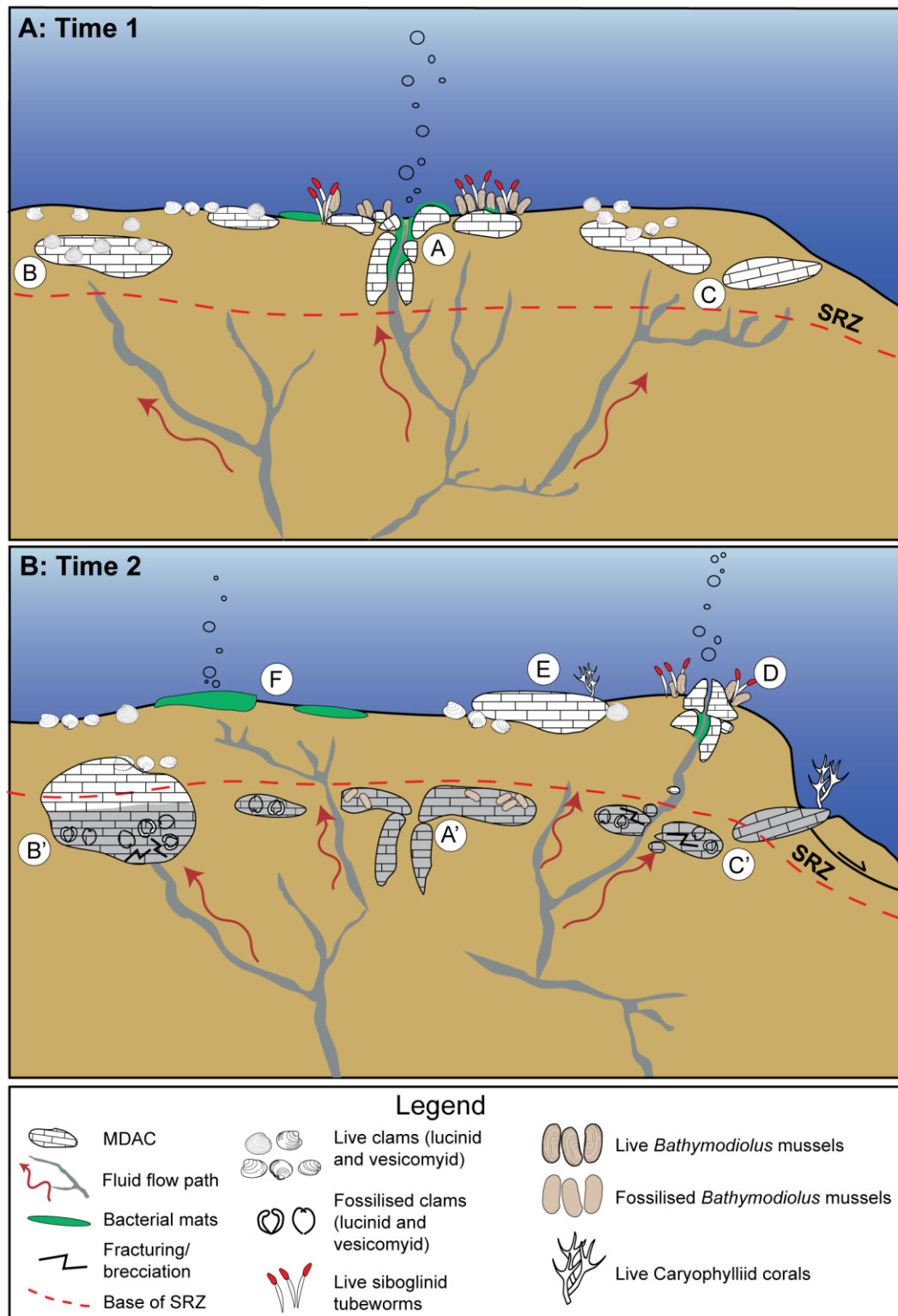
In this study no mega-invertebrate fossils have been found in the host mudstone formations, like in some other ancient cold seep localities elsewhere (e.g. western Washington State, USA, Peckmann *et al.* 2002; Hokkaido, Japan, Jenkins *et al.* 2007). This is analogous to the Mesozoic seep carbonate deposits of California (K. Campbell *pers comm.* 2010). However, recall that outcrops of host mudstone are very rare in the vicinity of the seep carbonates in the southern Hawke's Bay area, which may be the limiting factor in the discovery of mudstone-hosted mega-invertebrate fossils.

7.2.5 Inferred outcrop formation

The abundance of small, isolated seep carbonate deposits reflects the unique formation mechanism of these rocks on the paleo-seafloor. As the precipitation of MDAC is dependent on the presence of chemosynthetic microbes and thus the concentration of methane and sulphide, carbonate deposits form around the locus of the seeping fluids. This can be within the fluid conduit, and within and upon the surrounding sediments. If hydrocarbon-charged fluids are escaping from the subsurface in multiple locations, a small field of seep carbonate deposits will result. In addition, the seep system is extremely dynamic, causing temporal variations within the system and therefore within the deposits themselves.

Figure 7.4 schematically illustrates the development of a small seep carbonate field showing the MDAC morphology and biota in relation to fluid flux, and expressing the effects that a dynamic fluid flux could have on the carbonate bodies over time. As the fluids reach the near-seafloor environment their path diverges because of increasing sediment porosity, allowing easier fluid migration. This results in fluids escaping from the subsurface at many localities and with varying flux, and the saturation of the surrounding sediments in methane and

sulphide. Where fluid is escaping from the seafloor rapidly MDAC is formed within the conduit (typically in multiphase layers of aragonite cements and thrombolites, see Section 7.2.3), at the seafloor, and possibly building small chimneys (Peckmann *et al.* 2001b). Bacterial mats, mussels, and worm tubes



inhabit these areas. With diffusive fluid escape comes the precipitation of nodules, slabs, and boulders comprised of micarb and other early cements. Clams are the major taxa which inhabit the sediments of this zone.

With time and ongoing sedimentation the sulphate reduction zone (SRZ), where AOM occurs, gradually rises above the deposits. If the fluid flux remains steady the upper part of the deposit, which may still be within the SRZ, can be built on with further MDAC precipitation. Changes in fluid flux can cause variations in biota, which can be recognised within individual ancient deposits as vertical variations of fossil species within an outcrop (e.g. Ngawaka East). As the SRZ progressively moves upwards new MDAC deposits are formed.

Many of the seep carbonate (sub)sites of southern Hawke's Bay are ancient analogues of these small seep carbonate fields. This includes Wanstead, Ngawaka, Ugly Hill, and Wilder Road. Outcrop NG.A at Ngawaka West marks the longest lived fluid flow locality, which has resulted in the largest deposit of this study (15 m by 8 m). The clustering of outcrops at each site or sub-site implies that they each are likely to have been fed by a single subsurface fluid source which has only branched out in the shallow subsurface.

The fossil content of each (sub)site is likely to be indicative of the maturity or formation environment of that particular seep system. For example, the lack of macrofossils at Wilder Road outcrops may be suggestive of formation in the

Figure 7.4 – A schematic time-sequence diagram illustrating the likely formation mechanisms for many of the seep carbonate outcrops in southern Hawke's Bay which comprise small, scattered MDAC boulders. **A:** Time 1. Fluid pathways diverge near the seafloor resulting in many seafloor seepage localities. Where more advective flow reaches the sediment-water interface (A) multiphase sequences of early cements and bacterial mats form at the top of the sediment and possibly as small chimneys with positive relief. Bacterial mats, mussels and tubeworms are biota typical of such sites. Areas with more diffuse fluid flow, (B) and (C), typically form micarb-dominated nodules, slabs, and boulders within the sediments. Lucinid and vesicomyid clams thrive within and atop the sediments here. Remnants of biota become locked up within the precipitating cements. **B:** Time 2. With ongoing sedimentation the earlier carbonate deposits ((A), (B), and (C), now shaded grey) become further buried and begin to move below the SRZ. Fluids pathways change, and fluids stop flowing through the vicinity of (A') causing the deposit at that site to cease growth. The fluid flux towards (B') remains constant, allowing ongoing MDAC precipitation at the top of the deposit here, ultimately resulting in a very large mound. Rising fluids and associated pressures cause the fracturing of (C'), while a second boulder is revealed by a submarine slide and acts as a hardground for coral to colonise. The fluids reaching the SRZ and seafloor are now forming a new suite/horizon of MDAC deposits - (D) and (E). Bacterial mats remain to thrive at the sediment-seawater interface where fluid flow is relatively high (F).

subsurface away from seep biota, or a very immature seep system - no biota had yet migrated to the seep site. In contrast, Haunui appears to have been a well developed seep system with zones containing clams, mussels and tubeworms, and corals and borings which are both late colonisers as they require hardgrounds.

The site Haunui exhibits structure based on its formational history. Although interpretation is limited by outcrop exposure in the lower flanks of the hill and quarrying at the summit, a basic history can be recognised. The sparse strike and dip records on bedding from seep carbonate outcrops around the hill, 033/65 SE at HA.D and 035/60 SE at HA.I (see Section 5.5.1), along with the strike and dip of the host strata recorded from nearby stream cuttings (D. Francis *pers comm.* 2009), reveal that the stratigraphy of the hill has a steep dip to the southeast. Taking these measurements into consideration, it appears that the seep carbonate deposit at Haunui formed at two separate stages, likely due to temporal changes in the fluid flux of the once-active seep. The lifespan of the ancient hydrocarbon seep is inferred to have involved two stages of fluid flow, with an intermittent period of very little to no seepage activity. This would then have allowed the formation of two horizons of seep carbonate mounds; the earlier mounds formed during initial activation of the seep, followed by a period of inactivity which allowed a thick layer of muddy sediment to be deposited on top of the seep, before a second phase of seep activity occurred to form the upper horizon of seep carbonate mounds (Fig. 7.5). In the 20 m. y. since formation of the Haunui seep carbonates they have been uplifted and tilted, to give the present day strike and dip angles seen in the field.

7.3 MINERALOGY

7.3.1 Carbonate content

Carbonate percentage data were gained from two sources, the LECO machine at the University of Waikato and analysis at GEOMAR in Germany. The data sets contrast somewhat (Table 7.1), with carbonate percentages of a single sample varying by up to 42%. Here the GEOMAR data are accepted, as it is suspected that the LECO machine gave irregular readings due to malfunction. Use of GEOMAR values is supported by petrography. For example, sample UH.3A.1A

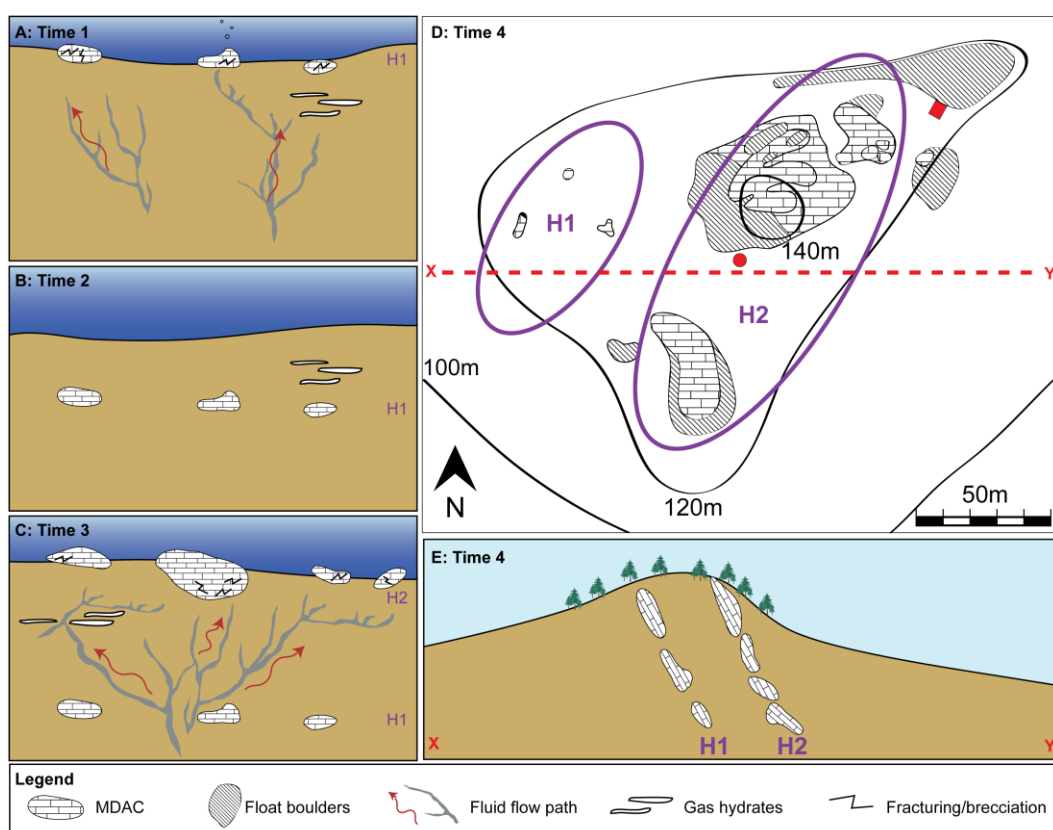


Figure 7.5 – Schematic time-sequence diagram illustrating how formational processes such as temporal variations in fluid flux, uplift, and tilting have affected the seep carbonate deposits at Haunui and allowed them to evolve to their present day structure and setting. **A:** Time 1. Ascending hydrocarbon-rich fluids (mainly via diffuse flow but also at least one conduit) reach the (near) seafloor environment and cause the precipitation of the MDAC deposits of Horizon 1 (H1). These are colonised by lucinid and vesicomyid clams. **B:** Time 2. Fluid migration halts, allowing the MDAC deposits and biota remnants to become buried by the ongoing sedimentation of the host mudstone. **C:** Time 3. Diffuse fluid flux resumes, instigating the formation of more MDAC deposits (Horizon 2, H2) which also hosts lucinid and vesicomyid clams. **D and E:** Time 4. The two horizons of seep carbonate deposits undergo burial, late diagenesis, uplift, and tilting (to approximately 65° SE) to reach the present day setting of the Haunui site. The two separate horizons are circled in purple on the field map (D), and portrayed in cross section (E).

from Ugly Hill (Fig. 6.1D) comprises many layers of pure aragonite fibrous cement (C2) and thrombolites (Th), with very little siliciclastic content due to the extremely sparse occurrence of micarb (M1). The LECO method gave about 66% CaCO_3 for this sample, whereas the GEOMAR analysis gave 100% CaCO_3 , the expected carbonate value.

The carbonate content of all 20 samples analysed at GEOMAR (Table 6.7) confirms their classification as limestones, as all samples contain greater than 50% calcium carbonate, values consistent with their petrographic mineralogies. Samples known to have a high siliciclastic content, such as many of those from

sites Haunui, Ngawaka, and Wanstead, have appropriately low carbonate content values (Fig. 7.6A). In contrast, those with few siliciclastics (e.g. Wilder Road) have high carbonate percentages (Fig. 7.6B).

Table 7.1 – Comparison of carbonate percentage range and site average data given by the two methods of carbonate percentage analysis (by GEOMAR, Germany, and using LECO at the University of Waikato) undertaken for this study.

Site	GEOMAR, Germany		LECO, University of Waikato	
	Range (%)	Site Average (%)	Range (%)	Site Average (%)
<i>Haunui</i>	68-82	73	69-83	75
<i>Ngawaka</i>	80-89	84	76-80	78
<i>Ugly Hill</i>	80-100	93	58-76	66
<i>Wanstead</i>	86-93	89	72-83	79
<i>Wilder Road</i>	93-99	97	76-86	82

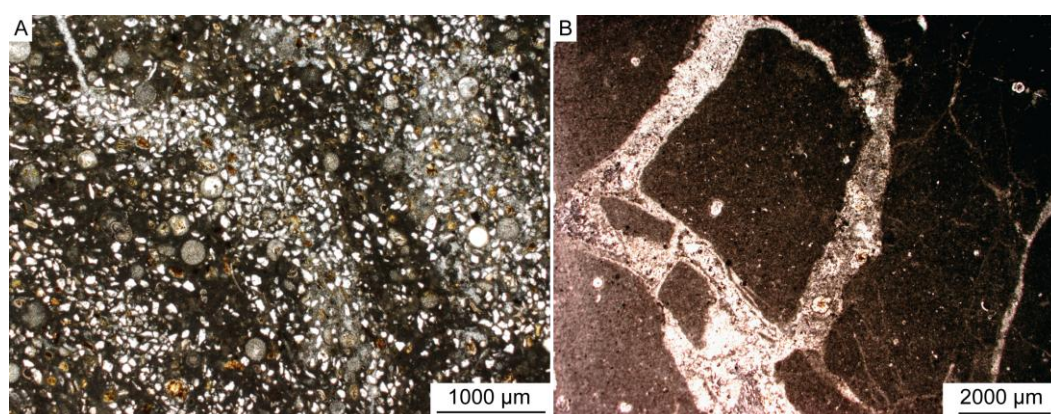


Figure 7.6 – The siliciclastic and foraminiferal content of micarb (M1) vary markedly over the five study sites. **A:** Thin section NG.M4 from Ngawaka contains abundant siliciclastic grains and foraminifera within the micarb (M1). This results in a significantly lowered carbonate content. **B:** In strong contrast to other sites, thin section W.8.1.1B from Wilder Road illustrates the lack of siliciclastic grains and foraminifera typical of samples from Wilder Road, leading to a very high carbonate content (up to 99%).

7.3.2 Carbonate mineralisation

Data gained from XRD analysis of 32 southern Hawke’s Bay seep carbonate samples confirmed the presence of calcite, aragonite, and minor dolomite carbonate phases within the samples, but for the calcite types failed to verify a dominance of either LMC, IMC, or HMC (Table 6.4). The latter was due to the lack of a large and constant “spiked” halite peak against which the “exact”

position of the calcite peak can be established (see Section 6.6), which is essential for determining the magnesium content of calcite. Studies on the modern cold seep deposits of the East Coast Basin by Ewen (2009) and Campbell *et al.* (in press) show the complete dominance of aragonite as the primary MDAC precipitate on the sea floor, with only minor HMC. Based on this, it is deemed unlikely that HMC or IMC were major sea floor precipitates in the Miocene seep carbonates. Further discussion of the XRD calcite mineralogy is based on peak positions in relation to the main quartz peak at $26.7^{\circ}2\theta$.

As earlier mentioned, there are a number of criteria which influence mineral precipitation. Of particular importance are the relative concentrations of sulphate and phosphate, magnesium concentration, and oxygenation of the environment. Aragonite tends to precipitate in high sulphate, low phosphate, and low magnesium conditions, such as occurs in very shallow sediments and at the seafloor (Greinert *et al.* 2001; Peckmann *et al.* 2001b). Lower in the sediments where it is a more restricted environment and magnesium concentrations are higher, precipitation of primary HMC becomes dominant, despite external conditions remaining appropriate for aragonite formation. This change is due to the lack of sulphate, a very important factor in the precipitation of HMC; sulphate reduction in the shallow sediments by SRBs reduces the sulphate concentration to levels low enough to allow HMC to form (Peckmann *et al.* 2001b; Aloisi *et al.* 2002). Dolomite is considered to precipitate in low-sulphate/high-phosphate anoxic environments and requires a high Mg/Ca ratio (Greinert *et al.* 2001). These conditions are often achieved at depth in the sediment, resulting in the concretionary/tubular structures of seep plumbing systems often being primarily composed of dolomite (Greinert *et al.* 2001; Aloisi *et al.* 2002; Nyman 2009).

Peckmann *et al.* (2001) concluded that modern carbonate mounds found in the Black Sea have morphologies tightly related to mineralogy and formational environments. In seafloor environments in which the water column is permanently oxic they found carbonate mounds in the anoxic zone of the underlying sediments which had no positive relief and were made up of HMC. In depths where the sea water at the seafloor was anoxic, they found aragonite dominated carbonates which were forming chimney structures up to 1 m high in the water column with active seepage through the central conduit (Peckmann *et al.* 2001b).

Those few samples of southern Hawke's Bay ancient seep carbonate deposits containing common to abundant aragonite (Table 6.4) are samples which, based on characteristics of the slabs and thin sections, are likely to have come from conduits within the sediments or elevated above the sea floor (chimneys). Evidence for this conclusion includes: (a) samples with polyphase mineral layers containing fibrous aragonite cements, yellow-brown cement, and thrombolites (whose bacterial source thrives in advective environments) (e.g. sample UH.3A.1A from Ugly Hill, Fig. 6.1D); (b) samples exhibiting marble-cake texture (Fig. 7.18) thought to be a result of bioturbation and therefore found at the (very near) seafloor environment; (c) an abundance of small (2 mm), well rounded peloids which can be formed by small micarb clasts being abraded and winnowed in high-flux environments; and (d) a lack of siliciclastic sediment in some samples, which may reflect conduits and chimneys elevated above the sea floor. The conduits/chimneys themselves are non-restrictive, anoxic, high-sulphate/low-magnesium environments due to the high rate of fluid flow and AOM. This is consistent with the results of Peckmann *et al.* (2001) who found chimney structures in anoxic, (near) seafloor seep environments formed from aragonite. In addition, it has been found that the viscosity of the host sediments can affect the mineral precipitates, with low viscosity sediments such as those closest to the sea floor favouring precipitation of aragonite over calcite (Buczynski & Chafetz 1991).

Alongside the precipitation of aragonite, it is also possible that some of the southern Hawke's Bay deposits were originally (partially) formed from HMC. As suggested by Peckmann *et al.* (2001), the precipitation of HMC would likely have taken place in the shallow sediments below the seafloor where the environment is more restricted, magnesium concentrations are higher, and sulphate concentrations lower. Deposits are likely to have formed as irregular lenses and slabs with no positive relief, much like the scattered mounds and boulders so abundant in the ancient southern Hawke's Bay sites. However, if this is the case there is no HMC seen in the current data. This will be due to the HMC content of the samples being lowered due to alteration in the burial realm. Aragonite and HMC are thermodynamically metastable carbonate phases which dominantly precipitate in the (near) seafloor environment, commonly so in modern seep carbonate deposits (Ewen 2009; Campbell *et al.* in press). During burial the

unstable nature of these minerals causes them to recrystallise and/or lose magnesium via calcitisation, changing them to LMC. Such an alteration process is reflected in the GADDs and petrographic data, where the mineralogy of neomorphosed cements shows remnants of an aragonite or possibly HMC precursor (see Section 6.3.9).

The few samples containing common to abundant dolomite could possibly have formed at depth in the sediment (Greinert *et al.* 2001). Seep plumbing systems typically constitute a significant amount of dolomite (cf. Nyman 2009), their mineralogy a function of formation at depth in areas of a high Mg/Ca ratio (Ewen 2009). The seafloor-sediment interface inhibits dolomite formation due to the sulphate content of seawater (Cavagna *et al.* 1999). However, these few samples with dolomite also have abundant aragonite or LMC. This implies initial precipitation in an area intermediate to the preferred zone of aragonite and dolomite precipitation, likely to be sourced from a conduit at shallow burial depth. Alternatively, the dolomite found in the samples could be a replacement mineral, formed in the burial realm where there typically is a plentiful magnesium supply.

7.3.3 Silica mineralisation

The presence of authigenic silica phases was noted within thin sections from all five sites of this study. Little is known about processes which induce silica precipitation within cold seep systems. Sources of silica in the deep marine environment include that from the dissolution of the opaline tests of siliceous marine organisms (e.g. sponge spicules, radiolarians, and diatoms), silica sourced from volcanic deposits, and silica released into pore fluids in the burial realm due to the dehydration of opaline silica and clay minerals (Boggs 2001). The source of silica in the southern Hawke's Bay seep carbonates remains open to interpretation, although a likely origin could be from the volcanic tuff beds which recur in the Miocene sediments (Field *et al.* 1997).

7.3.4 Lipids

The preliminary lipid results for some southern Hawke's Bay ancient seep carbonate samples confirmed the presence of microbes which carry out the anaerobic oxidation of methane (e.g. PMI and biphytanic diacid) and sulphate reduction (e.g. iso-and anteiso fatty acids). It is these microbes which drive carbonate precipitation at the seep site and ultimately give rise to the formation of the MDAC deposits. This data therefore authenticates the cold-seep origin of these deposits, as has been previously assumed.

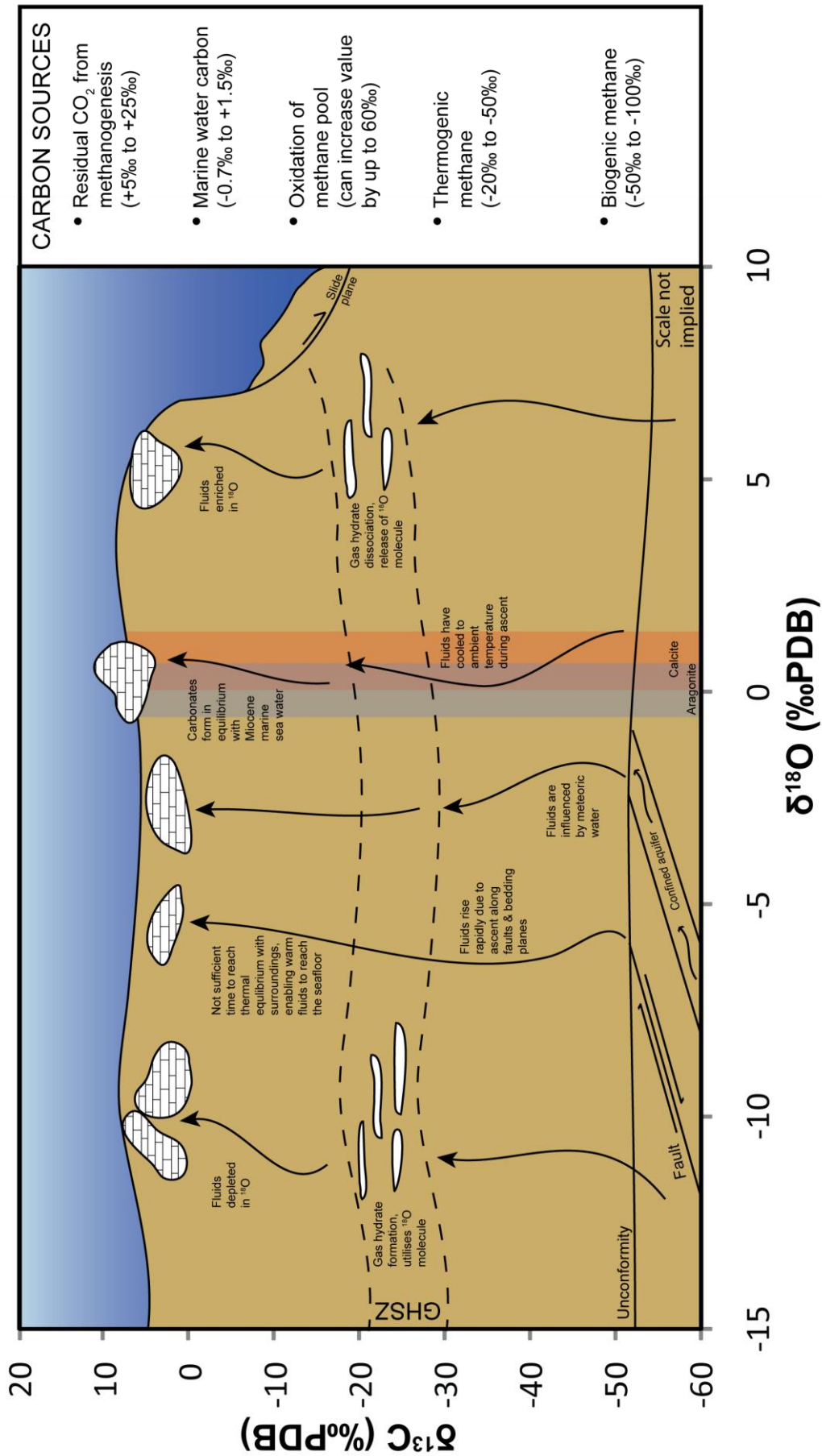
7.4 ISOTOPIC SIGNALS

As earlier mentioned (see Section 2.5.4), MDAC deposits typically have anomalously negative $\delta^{13}\text{C}$ signatures. The stable $\delta^{13}\text{C}$ signatures allow one to assess the origin of carbonate-carbon. Stable oxygen isotopic ($\delta^{18}\text{O}$) values of MDAC give a general indication of the water temperature and origin at the time of formation (Greinert *et al.* 2001; Judd & Hovland 2007). However, diagenesis can substantially affect the $\delta^{18}\text{O}$ values, adding difficulty to the interpretation of isotopic results (Campbell 2006). Figure 7.7 lists the major sources of carbonate-carbon, and depicts how numerous processes can affect the $\delta^{18}\text{O}$ value of the migrating methane-charged fluids and subsequent MDAC deposits..

