An investigation into the influence of methane seepage on calcium, calcium carbonate and other elemental concentrations in shallow water sediments in Dunmanus Bay, Ireland.

Thesis presented for the award of
Master of Science Degree

by

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Dr. Brian Kelleher (Dublin City University)

Submitted to the University of Limerick
ABSTRACT

In the marine environment, hydrocarbon seeps are known to be common and recognisable features and occur in shallow water and in the deep ocean. These seeps tend to be located at distinctive geotectonic, geochemical and biological interfaces where gas-rich fluids (e.g. methane) migrate upwards to the seabed. Seep characteristics range from diffuse seafloor venting to more focused low emission gas escape and these characteristics can be associated with morphological features on the seabed such as pockmarks and mud volcanoes. These seeps can host microbial communities that thrive on the venting methane and are also associated with methane-derived authigenic carbonates which under certain conditions can precipitate as concretions.

A pockmark field was first discovered in Dunmanus Bay, in Co.Cork, Ireland, in 2007 during multibeam mapping of the Bay. In shallow water depths of around 40 m, 60 pockmarks have been mapped with the largest reaching up to 20 m in diameter and up to 1 m in depth. The overall lithology of the Bay is characterised by coarse to medium sand, with mud to fine sand dominating closer to the mouth of the Bay. The pockmark field is located in an area of relatively finer particle size. Surveys show evidence of minor subsurface gas seepage in the region and also provide evidence of gas accumulations specific to the fine-grained muddy seabed in the pockmark field. In addition to this, a number of faults cross the region and these are thought to be likely pathways for gas migration to shallow sediments.
The aims of this research are twofold: (1) To investigate the influence of methane seepage on calcium and calcium carbonate concentrations and (2) to determine if methane seepage influences the concentration and distribution patterns of major and trace elements in the Bay. To investigate calcium and calcium carbonate concentrations, three 6m vibrocores were collected. One core was collected from within a pockmark, one from beside a pockmark but still in the gas seepage area and another core taken for comparison away from the pockmark field. To determine elemental concentrations and distribution patterns for major elements (Ca, Fe, Ti, Sr) and trace elements (Ba, Mn, Zr, Sc, Rb) twenty-two surficial sediments were collected throughout the bay and within the pockmark field.

All samples were analysed for their geochemical and physical properties. In conjunction with Particle Size Analysis, advanced analytical techniques such as Field-Portable X-ray Flourescence (FP-XRF), Bench XRF (XRF), X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM-EDS), were used. In addition, statistical analysis was carried out on the FP-XRF results data from the surficial sediments. All the results obtained were used to provide an insight in to marine calcification and elemental concentration and distribution patterns in seep environments.

The results show a decrease in Ca concentrations with depth and indicate that no obvious precipitation of CaCO₃ minerals occurs. This is due to a combination of factors which include (1) a low methane seepage rate, (2) microbially mediated reactions in the sulphate-methane-transition-zone that affect the calcium carbonate equilibrium and (3) the possibility of lateral migration of seawater (carrying CO₂)
from depth through a permeable gravel layer located approximately 4 meters below the seafloor.

The concentration and spatial distribution patterns of major elements (Ca, Fe, Ti, Sr) and trace elements (Ba, Mn, Zr, Sc, Rb) suggest that all were associated with all sediment types. Levels of concentration of Fe, Ti and Ba were broadly similar to levels in the soils in the surrounding landmass. Ca concentrations were high throughout the Bay, suggesting a large biogenic influence in the sediment. Sr followed similar trends to Ca. Mn was lower in the surficial sediments compared to regional soil concentration. Zr and Sc had higher concentrations in the pockmark field compared to the rest of the Bay and seem to be associated with the fine-grained sediments which occur here due to the high surface to volume ratios and adsorption capacities of their grains. Statistical analysis indicated that there was no significant difference between medians in the pockmark field and the rest of the Bay for Ca, Ti, Ba and Zr while statistical analysis confirmed that there was significant difference between the two areas for Fe, Sr, Mn, Sc and Rb.
Declaration

I declare that this thesis is entirely my own work and has not been submitted for an award at any other University.

Signed: Nigel Coleman

Date: 20/11/2015
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- Atlantic Ireland 2011 Conference, Dublin, Oct 17th
- INFOMAR Conference 2011, Galway, Nov 16th
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AOM</td>
<td>Anaerobic Oxidation of Methane</td>
</tr>
<tr>
<td>BC</td>
<td>Box Core Sample</td>
</tr>
<tr>
<td>DG</td>
<td>Day Grab Sample</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive System</td>
</tr>
<tr>
<td>EDXRF</td>
<td>Energy Dispersive X-ray Fluorescence</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>FP-XRF</td>
<td>Field Portable X-ray Fluorescence</td>
</tr>
<tr>
<td>GC</td>
<td>Gravity Core Sample</td>
</tr>
<tr>
<td>GPS</td>
<td>Global Positioning System</td>
</tr>
<tr>
<td>GSI</td>
<td>Geological Survey of Ireland</td>
</tr>
<tr>
<td>INFOMAR</td>
<td>Integrated Mapping for the Sustainable Development of Ireland's Marine Resources.</td>
</tr>
<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
</tr>
<tr>
<td>ODV</td>
<td>Ocean Data View</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>PSA</td>
<td>Particle Size Analysis</td>
</tr>
<tr>
<td>SMI</td>
<td>Sulphate-Methane Interface</td>
</tr>
<tr>
<td>SMTZ</td>
<td>Sulphate-Methane Transition Zone</td>
</tr>
<tr>
<td>SRB</td>
<td>Sulphate Reducing Bacteria</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>USGS</td>
<td>United States Geological Survey</td>
</tr>
<tr>
<td>VC</td>
<td>Vibrocore</td>
</tr>
<tr>
<td>WDXRF</td>
<td>Wave Dispersive X-ray Fluorescence</td>
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<tr>
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Chapter One