7.4.1 Influences on carbon signatures

The carbon isotopic signature of seep carbonate deposits reflects their source of carbon as the $\delta^{13}\text{C}$ value of the source is transferred into carbonates precipitating at the seep site. Carbon sources include methane produced diagenetically (thermogenic methane) and microbially (microbial methane), residual carbon from microbial methanogenesis (CO_2 by-product of methane production), sea water, and organic carbon and shell material deposited on the sea floor (Roberts & Aharon 1994; Judd & Hovland 2007). Some of these carbon sources and their $\delta^{13}\text{C}$ values are listed below. It is rare for $\delta^{13}\text{C}$ values to be altered during burial diagenesis (Aharon 2000)

- *Biogenic methane*: The microbial degradation of organic matter results in biogenic methane, which carries $\delta^{13}\text{C}$ values from -90‰ to -50‰ (Roberts & Aharon 1994; Whiticar 1999; Campbell 2006).
- *Thermogenic methane*: Formed due to the thermal maturation of organic matter, thermogenic methane passes on $\delta^{13}\text{C}$ values from -50‰ to -20‰ (Whiticar 1999; Judd & Hovland 2007; Nyman 2009).
- *Oxidation of methane pools*: Adding complication to the interpretation of the origin of carbon in MDAC deposits is the occurrence of oxidation in residual methane pools. This reaction favours the uptake of isotopically lighter carbon, to leave a residual methane pool which becomes increasingly enriched with heavy ^{13}C (Whiticar 1999; Nyman 2009). According to Whiticar (1999), the oxidation of 80% and 99% of a methane pool will enrich the residual pool by 10-30‰ and 20-60‰, respectively. This process, therefore, could significantly complicate to the identification of carbon sources in MDAC deposits. For example, extensive oxidation of a biogenic methane pool can change its $\delta^{13}\text{C}$ value from -90‰ to -30‰, giving it a final value otherwise indicative of thermogenically produced methane (Nyman 2009).
- *Sea water and organic carbon*: Some of the heavier $\delta^{13}\text{C}$ values may also be attributed to mixing with marine water dissolved organic carbonate (+2 to -2‰) and/or shell carbonate signatures (near that of sea water if shell secretion has occurred in equilibrium conditions) (Rio *et al.* 1992).
- *Residual CO_2* : Carbonate samples featuring enriched $\delta^{13}\text{C}$ signatures, $\geq +5\text{‰}$, may reflect carbon sourced from reduced CO_2 . This CO_2 is a by-product of methanogenesis (methane production) - the anaerobic remineralisation of organic matter by fermentative archaeobacteria known as methanogens, which may occur in the sediments beneath the zone of AOM (Whiticar 1999; Campbell 2006). This CO_2 typically has a relatively heavy $\delta^{13}\text{C}$ value of +5 to +24‰ due to kinetic isotopic fractionation. This methanogenesis preferentially utilises carbon molecules with a lighter isotopic mass (^{12}C), which leaves abundant ^{13}C in the



residual substrate (Whiticar 1999; Aloisi *et al.* 2000; Peckmann *et al.* 2002). During the ensuing CO₂ formation (part of the fermentation reaction) this ¹³C is utilised. The eventual product is MDAC with carbon sourced from this ¹³C-enriched CO₂ resulting in carbon isotopic values in the vicinity of +5 to +24‰.

Methane sources of a cold seep can become physically mixed due to vertical and/or lateral migration of the fluids. The convergence of methane derived via a variety of methanogenic pathways (e.g. marine carbonates, microbial and thermogenic methane), occurring either concurrently or successively within a region, will impact the resultant MDAC carbon isotope values (Whiticar 1999). This mixing, coupled with the overlapping of the $\delta^{13}\text{C}$ compositions of the many carbon sources, means that no exact source for any $\delta^{13}\text{C}$ value can be pinpointed - we can only speculate on the likelihood of a particular process or methane type contributing to the $\delta^{13}\text{C}$ values of deposits.

7.4.2 Influences on oxygen signatures

The $\delta^{18}\text{O}$ value of MDAC deposits is affected by water temperatures during formation, the isotopic composition of the source water, gas hydrate formation and dissociation, and fractionation of the carbonate phases (Aloisi *et al.* 2000; Greinert *et al.* 2001; Dahlmann & de Lange 2003). Using estimates of normal marine water composition and bottom water temperatures in the Miocene, a

Figure 7.7 – A schematic model illustrating the various causes of $\delta^{18}\text{O}$ enrichment and depletion in the Miocene, and sources of carbonate carbon with their associated $\delta^{13}\text{C}$ ranges. No scale implied. Gas hydrates form in the Gas Hydrate Stability Zone (GHSZ) where pressures and temperatures are ideal, with their formation and dissociation having effect on $\delta^{18}\text{O}$ values of local MDAC. Rapid migration of fluids (along weaknesses such as faults and bedding planes) will allow fluids to ascend without time to cool to equilibrium with surrounding strata, resulting in warm fluids at the sea floor and, consequently, $\delta^{18}\text{O}$ depletion in MDACs. Mixing with meteoric water will bring $\delta^{18}\text{O}$ values closer to 0‰. Finally, fluid which reach the (near) seafloor environment without interference and in thermal equilibrium with the surroundings will produce aragonite with $\delta^{18}\text{O}$ values from -0.5‰ to +0.7‰ (blue shaded rectangle) and calcites with $\delta^{18}\text{O}$ values from 0‰ to +1.5‰ (red shaded rectangle) (Roberts & Aharon 1994; Ussler & Paull 1995; Whiticar 1999; Campbell *et al.* 2002; Pierre & Rouchy 2004; Campbell 2006).

prediction can be made as to whether these carbonates formed in equilibrium with sea water or were affected by one of the above mentioned processes. Feary *et al.* (1991) estimated New Zealand Miocene marine water to have had an average $\delta^{18}\text{O}$ value of -0.7‰ SMOW. Ridgway (1969) recorded a series of modern upper slope bottom water temperatures ranging from 5–10°C, which are inferred to be similar to those during the Miocene.

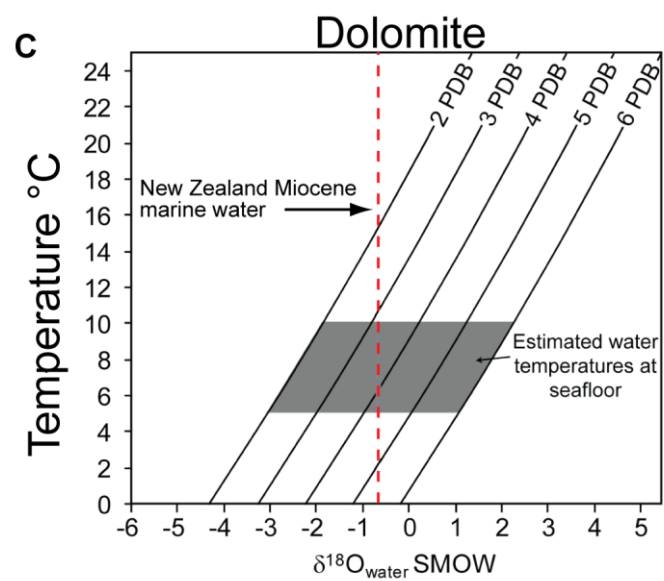
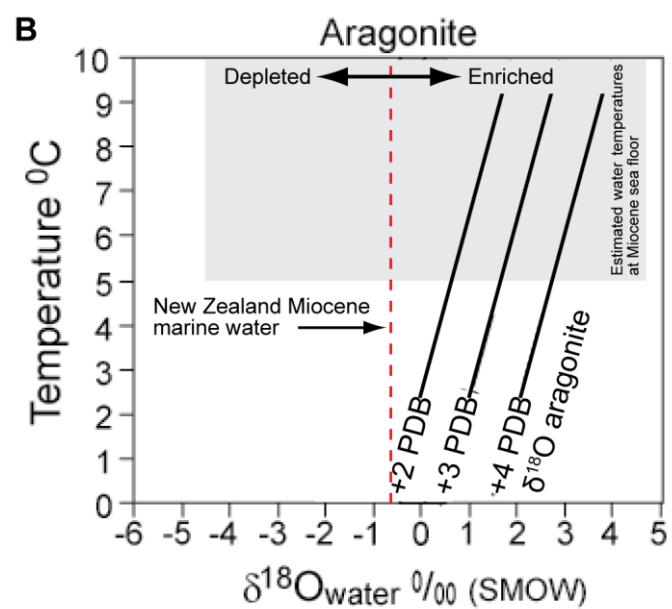
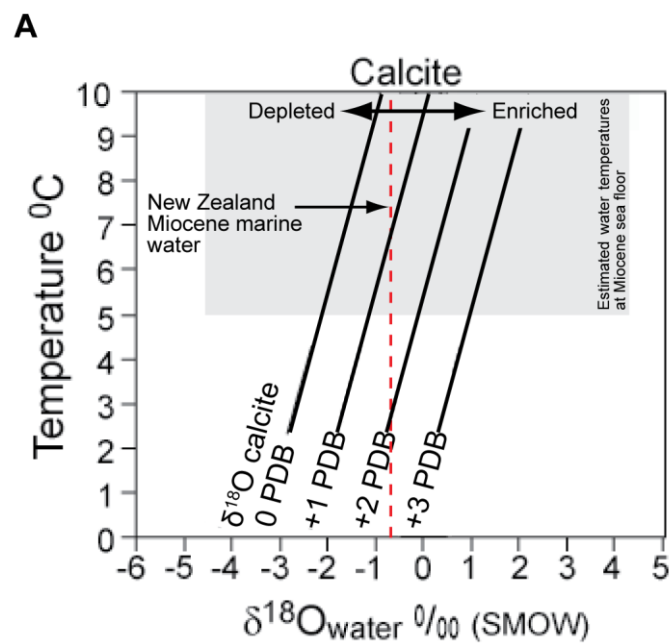
Fluid compositions at the time of calcite, aragonite, and dolomite precipitation can be determined based on the methods of Friedman & O'Neil (1977), Grossman & Ku (1986), and Fritz & Smith (1970). Calcite, aragonite, and dolomite precipitated in equilibrium with the above Miocene isotopic and temperature constraints would exhibit $\delta^{18}\text{O}$ values of 0 to +1.5‰ PDB (Fig. 7.8A), -0.5 to +0.7‰ PDB (Fig. 7.8B), and +3.2 to +4.2‰ (Fig. 7.8C), respectively. Authigenic calcite, aragonite, and dolomite with $\delta^{18}\text{O}$ values less than these equilibrium ranges are depleted with respect to Miocene marine water, and those deposits with $\delta^{18}\text{O}$ values greater than these ranges are enriched in ^{18}O .

With respect to the above estimates of the equilibrium precipitation conditions of the Miocene carbonates, samples which have relatively more depleted and enriched $\delta^{18}\text{O}$ values can be identified. Depletion and enrichment values for $\delta^{18}\text{O}$ can be a function of fluid temperatures, be affected by gas hydrate formation and dissociation, and be influenced by marine water, recrystallisation and dehydration of minerals, and evaporites, as described in more detail below. All of these factors should be taken into consideration when attempting to interpret the $\delta^{18}\text{O}$ enrichment or depletion mechanism for an MDAC deposit.

- *Fluid temperatures:* During MDAC formation, high fluid temperatures will result in more depleted $\delta^{18}\text{O}$ values (Mozley & Burns 1993). The local geothermal gradient for the East Coast region of the North Island, 23°C/km (Field *et al.* 1997), is an important characteristic to take into account - a high fluid temperature during MDAC precipitation can be achieved by formation occurring in the subsurface. However, this method of $\delta^{18}\text{O}$ depletion is unlikely for the southern Hawke's Bay seep carbonates as the fossil assemblages and earlier stage mineralogy indicate formation in the (near) seafloor environment. If fluid expulsion rates at the

seep are high, this can allow for burial fluids of a high temperature to reach the (near) seafloor environment. In this case the high fluid flux does not allow enough time for the heated fluid to come into equilibrium with its surroundings before the carbon is utilised in MDAC formation (De Boever *et al.* 2006a). Low fluid temperatures during MDAC formation will result in relatively enriched $\delta^{18}\text{O}$ values in associated MDACs (Mozley & Burns 1993).

- *Gas hydrates:* The local formation and destabilisation of gas hydrates has a pronounced effect on the $\delta^{18}\text{O}$ signature of any contemporaneously precipitating MDACs. As gas hydrates form, the incorporation of the heavier oxygen isotope (^{18}O) into the clathrate structure is preferred (Ussler & Paull 1995; Aloisi *et al.* 2000; Pierre & Rouchy 2004). The interstitial pore water therefore becomes increasingly depleted in ^{18}O by a few per mil relative to the original value (Ussler & Paull 1995). MDAC precipitating in the vicinity of active gas hydrate formation adopts this depleted $\delta^{18}\text{O}$ value of the pore water. It is therefore logical that upon gas hydrate destabilisation the water molecules lead to enriched $\delta^{18}\text{O}$ values (Aloisi *et al.* 2000; Pierre & Rouchy 2004). MDAC which has precipitated in association with these waters inherits these enriched $\delta^{18}\text{O}$ signals. This method for influencing $\delta^{18}\text{O}$ enrichment and depletion values in ancient seep carbonates formed in the East Coast Basin is particularly credible due to the presence of vast amounts of gas hydrates in the modern basin (Gorman *et al.* 2004). It is likely that these hydrates were also present in the Early Miocene, and consequently that they had an effect on the formational fluids and thus $\delta^{18}\text{O}$ values of the southern Hawke's Bay seep carbonate bodies.
- *Meteoric water:* The influence of meteoric water is a well documented explanation for $\delta^{18}\text{O}$ depletion (Mozley & Burns 1993). This can be a common occurrence in the offshore environment, as meteoric water-rich formations can be exposed at the sea floor and are common in the subsurface. This is regarded to be a minor factor in the depletion of the southern Hawke's Bay seep carbonate $\delta^{18}\text{O}$ values.



- *Recrystallisation:* The recrystallisation of minerals has been suggested to account for some cases of oxygen depletion (Mozley & Burns 1993). Recrystallisation of unstable minerals allows the isotopes to re-equilibrate with the ambient conditions (Allan & Matthews 1977). Re-mineralisation of a MDAC deposit at depth would result in new minerals forming with more depleted $\delta^{18}\text{O}$ values associated with higher temperatures. The $\delta^{13}\text{C}$ signature is more resistant to modification in the burial realm and is typically not affected by this recrystallisation.
- *Dehydration of clay minerals:* This can cause $\delta^{18}\text{O}$ enrichment in interstitial waters. Clay mineral transformation, due to high temperatures and pressures in the subsurface, commonly involves the alteration of smectite to illite (or in the case of silica minerals, opal dehydration). The water lost from these molecules is characteristically enriched in ^{18}O , refreshing the pore waters and increasing its overall $\delta^{18}\text{O}$ value (Dahmann & de Lange 2003). Given the preponderance of smectite in the host sediments (Campbell Nelson *pers. comm.* 2009) it is unlikely that the diagenetic transformation of clay minerals has influenced the seafloor to shallow burial cold seep carbonate deposits in the southern Hawke's Bay situation, therefore making this method of $\delta^{18}\text{O}$ enrichment also unlikely.
- *Evaporites:* It is exceedingly unlikely that evaporative conditions prevailed in this open marine, deep sea floor to subsurface environment, so that $\delta^{18}\text{O}$ enrichment must result from other factors.

Due to the many processes that may affect the $\delta^{18}\text{O}$ signature of MDAC deposits, there is some uncertainty in the confirmation of any of these processes influencing the values occurring in the southern Hawke's Bay seep carbonates. Some processes may overprint or mask the effects of others, making interpretation

Figure 7.8 – Possible water compositions responsible for the precipitation of calcite, aragonite, and dolomite. Red line encompasses the range of possible $\delta^{18}\text{O}$ PDB values of carbonate minerals formed in equilibrium with estimated Miocene marine water isotopic and temperature constraints. Adapted from Campbell *et al.* (in press), originally adapted from **(A)** Friedman & O'Neil (1977), **(B)** Grossman & Ku (1986), and **(C)** Fritz & Smith (1970).

difficult without further analysis. However, based on the slope (bathyal) environmental conditions and other contemporaneous hydrocarbon-related events during the Early Miocene it is probable that the $\delta^{18}\text{O}$ signatures of the southern Hawke's Bay seep carbonates were most likely affected by varying combinations of high fluid temperatures, gas hydrate formation and dissociation, and the re-mineralisation of minerals during burial diagenesis.

7.4.3 Wanstead stable $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values

Wanstead samples all have relatively negative stable carbon isotope values of -15 to -30‰ (Fig. 7.9). This could suggest that thermogenic methane was the major source of carbon during precipitation of the Wanstead deposits (Fig. 7.7). There may be a small influence from marine water and/or oxidation of the methane pool to bring a few of the samples above $\delta^{13}\text{C}$ -20‰.

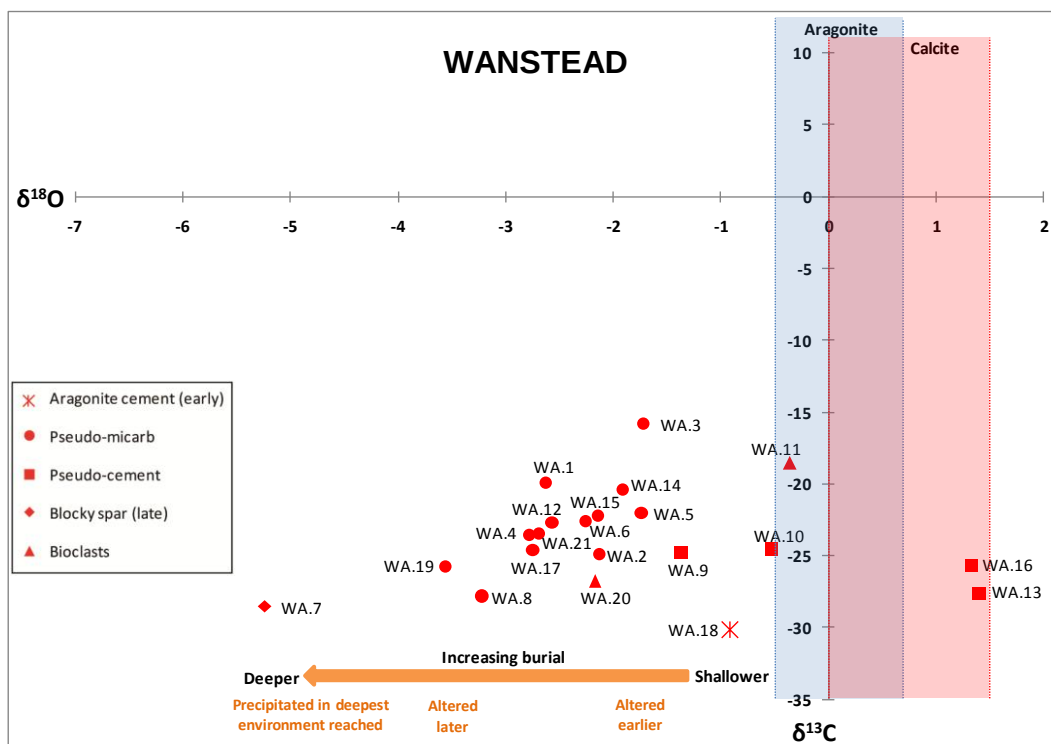


Figure 7.9 – Stable $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ cross plot showing the values of the 21 bulk and component-specific powders from Wanstead samples. Blue shaded area covers the $\delta^{18}\text{O}$ values of aragonite precipitated in equilibrium with sea water, based on methods by Grossman & Ku (1986). Red shaded area covers the $\delta^{18}\text{O}$ values of calcite precipitated in equilibrium with sea water based on methods by Friedman & O'Neil (1977). Orange arrow illustrates the trend of increasing burial and therefore temperatures relating to increasingly negative $\delta^{18}\text{O}$ values.

There is a large range of stable oxygen isotopic values for Wanstead samples (Fig. 7.9). Based on the aragonite equilibrium plot of Grossman & Ku (1986) the single aragonite sample (WA.18), which precipitated during the early diagenetic stage in the (near) seafloor environment, precipitated just outside of equilibrium with sea water. This could be due to a slight increase in the fluid temperature - temperatures are required to reach only 12°C to produce MDAC deposits with a $\delta^{18}\text{O}$ value of -0.9‰ (Fig. 7.8B). Alternatively, this slightly negative stable oxygen isotope value could be a result of mixing with meteoric water or due to access to upwardly advected (warm) burial fluids.

The pseudo-micarb and pseudo-cement samples, all of which likely originally precipitated as aragonite in the (near) seafloor environment and have since been neomorphosed to calcite, show a spread in $\delta^{18}\text{O}$ values. It is probable that these fabrics have inherited the stable oxygen values of the environment in which recrystallisation took place – a burial environment in which formation temperatures would be somewhat higher than those at the seafloor.

The blocky spar (Sp1) which precipitated in the later diagenetic stage (sample WA.7) has the most negative $\delta^{18}\text{O}$ value of the site (-5.24‰). This likely reflects the paragenetic sequence of events responsible for forming the deposits; early on in the late diagenetic stage the aragonitic micarbs and cements were neomorphosed to stable calcite, followed by further burial (bringing higher temperatures dictated by the geothermal gradient) and precipitation of blocky spar. These latest blocky spars carry the negative $\delta^{18}\text{O}$ value of the higher temperature pore fluids of this deeper burial environment. Based on the methods of Friedman & O'Neil (1977) and a geothermal gradient of 23°C/km (Field *et al.* 1997), and assuming the $\delta^{18}\text{O}$ value in the burial environment is similar to that of the sea floor environment, precipitation of these blocky calcite spars could be achieved at burial depths of about 1100 m.

7.4.4 Ugly Hill stable $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values

The $\delta^{13}\text{C}$ values of the Ugly Hill samples cover a large spread, from -5 to -27‰ (Fig. 7.10). Many of these are considerably negative, <-20‰, and have likely sourced their carbon from thermogenic methane. As with some of the Wanstead

samples, it is possible that there has been a small influence from marine water and/or oxidation of the methane pool to bring some of the samples above $\delta^{13}\text{C} - 20\text{‰}$.

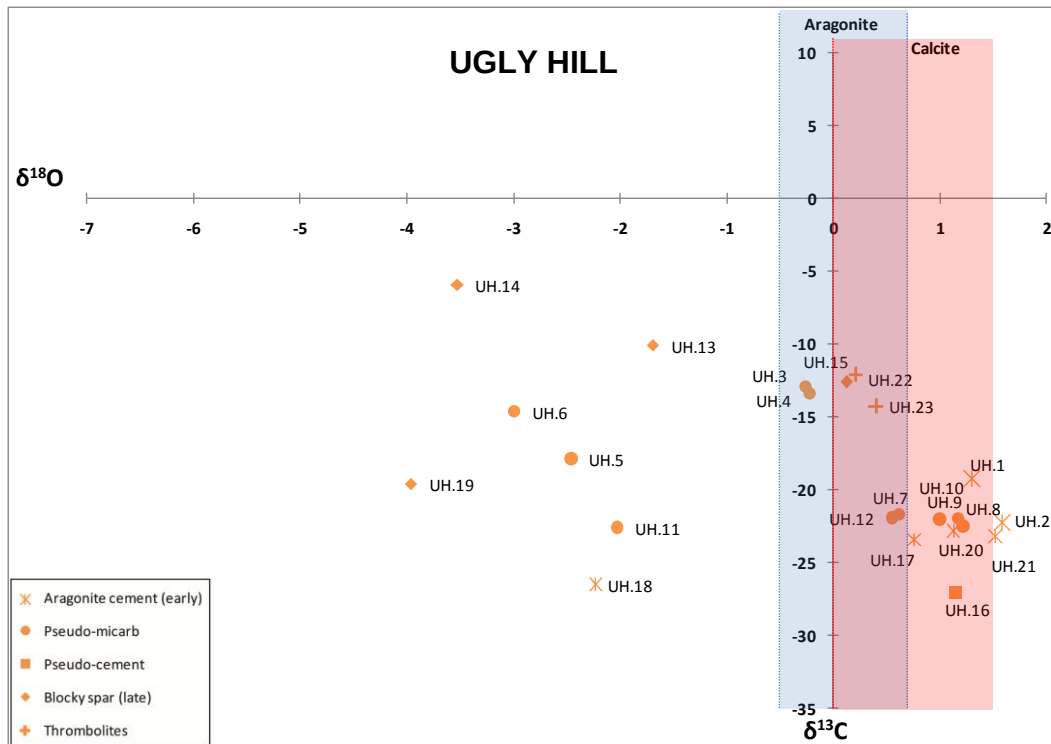


Figure 7.10 – Stable $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ cross plot showing the values of the 23 bulk and component-specific powders from Ugly Hill samples. Shaded areas defined in Figure 7.9.

Most of the aragonite precipitated in the seafloor environment early in the history of the Ugly Hill seep carbonate deposits has not formed in equilibrium with marine water conditions, but has enriched $\delta^{18}\text{O}$ values (Fig. 7.10). This may be a result of periodically lower water temperatures – based on methods by Grossman & Ku (1986), the water temperature would have to decrease to 1°C in order to precipitate aragonite cement with a $\delta^{18}\text{O}$ value as high as 1.6‰ . As such a seawater temperature is unlikely. Alternatively, these enriched aragonite fabrics could have formed contemporaneously with a local gas hydrate dissociation event which causes pore water to become enriched with ^{18}O , or have formed from fluids enriched in $\delta^{18}\text{O}$ due to the dehydration of clay minerals in the subsurface (Dahlmann & de Lange 2003). The one aragonite outlier (UH.18) with a depleted

$\delta^{18}\text{O}$ value with respect to marine water equilibrium is possibly due to periodic or local flow of high temperature fluids.

Two thrombolites were sampled from Ugly Hill. These microbial layers likely precipitated as microcrystalline aragonite (see Section 6.3.4), and as shown by the plot (Fig. 7.10) this appears to have occurred in equilibrium with Miocene marine water (Friedman & O'Neil 1977).

Many of the neomorphosed fabrics show relatively negative $\delta^{18}\text{O}$ values, and increasingly so with paragenesis (Fig. 7.10). As recrystallisation of the fabrics allows the minerals to adopt the $\delta^{18}\text{O}$ value of their new burial environment, it can be assumed that those with higher $\delta^{18}\text{O}$ values (e.g. UH.9, UH.10, UH.12, and UH.16) underwent neomorphism early on in the late diagenetic phase, before too much burial and when temperatures had only increased a small amount compared to those at the seabed. Those with increasingly more negative $\delta^{18}\text{O}$ values underwent neomorphism during deeper burial and hence with higher temperatures, which gave rise to their more negative values.

$\delta^{18}\text{O}$ values of blocky calcite spars precipitated in the burial realm are depleted, reaching values of -3.96‰ (Fig. 7.10). Based on the methods of Friedman & O'Neil (1977), a geothermal gradient of $23^{\circ}\text{C}/\text{km}$ (Field *et al.* 1997), and assuming the $\delta^{18}\text{O}$ value in the burial environment is similar to that of the seafloor environment, precipitation of these blocky calcite spars could be achieved at burial depths of 800-900 m. It can also be noted that the fabrics which precipitated in this deep burial environment formed after most of the neomorphism had taken place, giving them more negative $\delta^{18}\text{O}$ values compared to the altered fabrics (Fig. 7.10).

In addition to the calcite and aragonite fabrics abundant in these samples, XRD revealed that UH.7 and UH.8 both contain a significant amount of dolomite (see Table 6.4). Dolomite that precipitated in equilibrium with Miocene marine water would have $\delta^{18}\text{O}$ values of $+3.2$ to $+4.2\text{‰}$ (Fig. 7.8C) (Fritz & Smith 1970). The samples have slightly depleted $\delta^{18}\text{O}$ values compared to this equilibrium range of values. This may be due to a number of factors such as mixed isotopic signals from the calcitic component of each sample, higher fluid temperatures, or remineralisation in the burial realm.

7.4.5 Ngawaka stable $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values

The $\delta^{13}\text{C}$ values of Ngawaka samples are clustered relatively high on the isotope plot (Fig. 7.11). All are positioned between $\delta^{13}\text{C}$ -20‰ and 0‰. As the carbon isotopic value typically is not altered during burial diagenesis (Campbell *et al.* 2002) this must be a function of fluid conditions in the seafloor environment. As all values have been enriched in the heavier ^{13}C isotope it is likely that a large-scale process, such as oxidation of the methane pool, has affected the major thermogenic methane carbon source. It is also possible that interaction with marine water and organic carbon has helped to increase the $\delta^{13}\text{C}$ values of these samples compared to those at most other sites.

The $\delta^{18}\text{O}$ values of Ngawaka samples are also anomalously negative (Fig. 7.11). Primary fabrics (aragonite cements) lie between -2.5 and -3‰, indicating that something has affected the cements from the seafloor environment to decrease the $\delta^{18}\text{O}$ values from those in equilibrium with marine water. Based on calculations by Grossman & Ku (1986), and assuming a geothermal gradient of 23°C/km (Field *et al.* 1997), burial to depths of only 650 m are required to produce aragonites with such $\delta^{18}\text{O}$ values. However, it is unlikely that aragonite would precipitate in such an environment due to the lack of sulphate (see Section 2.5.3). Therefore, it is more probable that heated fluids (19-23°C) have reached the sea floor to influence the precipitation of these primary fabrics. Alternatively, the $\delta^{18}\text{O}$ values of these aragonite fabrics could be a result of gas hydrate formation or mixing with meteoric water.

Neomorphosed cements (pseudo-micarb and pseudo-cement) have $\delta^{18}\text{O}$ values between -1.7 and -6.5‰ (circled in orange in Fig. 7.11). These fabrics have remineralised in the burial realm, and are likely to have picked up their current $\delta^{18}\text{O}$ values during that process. The spread of values becomes increasingly more negative, which may be a reflection of the ever-increasing temperature associated with continual burial. Of note is the earlier neomorphism of many of the pseudo-micarb samples compared to the pseudo-cements. As earlier mentioned (see Section 6.3.9), neomorphism appears to have preferentially affected fine grained and loosely packed fabrics (e.g. micarb) over coarser, tightly packed ones (e.g. early spar cements).

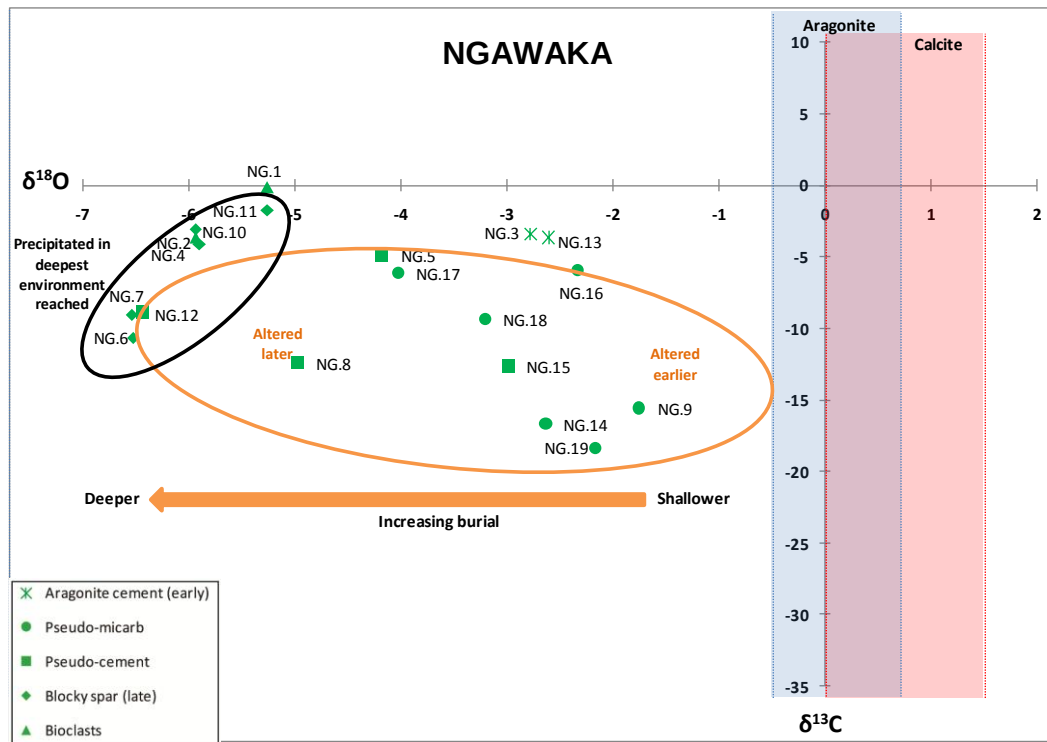


Figure 7.11 – Stable $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ cross plot showing the values of the 19 bulk and component-specific powders from Ngawaka samples. Shaded areas defined in Figure 7.9. Orange circle encompasses most of the neomorphosed fabrics (pseudo-micarb and pseudo-cement). These fabrics have remineralised from aragonite to calcite as burial was occurring. The negative $\delta^{18}\text{O}$ values reflect the ever-increasing depth of burial and temperature. Black circle encompasses the blocky spars precipitated last in the deep burial environment.

All of the blocky spar fabrics (Sp1-3), which precipitated in the late burial stage, also reflect the high temperatures of the burial environment in their very negative $\delta^{18}\text{O}$ values (circled in black in Fig. 7.11). These data also suggest that most of the neomorphic events occurred earlier on in the burial stage (giving mildly depleted $\delta^{18}\text{O}$ values), which slightly overlapped with the precipitation of blocky calcite spar (which has very negative $\delta^{18}\text{O}$ values). Based on the methods of Friedman & O'Neil (1977) and a geothermal gradient of $23^\circ\text{C}/\text{km}$ (Field *et al.* 1997), and assuming the $\delta^{18}\text{O}$ value in the burial environment is similar to that of the sea floor environment, precipitation of these blocky calcite spars could be achieved at burial depths of 1480 m. These blocky calcite fabrics also have a slightly higher range of $\delta^{13}\text{C}$ values than some of the other samples, perhaps indicating further oxidation of the methane pool by this stage of the deposit's history.

7.4.6 Haunui stable $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values

All of the Haunui samples have low $\delta^{13}\text{C}$ values, which lie in the range of -19 to -29‰ (Fig. 7.12). These samples have carbon sourced mainly from thermogenic methane, possibly with a small influence from marine water and organic carbon, or oxidation of the methane pool.

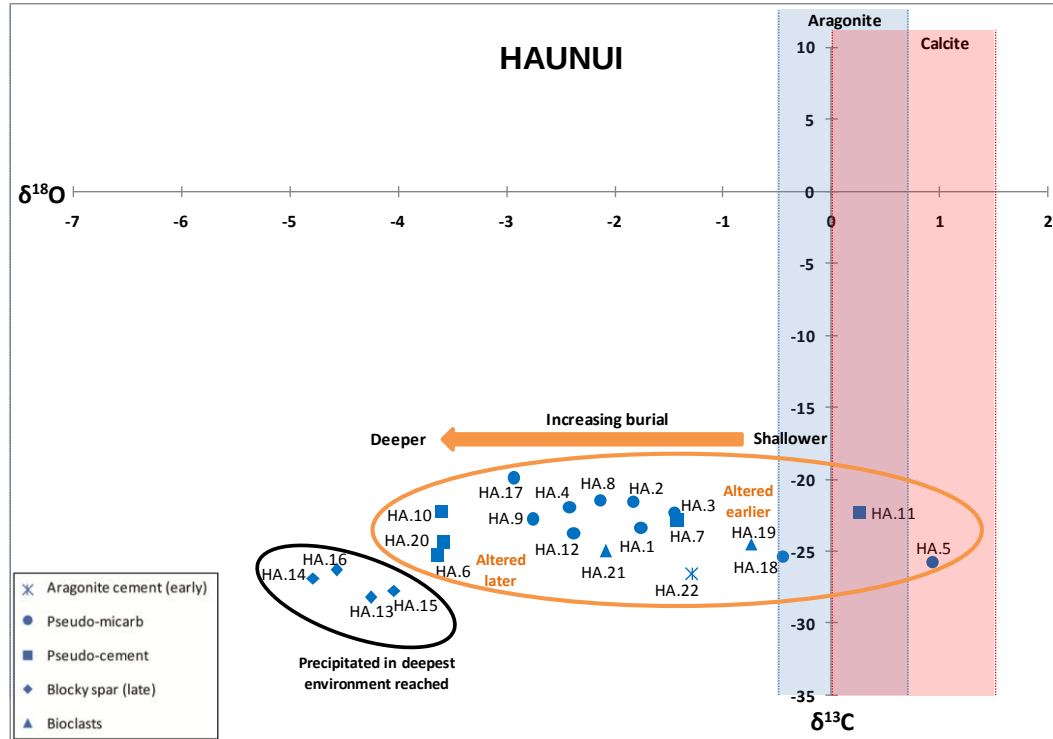


Figure 7.12 – Stable $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ cross plot showing the values of the 22 bulk and component-specific powders from Haunui samples. Shaded areas defined in Figure 7.9. Orange circle encompasses most of the neomorphosed fabrics (pseudo-micarb and pseudo-cement). These fabrics have remineralised from aragonite to calcite as burial was occurring. The negative $\delta^{18}\text{O}$ values reflect the ever-increasing depth of burial and temperature. Black circle encompasses the blocky spars precipitated last in the deep burial environment.

The single aragonite sample (HA.22) lies outside of the $\delta^{18}\text{O}$ range which forms in equilibrium with normal Miocene marine water. It is depleted in ^{18}O , perhaps due to periodically hotter advective fluids mixing with sea water, or a slight influence by a gas hydrate formation event.

The neomorphosed fabrics show a progressively more negative trend (orange circle in Fig. 7.12). As with the pseudo-cements of Ngawaka, these fabrics have remineralised in the burial realm and have likely inherited their $\delta^{18}\text{O}$ values from new environments as burial progresses. This results in a range of data points with increasingly negative $\delta^{18}\text{O}$ values that correspond to warmer burial fluid temperatures. Again, the micarb fabrics appear to have neomorphosed before many the other early cements.

The blocky spars (circled in black in Fig. 7.12) precipitated at the deposit's greatest burial depth. The carbon source remains thermogenic methane, and the low $\delta^{18}\text{O}$ values of these samples (-4 to -5‰) indicate the depth and warm temperatures at which they were precipitated. These blocky calcite spars could be achieved at depths of 1000-1100 m, based on the methods of Friedman & O'Neil (1977) and a geothermal gradient of 23°C/km (Field *et al.* 1997), and assuming that the $\delta^{18}\text{O}$ value of the fluids in the burial environment is similar to that of the sea floor environment.

7.4.7 Wilder Road stable $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values

The $\delta^{13}\text{C}$ values of Wilder Road samples have the largest range of the five study sites (Fig. 7.13). There are values at the lower end of the range ($\delta^{13}\text{C}$ -18 to -26‰) which are likely to be sourced from thermogenic methane. Those with higher values are also likely to be sourced from thermogenic methane; however, they appear to have been somewhat affected by methane oxidation or mixing with marine water to increase the $\delta^{13}\text{C}$ value above -20‰. Alternatively, samples with the highest values (>+5‰) could possibly have carbon sourced from residual CO_2 .

All but one of the aragonite samples falls outside of the range of $\delta^{18}\text{O}$ values for aragonite which has formed in equilibrium with Miocene marine water (Fig. 7.13). Burial to depths of 1000 m could result in aragonite fabrics with such depleted values, however precipitation of aragonite in such an environment is highly unlikely (see Section 2.5.3). This $\delta^{18}\text{O}$ depletion probably relates to a slight increase in water temperature (16-23°C would be required to precipitate fabrics with the appropriate $\delta^{18}\text{O}$ values), or a prolonged period of gas hydrate formation to deplete pore waters of ^{18}O (cf. Bohrmann *et al.* 1998).

$\delta^{18}\text{O}$ values of the pseudo-micarb and pseudo-cement fabrics are increasingly negative, likely due to neomorphism in progressively deeper and warmer environments in which they adopt the local $\delta^{18}\text{O}$ value. If this is the case, neomorphism of many of the micarb samples can be seen to pre-date that of the early cement fabrics (i.e. the neomorphism would have been occurring close to the seabed).

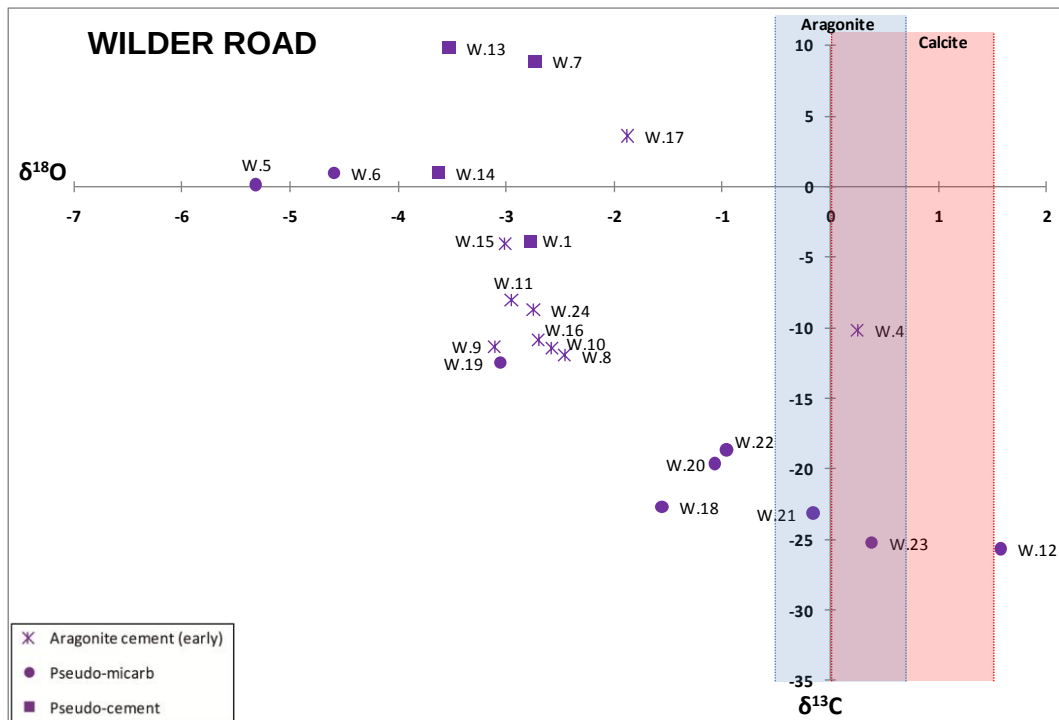


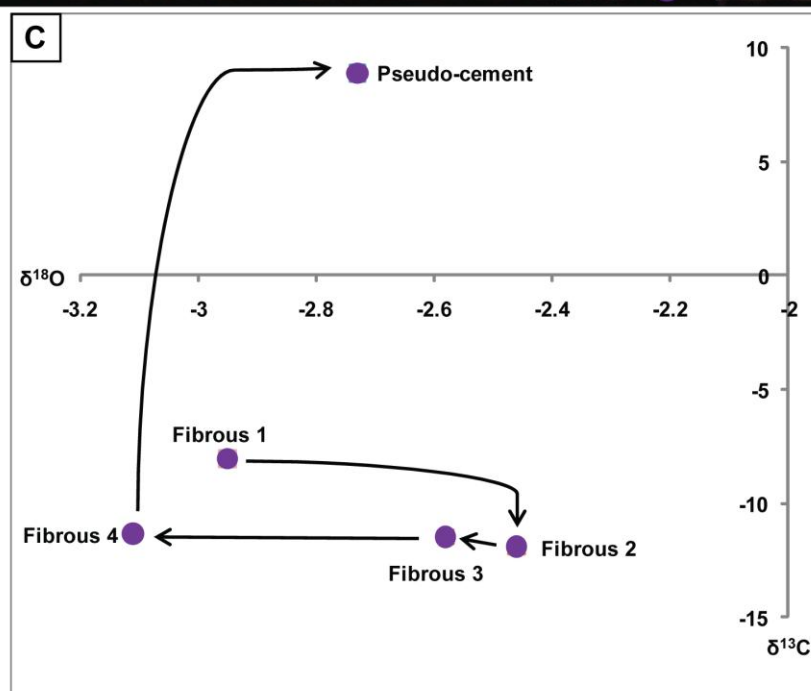
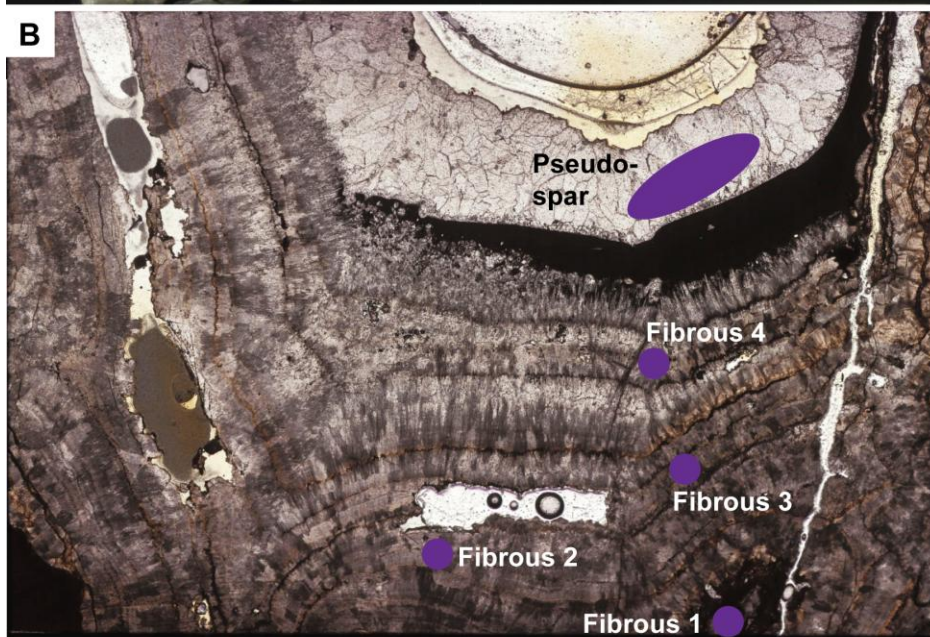
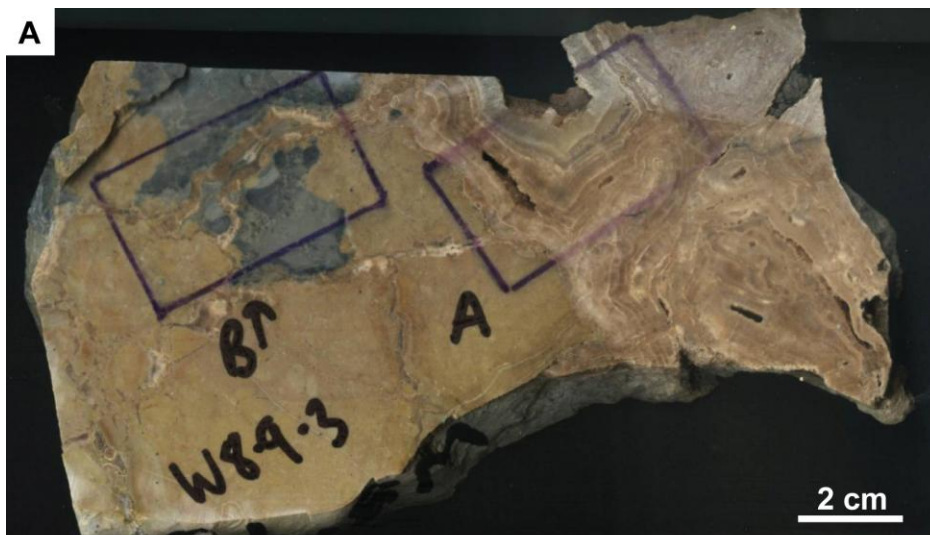
Figure 7.13 – Stable $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ cross plot showing the values of the 22 bulk and component-specific powders from Wilder Road samples. Shaded areas defined in Figure 7.9.

Sample W.8.9.3A was extensively analysed for isotopic values to assess any temporal trends. Figure 7.14 depicts the slab, thin section, sampling locations, and the isotopic values of each sample. The slab contains a very thick, multiphase vein within beige and blue-grey micarb (M1) (Fig. 7.14A), likely to be a fluid flow conduit (see Section 7.2.3). The thin section was cut from the thick vein, which consists of many layers of fibrous cements (C2) followed by a thinning band of micarb (M2) (Fig. 7.14B). The final fill is neomorphosed pseudo-cement (PC). The first 4 samples drilled were all earlier stage fibrous aragonite fabrics. They were collected incrementally, ensuring sampling across the older layers to the

younger layers. The final sample was taken from the innermost and therefore most recent fabric of neomorphosed pseudo-cement.

The isotopic results show some trends through the cement stratigraphy (Fig. 7.14C). In the early diagenetic stage of hydrocarbon seepage, the source of carbonate carbon was relatively constant – the 4 samples taken at this interval vary little, all with $\delta^{13}\text{C}$ values between -8 and -12‰. As earlier mentioned, this is likely to be thermogenic methane somewhat affected by oxidation of the methane pool or mixing with normal marine water carbonate. The $\delta^{18}\text{O}$ values fluctuate within 1‰, likely due to small variations in the fluid temperature. This begins with cooling to jump from precipitation of fibrous cement 1 ($\delta^{18}\text{O} = -2.95\text{‰}$) to fibrous cement 2 ($\delta^{18}\text{O} = -2.46\text{‰}$), a slight warming to precipitate fibrous cement 3 ($\delta^{18}\text{O}$ value -2.58‰), and with continued warming fibrous cement 4 ($\delta^{18}\text{O}$ value -3.11‰) was precipitated.

As the pseudo-cement was originally precipitated in the (near) seafloor environment, with re-mineralisation in the burial realm having little effect on $\delta^{13}\text{C}$ values (Campbell *et al.* 2002), this cement therefore carries a $\delta^{13}\text{C}$ value inherited from sea floor conditions. In the transition from precipitation of the latest fibrous cement to the pseudo-cement fluid conditions must have changed considerably as the system must have undergone change to precipitate micarb (M2) and back to aragonite cement (Fig. 7.14B). The pseudo-cement has a high $\delta^{13}\text{C}$ value, the source of which is either substantial oxidation of the methane pool or residual CO_2 from methanogenesis. This fabric appears to have retained its original $\delta^{18}\text{O}$ value, despite this often being altered in the burial environment due to recrystallisation.



7.4.8 Isotopic conclusions

The source of carbonate carbon for the ancient cold seep deposits of southern Hawke's Bay is highly likely to be thermogenic methane, based on the moderate depletion of $\delta^{13}\text{C}$ in the samples (e.g. Haunui). It is possible, but less likely, that some of the more negative $\delta^{13}\text{C}$ values could in fact be sourced from microbial methane which has been oxidised to give a heavier $\delta^{13}\text{C}$ value indicative of thermogenic methane.

The influences of a number of processes and carbon sources can be seen in the cumulative $\delta^{13}\text{C}$ results. Some sites, such as Wanstead, Ugly Hill, and some of the Wilder Road samples, show a small to moderate influence by either methane pool oxidation or marine water to result in slightly elevated $\delta^{13}\text{C}$ values. Other sites clearly were influenced by another process to result in noticeably higher $\delta^{13}\text{C}$ values, such as Ngawaka and most of the Wilder Road samples, which result from either extensive oxidation of the methane pool or carbon sourced from residual CO_2 .

These results can be compared to other isotopic data of modern seep carbonates from the Hikurangi Margin, compiled by Campbell *et al.* (in press). These samples have $\delta^{13}\text{C}$ values which cover a large spectrum of carbon sources and influential processes. This includes possible microbial and thermogenic methane sources, plus mixing with seawater bicarbonate and oxidation of the methane pool (Campbell *et al.* in press). In addition, modern hydrocarbon seeps and pore fluids sampled from both onshore and offshore East Coast Basin have verified methane sourced from purely biogenic and purely thermogenic methane, as well as mixed sources (Lyon *et al.* 1992; Lowry *et al.* 1998; Davies *et al.* 2000).

Figure 7.14 – Sample W.8.9.3A from Wilder Road contains a thick, multiphase vein within beige and blue-grey micarb which is sampled and analysed to show temporal isotopic fluctuations. **A:** Scanned slab of sample W.8.9.3A, rectangles indicate thin section locations. **B:** An entire thin section scan (2.5 x 4 cm) of thin section A in Image A. Purple circles show drilling/sampling localities with the fabric type labeled. **C:** The fibrous cements of the Wilder Road locality show slight fluctuations in $\delta^{18}\text{O}$, likely a result of small fluid temperature changes. Pseudo-cement has a much higher $\delta^{13}\text{C}$ value, a result of changes to the seep system which bring either oxidised methane or residual CO_2 into the (near) seafloor environment.

Many of the original fabrics remaining in these ancient samples (fibrous aragonites) show $\delta^{18}\text{O}$ depletion or enrichment in relation to aragonites formed in equilibrium with Miocene marine water. Depletion and enrichment of $\delta^{18}\text{O}$ implies that fluid temperatures were fluctuating (as illustrated in Section 7.4.2) (Mozley & Burns 1993; De Boever *et al.* 2006a), gas hydrates were locally forming or dissociating (Ussler & Paull 1995; Aloisi *et al.* 2000; Pierre & Rouchy 2004), or the deposits were affected by meteoric water (Mozley & Burns 1993). Affects caused by gas hydrate formation and dissociation are favoured due to the modern day presence of a vast gas hydrate field in the East Coast Basin (Barnes *et al.* in press), although clay mineral dehydration from advecting deeper fluids also could have played a role (Campbell *et al.* in press).

The neomorphosed fabrics (pseudo-micarb and pseudo-cement) show a typical trend of decreasing $\delta^{18}\text{O}$ values related to burial and warmer temperatures. This can be referred to in a temporal sense, as over time the deposits become increasingly buried which causes formation temperatures to increase and therefore $\delta^{18}\text{O}$ values of the pore fluids to decrease. When the aragonite fabrics neomorphose (with micarb typically altering before sparry cements), they adopt the $\delta^{18}\text{O}$ value from the pore fluids, and therefore can be tracked during burial. Last to precipitate were the blocky spars. They formed during deeper burial, as implied by the negative $\delta^{18}\text{O}$ values of most of the blocky spar samples.