Introduction
1.0 Introduction

The origins of the study of marine sediments can be traced back to expeditions by the HMS Challenger between 1872 and 1876 (e.g., Tizzard et al., 1885; Murray and Renard, 1891). Since then numerous research papers on marine sediment composition have been published including ones by Revelle (1944), El Wakeel and Riley (1961), Arrhenius (1963), Goldberg (1963), Chester and Aston (1976), Glasby (1977), Bischoff and Piper (1979), Baturin (1982, 1988), Notholt and Jarvis (1990), Nicholson et al. (1997), Glenn et al. (2000), and Li (2000). Although the analysis of marine sediments can present many exceptional challenges (e.g. difficulties obtaining samples), the diverse composition of sediments does provide extremely valuable data which can be used to study past climate change for environmental prediction and gives insight into the impact of benthic habitats on fisheries and other biological communities (Balsam et al., 2007). It also helps interpret the significance of events like gas hydrate releases (i.e. hydrocarbon molecules formed under low temperature and high pressure) and can determine suitable sites for seabed communications cables, drilling platforms and other structures (Green et al, 1985). All this vital information derived from marine sediments leads to a greater understanding of how the earth and its environmental systems function.

As an island nation, Ireland has a vast and largely unexplored marine resource. INFOMAR (Integrated Mapping for the Sustainable Development of Ireland’s Marine Resource) is a joint initiative between the Geological Survey of Ireland and the Marine Institute and is the successor to the Irish National Seabed Survey. INFOMAR covers almost 125,000 km² of Ireland’s inshore waterways and
is responsible for producing integrated mapping products covering the physical, chemical and biological features of the seabed. It has prioritised the surveying of 26 bays and 3 priority areas around the coast of Ireland (Figure 1.1). One of these priority bays is Dunmanus Bay, in the south-west of Ireland. This bay is of particular interest as crater-like depressions, known as pockmarks, were discovered on the seabed here during the INFOMAR survey in 2007.

![INFOMAR map showing priority bays and areas](www.infomar.ie)

*Figure 1.1: INFOMAR map showing priority bays and areas (www.infomar.ie).*
1.1.1 Geographical Details of Study Area

Dunmanus Bay is located in County Cork, Ireland (Figure 1.2). A bay is defined as an inlet of the sea extending inland with a wide mouth. In general, bay environments have a relatively wide sea area with a shallow near-shore. Dunmanus Bay is a southwest facing bay and is located between Bantry Bay to the north and Mizen Head to the south. Like other bays along this coastline, Dunmanus Bay is an example of a ria (or drowned valley) separated by peninsulas of Old Red Sandstone. The bay is almost 7 km wide from Sheep’s Head to Three Castle Head and 25 km long from its mouth to its head at Four Mile Water (www.infomar.ie). The bay is out of the main tidal flow with the river Durrus being the only significant river flowing into it.

Figure 1.2: Map of Ireland showing location of Dunmanus Bay (www.infomar.ie)

While there has been no direct study of the bedrock geology of Dunmanus Bay, the area has been referred to in studies dating back as far as the mid-nineteenth century by Jukes et al., (1861) and Jukes (1864). In more recent times, the area has
also been referred to in stratigraphical studies by Naylor (1975), Naylor and Sevastopulo (1993) and MacCarthy (2007).