7.5 PARAGENETIC SEQUENCE

The relative chronological order of mineral precipitation has been identified based upon plane polarised light (PPL), cathodoluminescent light (CL), and scanning electron microscope (SEM) petrography, isotopic values, and mineralogical data. Thirteen fabrics were identified, as well as four fracturing and/or corrosion events and two alteration phases (see Section 6.3 for descriptions) to form a paragenetic sequence of 17 events (Fig. 7.15). The sequence has been divided into two stages, an early diagenetic stage, which includes all minerals and events that occurred at the (near) seafloor environment, followed by a late diagenetic stage in which all minerals and events occurred in the burial realm. This sequence is necessarily somewhat generalised due to the patchy occurrence of many of the 13 mineral

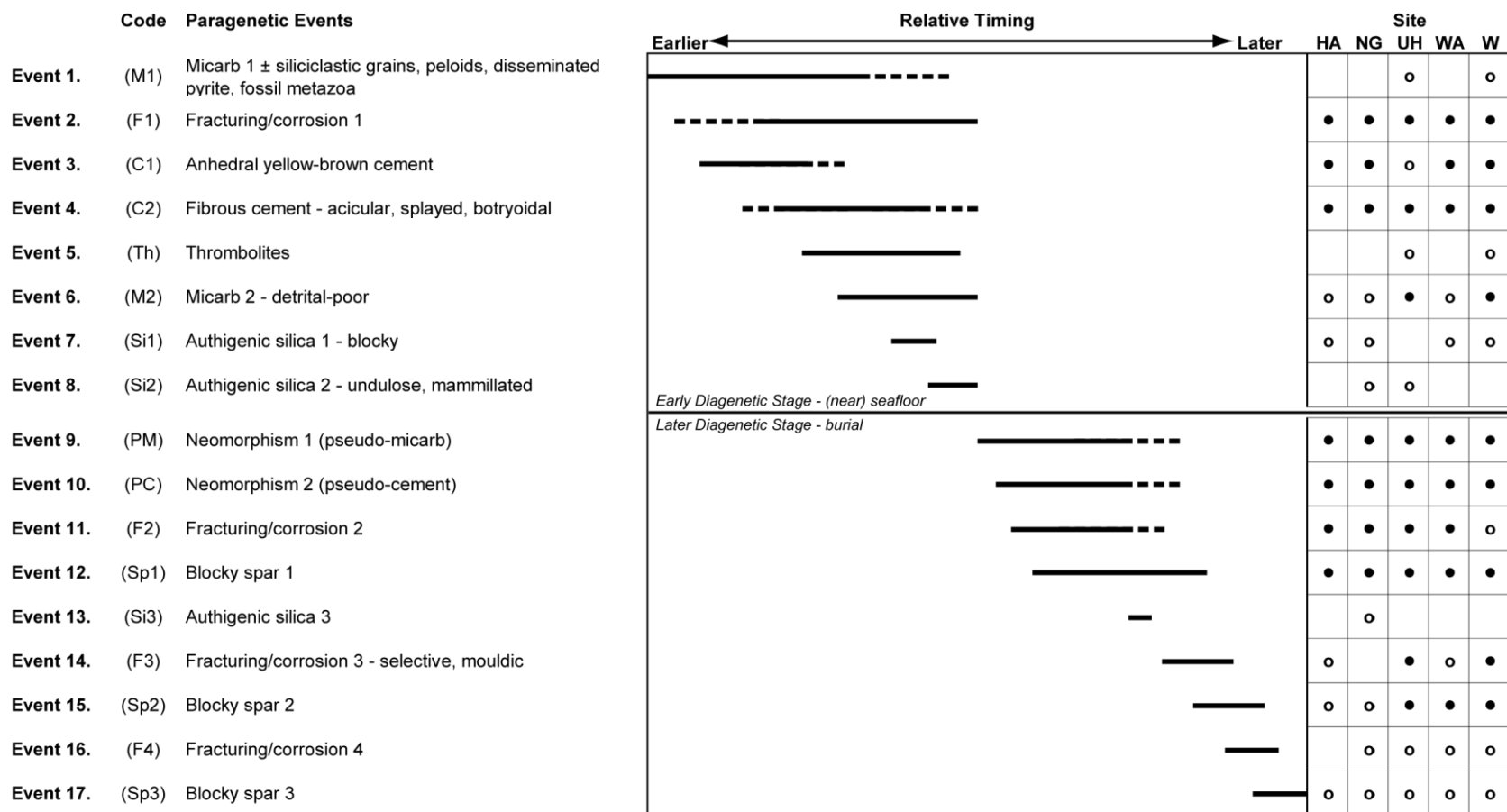


Figure 7.15 – A paragenetic sequence illustrating the relative timing of mineral precipitation and other events recorded in the formation of the southern Hawke’s Bay ancient cold seep carbonate deposits. The upper section of the diagram includes all minerals which initially made up the deposits in the seafloor environment, plus one fracturing/corrosion event. The lower section of the diagram includes all minerals which were precipitated once burial had occurred, plus multiple fracturing/corrosion and neomorphic events. The dark, solid lines indicate the major period when each event was occurring, with dashed lines where the event could have been occurring as a minor phase and showing the probable maximum extent of that event. The far right shows the distribution of events over the five sites (HA = Haunui, NG = Ngawaka, UH = Ugly Hill, WA = Wanstead, W = Wilder Road), with filled circles indicating a major occurrence of that event/mineral and open circles indicating that the event is rare at that site.

phases across outcrops and sites (as shown on the right in Figure 7.15). Note that the relative timing of each phase overlaps, sometimes considerably, with adjacent events to explain contemporaneous and alternating precipitation of mineral phases. Figures 7.18 through to 7.22 provide evidence to show the relative ordering of events given in the paragenetic sequence.

7.5.1 Early diagenetic stage

This stage involved the initial precipitation and fracturing/corrosion events of the carbonate deposits which occurred in the (near) seafloor environment. After initial micarb precipitation, many of the events occurred in a cyclic pattern – alternating phases of mineral precipitation are seen, as well as repeated fracturing events resulting in networks of cross-cutting veins.

Fluid migration and seep initiation

In the Early Miocene, the inception of the convergent plate boundary through New Zealand resulted in large-scale compression and deformation of pre-Miocene strata (Lewis & Pettinga 1993; Field *et al.* 1997). This immense deformation, coupled with sediment loading, increased lithostatic and pore pressures, forcing fluids to migrate up through the strata towards the sea floor (Lewis & Marshall 1996; Darby & Funnell 2001; Barnes *et al.* in press). When the hydrocarbon-charged fluids first began to escape at the sea floor, the fluid flow was diffuse and the sediments gradually became saturated in methane and hydrogen sulphide.

In the anoxic pore water of the sulphate reduction zone (SRZ), in the sediments sulphate-reducing bacteria (SRB) and methanotrophs thrived in utilising the methane and sulphate. This zone is marked by a rapid decrease in SO_4^{2-} (due to the SRBs) and an increase in the concentration of CH_4 due to the process of anaerobic oxidation of methane (AOM) which is carried out by the methanotrophs (Cavagna *et al.* 1999; Judd & Hovland 2007). AOM has an associated alkalinity increase, leading to the production of methane-derived authigenic carbonates (MDAC) (Event 1, see Fig. 7.15). These microbes are all dependent on methane

and sulphide in the environment, which is dictated by the rate of hydrocarbon-rich fluid flow through the seep (Cavagna *et al.* 1999).

Some authors (e.g. Beauchamp & Savard, 1992) have suggested that thiotrophic (sulphide oxidising) bacteria, such as *Beggiatoa* spp. and the less abundant *Thiothrix* and *Thioplaca* spp, are the first seep colonisers. These species grow in mats and thrive on top of the sulphide-rich sediments, and their remnants (cells, sheaths, and biofilms) can be found in both modern and ancient seep deposits (Savard *et al.* 1996; Trehu *et al.* 1999; Riding 2000; Boetius & Suess 2004; Judd & Hovland 2007). The presence of these bacterial mats results in steep chemical gradients; they create an interface between the oxic seawater above and an anoxic environment below which is similar to the SRZ at depth in normal marine sediments (Beauchamp & Savard 1992; Orphan *et al.* 2004). Methanotrophic and sulphate-reducing bacteria inhabit this anoxic environment below the bacterial mats, and sulphate reduction and AOM occurs, producing methane-derived authigenic carbonates (MDAC) as a by-product (Peckmann 2005). Some authors argue that the minimal volume of bacterial mats found within ancient samples indicates a sparse colonisation by thiotrophic bacteria which could not mediate such a large mass of early cements (Campbell *et al.* 2002), attributing MDAC precipitation to the presence of bacteria in the SRZ of the underlying host sediments.

Micarb (M1) is the dominant fabric present throughout all five study sites. As ascending methane-charged fluids reach the base of the SRZ they become anaerobically oxidised by the methanotrophic microbes (Cavagna *et al.* 1999; Campbell 2006). An associated alkalinity increase induces the precipitation of MDAC in the form of micarb. This zone in which the AOM occurs can be located at depth within the sediment or only centimetres below the sediment-water interface, driven by the flux of ascending methane (Campbell 2006). It can also occur at the top of the sediment and within the water column, if environmental conditions permit (oxygen-depleted sea water) (Campbell 2006).

As earlier described (see Section 6.3.1), micarb often has a clotted fabric, similar to structure grumeleuse (Fig. 7.16) (Bathurst 1971), which is generally associated with microbial precipitation (Peckmann *et al.* 2002). The microbes are thought to

induce precipitation of small (tens of μm in size), roughly spherical peloids with gradational boundaries which collectively form the structure grumeleuse fabric (Bathurst 1971; Cavagna *et al.* 1999). Micarb precipitates as aragonite, as shown by CL petrography and XRD results, due to the high-sulphate/low-phosphate conditions of the (near) seafloor environment (see Section 2.5.3). This microcrystalline carbonate cement contains varying amounts of siliciclastic material and foraminifera, sourced from the host sediment. The presence of disseminated pyrite is due to mixing of reduced sulphur (from AOM) with iron, and confirms that micarb precipitation was occurring in an overall reducing and oxygen depleted environment (Beauchamp & Savard 1992; Peckmann *et al.* 2001b). This pyrite is scattered throughout the host sediment and within foraminifera tests. Some samples have an abundance of rusty grains and stains which indicate the former presence of disseminated pyrite, now oxidised.

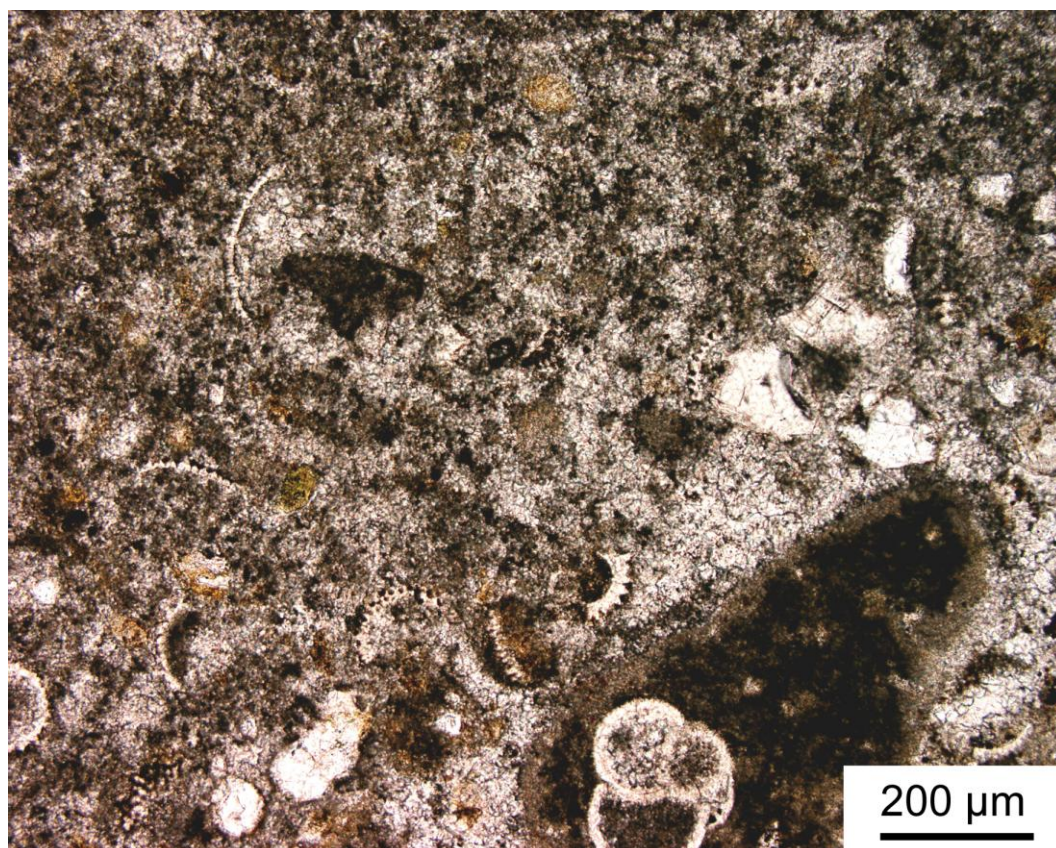


Figure 7.16 – Photomicrograph of thin section HA.13.5.1B from Haunui illustrates the mottled texture of structure grumeleuse, a common texture exhibited by micarb (M1). This micarb contains scattered grains of quartz, glauconite, and disseminated pyrite. A large, dense intraclast can be seen in the lower right of the image.

Although outcrop sizes vary across each of the five study sites, the sheer volume of micarb implies that methane migration, chemosynthesis, and MDAC precipitation must have gone on for a significant period of time. Numerical modelling by Luff *et al.* (2004) estimates 100-500 years of methane seepage at a flux appropriate for the methanotrophs can produce carbonate slabs several centimetres thick. Upon comparing this rate to the southern Hawke's Bay deposits, which range from a few centimetres thick to 8 m in height (Ngawaka West), precipitation of some of these large deposits could have taken several tens of thousands of years. This is not taking into account high sedimentation rates, waning of the methane supply, or an exceptionally advective fluid flux, all of which are factors that may decrease the rate at which MDAC is generated (Luff *et al.* 2004).

Colonisation by macro-invertebrates

Contemporaneous with initial micarb precipitation is colonisation by a variety of organisms. Many types of bivalves, tube worms, corals, and gastropods inhabited the sites, likely due to an abundance of food, in high density yet low diversity which is typical of hydrocarbon seep sites (Sibuet & Olu 1998). For a list of fossils and trace fossils found at the five southern Hawke's Bay seep carbonate deposit sites see Table 6.2. These taxa arrived after activation of the seep when hydrocarbon-rich fluids were entering the near-seafloor environment and mineral precipitation was initiating – the chemosynthetic microbes are the lowest trophic level of the ecosystem.

The requirement of a hardground for mussel and coral attachment assures that some of these carbonate deposits formed in seafloor sediment in contact with the water column, and that colonisation of the site did not occur pre-seepage. Nevertheless, burrows, probably assigned mainly to *Thalassinoides*, indicate that biological activity was evident in the earlier stages of MDAC precipitation or distal areas of the seep when sediments were only mildly cemented by authigenic carbonate (softgrounds). Borings (Fig. 5.18) imply colonisation based on the presence of a hardground.

Remains of seep biota are found entombed within micarb, which often provided micro-environments giving rise to features such as geopetal infills, umbrella voids, dense peloids, and the build-up of siliciclastic grains. The burrows and borings provided secondary pore spaces in which fluids continued to flow and deposit mineral phases after initial sediment porosity was reduced or lost. This has often resulted in a marble-cake texture in samples as new mineral phases of a different colour infill the bioturbation structure (Conti & Fontana 2002; Campbell *et al.* 2008). Slabs from the Ugly Hill and Haunui sites show this marble-cake fabric well (Fig. 7.17). Some borings aid in definition of the paragenetic sequence as their layered infill reflects the sequence in which late diagenetic minerals were precipitated (Fig. 7.18).

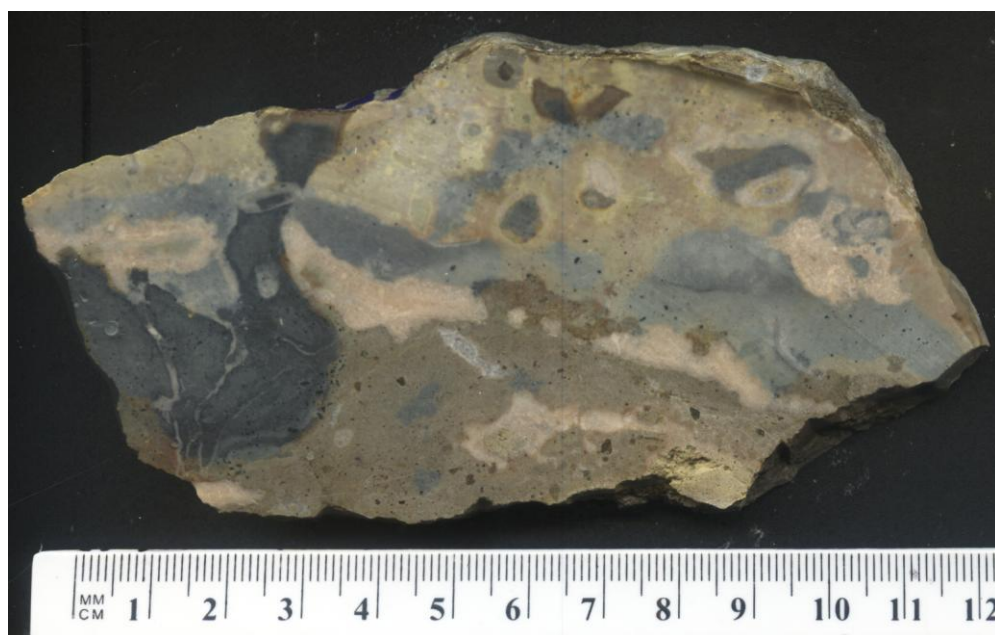


Figure 7.17 – Sample HA.M1 from outcrop HA.C at Haunui exhibits a marble-cake texture due to extensive burrowing or boring of the soft- or hard-ground. Later cements then infill the bioturbation structures to give such an irregular cement/phase distribution.

Early fracturing and corrosion

Corrosion, fracturing, and general erosion of the mounds (Event 2, F1) continually occurred during their initial seafloor formation (Fig. 7.15). Fracturing of intact carbonate mounds/hardgrounds occurred due to sediment instability, tectonics, gravity sliding, diapiric expansion, and liquefaction episodes (possibly gas

hydrate related). Autobrecciation occurs as the methane rich fluids migrate up through the sediments and the network of voids within the carbonate mass, continually precipitating MDAC which further reduces pore space. Portions of the network eventually become plugged, and pressures increase below the blockage due to the constant upwards fluid flux until explosive venting of the fluids occurs causing brecciation of the carbonate body (Conti & Fontana 2002, 2005). Clasts of the aragonitic micarb deposits become dislodged, which can range from millimetres to tens of centimetres in size, some of which are subject to winnowing and further erosion resulting in rounding. Most importantly, this erosion opened up new surfaces upon which the next phases of mineralisation could precipitate.

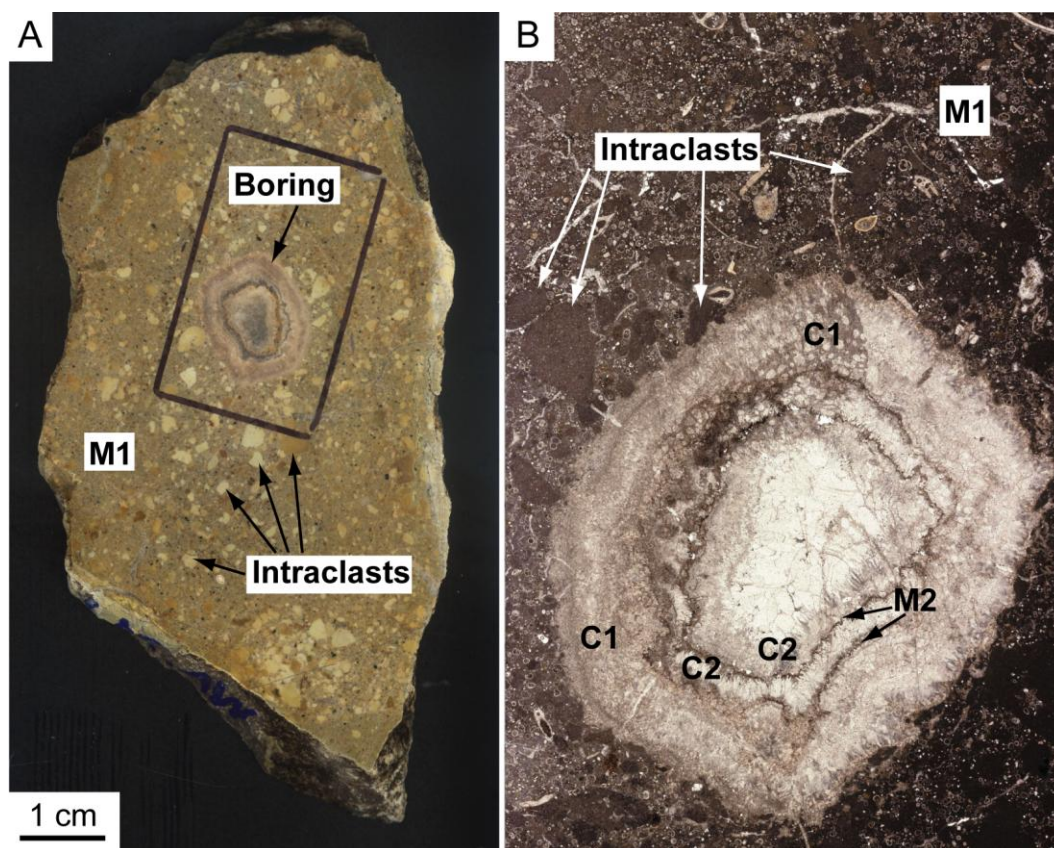


Figure 7.18 – Sample WA.M1 from Wanstead contains a large boring with many layers of infill. **Image A:** The scanned slab shows a very coarse-grained facies due to the large amount of intraclasts within the micarb (M1). The boring structure has a well defined rim and is completely infilled with many layers of pink to grey cements. **Image B:** The entire scanned thin section (2.5 x 4 cm) shows the infill consists of yellow-brown (C1) and fibrous cement (C2) layers, with two thin layers of micarb (M2) and a central blocky cement, a late diagenetic fabric).

The eroded clasts often ended up being re-cemented into lower sections of the growing deposit, as many of the later fabrics precipitated upon these new surfaces to act as cements which ‘healed’ the eroded micarb clasts back into an intact rock mass once again (Fig. 6.8C). These eroded clasts, when seen in slabs and thin sections, can later become small, regular, elliptical micarb peloids (Fig. 6.2C), intraclasts (irregular to angular micarb clasts, typically larger than peloids; Fig. 7.18), and monomictic breccias (volumes of coarse, angular, micarb clasts) healed by later cements or fall to the lower slopes of the carbonate mounds to be encompassed by the host material to result in talus breccias (Conti *et al.* 2008).

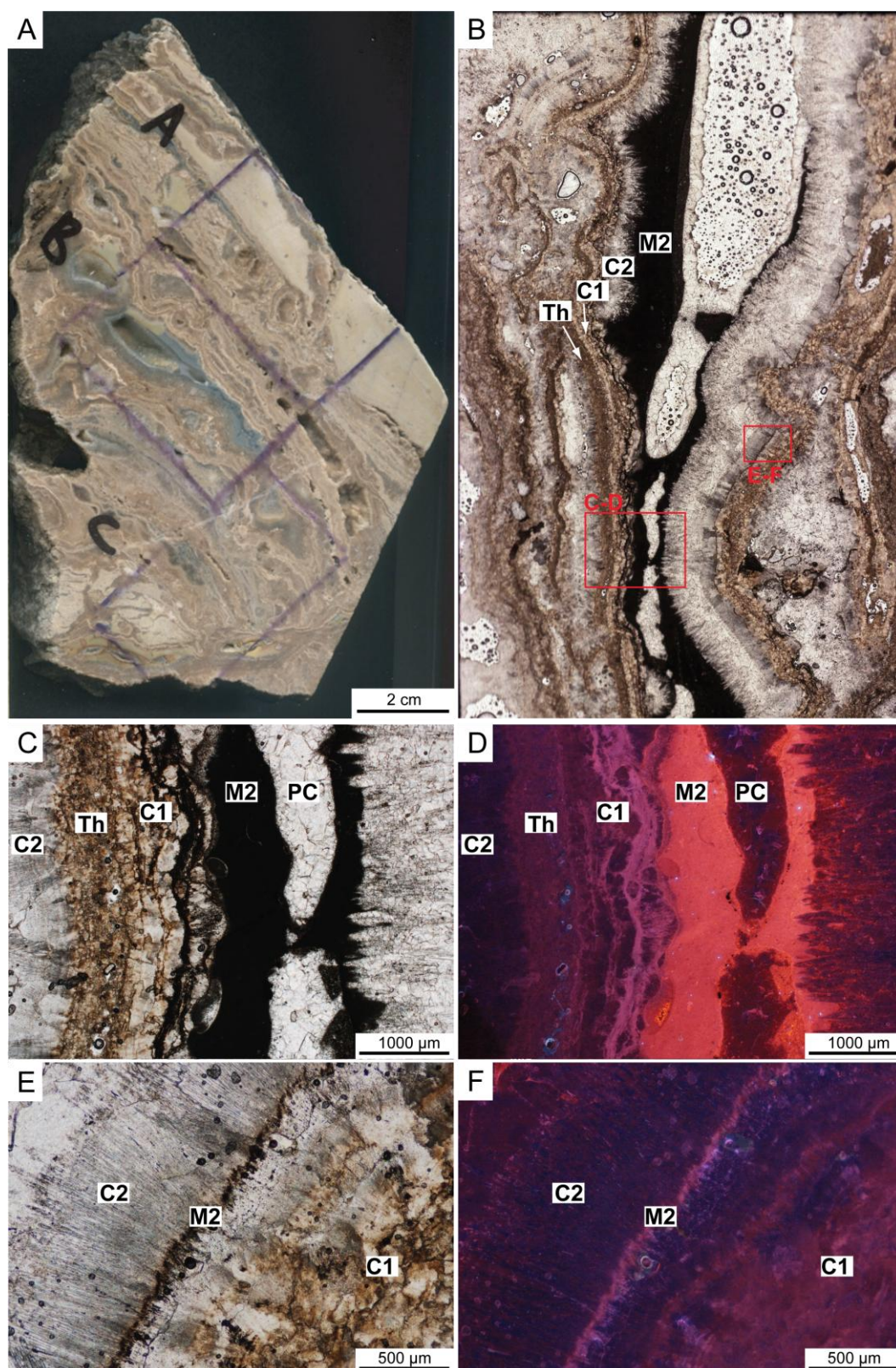
Corrosion of carbonate fabrics occurred as dissolution affected the surface of the micarb mounds. Sulphuric acid is produced during sulphide oxidation by thiotrophs, which sat in the anoxic zone and slowly dissolved impermeable aragonite surfaces (Cavagna *et al.* 1999).

Early cements

The following carbonate layers of the early diagenetic stage are often seen to be alternating with one another in a complex way. Figures 7.20 and 7.21 illustrate the complex relationships that can occur within these early carbonate fabrics. Beauchamp & Savard (1992) suggested that such an intermingling of early fabrics is due to changes in the seep environment from oxic to anoxic. Such changes may be linked to the growth and demise of bacterial mats such as *Beggiatoa* – the mat forms an oxic-anoxic interface, bringing conditions similar to that of the SRZ (in which AOM is carried out) to the sediments beneath the mat (Beauchamp & Savard 1992; Peckmann *et al.* 2004). A dynamic fluid flux can bring about phases of “boom and bust” to the bacterial mats, thus resulting in continual changes to the oxygenation of the environment. Within many of these early cement phases, hydrocarbon-bearing inclusions can be identified in PPL and UV, relating these fabrics back to carbon source origins.

Thin layers of anhedral yellow-brown cement (Event 3, C1) are found, somewhat inconsistently, upon micarb surfaces (Figs. 6.4A, 6.4C) and fibrous cements (Fig. 7.18). It appears that, like most other carbonate phases which form in this early diagenetic stage, anhedral yellow-brown cement was initially aragonitic but it has

subsequently undergone neomorphism to calcite. We can interpret this from the visible remnants of aragonite under CL, where small areas of purple can be seen amongst mottled pink of the calcite fabric (Fig. 6.4B), and also from GADDs



analysis which indicates a calcitic mineralogy with minor (remnant) aragonite. The yellow-brown tinge to this fabric could be attributed to the inclusion of crude lipids or an expression of the fabric's iron content, as suggested by Pearson & Nelson (2005). Peckmann *et al.* (2002) noted the common sequence of yellow aragonite cement (which is very similar to the anhedral yellow-brown cement of this study) followed by clear aragonite cement in Oligocene seep carbonate deposits from western USA and the Black Sea. It appears from the sharp boundary between yellow-brown cement and irregular (?corroded) micarb, that the yellow-brown cement of this study does indeed post-date micarb precipitation and is typically followed by clear, fibrous cement formation. This differs from the yellow cement of Campbell *et al.* (2002) who suggested that it represents an *in situ* replacement of micarb, perhaps related to dissolution.

In much the same time frame as the precipitation of yellow-brown cement, came the formation of a variety of fibrous cements (Event 4, C2). This phase is pervasive, occurring in abundance at every study site and in most thin sections. It formed upon all surfaces present (M1 and C1) (Fig. 6.4) and can occur in many consecutive layers or layers alternating with other early cements (e.g. C1, other C2 types, Th, and M2) (Figs. 6.4E, 6.4G, and 7.19). Also common are masses of spar made up of fibrous cement (typically splayed). This cement is often found healing clasts of angular, eroded micarb back into the main carbonate deposit (Fig. 6.8C; cf. Campbell *et al.* in press, Fig. 7L). Hydrocarbon-bearing inclusions are found in greatest abundance within fibrous crystals, indicating that liquid

Figure 7.19 – A of collection images and photomicrographs of sample W.2.1.1B from Wilder Road to illustrate the complicated sequence of mineral precipitation which led to the final fabrics and facies of the ancient samples. **Image A:** The scanned slab shows a thick sequence of alternating pink-grey, brown, and white cement layers and areas of beige and blue-grey micarb. The rectangles indicate the locations from where thin sections were made. **Image B:** An entire thin section scan (2.5 x 4 cm) of thin section B, as seen in Image A. The thin section reveals alternating layers of fibrous cements (C2), thrombolites (Th), yellow-brown cement (C1), and micarb (M2). Red boxes indicate the locations of images C-D and E-F. **Images C and D:** Photomicrographic pair of images under PPL and CL, respectively. A thick vein has precipitates on both sides which eventually reached the middle to completely fill the void. The final void fills shown in these images are fibrous cement (C2), followed by thrombolites (Th), yellow-brown cement (C1), and a mix of micarb (M2) and fibrous cements (C2) on the left side, before a final last infill of late micarb (M2) and a pseudo-cement (PC) - likely to have originally been fibrous cements. **Images E and F:** A close up view showing a layer of fibrous cement (C2) interrupted by a thin band of micarb (M2). This image illustrates how fabric changes can occur on such a fine scale, giving rise to the need for generalisation of the paragenetic sequence to allow for such relationships.

hydrocarbons were present in high concentrations within the migrating fluids (Campbell *et al.* 2002). All three varieties of fibrous cements precipitated as aragonite, as confirmed by GADDs analysis on these fabrics, and appear purple to blue under CL unless neomorphosed (Fig. 6.4).

The next event (Event 5) is the precipitation and preservation of thrombolites (Th) – dense layers of clotted, microbially-induced micrite containing bacterial remnants (Riding 2000). These layers are typically associated with fibrous cements, but have also been preserved upon micarb (M1, M2) and yellow-brown cement (C1) (Fig. 7.19). The scattered occurrence of thrombolites in the samples may be a function of a rapid geochemical change in the environment – the oxic conditions above the mat suddenly change to anoxic, encouraging MDAC precipitation due to intensive AOM which encases and thus preserves the bacterial mat (Peckmann *et al.* 2004). The mottled, blotchy fabric of thrombolitic layers is a consequence of the substantial amount of authigenic micarb (M1, M2) crystals within these microbial mats. It is surprising that no siliciclastic grains are trapped within these layers, as is commonly seen in other microbial mats (Riding 2000). This may be due to considerable build-up of the carbonate mounds above the seafloor when the thrombolite layers were forming, or be a function of microbe size, mobility, or orientation (Riding 2000).

Throughout horizons of yellow-brown cement, fibrous cement, and clotted thrombolites are layers of the detrital-poor, dense appearing micarb 2 (Event 6, M2). This fabric precipitates as very fine bands between successive layers of other fabrics (Fig. 6.4E), or can act as a major cavity fill (Fig. 7.19; cf. Campbell *et al.* 2002).

Present in relatively few samples from the southern Hawke's Bay cold seep carbonate collection are the two early silica phases (Si1 and Si2). These fabrics occur as one of many layers of cavity/vein fill and as the final void fill (Fig. 7.20). Where both phases are present together, the blocky variety (Si1) has precipitated before the mammillated variety (Si2) (Figs. 6.6C-F).

With the ongoing precipitation of early stage carbonate cements and episodes of fracturing and healing, colonisation of biota, and influx of sediment, the MDAC deposits built up to a significant volume and became relatively impermeable –

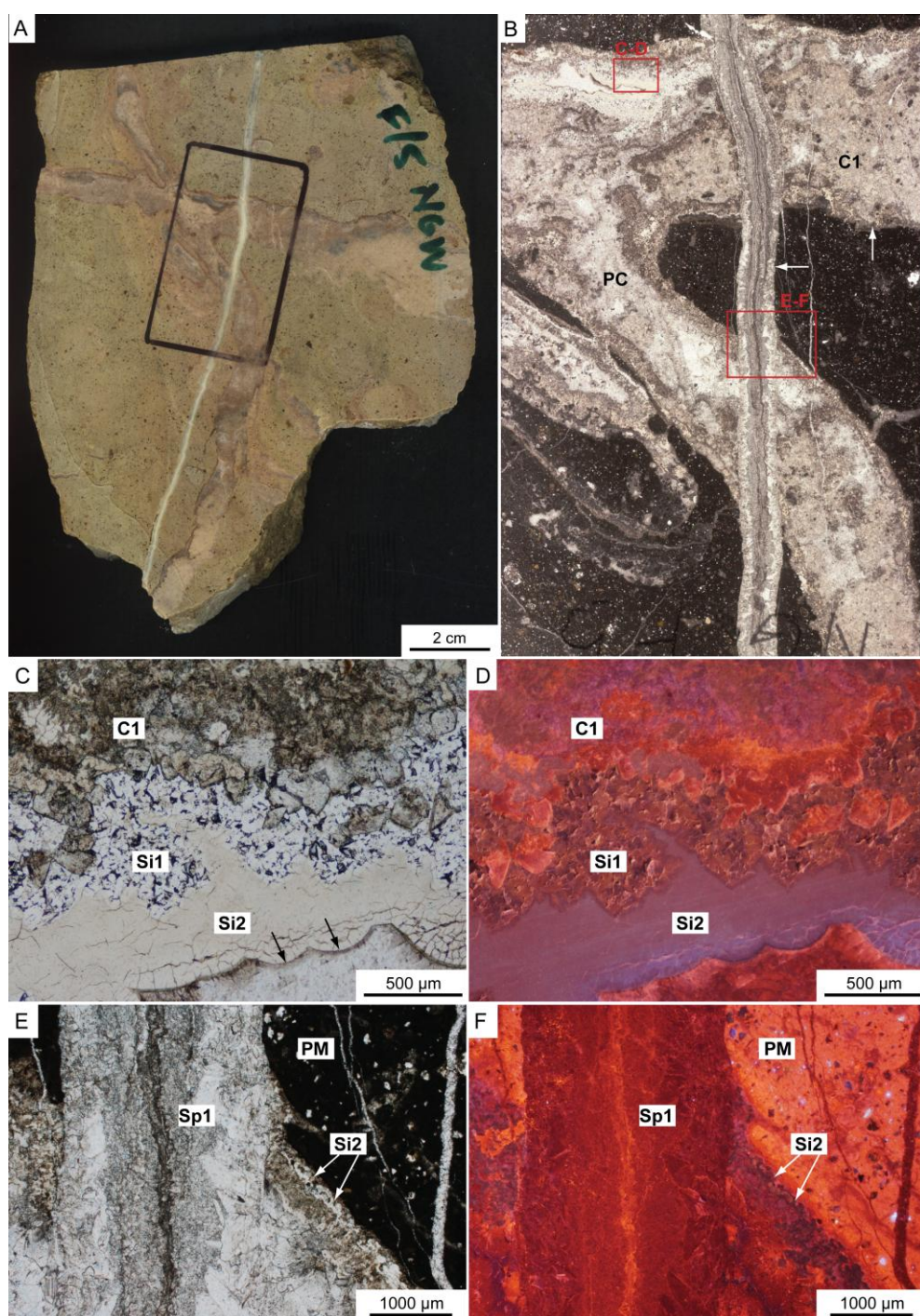


Figure 7.20 - A collection of images and photomicrographs of sample NG.F5 from Ngawaka illustrate the complicated sequence of mineral precipitation which led to the final fabrics and facies of the ancient samples. **Image A:** The scanned slab shows a pink to grey, thick, branching vein cutting through beige micarb (M1). A much thinner, white vein then cuts vertically through the slab. The rectangle illustrates the position of the thin section (image B). This slab illustrates the differences between earlier and later cements – early cements are typically pink-grey in slab form, and later cements are sparry white to grey. Red boxes indicate the locations of images C-D and E-F. **Image B:** An entire thin section scan (2.5 x 4 cm) shows an abundance of yellow-brown cement (C1) and pseudo-cement (PC) in the earlier vein. **Images C and D:** Within the early vein is a patch containing two silica fabrics. The first, blocky silica phase (Si1) has precipitated off yellow-brown cement (C1). The second silica phase (Si2) has grown off the first, free of physical constraint as suggested by the mammillated outer surface (arrowed). **Images E and F:** The earlier vein, here containing a thin band of silica (Si2) at its outer edge, is cross cut by the later vein comprised of layers of late blocky spar (Sp1) with varying crystal sizes.

most of the porosity became infilled with authigenic cements or siliciclastic host grains (Beauchamp & Savard 1992).

7.5.2 Late diagenetic stage

The second major diagenetic stage which affected the seep carbonates occurred once the seep system began to undergo burial. The chemosynthesis-based community died off due to the lack of methane and sulphate, and sedimentation of the host formation eventually smothered the carbonate deposits. In this burial realm, dewatering of strata due to compaction ensured plentiful pore fluids, and the overall environmental conditions (temperature, pressure, and geochemistry) were significantly different. This brought rise to a new suite of processes which would have affected the fabric and geochemical character of the seep carbonate deposits.

Neomorphism

A major process that occurred during the late diagenetic stage was neomorphism. It is unclear whether this neomorphic alteration occurred mainly early on, during, or at the late stages of burial, although it was likely to have occurred gradually throughout burial. The term covers all transformations where the primary mineral is altered and simultaneously replaced with secondary crystals of the same mineral type or a polymorph, and the resultant mineral structure can have a larger or smaller crystal size, and it may be of a different morphology/shape and texture than that of the original mineral (Bathurst 1971). Following Bathurst (1971), in this study such altered phases have been prefixed by pseudo, thus pseudo-micarb and pseudo-cement.

Event 9 represents the neomorphism of aragonitic micarb (M1 and M2) into calcitic micarb, referred to as pseudo-micarb (PM). Micarb is known to be prone to neomorphism due to the mineralogically meta-stable nature of aragonite, the primary precipitate in the seafloor environment (see Section 2.5.3) (Tucker & Wright 1990). In the southern Hawke's Bay ancient seep carbonate samples, the original aragonitic micarb (M1) is indeed rarely preserved and has largely

undergone aggrading neomorphism to pseudo-micarb (Fig. 6.7). This is revealed through CL petrography by the abundance of pink to orange micarb (calcitic) and rare sighting of blue to purple aragonitic micarb (only in Ugly Hill and Wilder Road thin sections). This pattern is typical, as shown also by Ewen (2009) who compared modern Hikurangi Margin seep carbonate samples containing only aragonitic micarb with seep carbonates from the Miocene at Tauwhareparae on Raukumara Peninsula, which contained a combination of both aragonitic and calcitic micarb.

Event 10 refers to the phase of neomorphism which affected early cements (M1, M2, C1, and C2). The degree to which these fabrics were altered varied between sites and outcrops. The end result is pseudo-cement (PC) which often retains remnants of the original cement texture (see Section 6.3.9) (Fig. 6.8). Under CL these fabrics can exhibit a range of colours from maroon, pinks, and peach in partially neomorphosed examples, to an orange colour in samples completely neomorphosed to calcite spar. In addition, hydrocarbon-bearing inclusions locked up in the original cement are commonly also present in the neomorphosed form, as identified by UV microscopy - typically the inclusions have migrated to crystal rims and/or neomorphic fabric borders. Typically, neomorphism of micarb and early cements occurs early on in the late diagenetic stage. This is revealed by comparison of $\delta^{18}\text{O}$ isotopic values of neomorphosed fabrics with late blocky spar fabrics (Sp1, Sp2, Sp3), which imply that the blocky spars tended to precipitate at greater depth and higher temperature than the zone in which neomorphism occurs (see Section 7.4).

Late fracturing and corrosion

A major phase of fracturing (Event 11, F2), in places with associated corrosion, also occurred during burial of the seep carbonate deposits. This destructive phase opened up porosity in the carbonate deposits to allow burial fluids (saturated in calcite) to flow along pathways and deposit the later stage cements (Figs. 7.20 and 7.22). It is likely that this fracturing was occurring sporadically throughout burial of the deposits, many repeating phases of fracturing and blocky spar (Sp1, Sp2, and Sp3) precipitation were observed.

Late burial cements

The precipitation of carbonate cement in the subsurface is represented in the paragenetic sequence by blocky spar 1, 2, and 3 (Sp1, Sp2, and Sp3). These three fabrics can have equant, dentate, or rhombohedral crystals with sizes ranging from the micro-equant variety up to about 900 μm in size (see Table 6.3). All three phases are calcite, as confirmed via GADDs (see Table 6.5), and were uncommonly found to host hydrocarbon-bearing inclusions (as identified with UV microscopy). Division into three phases of blocky spar was based upon the spar's relationships with other fabrics, fractures and the basic geological rule of cross-cutting relationships, as well as their characteristic CL colours.

Blocky spar 1 (Event 12, Sp1) is the major variety of late stage spar found in the samples. It continued to precipitate over an extended period of time, as alluded to by the multiple layers of blocky spar 1 that were common in large cavities and veins (Figs. 6.9E-F and 7.20). The concentric to oscillatory zonation commonly seen within individual calcite crystals under CL (Fig. 6.10) indicates that the system experienced far from equilibrium conditions, and that (slight) changes in fluid composition were occurring over a relatively short time-scale (Pagel *et al.* 2000).

For a short period of time, fluid composition was significantly altered to result in the precipitation of a late silica phase (Event 13, Si3). This silica, found only in thin sections from Ngawaka, is given its position in the paragenetic sequence based on its formation only upon blocky spar 1 (Sp1). Peckmann *et al.* (2002) suggested that authigenic quartz formation can be associated with igneous intrusions, although such an association is unlikely in the current study. However, a silica source from scattered silicic tephras within the Miocene sediment pile itself is a possibility (Field *et al.* 1997).

A third phase of fracturing and significant corrosion (Event 14, F3) occurred after the precipitation of blocky spar 1. This event opened up further pore space (thin veins and small fenestrae) and provided new surfaces for corrosion and eventual precipitation of blocky spar 2 (Event 15, Sp2) (Figs. 6.9, 7.21). The final two events of the paragenetic sequence were a fourth fracturing/corrosion event (Event 16, F4) which often resulted in creation of new surface areas for the precipitation

of blocky spar 3 (Event 17, Sp3). Consequently, this fabric occurs in veins and cavities which cross-cut and/or post-date all other fabrics (Figs. 6.9, 7.21, and 7.22).

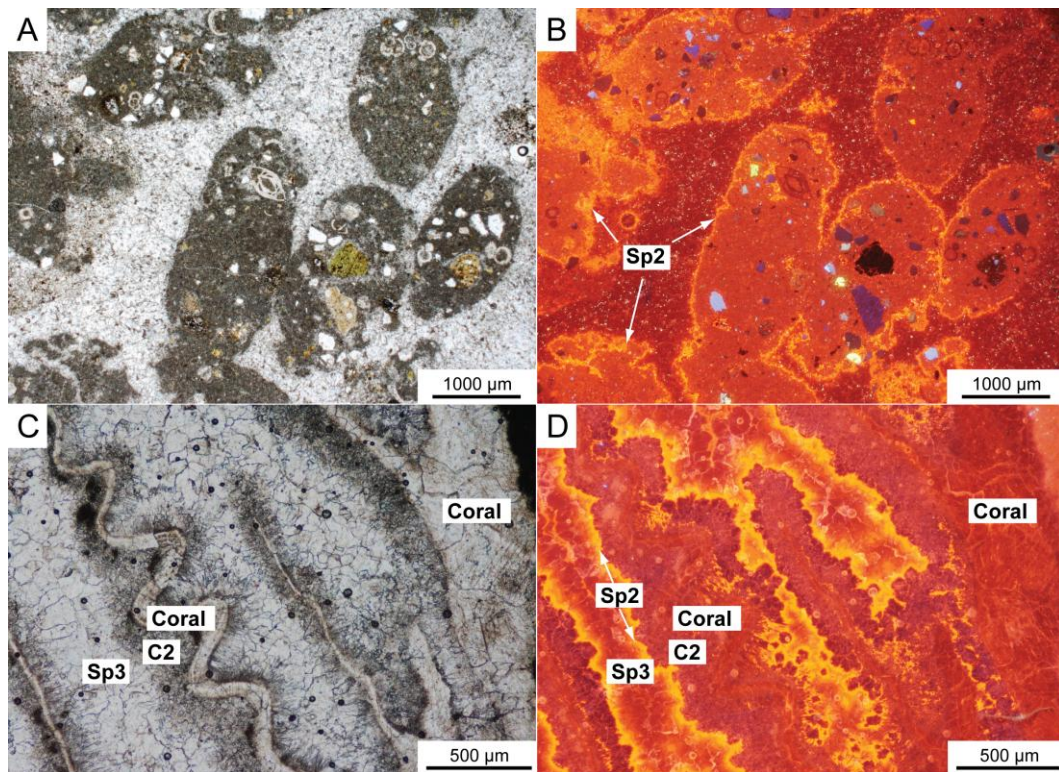


Figure 7.21 – Photomicrographic pairs of images under PPL and CL, respectively. **Images A and B:** Corrosion around peloid margins has allowed precipitation of blocky spar 2 (Sp2). This is not visible in PPL, however, the bright yellow colour of this fabric under CL is very obvious. Thin section WA.3B.1 from Wanstead. **Images C and D:** An array of cements has precipitated around the inner septa of a coral in thin section WA.13.1.1B from Wanstead. The first to precipitate was aragonitic acicular cement (C2), which can be seen to contain hydrocarbon-bearing inclusions in PPL and UV. This was followed by blocky spar 2 (Sp2), with bright yellow CL colours. The last phase of mineralisation, in the centre of the coral, is a blocky spar with an orange to maroon CL colour. This fabric is blocky spar 3 (Sp3), which has formed after Sp2.

A paragenesis example

A sample from Ngawaka (NG.M7; Fig. 7.22) can be used to support the relative ordering presented in the paragenetic sequence given in Figure 7.15. It illustrates many of the early and late spar phases, and gives insight into the ongoing fracturing which must have been occurring to create the often rather complex relationships among the various fabrics. The different fabrics present can be

identified based on their PPL and CL characteristics (Fig. 7.22). The events required to develop this series of fabrics are:

1. Precipitation of aragonitic micarb (M1).
2. Fracturing (F1) to create new internal surfaces for step 3.
3. Precipitation of fibrous cement (C2) in the thin, diagonal vein.
4. Burial, which resulted in neomorphism of micarb (M1) into pseudo-micarb (PM) and earlier fibrous cements into pseudo-cement (PC).
5. Fracturing (F2).
6. Precipitation of blocky spar 1 (Sp1a) into thin, diagonal vein created in step 5.
7. Fracturing (F2).
8. Blocky spar 1 (Sp1b) precipitated into a thin vein formed in step 7, cross-cutting the spar-filled vein of step 6.
9. Further fracturing (F2) of above vein.
10. A second phase of blocky spar 1 (Sp1c) with a larger crystal size precipitated along one side of the vein formed in step 7.
11. The system remained dormant for an unknown period of time. This is inferred by the lack of blocky spar 2 (Sp2) in this thin section. Once the system resumed seepage, the pore fluid chemistry changed somewhat.
12. Fracturing (F2).
13. Blocky spar 3 (Sp3) precipitated in multiple veins which were created in step 12. Events 12 and 13 repeat numerous times, resulting in the many thin veins containing blocky spar 3 (Sp3).

7.6 SYNTHESIS

A combination of field observations and results from the laboratory analyses of samples allows elucidation of the individual formational history of each of the five study sites. Many sites appear to have undergone specific, and often unique, processes which have led to the particular mineralogical and geochemical characteristics seen at each site. This section reviews data and observations on a site by site basis, endeavouring to highlight particularly important episodes and processes that have occurred during the lifespan of each site's deposits.

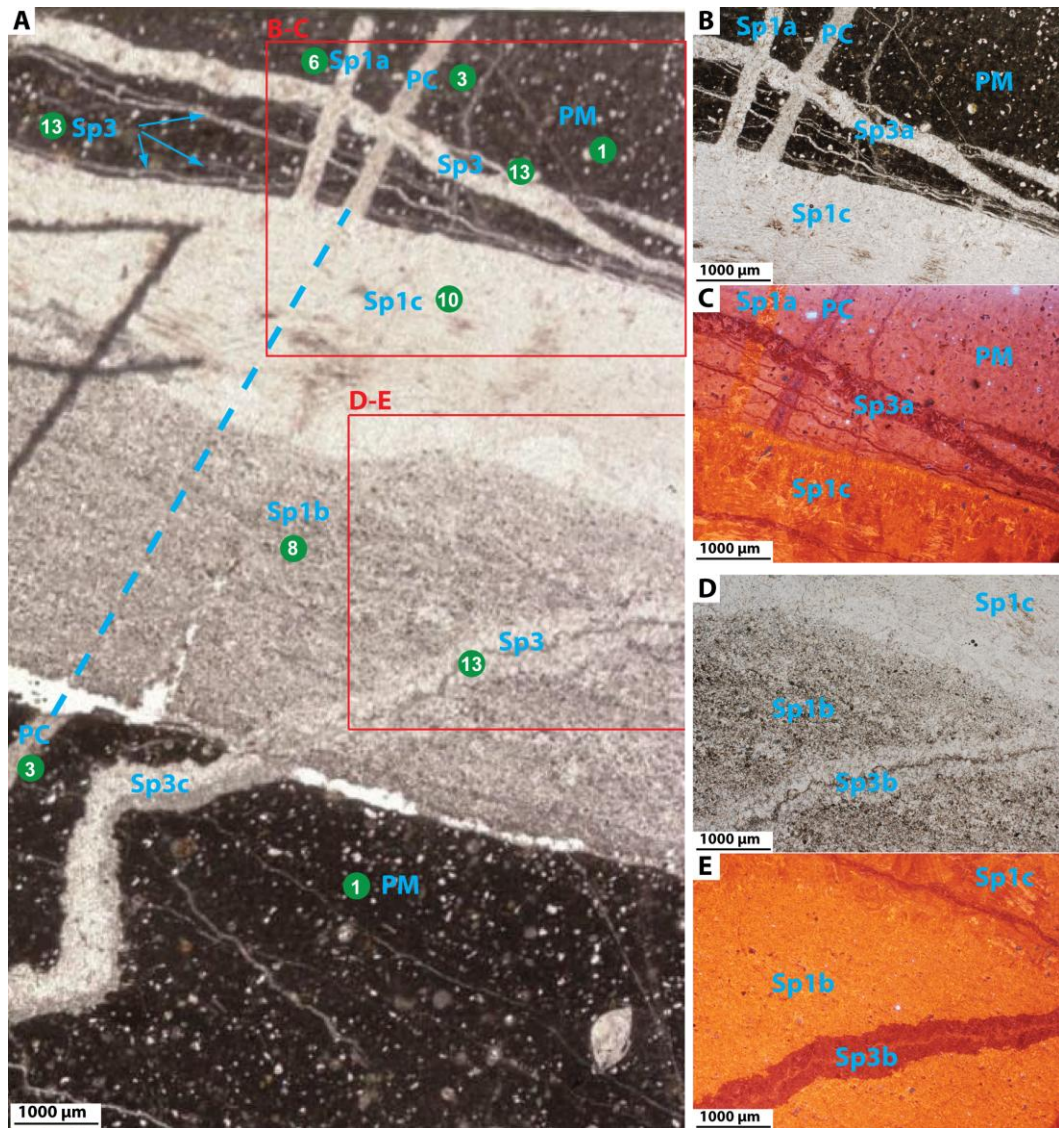


Figure 7.22 – Part of a thin section scan and two photomicrographic pairs under PPL and CL of thin section NG.M7 from Ngawaka. These images support the ordering of the paragenetic sequence of events (green-circled numbers) and give insight to the amount of fracturing and precipitation which has occurred to result in such a mosaic of fabrics. Red boxes indicate positions of images B-C (PPL and CL, respectively) and D-E (PPL and CL, respectively). Fabric codes are defined in Fig. 7.15.

7.6.1 Wanstead

At a slab scale it is evident that the seep carbonate environment which gave rise to the deposits at Wanstead was relatively mature. The dominant facies of the site include many containing abundant intraclasts (Table 6.1), indicative of prolonged physical disturbance to the seep deposits as they sat in the (near) seafloor environment (Event 2, Fig. 7.15). The biota identified in the samples is relatively diverse – many species were able to colonise the site over its time spent on/near

the sea floor. This includes coral species and borings, indicating that the deposits spent considerable time exposed on the seafloor, acting as hardgrounds. The presence of the carbonate boulders at the sediment surface could be due to erosion or environmental conditions allowing MDAC formation in contact with the open water (i.e. an anoxic water column).

The mineralogy of the samples is dominated by LMC, with minor aragonite (Table 6.4); however, this mineralogy only implies thorough neomorphism of minerals in the burial realm rather than indicating it was the primary mineralogy of precipitants on the seafloor. Total carbonate values ranging from 86-93% indicate that some samples contain a significant amount of siliciclastic material. The lack of multiphase sequences of early cements (see Section 7.2.3) at this site suggests that the seep carbonate environment was driven by a steady, diffuse flow of hydrocarbon-charged fluids from the subsurface. This is also supported by the lack of *Bathymodiolus* mussels, which are well known to inhabit areas of high fluid flux (Barry *et al.* 1997). Additionally, UV microscopy confirms the presence of hydrocarbon-bearing inclusions within sparry fabrics (Fig. 6.11F), with organic carbon contents ranging from 0.07 to 0.10% (Table 6.7).

The source of carbonate carbon for Wanstead cold seep deposits is highly likely to be thermogenic methane, based on the moderate depletion of $\delta^{13}\text{C}$ in the samples (Judd & Hovland 2007). It is possible, but less likely, that some of the more negative $\delta^{13}\text{C}$ values could in fact be sourced from microbial methane which has been oxidised to give a heavier $\delta^{13}\text{C}$ value indicative of thermogenic methane (Fig. 7.9). Some samples show a small influence by either methane pool oxidation or marine water to result in slightly elevated $\delta^{13}\text{C}$ values. The $\delta^{18}\text{O}$ value of the single aragonite sample (WA.18) has precipitated just outside of equilibrium with sea water (Fig. 7.9). This could be due to a slight increase in the fluid temperature, a result of mixing with meteoric water, or due to contact with upwardly advected (warm) burial fluids.

The slightly negative $\delta^{18}\text{O}$ values of many of the neomorphosed fabrics (pseudomicarb and pseudo-cement – events 9 and 10, Fig. 7.15) indicate minimal alteration in the burial realm, or alteration in a shallow environment. A single

blocky spar fabric indicates precipitation of late calcites in a deeper burial environment through its very negative $\delta^{18}\text{O}$ value ($<-5\text{‰}$).

7.6.2 Ugly Hill

Lipid biomarkers confirm that these outcrops have indeed formed based on AOM and sulphate reduction (Table 6.10). The spread of outcrops over such a large area (the site contains three sub-sites, see Section 5.3) implies that this was a large seepage field in the Early Miocene. The array of facies throughout the site (Table 6.1) and their often chaotic intermingling (see Section 5.3) indicate varying fluid fluxes and processes operating across the paleo-seep environment. Figure 7.2 highlights the areas of advective fluid flow, while the outcrops hosting lucinid and vesicomyid bivalve fossils suggest areas of diffuse fluid flow. The presence of *Bathymodiolus* mussels, in particular abundance at outcrop UH.E, indicates that at least some of the Ugly Hill deposits spent time exposed on the seafloor, as this taxa requires a hardground on which to anchor.

XRD analysis also strengthens the inferred localities of high fluid flux, as samples from these outcrops retain a significant amount of aragonite (Table 6.4). Additionally, carbonate percentage data gave very high readings (up to 100% carbonate, Table 6.7) for some of these samples, adding to the likelihood that they were derived from conduits or chimneys which form with high fluid flux and receive little siliciclastic input. However, most samples were dominated by LMC, due to alteration of much of the early cement during burial diagenesis, and had lower total carbonate percentages due to their siliciclastic content.

XRD also revealed that two samples contain a significant amount of dolomite (see Table 6.4). Dolomite typically precipitates in restricted environments with an abundance of magnesium (Cavagna *et al.* 1999), such as in sediments at depth below the seafloor. Some carbonate deposits may have formed deep enough within the sediments to reach the zone of dolomite precipitation. Alternatively, this dolomite could have formed due to an excess of magnesium in pore fluids during burial diagenesis.

The $\delta^{13}\text{C}$ values of the Ugly Hill samples cover a large spread (Fig. 7.10), many of which are considerably negative, $<-20\text{‰}$, and have likely sourced their carbon from thermogenic methane (Judd & Hovland 2007). As with some of the Wanstead samples, it is possible that there has been a small influence from marine water and/or oxidation of the methane pool (Whiticar 1999). Most of the aragonite precipitated in the seafloor environment is likely to have formed contemporaneously with a local gas hydrate dissociation event which causes pore water to become enriched with ^{18}O , or have formed from fluids with enriched $\delta^{18}\text{O}$ values due to the dehydration of clay minerals in the subsurface (Dahlmann & de Lange 2003).