Stratigraphically, Dunmanus Bay is in the South Munster Basin. The Munster Basin developed as a half-graben during the Devonian as a result of north-south crustal tension (MacCarthy, 2007). The subsequent formation of the South Munster Basin began with the development of the Killarney-Mallow Fault which divided the original Munster Basin into the North Munster Shelf and the South Munster Basin. Upper Devonian and Upper and Lower Carboniferous formations dominate the stratigraphy of the South Munster Basin. These formations consist of deep and shallow marine shelf siliciclastic, non-marine fluvial siliciclastic and non-marine coastal plain siliciclastic rocks (MacCarthy, 2007) and sit on caledonian granite and older pre-caledonian basement formations (Naylor, 1975; Naylor and Sevastopulo, 1993). A number of surveys and studies of the Munster Basin (Vermeulen et al, 2003 and Quin, 2008) refer to several faults present in this area. In terms of Dunmanus Bay, its major sedimentation controlling fault is the Dunmanus Fault, which runs along the entire bay parallel to the landmass and just north of the pockmark field. In the vicinity of this pockmark field there are two major branches of the Dunmanus Fault, the Gortavallig Fault and the Letter Fault. In addition to these two faults, there are several minor faults in the northern part of the Dunmanus syncline, that are not connected to the Dunmanus Fault itself. The most notable of these are the Glanlough Fault and Rossmore Fault (Szpak, 2012a). A recent study of this area describes the coastal catchments along the headlands as comprising of resistant Devonian Old Redstone with bays underlain by less resistant Dinatian limestone and mudstone (OPW Report 2014)
The pockmarks in Dunmanus Bay were identified on the seabed here during an INFOMAR multibeam survey in 2007. Acoustic and ground-truthing methods were used to characterize the Quaternary sediments of the bay and sediment classification revealed a diverse seabed structure (Monteys et al., 2010). The northern part of the bay is dominated by sand areas with a high mud constituent and bedrock outcrops with coarse sand and gravel being infrequent and mainly confined to the centre of the syncline and close to the landmass. Along the mouth of the bay, the main sediment feature is mud with coarser sediment unevenly distributed and only occurring in patches.

Figure 1.3: Bathymetry Contour Chart of Dunmanus Bay (www.infomar.ie)

The specific survey area (Figure 1.3) is located approximately 650 metres east of Dooneen Point and approximately 2.4 kilometres west of Carbury Island. This is an area of 225000 m² and seabed sediments mainly contain mud and fine sands with two major rock outcrops southeast and northwest of the pockmark field.
A Shellfish Water Report in 2006, which reviewed the Dunmanus Inner Shellfish Area, documented that in the catchment area there were 976 on-site-waste-water systems. This density, it noted, was higher than the national average (SPRP 2006). On a potentially relevant historical note, it is worth mentioning that Barite was mined in nearby Dreenanalomane initially by Dunmanus Bay Barytes Co. and later Durrus Baryte Co. until 1920. Records show that 6339 tons was exported in 1916. Ships were loaded in Dunmanus Bay for export to Liverpool, England. The barite mined was known to be particularly pure and the product name was “Dunmanus White” (Hallissy, 1923).

1.1.2 Research Expedition

AQUAFACT International Services Ltd. and Dublin City University (DCU) were grant aided by INFOMAR to carry out a ground-truthing survey of pockmark areas in Dunmanus Bay. This project employed a combined acoustic and electromagnetic geophysical approach to study the near-seabed composition in the recently discovered shallow gas bearing area in the bay. This involved gravity core, day grab, box core and vibrocore sample analysis, multi-beam and single-beam backscatter classification and a marine controlled-source electromagnetic method. This combined method enabled the mapping, in an unprecedented way, of the upper 20m of the seabed and correlated the main geophysical parameters with the geological properties of the seabed, thus providing a unique tool for geohazard identification, seabed classification, fluid flow migration paths and sediment porosity. Knowledge of the sediment composition of these areas is vital to
understanding the natural processes occurring at such sites and also for the potential
discovery and extraction of hydrocarbons. During a seven day sampling expedition
on the RV Celtic Voyager (Figure 1.4) in April 2009 a range of seabed samples were
taken, including gravity cores, box cores and day grab samples. In 2011, another
sampling expedition to the bay successfully obtained three 6 m Vibrocores samples.

Figure 1.4: The RV Celtic Voyager, a multipurpose research vessel suited to coastal
research and offshore survey operations (Image courtesy of www.marine.ie).

1.1.3 Dunmanus Bay Pockmark Field

The pockmark field in Dunmanus Bay contains in excess of 60 pockmarks.
Some of the pockmarks are up to 20 m in diameter and they range from 0.3 m to 0.8
m in depth. The pockmarks occur in clusters, with each cluster containing 5 to 9
larger features (pockmark formations) and typically in the vicinity of this cluster are small, random “satellite” or “parasite” pockmarks which can vary from 1.0 m to 1.2 m wide (Figure 1.5). Initially the pockmark clusters seem to be parallel to one another although observing the entire pockmark field, as a whole, there is a distinct northeast-southwest orientation, with the two rock outcrops at either end.

![Figure 1.5: Bathymetry image and depth profiles of pockmark features in Dunmanus Bay. The white line depicts transect lines along the Bottom. Shallow seismic cross section along white line indicated in top image. Image courtesy of Xavier Monteys, GSI, Ireland.](image)

**1.2 Background to Marine Pockmarks**

Pockmarks are crater-like depressions on the seafloor (King & MacLean, 1970; Hovland, 1982; Hovland & Judd, 1988) (Figure 1.6). These features occur worldwide in the ocean at all depths and in lakes. They typically reach diameters of hundreds of metres and depths of tens of metres. They were first discovered off Nova Scotia, Canada by Lew King and Brian MacLean in 1970 and as methods of acoustic
detection and mapping of the seafloor have advanced (Ussler III et al., 2003) they have become widely recognised morphological features on the continental margins of the world.

Figure 1.6: Bathymetry image and depth profiles of pockmark features of the Malin Sea, off the northern coast of Ireland. Dotted lines depict transect lines of the vessel, red and white dots depict sampling sites (Image courtesy of Xavier Monteys, GSI, Ireland).