The $\delta^{18}\text{O}$ values of neomorphosed fabrics indicate that this site has undergone the least amount of diagenetic alteration of the five study sites. This is implied by the bulk of neomorphosed samples having positive to slightly negative $\delta^{18}\text{O}$ values – samples typically pick up increasingly negative $\delta^{18}\text{O}$ values during burial diagenesis. The abundance of veins containing late cements found throughout many of the outcrops hints at a significant amount of physical disturbance and fracturing of deposits once they had left the seafloor environment.

7.6.3 Ngawaka

Similar to outcrops at Wanstead, the lack of multiphase sequences of early cements (see Section 7.2.3) and *Bathymodiolus* mussels indicates that the seep carbonates of Ngawaka formed under diffuse fluid flow conditions (Barry *et al.* 1997; Conti & Fontana 2002). The $\delta^{13}\text{C}$ values of Ngawaka samples are clustered relatively high on the isotope cross-plot (Fig. 7.11) – they are enriched in the heavier ^{13}C isotope. This implies that the hydrocarbons contained within the fluids supporting this paleo-seep site are likely to have undergone thorough oxidation of the methane pool or extensive mixing with marine water and organic carbon on their journey up to the seafloor environment, as earlier mentioned (see Section 7.4.5). The large size of the Ngawaka West outcrop NG.A (the largest intact outcrop of this study) hints at this diffuse fluid flow being broadly steady over many tens of thousands of years (see Section 7.5.1; Luff *et al.* 2004).

The lack of positive relief on many of the Ngawaka East and West outcrops (Peckmann *et al.* 2001b), coupled with total carbonate values averaging 84% indicating that many samples contain a significant volume of siliciclastic material, points towards deposits having formed in the shallow subsurface. These samples could possibly have precipitated as HMC (Peckmann *et al.* 2001b); however this cannot be confirmed due to the complete alteration of all carbonate fabrics to LMC.

Despite the diffuse fluid flux and extremely steady/long-lived seepage, fluctuations in environmental conditions can be acknowledged at Ngawaka. Outcrop NG.A exhibits lithological variations stratigraphically up the major outcrop face (see Section 5.4.1), including changes in texture and fossil content. This is reflective of the dynamic state of the fluid flux reaching these sites, which impacts many geochemical and biotic processes occurring. Additionally, lipid biomarkers confirm that these outcrops have indeed formed based on AOM and sulphate reduction (Table 6.10).

XRD shows that the carbonate within the samples is completely dominated by LMC. Coupled with the $\delta^{18}\text{O}$ values of Ngawaka samples, it is obvious that the seep carbonate deposits of this site have undergone extensive burial alteration (events 9 and 10, Fig. 7.15) – in fact Ngawaka contains the most altered samples of this study. This statement is supported by the anomalously negative $\delta^{18}\text{O}$ values (Fig. 7.11) exhibited by the samples, which have come about due to remineralisation in the burial realm that allows the new minerals (LMC) to adopt the depleted $\delta^{18}\text{O}$ value of the burial environment (Mozley & Burns 1993). The lack of any other carbonate phases (aragonite, HMC, and even dolomite) implies that neomorphism of early fabrics was thorough. Additionally, the latest calcite cements to precipitate in the burial realm have increasingly negative $\delta^{18}\text{O}$ values, implying precipitation at even greater depths than where neomorphism was taking place.

7.6.4 Haunui

As earlier described (see Section 7.2.5), the seep carbonate outcrops at Haunui have formed over two separate stages, likely due to temporal changes in the fluid

flux of the once-active seep. This resulted in the formation of two horizons of seep carbonate mounds encased in the host mudstone. On a smaller scale, similar variations in fluid flux have led to textural and biological changes stratigraphically up outcrop HA.D (see Section 5.5.1). Extensive or long-lived physical disturbance to the seep environment occurred (event 2, Fig. 7.15), hinted at by the abundance of intraclasts and veins within the samples (Table 6.1). Additionally, it is possible that many of these deposits have formed in the shallow subsurface, as suggested by the low carbonate values exhibited by many samples (ranging from 68-82% carbonate, Table 6.8) and obviously high siliciclastic content as noted during PPL petrography. In contrast, the presence of scattered coral (caryophylliids) in some outcrops indicates time spent exposed on the seafloor as a hardground.

All of the Haunui samples have low $\delta^{13}\text{C}$ values (Fig. 7.12). These samples have carbon sourced from thermogenic methane, perhaps with small influences acting to slightly increase the $\delta^{13}\text{C}$ values (see Section 7.4.6) (Judd & Hovland 2007). Organic carbon ranges from 0.07–0.12%, lipid biomarkers confirm that these outcrops have indeed formed based on AOM and sulphate reduction (Table 6.10), and hydrocarbon-bearing inclusions have been identified in blocky fabrics via UV microscopy.

The neomorphosed fabrics show a progressively more negative trend (orange circle in Fig. 7.12) which is a result of remineralisation in the burial realm to inherit a $\delta^{18}\text{O}$ value from the new burial environments (Mozley & Burns 1993). This results in a range of data points with increasingly negative $\delta^{18}\text{O}$ values that correspond to warmer burial fluid temperatures. The blocky spars (circled in black in Fig. 7.12) have precipitated at the deposit's greatest burial depth as indicated by their highly negative $\delta^{18}\text{O}$ value.

7.6.5 Wilder Road

Outcrops of Wilder Road are all accumulations of mainly small to medium sized boulders scattered over more than 1 km of gently rolling hills (see Section 5.6). Lithological evidence points to areas of diffuse and advective fluid flow, with multiple chimney/conduit features proposed (Fig. 7.2). Of particular importance,

this site hosts no fossilised macrofauna of the paleo-seep environment. As mentioned earlier (see Section 7.2.5), this could be due to a number of possible scenarios: (a) this seep system was very immature, with insufficient time to allow colonisation by macrofauna; or (b) these deposits formed at shallow depth within the sediment, away from the zone inhabited by seep taxa. The lack of siliciclastic material seen in PPL petrography and the high carbonate content of the samples (93-99% carbonate) points to the former; however, more direct evidence is needed to form a positive conclusion.

The $\delta^{13}\text{C}$ values of Wilder Road samples have the largest range of the five study sites (Fig. 7.13). The values at the lower end of the range are sourced from thermogenic methane, with higher values likely to be affected by methane oxidation or mixing with marine water. Alternatively, samples with the highest values ($>+5\text{‰}$) could possibly have carbon sourced from residual CO_2 (Whiticar 1999). Lipid biomarkers confirm that these outcrops have indeed formed based on AOM, sulphate reduction, and also possibly aerobic oxidation of methane (Table 6.10), and UV microscopy reveals abundant hydrocarbon-bearing inclusions are housed within the fabrics of these samples (Fig. 6.11). The $\delta^{18}\text{O}$ values for primary aragonite fabrics indicate either a slight increase in water temperature or a prolonged period of gas hydrate formation to deplete pore waters of ^{18}O (cf. Bohrmann *et al.* 1998).

$\delta^{18}\text{O}$ values of the pseudo-micarb and pseudo-cement fabrics are increasingly negative, likely due to neomorphism in progressively deeper and warmer environments in which they adopt the local $\delta^{18}\text{O}$ value (Mozley & Burns 1993). This neomorphism is somewhat extensive, with most fabrics now altered to LMC (Table 6.4).

7.7 COMPARISON WITH ITALIAN SEEP CARBONATE DEPOSITS

The Early Miocene seep carbonate deposits of southern Hawke's Bay, New Zealand, have a number of often striking similarities with the Miocene deposits of the Italian Apennines. Firstly, they share a similar age; deposits of this study are of Early Miocene age, with those in the Apennines of Middle to Late Miocene age (Ricci Lucchi & Vai 1994). Both groups of cold seep deposits formed in fine-

grained sediments: New Zealand deposits are hosted within calcareous slope mudstones; Italian deposits are found within marly and clayey hemipelagites and fine grained turbidites (Conti & Fontana 2005; Conti *et al.* 2007). Migration of the fluids which drove the paleo-seeps was, in both settings, initiated due to convergence (see Chapter 3; Conti & Fontana, 2005). Isotopic evidence at both settings points to a methane-related origin for the carbonate carbon (Clari *et al.* 1994; Conti *et al.* 2008).

Lithologically, the deposits also exhibit similarities. Throughout the southern Hawke's Bay deposits there are a multitude of facies (see Section 6.2), which are often chaotically intermingled and can vary between sites, outcrops, and even throughout a single boulder. Conti & Fontana (2005) identified 17 facies over the Apennine deposits which vary in aspects such as grain size, (trace) fossil content, degree of brecciation, and vein content. Similarities in these lithologies include brecciated fabrics, thick sequences of early aragonite cements, peloidal fabrics, dense networks of anastomosing carbonate-filled veins, cavities featuring polyphase infillings, and chaotic mixing of lithologies at an outcrop scale (Conti & Fontana 2002, 2005; Conti *et al.* 2008). Additionally, features of the Italian deposits such as flank breccias and conduit structures are akin to some ancient seep carbonate deposits in the northern East Coast Basin (Collins 1999; Conti & Fontana 2005; Conti *et al.* 2007; Campbell *et al.* 2008; Nyman 2009).

Fossil content can be compared between the sites, with both sets of seep carbonate deposits hosting lucid and vesicomid bivalves often in dense accumulations, modiolid mussels, burrows and other evidence of bioturbation (Clari *et al.* 1994; Conti & Fontana 2002, 2005).

CHAPTER 8

Conclusions

8.1 OVERVIEW

This study has focused on five sites of seep carbonate outcrops in southern Hawke's Bay, onshore East Coast Basin, New Zealand, namely at Wanstead, Ugly Hill, Ngawaka, Haunui, and Wilder Road. These are ancient seep carbonate outcrops, hosted within Early Miocene calcareous mudstones of the Ihungia Formation (Reid 1998; Campbell *et al.* 2008). They are situated within the accretionary wedge setting of the convergent Hikurangi Margin (Fig. 3.1), where there is known to be a sizable field of modern cold seeps and associated carbonate deposits, in addition to a vast gas hydrate province (Lewis & Marshall 1996; Henrys *et al.* 2009; Barnes *et al.* in press; Campbell *et al.* in press).

Aims of this study were to document the field nature and distribution of the five sites and their outcrops, to determine the minerals present and characterise the petrographic fabrics observed, to carry out a variety of geochemical analytical techniques to identify processes which may have affected the deposits, and ultimately to unravel the complex evolution of the ancient cold seep carbonates by means of a paragenetic sequence. Field work included lithological descriptions, (trace) fossil identification, mapping, stratigraphic logging, and extensive sampling (Chapter 5; see Appendix 2 for sample list). Laboratory analyses included plane polarised light (PPL), cathodoluminescent light (CL), and ultraviolet (UV) light petrography, scanning electron microscopy, bulk mineralogy via X-ray diffraction (XRD), component specific mineralogy by general area detector diffraction (GADD), stable $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ analysis, carbonate percentage, total organic carbon (TOC), and lipid biomarkers (Chapter 6).

This chapter gives concluding remarks on the patterns and processes identified through discussion of the results (Chapter 7). Trends across the five seep sites are summarised, along with overall formation mechanisms, processes, and products.

8.2 EVIDENCE TOWARDS SEEP ORIGIN

The methane-related origin of these deposits is confirmed by a number of evidential factors which can be identified at the outcrop/slab scale, through petrography, and via geochemical and isotopic analysis. These include:

1. Lipid biomarkers. These confirm the presence of microbes which carry out AOM and sulphate reduction (see Section 6.11), the two major biogeochemical processes which drive MDAC precipitation at cold seep sites.
2. The very patchy occurrence of the outcrops and limited lateral extent (Chapter 5) indicates an unusual process has taken place in restricted areas of the paleo-East Coast Basin. This reflects the formation based upon the focused expulsion of hydrocarbon-charged fluids on the sea floor, with carbonate cementation of the host formation laterally restricted by proximity to the seep site (and thus chemosynthetic microbes) and stratigraphically by the longevity of the seep.
3. The complex intermingling of authigenic fabrics, fractures, and cavities is recognisable at both outcrop and microscopic scales. These polyphase cements record the dynamic fluid flux and geochemical changes which occurred in the paleo-seep environment, with phases of fracturing resulting from blockage of the fluid conduits and/or dramatic increases to the fluid flux.
4. The dominance of authigenic micro-crystalline carbonate cements (micarb) which have precipitated throughout the host formation (see Section 6.3). These are dominantly composed now of low magnesium calcite (LMC) which has probably originated from the alteration of an original aragonite (and possibly high magnesium calcite) mineralogy. Also included are some aragonite, and minor dolomite and silica. There are many cavity filling cements, observed in a variety of morphologies, all of which differ significantly from the surrounding mudstone strata.
5. The abundant remains of chemosynthetic communities. All of the species present have been identified within other ancient cold seep deposits worldwide, and many are similar to, or in the same family as, species reported at modern seeps (Sibuet & Olu 1998; Campbell 2006).

6. Isotopic results reveal depleted $\delta^{13}\text{C}$ values (see Section 6.9) characteristic of seep carbonate deposits (Roberts *et al.* 1993; Campbell *et al.* 2002). The bulk of the $\delta^{13}\text{C}$ values are below -20‰, which is indicative of carbonate carbon sourced from thermogenic methane (Judd & Hovland 2007).

8.3 OUTCROP FORMATION

The development history of the seep carbonate deposits of southern Hawke's Bay, from fluid source to seep, has been discussed in Chapter 7. The source of the fluids and their likely migration paths has been inferred through isotopic data and the regional and stratigraphic positioning of the carbonate deposits, and two phases of diagenesis have been proposed - an early phase which takes place at or near the sediment-water interface of the deep marine environment, and a late diagenetic phase which occurs during burial of the deposits. The processes and products of these formational phases are outlined in this section.

8.3.1 Subsurface fluid migration

Cold seep systems are initiated by the onset of fluid migration from the subsurface to the seafloor environment. They are generated at various depths in the subsurface and must migrate from their source formation or storage reservoir up to the sea floor to produce a seepage area.

The migration of fluids is dynamic and dependent on, among other things, the availability of migration pathways. Dispersed fluid flow in the shallower sediments (due to increased pore space) results in a scattering of deposits, which is seen over much of the field area by the distances between outcrops and sites (Chapter 5). Additionally, outcrop NG.A at Ngawaka West gives a seepage time period of many tens of thousands of years, based on the large size of the deposit and MDAC precipitation models by Luff *et al.* (2004).

The regional stratigraphy and structure of the southern Hawke's Bay region allow little inference as to the pathways which hosted the fluids resulting in the seep carbonate deposits. There are numerous strike-slip and thrust faults in the region

(see Chapter 3, Fig. 3.5); however, there is no direct evidence of an ascending pathway via faults in close proximity to each of the ancient seep carbonate outcrop occurrences. The basal unconformity of the Ihungia Formation (which hosts the seep carbonate deposits) could possibly have acted as an important fluid migration pathway, directing fluids towards the East Coast Basin paleo-seafloor (D. Francis, *pers. comm.* 2009).

The methane within the fluids is dominantly sourced from a thermogenic methane pool. This is drawn from the stable $\delta^{13}\text{C}$ values of the seep carbonates (see Section 6.9), the bulk of which are from -20 to -30‰. Slightly enriched ^{13}C values of the fluids reaching some sites (Ugly Hill, and particularly Ngawaka and Wilder Road) are likely due to influence from marine water and/or oxidation of the methane pool (see Section 7.4.1). Significant enrichment of stable $\delta^{13}\text{C}$ values is seen within some samples from Wilder Road (Fig. 7.13) and may be sourced from residual CO_2 .

Stable $\delta^{18}\text{O}$ values of MDAC give a general indication of the water temperature and origin at the time of formation (Greinert *et al.* 2001; Judd & Hovland 2007). Results from the southern Hawke's Bay seep carbonate samples (see Section 7.4) indicate that numerous processes have affected the $\delta^{18}\text{O}$ values of the fluids. These include: (a) warm fluids due to either a rapid ascent to the seafloor or contact with upwardly advected (warm) burial fluids (Wanstead, Haunui); (b) mixing with meteoric water (possibly Wanstead and Ngawaka); (c) formation contemporaneous with local gas hydrate formation (Ngawaka, possibly Wilder Road) or dissociation events (possibly Ugly Hill); (d) influence from fluids with enriched $\delta^{18}\text{O}$ values due to the dehydration of clay minerals in the subsurface (possibly Ugly Hill) (Dahlmann & de Lange 2003); and (e) the recrystallisation of unstable minerals in the burial realm (all sites) (Allan & Matthews 1977).

8.3.2 Early diagenesis

With fluids reaching the seafloor environment came colonisation by a suite of chemosynthetic microbes (methane oxidisers and sulphate reducers) and the precipitation of authigenic carbonates (Judd & Hovland 2007). There are multiple phases of early carbonate cements which took on a variety of crystal habits such

as microcrystalline, fibrous, equant, and anhedral forms (see Section 6.3). Alternations between precipitation of these cement varieties is due to slight biogeochemical changes throughout the seep (micro)environments, which affect the fabrics precipitating.

These early carbonate cements initially formed as aragonite due to the high sulphate, low phosphate, and low magnesium conditions of the (near) seafloor environment (Greinert *et al.* 2001; Peckmann *et al.* 2001). It is possible that some of these deposits may have formed as high magnesium calcite (HMC); however, if this is the case, there is no longer any evidence of this mineralogy due to later alteration of this metastable carbonate phase. A few sites contain some dolomite (Haunui and Ugly Hill; Table 6.4), which could reflect formation slightly deeper in the sediments bordering the zone in which dolomite can precipitate (low-sulphate/high-phosphate anoxic environments with a high Mg/Ca ratio; Greinert *et al.* 2001). Also, minor siliceous phases formed as an early cement at each site, with Miocene tuff beds within the host mudstones a possible silica source (Field *et al.* 1997).

Physical disturbance to the deposits on the sea floor resulted in fracturing and brecciation of deposits, extensive in some areas (e.g. Wilder Road, Facies W.F2, Chapter 5). Additionally, corrosion, likely due to the local generation of sulphuric acid produced during sulphide oxidation by thiotrophs, slowly dissolved impermeable aragonite surfaces (Cavagna *et al.* 1999).

Lithologies and morphologies of the deposits are seen to be related to fluid flux, with multiphase sequences of early cements found in conduits/chimneys with advective flows, and diffuse seepage marked by lenses and mounds dominated by micarb. Biota are also zoned around and stratigraphically up deposits, largely based on fluid flux (e.g. species such as *Bathymodiolus* mussels and siboglinid tube worms thrive in advective areas of the seep; Campbell *et al.* in press), but also on niche requirements such as hardgrounds (e.g. coral species and *Bathymodiolus* mussels) and softgrounds (lucinid bivalves).

8.3.3 Late diagenesis

After initial formation at the (near) seafloor, the deposits eventually became buried by the host and other post-Miocene formations. In the burial realm extensive neomorphism took place, altering the metastable aragonite (and possibly HMC) into LMC. These new cements are termed pseudo-micarb and pseudo-cement (see Sections 6.3.8, 6.3.9).

Additionally, new minerals precipitated in the burial realm due to calcium-saturated pore waters. A suite of blocky spar fabrics formed, with equant, dentate, and rhombohedral crystal habits. Zoning within crystals (see Section 6.3.10) reflects the constantly changing pore-fluid chemistry. It is also possible that minor dolomite formed in the deposits at Haunui and Ugly Hill, due to a high Mg/Ca ratio of the burial environment. Fracturing of the deposits during burial provided many new surfaces for these mineral phases to form upon.

8.4 CONCLUSIONS

1. Seep carbonate deposits of southern Hawke's Bay formed due to the migration of hydrocarbon-rich fluids from the subsurface to the sediment-water interface during the Early Miocene, causing the localised cementation of the host mudstone – the Ihungia Formation.
2. These ancient seep carbonates still contain traces (lipid biomarkers) of the chemosynthetic microbes which drove MDAC precipitation.
3. Deposits are dominated by carbonate (>68% CaCO_3), and can be classed as limestones. Based on the modified limestone classification scheme of Dunham (1962) these carbonate deposits comprise floatstones, mudstones, and wackestones.
4. The seep carbonate deposits are today seen as weathered groups of boulders, often with individual boulders >2 m in size. These groups, or outcrops, are typically separated from one another and scattered over small fields (each field comprising a site or sub-site). Many outcrops have associated 'float' zones of

repositioned boulders, chiefly a result of host mudstone erosion, local geologic structure, or quarrying.

5. Deposits encompass abundant fossils of seep-related macrofauna – remnants of the paleo-seep environment. These biota are zoned, largely based on fluid fluxes and species niches.

6. The boulders are lithologically complex, so that there are a multitude of facies identified in the field and in slabbed samples. These facies are often chaotically intermingled, and some can also be related back to aspects of the paleo-seep environment, such as fluid flux and biota distribution.

7. The seep carbonate deposits formed over two major diagenetic stages. Initially, they likely precipitated as aragonite at the (near) seafloor environment. With burial came alteration resulting in neomorphism of the metastable aragonite into LMC. Additionally, the later mineral phases formed in the burial environment were calcitic (LMC).

8. Minor dolomite and silica phases are also present in the deposits, although their timing and formational mechanisms are presently uncertain.

9. Stable $\delta^{13}\text{C}$ isotopic analysis shows the carbonate carbon was largely sourced from thermogenic methane, with minor influences from marine water, methane pool oxidation, and residual CO_2 .

10. Stable $\delta^{18}\text{O}$ isotopic analysis indicates that numerous processes have affected the fluid supply to the deposits. This includes warmer fluids, mixing with meteoric water, formation contemporaneous with local gas hydrate formation and dissociation events, dehydration of clay minerals, and the recrystallisation of unstable minerals in the burial realm.

8.5 RECOMMENDATIONS FOR FUTURE RESEARCH

This research has given a greater insight to, and understanding of, the processes that form seep carbonate deposits. The results of this study can be applied and compared to other New Zealand and international ancient cold seep deposits. In

light of the findings of this study and its limited scope, some recommended research aspects are highlighted:

- Detailed elemental analysis via laser ablation or microprobe to determine the composition of specific fabrics would aid the recognition of primary and secondary minerals and provide insights into the degree of neomorphism that a fabric has undergone.
- Further stable isotope data for a larger suite of minerals would allow for better recognition of processes that the ancient seep deposits have undergone. In particular, data for non-carbonate minerals such as pyrite (e.g. $\delta^{34}\text{S}$ values) could help source the sulphide (?bacterial sulphate reduction), and historical methane fluxes to the seep environment could be revealed by $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of benthic foraminiferal tests.
- Analysis of the hydrocarbon-bearing fluid inclusions found within many of the carbonate phases would be highly beneficial in determining the exact source and nature of the primary methane-rich fluids.

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APPENDIX 1

Field Information

APPENDIX 1.1

Additional descriptions, location data, and land owner details for the 16 known ancient seep carbonate sites in the onshore East Coast Basin.

Table A1.1 – Grid references (NZMS260 map number and NZMG northing and easting), brief descriptions, and land owner details (where known) for the 16 East Coast Basin ancient seep carbonate sites.

Site	Grid reference	Nature/description	Landowners
Bexhaven	Y16 2955810E 6333237N	Scattered boulders on left hand side of road. Common marble cake texture, plus fossil beds.	N/A
Karikarihuata Stream	Y16 2965700E 6335100N	Large carbonate mound high on cliff, with mudstone & carbonate beds upstream.	Forest Block managers: Leigh & Sheree Phillips, Gate - 56.5 km along road.
Moonlight North	Y16 2943343E 6314003N	Large volume of material, 2 main sites. Outcrop < 10 m thick. Micritic marble cake, plus fine micrite dominates. Old fossil beds.	Olsen Forestry 06-8685426, 396 Childers Rd, Gisborne.
Puketawa	Y16 2955655E 6320635N	A large (1.8 m) boulder. Fossil-rich - includes Bivalvia (articulated mussels common), Gastropoda, and possible Scaphopoda.	Gisborne Port
Rocky Knob	Y16 2941200E 6310300N	Large amounts of Lst, varying facies. Cross bedding, plus several dominant fossil types. Largest outcrops in NZ.	Olsen Forestry 06-8685426, 396 Childers Rd, Gisborne.
Tauwhareparae	Y16 2946283E 6324166N	Carbonate underlain by plumbing tubes & host mudstone. Shows pervasive bioturbation, brecciation & fossil beds.	Scotty & Margo Wallace 06-8638944
Totaranui, upper Waian River	Y16 2960605E 6319160N	Several small outcrops of seep carbonate. Difficult access.	Olsen Forestry 06-8685426, 396 Childers Rd, Gisborne.
Turihaua	Y18 2958065E 6274500N	Small fossiliferous boulders.	Hamish & Angela Williams, 06-8688421

Waiapu	Z15 2991680E 6365369N	Described by McKay (1877) in passing as a limestone bearing similar fossils to Waipiro.	Unknown.
Waikairo	Y16 2960020E 6306500N	A single, large, block of carbonate. Micritic with yellow-orange weathering. Mussels observed.	Unknown.
Waipiro Stream	Z16 2976260E 6339430N	Large boulders of carbonate within 1 km either side of the stream. Fossil content of main site includes Modiolus, Gastropoda, and corals. Many local gas and brine seeps.	Unknown.
Haunui	U23 2807284E 6104438N	Large pine-covered hill. Abundant fossil material & burrows, siliciclastic rich facies with varying amounts of micritic cements.	James & Sue Hewett, 348 Epae Rd. 06-8554947
Ngawaka	U23 2804365E 6107214N	Several outcrops across 4 paddocks. Fossil material varies spatially. Main outcrop has undergone brecciation, veining seen throughout.	Ngawaka West: Richard Barrett, 06-8554846 Ngawaka East: Marcus & Jeanette Louisson, 06-8554738
Ugly Hill	U23 2809540E 6106608N	Small groups of boulders & associated float, & a quarry. Localised fossil accumulations. Some boulders exhibit many cement phases & vugs.	UH North: Tim & Maggie Simcock, 06-8554731. UH South: Paul & Kate Dearden, 72 Epae Rd, 06-8554878
Wanstead	U23 2813326E 6111126N	Strewn boulders right down through valley. Coral & bioclastic rich facies.	Tim Hodge, 2413 Porangahau Rd, 06-8554841
Wilder Road	U23 2806268E 6102668N	2 small zones of boulders throughout back paddocks, central oil seep. Boulders on ridge with associated float. Fossil barren, thrombolites abundant.	Wilder Rd North: Paul & Kate Dearden, 72 Epae Rd, 06-8554878. Wilder Rd South: Rod & Emma Bremmer, 06-8555370

APPENDIX 2

Sample Catalogue

APPENDIX 2.1

Full sample list of ancient seep carbonate samples from the five sites of this study (Wanstead – WA; Ugly Hill – UH; Ngawaka – NG; Haunui - HA; Wilder Road – W) with the field sample numbers used in this thesis, the corresponding University of Waikato sample numbers which are logged in the PETLAB database, facies codes (see Table 6.3 for code descriptions) and brief sample descriptions.

Running number	Field sample number	UoW number	Out-crop	Facies code	Sample description
1	WA-1A	20100200	WA.A	R2/Int,Vn,Vg	Coarse. Large corals. Gently dipping.
2	WA-1C	20100201	WA.A	R1/Int,Vg	Large vugs, fossils often fragmented.
3	WA-2A	20100202	WA.A	A1,2/Vn	Borings and spar filled vugs. Abundant corals.
4	WA-2B	20100203	WA.A	A1,2/Vn	Abundant corals, bivalves, borings.
5	WA-2C	20100204	WA.A	A1,2/Vn	Thick, sparry veins, vugs, and bivalve hash.
6	WA-2D	20100205	WA.A	A1,2/Vn	Corals. Spar-filled vugs.
7	WA-3A	20100206	WA.a	A6/Int,Vg	Dark micarb with large, light coloured intraclasts. Borings.
8	WA-3B	20100207	WA.a	R1/Int,Vn	Coarse. Large bivalves. Peloid-filled vugs.
9	WA-3C	20100208	WA.a	A1/Int,Vn,Vg	Veins, vugs, blue-grey patches.
10	WA-3D	20100209	WA.a	R1/Vg	Very coarse. Thin veins and vugs.
11	WA-3E	20100210	WA.a	A1/Int,Vg	Dark micarb with large, light coloured intraclasts. Borings.
12	WA-3F	20100211	WA.a	A1/Int, Vn	Bivalves, thick sparry veins.
13	WA-6B	20100212		~	Central blue-grey core. Small vugs.
14	WA-6C	20100213	WA.G	~	Ihungia host rock
15	WA-7A	20100214	WA.F	A6/Vn,Vg	Calyptogena, burrows, large bivalves.
16	WA-7B	20100215	WA.F	A1/Vg,Pe	Peloidal. Tiny bivalves.

17	WA-7C	20100216	WA.F	A1/Vn,Vg	Small bivalves. Thrombolites?
18	WA-7D	20100217	WA.F	A1/Vg	Fossils, burrows. Small, spar-filled vugs.
19	WA-7E	20100218	WA.F	A1/Vn	Pseudo-bedding.
20	WA-7F	20100219	WA.F	A3/Vn,Vg,Br	Veins, vugs, borings. Pseudo-bedding. Some thick sparry veins.
21	WA-8B	20100220	WA.B	A1/Vg,Br	Complex, mottled fabric. Beige and blue-grey.
22	WA-1E	20100221	WA.A	A1/Int,Vn	Fine intraclasts, large bivalves.
23	WA-13.1	20100222	WA.E	L2/Vn	Fine grained and coral-rich micarb.
24	WA-13.2	20100223	WA.E	L2/Vn	Fine grained and coral-rich micarb.
25	WA-13.4	20100224	WA.F	A1/Vg,Vn	Sandy micarb with rusty clasts. Sparry vugs.
26	WA-13.5	20100225	WA.a	A6/Int,Vn	Veined, stylo-bedded, intraclasts, thick veins.
27	WA-13.6	20100226	WA.a	~	Small paper bag of lucinid shell material
28	WA-13.7	20100227	~	~	Host Ihungia Fm.
29	WA.M1	20100228	WA.C	A5/Int,Vg	Large continuous worm tube. Coarse grained, abundant intraclasts.
30	WA.M2	20100229	WA.E	L2/Vn	Fine grained and coral-rich micarb.
31	WA.M3	20100230	WA.F	A1/Vg,Vn	Intermingling fine grained micarbs, a large crystal filled burrow.
32	UGL-1-5	20100231	UH.L	A4	Tubeworm rich.
33	UH-1A	20100232	UH.L	A1/Vn	Macro vesicomyids, thick veins. Oil smell.
34	UH-1B	20100233	UH.L	A1/Vn	Macro vesicomyids, thick veins. Oil smell.
35	UH-1C	20100234	UH.L	A6	Thick veins. Oil smell.
36	UH-1D	20100235	UH.L	A6,7/Vn,Pe	Sandy micarb with thick vein sequence and thrombolites.
37	UH-1F	20100236	UH.L	A1/Vn	Sandy micarb with thick sparry veins and bivalve hash.
38	UH-2A	20100237	UH.J	L6/Vn	Few bivalves & corals; weak oil smell. Float.
39	UH-2B	20100238	UH.J	A1/Int,Pe	Very patchy looking micarb, with burrows.
40	UH-2C	20100239	UH.J	A3/Vn,Int	Very patchy looking micarb, with burrows.
41	UH-2D	20100240	UH.J	A6/Vn,Int	Sandy, brown micarb with thick white veins.
42	UH-3A	20100241	UH.I	A6,7/Vn,Pe	Very thick vein sequence with white, p ink-grey, and thrombolite layers.

43	UH-4A	20100242	UH.C	L1,4/Vg,Vn	Brown micarb with abundant veins and sparry vugs.
44	UH-4B	20100243	UH.C	A1/Vn,Vg	Many different micarb fabrics, bioturbated?
45	UH-5A	20100244	UH.G	A1,4/Vg	Mussels and tubeworms. Often with sparry central mineralisation.
46	UH-5C	20100245	UH.G	A1,4	Mussels and tubeworms. Often with sparry central mineralisation.
47	UH-6	20100246	UH.A	L1	Bivalve hash.
48	UH-100.8	20100247	UH.a	A4,7/Pe,Vn,Vg	Dark micarb, brecciated, veined.
49	UH-100.9	20100248	UH.a	A1,4/Vg	Brown micarb, brecciated, veined, tubeworm rich.
50	UH-100.10	20100249	UH.A	A4	Sandy, wormtube rich.
51	UH-100.11	20100250	UH.A	A6/Vn	Small micritic vein.
52	UH-102.1	20100251	UH.E	A6	Beige, sandy micarb with fossils and veins.
53	UH-103.1	20100252		A1/Vn	1 large piece, bivalve-rich.
54	UH-104.1	20100253	UH.E	A6/Vn	Beige, sandy micarb with fossils and veins.
55	UH10.1	20100254	UH.a	A1,4/Vg,Vn,Pe	Blue grey and beige micarb, bivalve-rich with veins and spar-filled vugs.
56	UH10.2	20100255	UH.A	A1,2/Vn	Sandy micarb with shell hash.
57	UH10.3	20100256	UH.a	A1,4/Vn	Wormtube and bivalve rich.
58	UH10.4	20100257	UH.A	A1	Bag of bivalve fossils.
59	UH10.5	20100258	UH.a	A6	Sandy hostrock, orange oxidation rind? concretionary tube with radial fractures.
60	UH11.1	20100259	UH.E	A1,3/Vn,Vg,Pe	Sparry vugs and veins.
61	UH11.2	20100260	UH.E	A1,3	Micarb base overlain by MDAC fossil mat.
62	UH11.3	20100261	UH.E	A6	Stylo-bedded, creamy, sandy with dark rusty flecks + burrows. Gentle dip 064/20
63	UH11.4	20100262	UH.E	A1,4/Vg,Vn	Mussell and tubeworm rich MDAC.
64	UH11.5	20100263	UH.E	A3	Bag of burrows
65	UH11.6	20100264	UH.C	A3,4/Pe,Vg	3 large+ 3 small pieces of sparry eyed Lst.
66	UH.M1	20100265	UH.A	~	North host mudstone. Calcareous.
67	UH.M2	20100266	UH.K	~	South host mudstone. Massive, dark grey with tiny microfossils.
68	UH.M5	20100267	UH.A	A1,5	Tiny sample containing gastropod.

69	UH.M6	20100268	UH.H	L1/Vn	Macro vesicomyids, thick veins. Oil smell.
70	UH.M7	20100269	UH.H	L1/Vn	Macro vesicomyids, thick veins. Oil smell.
71	UH.M8	20100270	UH.F	A6/Vn	Sandy brown micarb with veins.
72	UH.M9	20100271	UH.E	A6/Vn	Beige, sandy micarb with fossils and veins.
73	UH.M16	20100272	UH.J	L1/Vn	Weathered looking, thick white veins.
74	UH.M17	20100273	UH.F	A1/Vn,Int	Coarse grained micarb with thin vein networks.
75	NG-1A	20100274	NG.B	A3/Vn	Hydro. Smell. Patchy micarb, veins, bedding. No fossils.
76	NG-1B	20100275	NG.B	A6/Vn	Thick, spar filled veins.
77	NG-2B	20100276	NG.A	A1,3/Vg,Int	Burrowing. Abundant tiny vugs.
78	NG-2C	20100277	NG.A	A3/Vn,Vg	Patchy micarb, pinkish in areas.
79	NG-3A	20100278	NG.J	A6/Vn	Silty micarb with bivalves. Sub-horizontal pseudo-bedding, vertical fractures @ 115 strike.
80	NG-3B	20100279	NG.J	A1/Vg	Lots of dark grains within micarb. Bivalve hash.
81	NG-5A	20100280	NG.E	A1/Vn	Cream silty limestone, v hard. Few lucinids but poorly preserved, diff to extract.
82	NG.5C	20100281	NG.B	A6/Vn	Pale coloured, brecciated.
83	NG-6	20100282	NG.B	A1/Vn	Lucinids, med size, smooth sculpture.
84	NG-7	20100283	NG.J	A6/Vn	Beige micarb, thin veins.
85	NG-1C	20100284	NG.B	A6/Vn,Int	Large sample with radial veins.
86	NG-2D	20100285	NG.A	A6/Vn,Int	Central, brecciated.
87	NG-2E	20100286	NG.A	A2,3	Fossils and burrows.
88	NG-2F	20100287	NG.A	A6/Vn	Pale coloured, with veins.
89	NG.2G.1	20100288	NG.A	A1/Vg	Lots of dark grains within micarb. Bivalves, mainly broken. Vugs.
90	NG.2G.2	20100289	NG.A	A1/Vg	Lots of dark grains within micarb. Bivalves, mainly broken. Vugs.
91	NG.8.1	20100290	NG.C	A6/Vn,Vg	Fossil-rich, far left. Veins.
92	NG.8.2	20100291	NG.C	A1/Vg,Int	Pigtail' veins.
93	NG.8.3	20100292	NG.C	A6/Vn,Vg	Fine grained, spar-filled vugs.
94	NG.8.4	20100293	NG.C	A6/Vn,Int	Some large dark intraclasts or grains. Thick sparry veins.
95	NG.8.5	20100294	NG.C	A1/Vn,Int	Patchy micarb, areas of green and orange tinged micarb.
96	NG-10.1	20100295	NG.J	A6/Vn	Veins
97	NG.A1	20100296	NG.A	A6/Vn,Vg	Sandy micarb.

98	NG.A3	20100297	NG.A	A6/Int	Sandy micarb.
99	NG.A4	20100298	NG.A	A1/Vn,Vg	Sandy micarb with veins and burrows.
100	NG.B1	20100299	NG.A	A3/Vn,Vg,Int	Sandy micarb with veins and burrows.
101	NG.B2	20100300	NG.A	A6/Vn,Int	Pale yellowish micarb with veins.
102	NG.C1	20100301	NG.A	A6/Vg,Int	Sandy micarb with sparry vugs.
103	NG.C2	20100302	NG.A	A6/Vn,Vg,Int	Patchy micarb with sparry veins and vugs.
104	NG.D3	20100303	NG.A	A6/Int	Sandy micarb with dark grains in concentrated zones.
105	NG.E1	20100304	NG.A	A6/Vg,Int	Sandy micarb with burrows and small vugs.
106	NG.E3	20100305	NG.A	A3/Vg,Vn	Many small samples of sandy micarb clasts.
107	NG.F1	20100306	NG.A	A3/Vn,Vg	Beige micarb with burrows.
108	NG.F2	20100307	NG.A	A6/Vn	Sandy micarb with complex veining.
109	NG.F4	20100308	NG.A	A3/Vn	Thin irregular veins.
110	NG.F5	20100309	NG.A	A6/Vn,Int	Sandy micarb with pink-grey and sparry vein networks.
111	NG.1E	20100310	NG.B	A6/Vn,Vg	Burrows and micarb-filled veins.
112	NG.M1	20100311	NG.a	A3/Vn,Vg	Weathered sample. Veins infilled with pure micarb.
113	NG.M2	20100312	NG.a	A1,2/Vn,Vg	Lucinid shell bed.
114	NG.M3A	20100313	NG.H	A1/Vg	Bivalve shell hash, small sparry vugs.
115	NG.M3B	20100314	NG.H	A1,2/Vg	Fossil rich.
116	NG.M4A	20100315	NG.J	A1/Vn	Lucinid-rich.
117	NG.M4B	20100316	NG.J	A3/Vg	Extensive vein network plus burrows.
118	NG.M5	20100317	NG.D	A3	Large burrow.
119	NG.M6	20100318	NG.B	A6/Vn,Vg	Veined and sparry vugs.
120	NG.M7	20100319	NG.A	A6/Vn	SE's "apricot pebbles". Pink-grey and white sparry vein systems.
121	NG.M8	20100320	NG.K	A6/Vn,Vg	Patchy micarb with varying siliciclastic grain content.
122	HA-1A	20100321	HA.J	A6/Int,Vn	Coarse grained with abundant intraclasts.
123	HA-1D	20100322	HA.J	A1/Int,Vg,Vn	Coarse grained with abundant intraclasts and sparry vugs.
124	HA-1E	20100323	HA.J	A1/Vg,Int	Coarse grained with abundant intraclasts and sparry vugs.
125	HA-1F	20100324	HA.J	A1/Vg,Int	Dark intraclasts and large bivalves.
126	HA-2D	20100325	HA.J	A6/Vg,Int	Coarse grained, large burrow/boring.

127	HA-3A	20100326	HA.G	A1/Vg,Int	Light coloured, contains shell hash.
128	HA-3C	20100327	HA.G	~	burrows prominent, some hollow calcite crystals infilled.
129	HA-3D	20100328	HA.G	A1/Vn,Int	burrows prominent, some hollow calcite crystals infilled.
130	HA-4A	20100329	HA.D	A3/Vg,Int	Fine and coarse grained micarb. Moderately sized bivs, concentric rings.
131	HA-5	20100330	HA.G	A1,3/Int	Bivalves
132	HA-11.1	20100331	HA.G	A1,3/Vg,Int	Coarse grained. Burrows.
133	HA-11.2	20100332	HA.G	A1,3/Vn,Int	Sparry veins.
134	HA-12.2	20100333	HA.D	A3/Vn,Int	Burrows, veins, patches of fine grained facies.
135	HA-12.3	20100334	HA.D	A5/Vn,Int	Veins. Tiny samples.
136	HA-12.4	20100335	HA.D	A1,3/Vg,Int	Burrows, veins, patches of fine grained facies.
137	HA-12.5	20100336	HA.D	A4/Vn,Int,Br	Meduim grained, veined. Beige micarb with patches of blue-grey.
138	HA-12.6	20100337	HA.D	L6/Vn*	Fine grained. Beige and blue-grey.
139	HA13.1	20100338		A6/Pe,Vg,Vn	Burrowed, peloidal infill. Veins. Spar-filled vugs.
140	HA13.2	20100339		A6/Vn,Vg	Extensive veining. Conduit?
141	HA13.3	20100340	HA.F	A1,2/Vg,Vn	Fine and coarse grained. Pseudo-flags.
142	HA13.4	20100341	HA.G	A3/Vg,Int	Sandy hill-top facies, blue core+orange outer+thin vein (side).
143	HA13.5	20100342	HA.G	A1,3/Vg,Int	Sandy boulder, scatt lucinids. Borings.
144	HA13.6	20100343	HA.G	A1/Vn,Int	Veins 0.5 cm wide
145	HA13.7A	20100344	HA.G	A1,5/Vg,Int	Has gastro, coarse sandy with sparry veins from large lucinid bearing boulder.
146	HA13.7B	20100345	HA.G	A1/Vg,Int	Coarse and sandy with sparry veins from large lucinid bearing boulder.
147	HA13.8	20100346	HA.H	A6/Vn,Int,Br	Extensively veined, blue sandy micarb.
148	HA.M1	20100347	HA.C	L1/Vg,Int	Marble-cake micarb patterns.
149	HA.M2	20100348	HA.F		Bivalve specimens.
150	HA.M3	20100349	HA.A	A1/Vg,Vn,Int	Host mudstone.
151	W1.1	20100350	W.G	L6,7/Vn,Vg	Top flag, vugs, veins, brecciation.
152	W1.2	20100351	W.G	L6,7/Vn	Vugs, veins, brecciation.
153	W1.3	20100352	W.G	L6,7/Vn,Vg	Vugs, veins, brecciation.
154	W1.4	20100353	W.G	L6/Vn	Thin veins, micarb-filled. Beige and blue-grey
155	W2.1	20100354	W.F	L6,7/Vn	Thick, multiphase

					sequence.
156	W2.2	20100355	W.F	L6,7/Br,Vn,Vg	2 phases of micrite, tiny vugs and fine brecciation.
157	W3.1	20100356	W.H	L6/Br,Vn,Vg	Coarse brecciation, veins.
158	W3.2	20100357	W.H	L6/Vn	Marbled micarb, beige and blue-grey areas.
159	W4.1	20100358	W.H	L6/Vn	Steaky, beige to orange.
160	W5.1	20100359	~	~	Flysch mudstone host - Ihungia Fm
161	W6.1	20100360	~	A6	Fine-grained, dark coloured.
162	W7.1	20100361	~	A6	Laminated
163	W7.2	20100362	W.H	A6	Streaked and offset, tectonised? Beige and grey.
164	W8.1	20100363	W.H	L6/Br,Vn	Beige micarb, stained. Multiple fine veins.
165	W8.2	20100364	W.H	L6/Vn	Blue, unoxidised core, complex zoning.
166	W8.3	20100365	W.F	L6/Vn,Vg	repres. Sample, brecc mic+vein
167	W8.4	20100366	W.F	L6/Vg,Vn	Thrombolites, tiny tension gashes.
168	W8.5	20100367	W.F	L6,7/Br,Vg,Vn	Veined and brecciated.
169	W8.6	20100368	W.F	L6,7/Vn,Br	Brecciation, veins, and vugs.
170	W8.7	20100369	W.H	L6/Vn	Stylo-bedded fabric
171	W8.8	20100370	W.H	L6/Br,Vn	Microbrecciation.
172	W8.9	20100371		L6,7/Vn	Thrombolitic boulder. Multilayered vein several cm thick.
173	W8.10	20100372		L6/Pe,Vg	Brecciated, dark fill.
174	W.M1	20100373	W.A	L6/Br,Vn	Brecciated micrite
175	W.M2	20100374	W.B	L6/Br,Vn,Vg	Brecciated micrite with some large clasts.
176	W.M3	20100375	W.C	L6,7/Br,Vn,Vg	Brecciated micrite and vugs
177	W.M4	20100376	W.D	L6,7/Br,Vn	Fine grained, brecciated.
178	W.M5	20100377	W.D	L6/Br,Vn	Highly brecciated, 2 phase micrite.
179	W.M6	20100378	W.C	L6,7/Br,Vn	Brecciated micrite with large veins and vugs.
180	W.M7	20100379	W.B	L6/Br,Vn,Vg	Complex mix of fine grained fabrics, stained orange.
181	W.M8	20100380	W.H	L6/Vg	Blue core to outer brown micrite. Complex mottling.
182	W.M9	20100381	W.H	L6/Vn	Pale, brecciated.
183	W.M10	20100382	W.H	L6/Vn	Pale, brecciated, fine veins.
184	W.M11	20100383	W.E	L6,7/Vn,Br,Pe	Fine grained micrite with thin and thick vein systems. Thrombolites.

APPENDIX 3

Laboratory Data

APPENDIX 3.1

Summarised (Table A3.1) and graphed (Figs. A3.1 to A3.20) component specific mineralogical results for the 20 areas from seven southern Hawke's Bay cold seep carbonate thin sections analysed using the General Area Detector Diffraction (GADD) technique. For raw data see Appendix disk. For fabric codes see Table 6.3.

Table A3.1 – Mineralogical summary based on GADDs analysis of 20 fabrics from seven thin sections from southern Hawke's Bay seep carbonate sites. Codes for target fabrics defined in Table 6.3.

Thin section / spot	Target fabric	Mineralogy, morphology
NG.2B.B_1	Si3	Quartz, large crystal size
NG.2B.B_2	Sp1	Calcite, large crystal size
NG.2B.B_3	PM	Calcite. Quartz. Possibly feldspar or clay
NG.F5_2	Si2	Quartz, small crystal size, randomly orientated
NG.F5_3	Si1	Quartz, a range of crystal sizes
NG.M7_1	Sp1	Calcite, perhaps enriched in Mg, large crystal size
NG.M7_2	Sp1	Calcite
NG.M7_3	Sp3	Calcite
NG.M7_4	Sp1	Calcite, well orientated crystals
NG.M7_5	PC	Calcite
UH.3A.1A_1	M1	Calcite, enriched in Mg. Quartz
UH.3A.1A_2	C2	Aragonite
UH.3A.1A_3	Th	Calcite, large crystals. Aragonite, many small crystals
UH.10.1.2A_1	C2	Aragonite. Minor calcite
UH.10.1.2A_2	Sp1	Calcite
W.2.1.1B_1	Sp1	Calcite
W.2.1.1B_2	M2	Calcite
W.2.1.1B_3	C1	Calcite, moderately orientated crystals. Minor aragonite
W.2.1.1B_4	Th	Calcite, moderately orientated crystals. Aragonite
W.M6	Sp2	Calcite

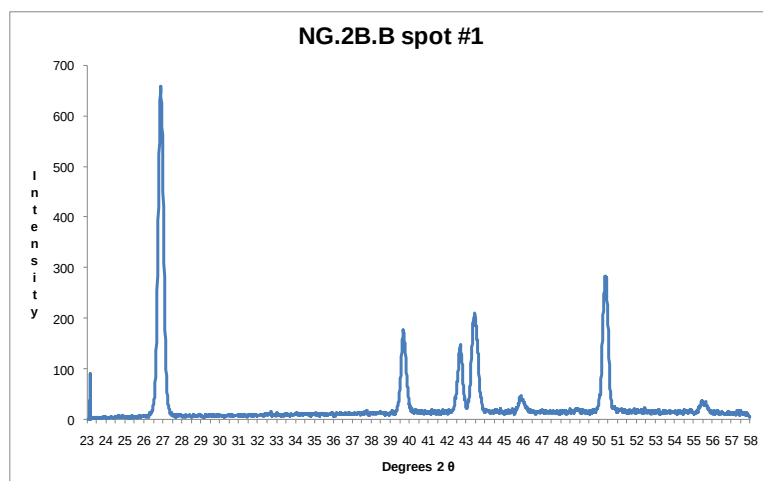


Figure A3.1 – Graphed GADDs data for spot 1 on thin section NG.2B.B from Ngawaka shows multiple strong quartz peaks for fabric Si3.

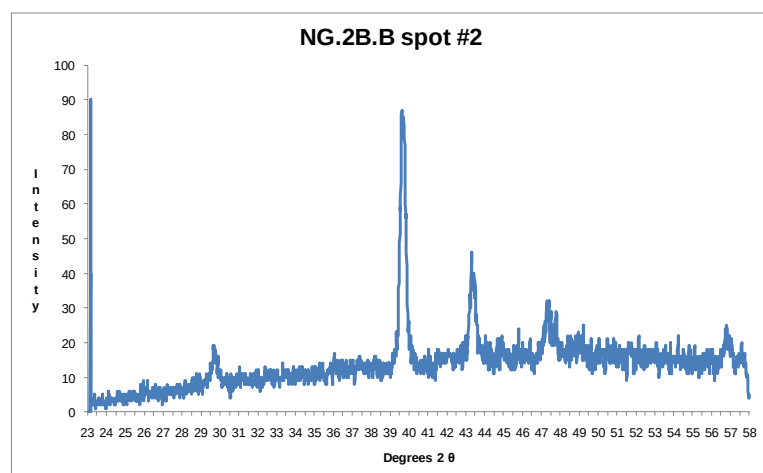


Figure A3.2 – Graphed GADDs data for spot 2 on thin section NG.2B.B from Ngawaka shows multiple strong calcite peaks for fabric Sp1.

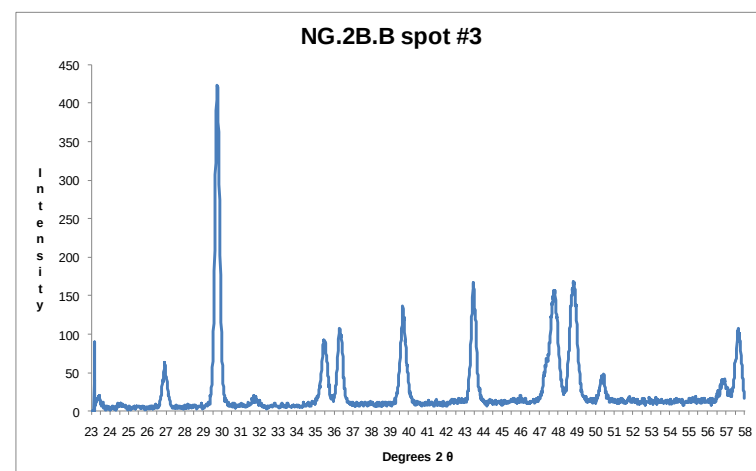


Figure A3.3 – Graphed GADDs data for spot 3 on thin section NG.2B.B from Ngawaka shows multiple strong calcite peaks and minor quartz peaks for fabric PM.

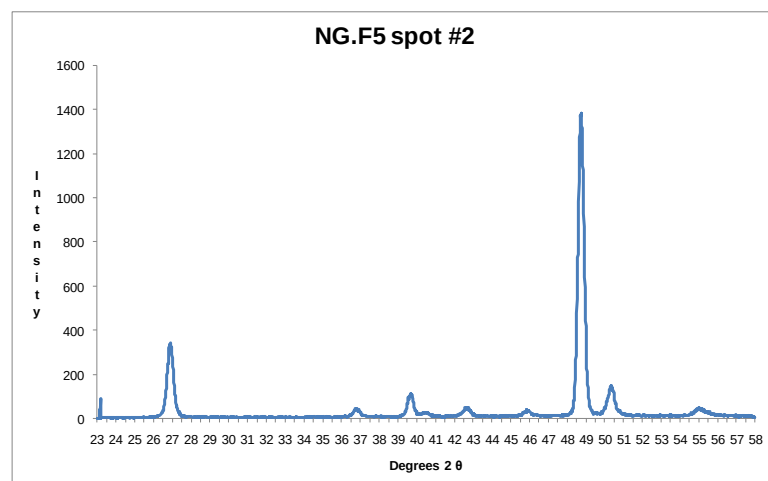


Figure A3.4 – Graphed GADDs data for spot 2 on thin section NG.F5 from Ngawaka shows multiple quartz peaks for fabric Si2.

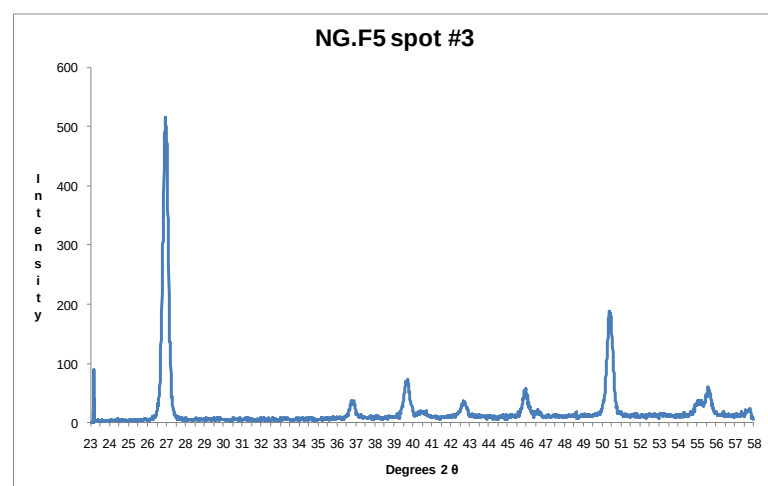


Figure A3.5 – Graphed GADDs data for spot 3 on thin section NG.F5 from Ngawaka shows multiple quartz peaks for fabric Si1.

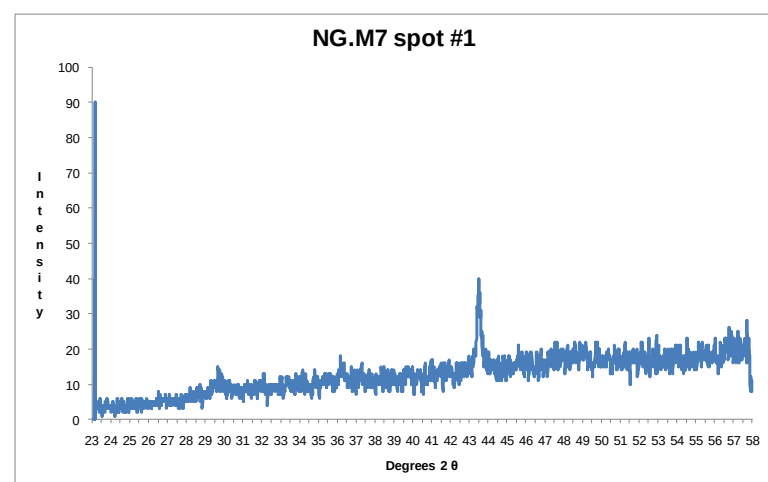


Figure A3.6 – Graphed GADDs data for spot 1 on thin section NG.M7 from Ngawaka shows calcite peaks for fabric Sp1.