Pockmarked areas of the seabed have historically been compared to the lunar surface. Indeed it has been suggested (Schuum, 1970) that some of the lunar surface features could have been formed in a similar manner to terrestrial pockmarks. Pockmarks are seen in several geological environments around the world e.g. on continental shelves, lakes, shallow bays and deep water (Hovland & Judd, 1988; Hovland et al., 2002). The phenomena has been known for the last 40 years and generally pockmarks are considered to be created by violent expulsions of fluids and sediments onto the seafloor (King & MacLean, 1970; Hovland & Judd, 1988; Judd & Hovland, 2007). The fluids that generate pockmarks can be of varying composition ranging from oil, thermogenic and biogenic gas (methane), to pore water (brine) and
even fresh water (ground water) (Hovland, 1985; Hovland & Judd, 1988; Fader, 1991; Paull et al., 1995; Bøe et al., 1998; Bünz et al., 2003; Schroot et al., 2005; Gay et al., 2006).

Pockmarks can occur as single isolated formations, as pockmark fields or as a string of pockmarks (Hovland, 1981; Rise et al., 1999; Hovland et al., 2002). Their size and shape depends on the capacity, overpressure and fluid composition of the fluid reservoir involved (Hovland & Judd, 1988), the nature of the fluid escape (Bøe et al., 1998), the rheology and grain size of the seabed sediments and their interactions with underlying structures that facilitate fluid flow (Gay et al., 2006). Several morphological classes have been identified by Hovland et al., (2002) who defined a normal pockmark to be a circular depression typically measuring 10-700m in diameter and 1-45m in depth. Current scour erosion, merging of individual pockmarks, inward gravity movement of unstable pockmark flanks and authigenic carbonate precipitation may alter the initial circular geometry of the pockmark. This can result in other geometric classes, such as elongated, composite, complex and eyed pockmarks (Hovland, 1982, 1983; Hovland & Judd, 1988; Stewart, 1999; Bøe et al., 1998; Cole et al., 2000; Hovland et al., 2002, 2005; Çifçi et al., 2003).

1.2.1 Pockmark Formation, Arrangement and Density

There have been a number of suggested mechanisms for pockmark formation. Kelley et al., (1994) has suggested that there are two models for pockmark formation;
(1) Organic matter deposited above an erosional surface decomposes, releasing gas that excavates the pockmark, once the excavation extends to the erosional surface, the pockmarks spread out laterally along the erosional surface.

(2) A catastrophic event such as an earthquake or tsunami reduces the confining pressure in the area, allowing gas and fluids to suddenly escape.

The first model can explain why U-shaped, V-shaped and flat-floored pockmarks are observed, and the latter model why pockmark formation and increased methane venting have been documented to occur in response to earthquakes (Hovland et al., 2002; Christodoulou et al., 2003).

Pockmarks have been identified by seismic profiling, side-scan solar surveys and visual observations (e.g. Hovland & Judd, 1988; Fader, 1991). They can occur as discrete features, or as coalescing structures forming extensive pockmark fields, up to 1000 km² (Kelley et al., 1994).

Additionally, a variety of formation mechanisms have been proposed, including:


(2) Pore water escape (Harrington, 1985; Soter, 1999)

(3) Seepage of freshwater (King & Maclean, 1970; Whiticar and Werner, 1981; Whiticar, 2002)

(4) Rafting of gas hydrate (Vogt et al., 1994; Paull et al. 1995)

(5) Rafting of water ice (Paull et al., 1999).

Hovland (1989) suggests that there are three phases of pockmark development (Figure 1.7):
1. A pressure build-up phase. This is where gas accumulates below the seabed.

2. The eruption phase. This is when liquid and solids are ejected into the water column.

3. The post-eruption phase, which can be either a dormant phase or one where gas is continually seeping through the pockmark floor.

![Figure 1.7: Suspected pockmark formation mechanism. A - seabed doming caused by increasing fluid pressure; B - blow-out of the gas charged sediment and creation of the sediment plume in the water column; C - sedimentation of the coarse material and the fine grains, joint with side walls slumping. Red dotted curve depicts initial seabed profile (Concept after Hovland & Judd, 1988).]

Though pockmarks have been historically hard to detect on single-beam sounding data, they are easily imaged using contemporary side-scan sonar and multi-beam surveys. Interest in pockmarks has increased in recent times because of the increasing availability of high quality multi-beam data that demonstrate that pockmarks are common continental margin geomorphic features (Paull et al., 2002). Because of their diverse occurrence, morphology, size, and character, pockmarks are probably formed by a variety of mechanisms.
Pockmarks are found to occur in both random and non-random distributions and in a wide range of spatial densities (Table 1.1). Pilcher & Argent (2007), use the term “random” to describe those pockmarks which either occur singly or appear to have irregular distribution on the seabed, with no discernable spatial relationship to each other or to a resolvable surface or sub-surface feature. They typically occur on low-gradient shelf and deep marine environments underlain by simple layered stratigraphy. Non-random pockmarks show one of several types of organised spatial arrangement, related either to more complex underlying geology or to local disturbance of the seabed. Non-random pockmarks occur in a variety of settings and their formation has been attributed to a variety of mechanisms.
<table>
<thead>
<tr>
<th>Type</th>
<th>Description</th>
<th>Causes</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Random pockmarks</td>
<td>Occur singularly, in small groups or extensive fields.</td>
<td>Single or prolonged fluid explosion</td>
<td>Fader,1991; Hovland, 1982; Hovland &amp; Judd,1988; Rise et al., 1999</td>
</tr>
<tr>
<td>Pockmark clusters and coalescing pockmarks</td>
<td>Pockmarks occurring in groups or clusters e.g. Gulf of Maine</td>
<td>Fluid explosion</td>
<td>Fader,1991; Hasiotas et al.,1987; Dimitrov &amp; Woodside,2003</td>
</tr>
<tr>
<td>Fault-strike pockmarks</td>
<td>Describes the linear arrangement of pockmarks along the strike of a subsurface fault</td>
<td>Underlying faults</td>
<td>Pilcher &amp; Argent,2007; Svyitski &amp; Praeg, 1989; Soter,1999; Hovland &amp; Judd,1988</td>
</tr>
<tr>
<td>Buried channel pockmarks</td>
<td>Observed above the length of buried channels, indicating fluid escape from channel sediment vertically upward to the seabed.</td>
<td>Fluid seepage</td>
<td>Pilcher &amp; Argent, 2007; Haskell et al.,1997; Gay et al.,2006; Gay et al.,2003; Haskell et al.,1999</td>
</tr>
<tr>
<td>Slump pockmarks</td>
<td>Slumps are common on unstable (steep) slopes. Causes include seismic activity, storm-wave action or local subsurface movement. Sediment slumping may promote preferential pockmark formation.</td>
<td>Fluid/Gas seepage</td>
<td>Schwab &amp; Lee,1988; Foland et al.,1999; McNeill et al.,1998; Sultan et al.,2004.</td>
</tr>
<tr>
<td>Current-modified pockmarks</td>
<td>Pockmarks originate as circular or near-circular features in plan view, but can be subsequently elongated through scouring and current action.</td>
<td>Fluid/Gas Seepage</td>
<td>Bøe et al.,1998; Josenahns et al.,1978; Fader,1991; Fader &amp; Miller,1998.</td>
</tr>
<tr>
<td>Iceberg scour pockmarks</td>
<td>Local scouring by grounded moving icebergs can cause sufficient reduction on lithostatic pressure to allow fluid in the shallow sediments to escape the seabed forming a pockmark.</td>
<td>Fluid/Gas seepage</td>
<td>Fader,1991; Hovland &amp; Judd, 1998</td>
</tr>
<tr>
<td>Anthropogenic pockmarks</td>
<td>Anthropogenic mechanism can disturb the seabed from above, locally reducing lithostatic pressure and causing fluid to be released to the seabed, resulting in pockmark formation.</td>
<td>Fluid/Gas seepage</td>
<td>Fader,1991; Hovland &amp; Judd, 1988.</td>
</tr>
</tbody>
</table>

Table 1.1: Table summarising Pockmark types as outlined by Pilcher & Argent (2007)
1.2.2 Pockmark Morphology and Size