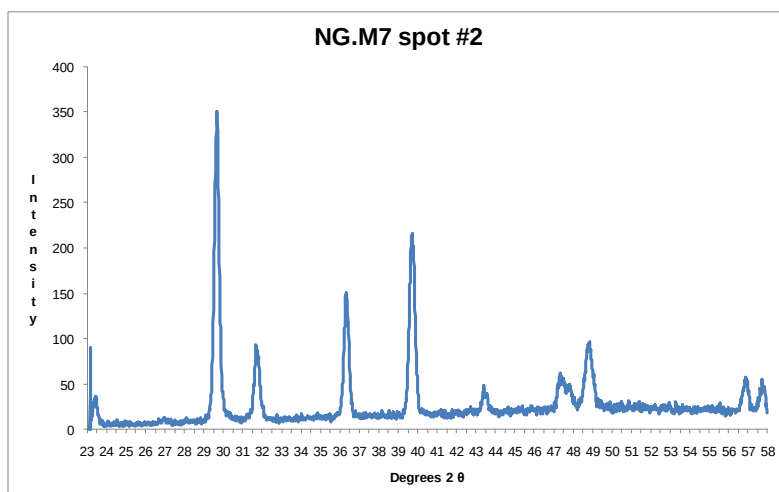


Figure A3.7 – Graphed GADDs data for spot 2 on thin section NG.M7 from Ngawaka shows many strong calcite peaks for fabric Sp1.

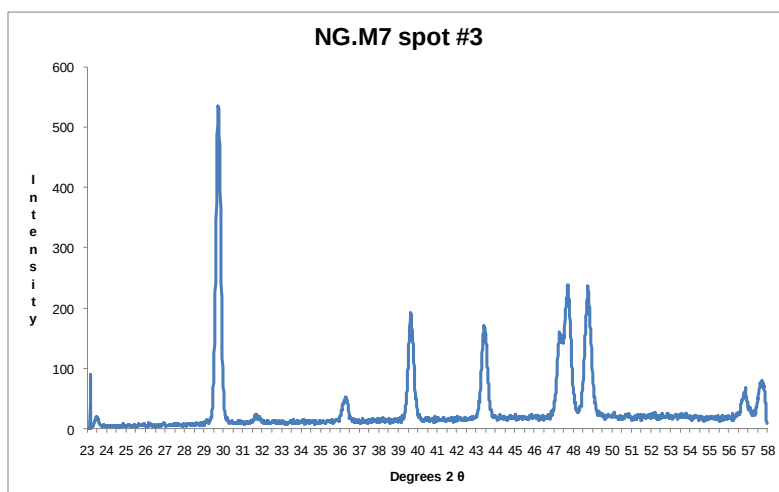


Figure A3.8 – Graphed GADDs data for spot 3 on thin section NG.M7 from Ngawaka shows multiple strong calcite peaks for fabric Sp3.

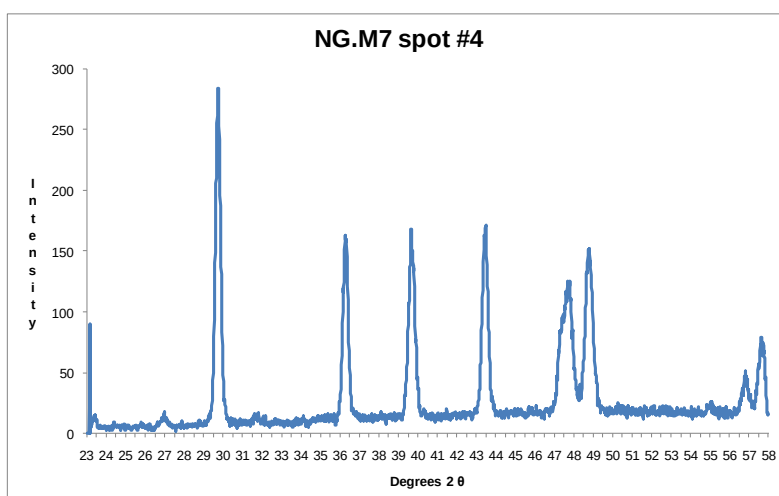


Figure A3.9 – Graphed GADDs data for spot 4 on thin section NG.M7 from Ngawaka shows multiple strong calcite peaks for fabric C2.

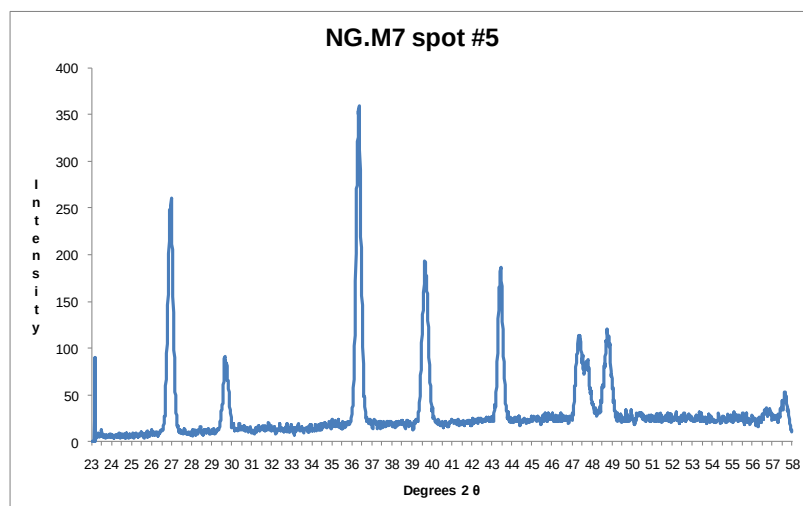


Figure A3.10 – Graphed GADDs data for spot 5 on thin section NG.M7 from Ngawaka shows multiple strong calcite peaks for fabric PC.

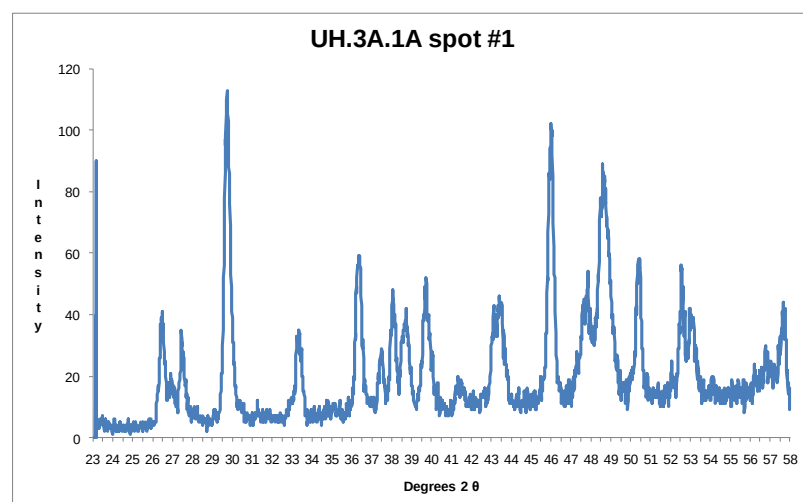


Figure A3.11 – Graphed GADDs data for spot 1 on thin section UH.3A.1A from Ugly Hill shows multiple strong calcite peaks and minor quartz peaks for fabric M1.

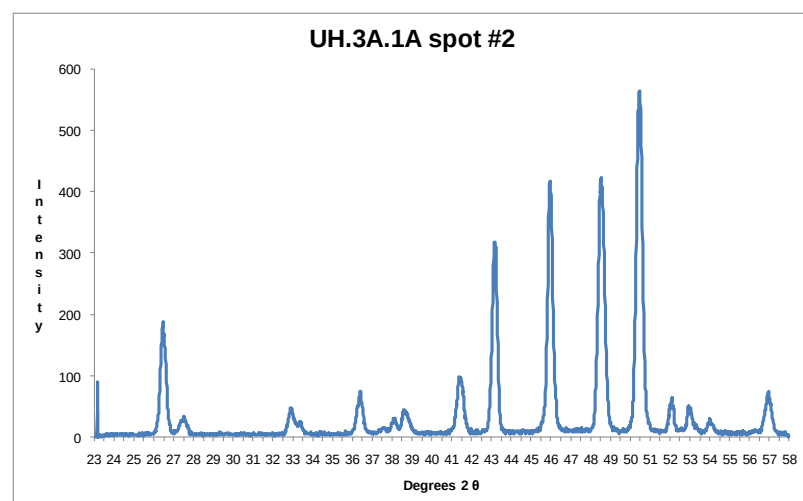


Figure A3.12 – Graphed GADDs data for spot 2 on thin section UH.3A.1A from Ugly Hill shows many strong aragonite peaks for fabric C2.

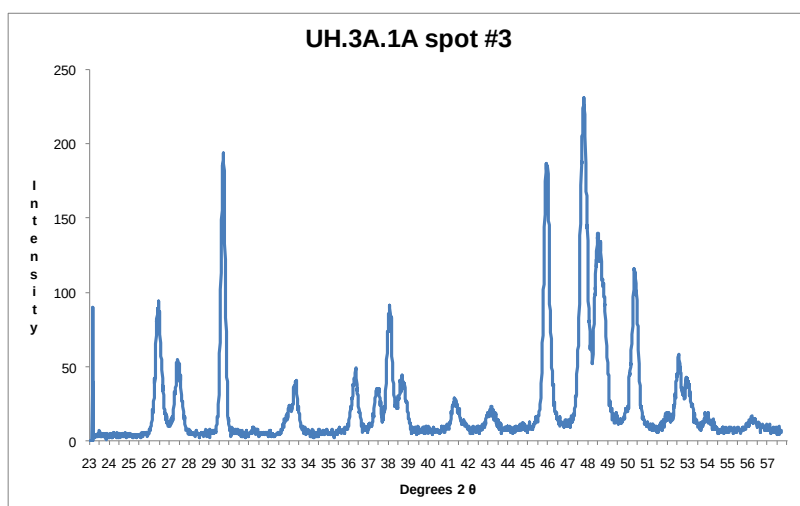


Figure A3.13 – Graphed GADDs data for spot 3 on thin section UH.3A.1A from Ugly Hill shows many strong calcite peaks and minor aragonite peaks for fabric Th.

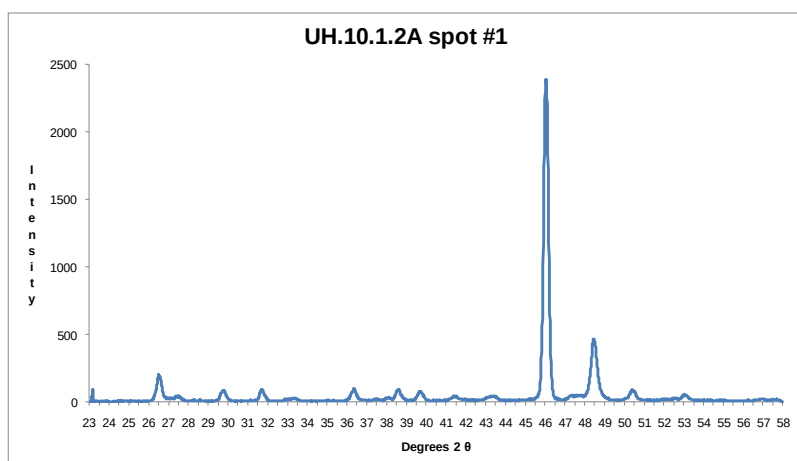


Figure A3.14 – Graphed GADDs data for spot 1 on thin section UH.10.1.2A from Ugly Hill shows aragonite peaks and minor calcite peaks for fabric C2.

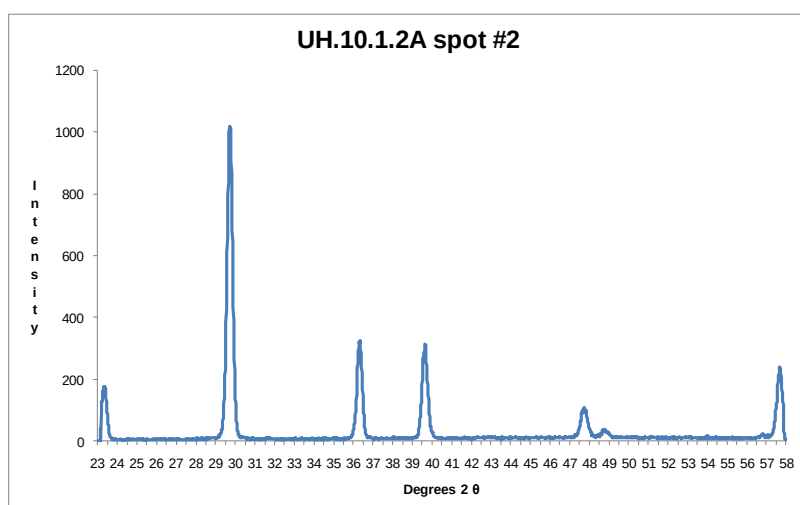


Figure A3.15 – Graphed GADDs data for spot 2 on thin section UH.10.1.2A from Ugly Hill shows calcite peaks for fabric Sp1.

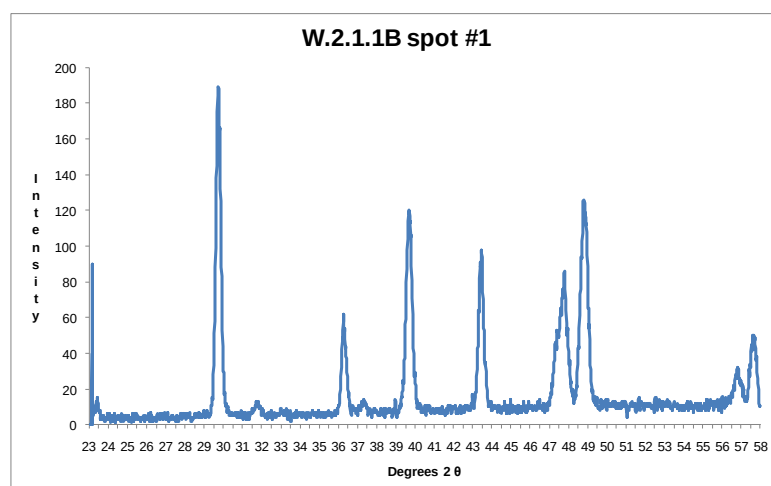


Figure A3.16 – Graphed GADDs data for spot 1 on thin section W.2.1.1B from Wilder Road shows strong calcite peaks for fabric Sp1.

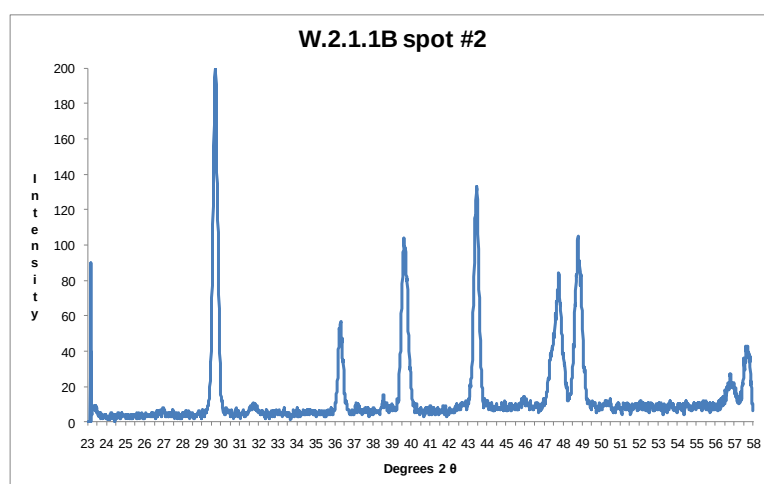


Figure A3.17 – Graphed GADDs data for spot 2 on thin section W.2.1.1B from Wilder Road shows strong calcite peaks for fabric M2.

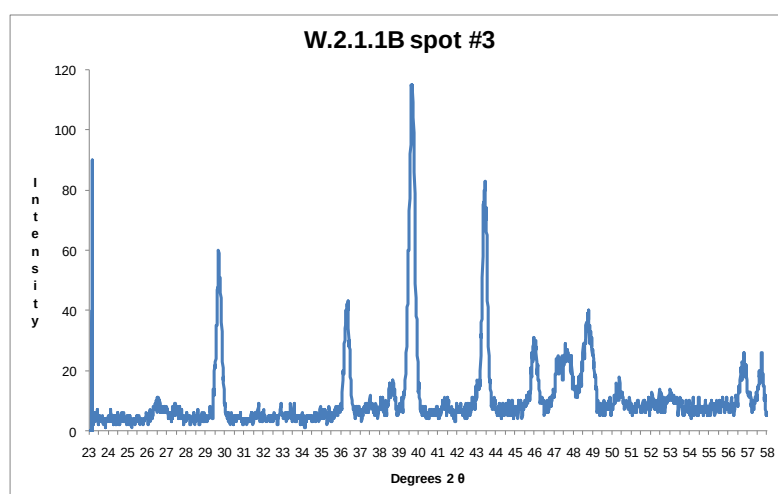


Figure A3.18 – Graphed GADDs data for spot 3 on thin section W.2.1.1B from Wilder Road shows strong calcite peaks and minor aragonite peaks for fabric C1.

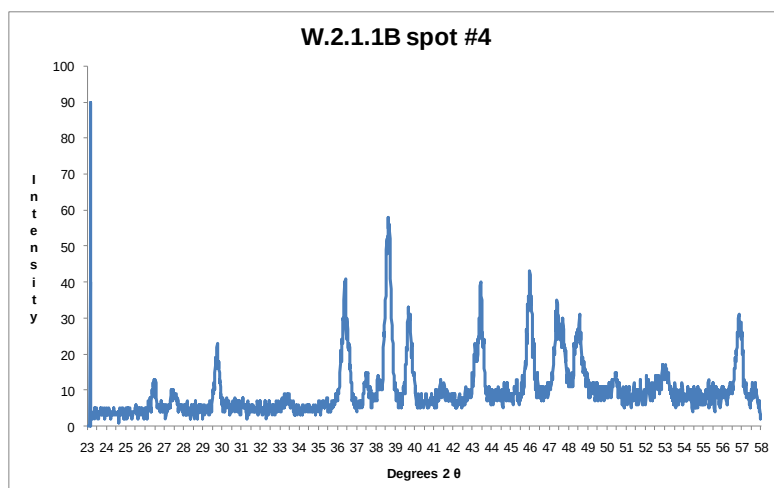


Figure A3.19 – Graphed GADDs data for spot 4 on thin section W.2.1.1B from Wilder Road shows strong calcite peaks and aragonite peaks for fabric Th.

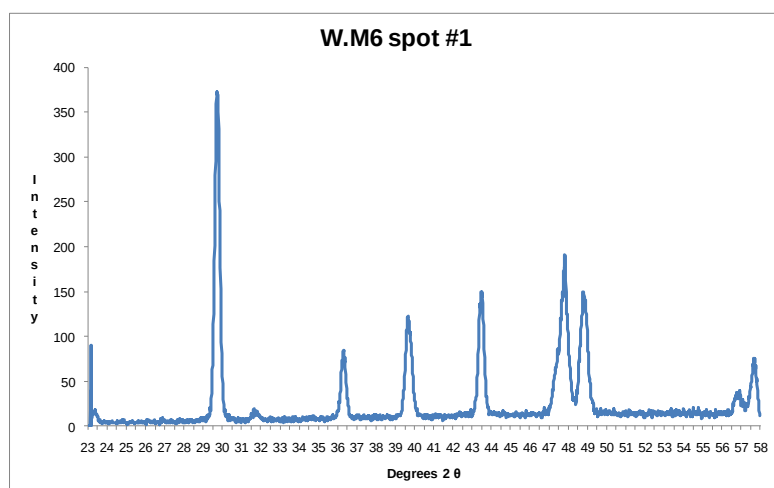


Figure A3.20 – Graphed GADDs data for spot 1 on thin section W.M6 from Wilder Road shows strong calcite peaks for fabric Sp2.

APPENDIX 3.2

Stable $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotope data for powders from the five sites of this study (Wanstead – WA; Ugly Hill – UH; Ngawaka – NG; Haunui - HA; Wilder Road – W) with the field sample numbers used in this thesis, the corresponding powder numbers, and the fabric analysed.

Table A3.2 – Stable $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotope data for southern Hawke’s Bay samples, with corresponding powder numbers and brief notes on the fabric analysed.

Sample number	Powder number	$\delta^{18}\text{O}_{\text{VPDB}}$	$\delta^{13}\text{C}_{\text{VPDB}}$	Fabric
W.1.2	W.1	-2.77	-3.89	Bulk powder
W.7.1.1	W.3	3.04	4.96	Odd micarb
W.8.4.1B	W.4	0.25	-10.15	Tension crack infill
W.7.2.1	W.5	-5.32	0.15	Banded micarb
W.7.2.1	W.6	-4.59	1.00	Banded micarb
W.8.9.3A	W.7	-2.73	8.87	Equant calcite
W.8.9.3A	W.8	-2.46	-11.90	Acicular & spherulitic aragonite
W.8.9.3A	W.9	-3.11	-11.32	Acicular & spherulitic aragonite
W.8.9.3A	W.10	-2.58	-11.47	Acicular & spherulitic aragonite
W.8.9.3A	W.11	-2.95	-8.03	Acicular & spherulitic aragonite
W.3.1.1	W.12	1.58	-25.66	Re-crystallised micarb
W.8.3.1A	W.13	-3.53	9.82	Micro-equant calcite
W.8.6.1	W.14	-3.63	0.95	Equant calcite
W.8.6.1	W.15	-3.01	-4.03	Light brown calcite stain
W.2.1.1A	W.16	-2.70	-10.87	Acicular & spherulitic aragonite
W.8.9.3B	W.17	-1.88	3.61	Acicular & spherulitic aragonite
W.8.5.1	W.18	-1.56	-22.66	Re-crystallised micarb
W.M11	W.19	-3.05	-12.48	Siliciclast-rich intrusion/vein
W.3.2	W.20	-1.07	-19.64	Bulk powder
W.8.2	W.21	-0.16	-23.13	Bulk powder
W.8.7	W.22	-0.96	-18.65	Bulk powder
W.M10	W.23	0.38	-25.23	Bulk powder
W.2.1	W.24	-2.75	-8.70	Bulk powder
WA.1A.1	WA.1	-2.63	-19.94	Bulk powder
WA.M1	WA.2	-2.13	-24.90	Bulk powder
WA.2B.1	WA.3	-1.72	-15.79	Bulk powder
WA.F7.1	WA.4	-2.78	-23.56	Bulk powder
WA.13.1	WA.5	-1.74	-22.01	Bulk powder
WA.M2	WA.6	-2.26	-22.59	Bulk powder
WA.13.5.1	WA.7	-5.24	-28.51	Equant calcite
WA.13.5.1	WA.8	-3.22	-27.81	Beige micarb

WA.13.4.1A	WA.9	-1.37	-24.79	Light brown calcite stain
WA.3B.1	WA.10	-0.53	-24.56	Peloids & spar
WA.13.1.1B	WA.11	-0.36	-18.53	Bioclasts
WA.13.1.1B	WA.12	-2.57	-22.68	Beige micarb, muddy
WA.M3	WA.13	1.40	-27.68	Micro-spar
WA.7B.2	WA.14	-1.91	-20.37	Beige micarb
WA.7B.2	WA.15	-2.14	-22.22	Beige micarb
WA.7F.1A	WA.16	1.33	-25.64	Burrow fill
WA.7F.1A	WA.17	-2.75	-24.62	Burrow fill
WA.7B.2	WA.18	-0.91	-30.16	Acicular/spherulitic aragonite
WA.7F.1A	WA.19	-3.56	-25.73	Siliciclastic-rich vein
WA.1C.1	WA.20	-2.17	-26.77	Bioclasts
WA.7F.1A	WA.21	-2.69	-23.48	Beige micarb
UH.3A.1	UH.1	1.30	-19.28	Bulk powder
UH.3A.2	UH.2	1.59	-22.28	Bulk powder
UH.104.1	UH.3	-0.26	-12.91	Bulk powder
UH.11.3	UH.4	-0.22	-13.37	Bulk powder
UH.5C.1	UH.5	-2.46	-17.87	Bulk powder
UH.11.4.2	UH.6	-2.99	-14.61	Bulk powder
UH.10.1.3	UH.7	0.62	-21.71	Bulk powder
UH.100.8.1	UH.8	1.22	-22.51	Bulk powder
UH.2A.1	UH.9	1.17	-21.99	Blue-grey micarb
UH.2A.1	UH.10	1.00	-22.03	Beige micarb
UH.100.8.1B	UH.11	-2.03	-22.60	Blue-grey micarb
UH.100.8.1B	UH.12	0.55	-21.93	Beige micarb
UH.10.1.2A	UH.13	-1.69	-10.10	Equant calcite
UH.11.4.1	UH.14	-3.53	-5.91	Equant calcite
UH.10.1.1B	UH.15	0.13	-12.59	Pseudo-sized spar
UH.10.1.1B	UH.16	1.15	-27.06	Micro-equant calcite
UH.10.1.1B*	UH.17	0.76	-23.42	Acicular needles
UH.10.3.1B	UH.18	-2.23	-26.51	Acicular needles
UH.2D.1	UH.19	-3.96	-19.59	Pseudo-sized spar
UH.3A.1A	UH.20	1.13	-22.84	Peloids in acic & micro-equant spar
UH.3A.1.A	UH.21	1.52	-23.22	Spherulitic needles
UH.3A.1A	UH.22	0.21	-12.08	Thrombolites
UH.3A.1A	UH.23	0.40	-14.25	Thrombolites
HA.13.1.1	HA.1	-1.76	-23.37	Bulk powder
HA.11.1.1	HA.2	-1.83	-21.57	Bulk powder
HA.M1	HA.3	-1.45	-22.34	Bulk powder
HA.1F.1A	HA.4	-2.42	-21.94	Bulk powder
HA.12.6.1	HA.5	0.93	-25.79	Bulk powder
HA.13.1.1A	HA.6	-3.64	-25.24	Peloids in acic & spar
HA.13.4.1	HA.7	-1.43	-22.86	Peloids in acic & spar
HA.13.4.1	HA.8	-2.13	-21.46	Individual Intraclasts
HA.13.8.1A	HA.9	-2.75	-22.76	Individual Intraclasts

HA.13.8.1	HA.10	-3.60	-22.25	Peloids in acic & spar
HA.11.1.1	HA.11	0.26	-22.32	Micro-equant calcite
HA.13.6.1	HA.12	-2.38	-23.76	Beige micarb
HA.13.6.1	HA.13	-4.25	-28.19	Equant calcite
HA.13.6.1	HA.14	-4.79	-26.88	Micro-equant calcite
HA.13.6.1	HA.15	-4.04	-27.78	Equant calcite
HA.13.1.1B	HA.16	-4.57	-26.28	Equant calcite
HA.13.8.1A	HA.17	-2.93	-19.90	Blue-grey micarb
HA.3A.1	HA.18	-0.45	-25.36	Individual Intraclasts
HA.3A.1	HA.19	-0.74	-24.49	Bioclasts
HA.1F.1A	HA.20	-3.58	-24.38	Spherulitic/acicular aragonite
HA.1F.1A	HA.21	-2.08	-24.96	Bioclasts
HA.13.2.1	HA.22	-1.29	-26.60	Spherulitic/acicular aragonite
NG.M2	NG.1	-5.27	-0.12	Bioclasts
NG.2G.2	NG.2	-5.94	-3.66	Bioclasts
NG.F5	NG.3	-2.78	-3.38	Yellow-brown calcite
NG.2B.B	NG.4	-5.91	-4.13	Equant calcite
NG.E3	NG.5	-4.18	-4.88	Yellow-brown calcite
NG.1B	NG.6	-6.53	-10.69	Micro-equant calcite
NG.1B	NG.7	-6.54	-9.06	Equant calcite
NG.1B	NG.8	-4.98	-12.39	Pseudo-spar
NG.1B	NG.9	-1.76	-15.56	Beige micarb
NG.M7	NG.10	-5.94	-3.04	Equant calcite
NG.M7	NG.11	-5.27	-1.72	Pseudo-spar
NG.M7	NG.12	-6.44	-8.82	Micro-equant calcite
NG.M7	NG.13	-2.61	-3.64	Yellow-brown calcite
NG.M7	NG.14	-2.64	-16.63	Beige micarb
NG.E3	NG.15	-2.99	-12.63	Bulk powder
NG.2B	NG.16	-2.34	-5.94	Bulk powder
NG.2G.2	NG.17	-4.03	-6.09	Bulk powder
NG.F4	NG.18	-3.21	-9.33	Bulk powder
NG.5A	NG.19	-2.17	-18.37	Bulk powder