Pockmarks are usually described as circular or near-circular depressions, generally 10-200m in diameter and up to 35m deep (Table 1.2). However several cases of non-circular pockmarks also exist (Pilcher & Argent, 2007). The cross-sectional shape of pockmarks varies from U-shaped to V-shaped seafloor depressions to truncated cones with steep low angled or asymmetric walls. Some are circular in plan view while others are elongate (Dimitrov & Woodside, 2002; Hovland et al., 2002). The internal shape of pockmarks ranges from cone shaped to flat-bottomed. The internal slopes of pockmarks average 9° with a range of 6° - 18° (Fader, 1991). Globally, contemporary pockmarks have been reported with diameters of less than 1m to hundreds of meters (Fader, 1991; Haskell et al., 1999; Hovland & Judd, 1988). Pockmarks greater than 250m in diameter are referred to as “giant” by Foland et al. (1999).
<table>
<thead>
<tr>
<th>Reference</th>
<th>Diameter 1 (m) (short axis)</th>
<th>Diameter 2 (m) (long axis)</th>
<th>Depth (m)</th>
<th>Form in plan view</th>
<th>Age</th>
</tr>
</thead>
<tbody>
<tr>
<td>King &amp; Maclean (1970)</td>
<td>15-45 (400)</td>
<td>-</td>
<td>5-10</td>
<td>Circular</td>
<td>Recent</td>
</tr>
<tr>
<td>Josenhans et al. (1978)</td>
<td>85</td>
<td>-</td>
<td>6</td>
<td>Oval</td>
<td>Recent</td>
</tr>
<tr>
<td>Hovland (1981)</td>
<td>2-300</td>
<td>-</td>
<td>4-15</td>
<td>Circular</td>
<td>Recent</td>
</tr>
<tr>
<td>Hovland (1982)</td>
<td>10-75 m</td>
<td>700</td>
<td>3.5</td>
<td>Circular</td>
<td>Recent and buried</td>
</tr>
<tr>
<td>Hovland (1985)</td>
<td>450</td>
<td>400</td>
<td>17</td>
<td>Elongated</td>
<td>Recent</td>
</tr>
<tr>
<td>Prior et al. (1989)</td>
<td>280</td>
<td>-</td>
<td>58</td>
<td>Elliptical</td>
<td>Recent</td>
</tr>
<tr>
<td>Fader (1991)</td>
<td>1-300</td>
<td>-</td>
<td>Up to 29</td>
<td>-</td>
<td>Recent</td>
</tr>
<tr>
<td>Kelley et al. (1994)</td>
<td>Up to 300</td>
<td>-</td>
<td>Up to 35</td>
<td>Circular</td>
<td>Recent</td>
</tr>
<tr>
<td>Paull et al. (1995)</td>
<td>50</td>
<td>2000</td>
<td>4</td>
<td>-</td>
<td>Recent</td>
</tr>
<tr>
<td>Bøe et al. (1998)</td>
<td>400</td>
<td>-</td>
<td>45</td>
<td>Elongated</td>
<td>Recent</td>
</tr>
<tr>
<td>Heggland (1998)</td>
<td>300</td>
<td>-</td>
<td>6-8</td>
<td>Circular</td>
<td>Recent and Pliocene</td>
</tr>
<tr>
<td>Rise et al. (1999)</td>
<td>70</td>
<td>-</td>
<td>6</td>
<td>Circular</td>
<td>Recent</td>
</tr>
<tr>
<td>Stewart (1999)</td>
<td>10-300</td>
<td>-</td>
<td>-</td>
<td>Circular</td>
<td>—</td>
</tr>
<tr>
<td>Cole et al. (1999)</td>
<td>500-4000</td>
<td>-</td>
<td>50-200</td>
<td>Circular to elliptical</td>
<td>Paleogene</td>
</tr>
<tr>
<td>Gemmer et al. (2002)</td>
<td>100-300</td>
<td>-</td>
<td>5-10</td>
<td>circular</td>
<td>Danian</td>
</tr>
<tr>
<td>Hovland et al. (2002)</td>
<td>1-700</td>
<td>-</td>
<td>0-45</td>
<td>Several Types</td>
<td>—</td>
</tr>
<tr>
<td>Paull et al. (2002)</td>
<td>8-12</td>
<td>2000-3000</td>
<td>130-260</td>
<td>Circular</td>
<td>Recent</td>
</tr>
<tr>
<td>Cifci et al. (2003)</td>
<td>50-200</td>
<td>-</td>
<td>10-25</td>
<td>Circular and elongated</td>
<td>Recent and buried</td>
</tr>
<tr>
<td>Ussler et al. (2003)</td>
<td>10-350</td>
<td>-</td>
<td>&gt;5</td>
<td>-</td>
<td>Recent</td>
</tr>
<tr>
<td>Sumida et al. (2004)</td>
<td>1000</td>
<td>-</td>
<td>100</td>
<td>Circular</td>
<td>Recent</td>
</tr>
<tr>
<td>Hovland et al. (2005)</td>
<td>Up to 320</td>
<td>-</td>
<td>Up to 15</td>
<td>Circular</td>
<td>Recent</td>
</tr>
<tr>
<td>Schroot et al. (2005)</td>
<td>40-150</td>
<td>-</td>
<td>2</td>
<td>Circular</td>
<td>Recent</td>
</tr>
<tr>
<td>Gay et al. (2006)</td>
<td>100-300</td>
<td>-</td>
<td>Up to 20</td>
<td>-</td>
<td>—</td>
</tr>
</tbody>
</table>

**Table 1.2:** Table showing the dimensions and geometry of pockmarks described by previous studies. (Recent (Holocene) = Approx. 12,000 years ago- Present. Pliocene = Approx. 5.3million- 2.6million years ago. Paleogene = Approx. 65.5million-23million years ago. Danian= Approx. 65.5million- 61.7million years ago).
1.2.3 Global Geographical Distribution of Pockmarks

Pockmarks are known to occur in a variety of marine environments from estuarine to marine shelf and have been recorded at all water depths from <10m to ~5000m (Hovland & Judd, 1988). They are also reported in lacustrine environments (Hovland & Judd, 1988; Pickrill, 1993). Besides a sub-aqueous environment, certain other factors seem to be important in pockmark formation. These include (1) a source of fluid to produce the pockmark: gas of thermogenic or biogenic origin or pore fluid from rapidly buried and compacting sediments and (2) a fine-grained clay-rich and soft substrate. In theory therefore, “true” pockmarks should not form in a crystalline or lithified substrate. Examples of crater-like structures that cut lithified strata are interpreted to form through catastrophic eruption of gas through a competent seal layer such as volcanoclastic tuffs (Cole et al., 2000) or gas hydrates (Solheim & Elverhøi, 1993). While fluid escape will occur through coarse-grained sandy substrates no pockmark will be formed, although other indications of fluid escape may be observed such as bioherms or bacterial mats (Fader, 1991).

Despite the above criteria, pockmarks have been observed in some surprising settings. For example in the Swedish Baltic Sea pockmarks occur in an area of crystalline rock with only a very thin sedimentary cover. Here they are interpreted to be sourced by thermogenic gas that has migrated through basement fractures from source beds (Hovland, 1992). To date, the only bays and estuaries along the Atlantic coast of North America that are known to contain pockmarks are those along the Fundy/Gulf of Maine coasts. A factor in the formation of these pockmarks could be the macrotidal setting of these areas. Changes in the delicate balance between the pressure of confined shallow gas and the pressure imparted by the overlying water,
brought about by the extreme tidal range, could be enough to cause periodic release of gas (Fader, 1991).

Pockmarks have previously been noted to occur in a variety of environments, including: in association with mud diapirs and mud volcanoes (Dimitrov & Woodside, 2003; Hovland, 1992; Hovland & Judd, 1988), on active faults (Dimitrov & Woodside, 2003; Fader, 1991; Soter, 1999; Syvitski & Praeg, 1989), in association with submarine slumps (Dimitrov & Woodside, 2003; Foland et al., 1999; Schwab & Lee, 1988). Environments with these geological or structural features may be more likely to develop pockmarks.

A link between pockmark occurrence and petroleum basins has been implied both in the literature (Hovland & Judd, 1988) and within the petroleum industry, particularly with respect to new venture exploration. In an area with an active petroleum system there is an additional source of migrating fluids (thermogenic hydrocarbons) that could form pockmarks and in some cases gas escaping from pockmarks has been shown to be thermogenic in origin (Hovland & Sommerville, 1985). While pockmarks may be more common in petroleum basins, many of their occurrences are in non-petroleum bearing basins as pockmarks will form equally from biogenic gas or sedimentary pore fluids. While several observations regarding the geographical distribution of pockmarks have been made it is probable that the apparent clusters of pockmark occurrence are largely due to sampling bias whereby many examples are documented from shallow coastal waters, often in heavily fished northern latitudes and many examples come from environments where active petroleum exploration and production is occurring. The seafloor of these areas tends
to be heavily investigated with echo-sounders, sonar and seismic surveys (Hovland & Judd, 1988).

1.3 Characteristics of Marine Sediment

Any solid fragment of inorganic or organic material may be termed sediment. Marine sediments include those found along the coast; rocks and pebbles on a beach, fragments of seashells, or sand and mud at the bottom of a bay. In general terms, marine sediments consist of rock and soil particles (insoluble material), organic matter and remnants of marine organisms that accumulate on the seabed. They are the oceanographers’s history book as they record the past biological, chemical and physical history of the ocean. There is a wide variation in the composition and physical characteristics of marine sediments depending on water depth, distance from land, variations in sediment source and the physical, chemical and biological factors of their environments (Romero et al, 2008). Marine sediments are often classified according to their origin (Goldberg, 1963) and broadly consist of detrital, biogenus and hydrogenous components (Li and Schoonmaker, 2005). The detrital part consists of lithogenous and cosmogenous materials. The lithogenous constituents of marine sediment are materials derived from the weathering of rock on land and on the seafloor or from volcanic eruptions and undergo little or no transformation during deposition in ocean basins (Windom, 1976). Cosmogenous constituents consist of cosmic spherules containing iron-nickel particles that are formed by the reactions of iron meteorites passing through the Earth’s atmosphere, and include fragments of silicate chondrules (Arrhenius, 1963). The biogenus component contains planktic, benthic organisms and biogenic apatite (Berger, 1976). The hydrogenous constituent
of marine sediments contains phases formed by inorganic precipitation from seawater (Elderfield, 1976, Piper and Heath, 1989).

Numerous studies have been carried out on marine sediments. Preda and Cox (2004) investigated the chemical and mineralogical composition of marine sediments and their source and transport in the Gulf of Carpentaria in Northern Australia. The results of their study indicated a complex history over a short time period, with sediment supply, biological production and current patterns being the main factors that controlled the sediment character and its regional distribution within the Gulf. Naimo et al., (2005) studied the mineralogy and geochemistry of sea sediments from a 6 meter core collected in the Gulf of Salerno, Italy. Their results indicated enhanced barium concentrations at 160cm and 320cm below the seafloor and an increased lead content on the seabed. Zinc, nickel and manganese were strongly bonded to residual mineral phases, likely of volcanic origin. Iron was found mainly associated with easily reducible oxide phases and as pyrite. Ohta and Imai (2012) studied multi-elements in coastal sea and stream sediments in the Island Arc Region of Japan, taking in to account the mass transfer of elements from terrestrial to marine environments. They found that elemental abundance patterns were consistent with those of local stream sediments and with Japanese upper crust materials and concluded that coastal sea sediments in the region were originally adjacent terrestrial materials.

Knowledge of the physical, chemical and biological properties of marine sediment is important and can determine potential uses of the seabed. Engineering behaviour depends on all three. For example, the strength of fine-grained sediments
is mainly controlled by the geochemistry (mineralogy) of the components, which in turn is then linked to biological processes. Conditions that affect physical properties and seabed conditions are dynamic loading by waves, earthquakes and sediment structure interactions, high carbonate content, gas in sediments and high inorganic content.

Inorganic material in marine sediments can be generally divided in to four categories; authigenic, biogenic, detrital and anthropogenic. Authigenic components apply to minerals formed in-situ during the formation of the rock in which they form e.g an igneous rock. Authigenic minerals include non-biogenic carbonates: like dolomite, CaMg(CO$_3$)$_2$ (Moore et al.,2004) and rhodochrosite, MnCO$_3$ (Burke and Kemp, 2002). Manganese oxides (MgO) and iron oxides (FeO) can sometimes contain nickel, copper and cobalt (Burdige, 2006). Sulphide minerals: mackinawite (FeS), greigite (Fe$_3$S$_4$) and pyrite (FeS$_2$) (Morse, 1999). They can also contain phosphate minerals and various types of phyllosilicates (Ruttenberg and Berner, 1993). Research in this area also includes analysis by Reichel and Halback (2007), where they investigated an authigenic calcite layer on sediments from the sea of Mermiera. Two piston cores and a gravity core were analysed using analytical techniques that included X-ray Diffraction (XRD), to calculate the weight percent (wt%) of CaCO$_3$. They used a Scanning Electron Microscope (SEM) with an Energy Dispersive System (EDS) and also an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) to determine element concentrations. As a result of their analysis they were able to calculate a calcite content of more than 30% (wt%) and were able to hypothesise that the calcite layer was the result of an authigenic precipitation. Cole and Shaw (1983) using gravity core samples
investigated the origin of authigenic smectites in marine sediments. They also used XRD to analyse bulk samples and clay fractions and SEM for further chemical analysis.

Biogenic components in marine sediment include sedimentary deposits e.g. shelly limestone (formed from once living organisms). Generally they are defined as containing at least 30% skeletal remains of marine organisms and cover approximately 62% of the deep ocean floor. They mainly contain biogenic carbonates; calcite and aragonite – CaCO$_3$ (Jahnke and Jahnke, 2004, Gehlen et al., 2005) and amorphous hydrated silica (Vreiling et al., 2002). The main contributors of calcium carbonate are planktonic foraminiferids, coccolithophorids and pteropods and contributing to the silica cycle are radiolaria, diatoms and to a lesser degree, dilicoflagellates and sponges. Pirrung et al., (2008) investigated biogenic barium in marine surface sediments of the European Nordic Sea. The majority of barium in marine surface sediments is normally of terrigenous origin and not of biogenic origin. They analysed box core and multi-core sediment samples using XRD, XRF and ICP-AES and were able to determine the distribution of biogenic barium in surface sediments across the study area.

Detrital components are fragmented rock material, formed by the breaking up and erosion of rocks. This is particularly relevant in coastal areas due to the closeness of a landmass. Mechanisms which result in the formation of detrital materials include redox processes and the dissolution of salt deposits (NaCl), limestone (CaCO$_3$) and silicate rocks (Burdige, 2006). The coarser constituents of detrital sediments include quartz, feldspars, amphiboles and a wide spectrum of other rock-forming minerals.
The finer-grained components also include some quartz and feldspars but here they mainly belong to a group of sheet-silicate minerals i.e. clay minerals. The most common of these are illite, montmorillonite, kaolinite and chlorite. Demory et al., (2005) investigated detrital input and early diagenesis on sediments in Lake Baikel. They used XRF and Transmission Electron Microscopy (TEM) to compliment continuous rock magnetic measurements.

Anthropogenic materials are relatively recent phenomena and are the result of human and industrial activity e.g. heavy metals (Gagnon et al., 1997). The increased use of metals in human society has significantly changed their original distribution patterns in natural environments (Gao and Li, 2012) and trace metals are recognised as an important indicator of the degradation of aquatic environments (MacDonald et al., 1996 and Allen Burton, 2002). Significant amounts of trace metals can enter the coastal environment each year from anthropogenic related activities like untreated industrial waste water and sewage effluent etc. Contaminants accumulating in coastal marine sediments from anthropogenic and natural sources can often serve as a record of natural and anthropogenic events that occur in drainage basins, local and regional air masses or several other factors can affect the marine environment (Callender, 2005). Gao and Li (2012) studied concentrations and fractionations of trace metals in marine surface sediments from Bohai Bay, China. They collected fifteen sediment samples from five different locations in the bay and used sediment quality guidelines and geochemical normalisation methods to monitor the potential risk and accumulation of metals. They concluded that trace metal concentration levels of Bohai Bay sediments are normal at present but need to be monitored as industrial development and urbanisation increases. Riyadi et al., (2011) studied the profile of
trace elements in marine sediments from Jakarta Bay, Indonesia. Fifteen surface marine sediments were analysed by XRF for heavy metal contamination. From their analysis they concluded that although there was an apparent anthropogenic impact on metal levels in the bay, their degree of contamination was moderate.

In terms of inorganic material from marine sediments in Dunmanus Bay, it is envisaged that they should contain a combination of authigenic, biogenic, detrital and anthropogenic materials. The 2011 National Census indicated that there were in excess of 7,000 people living in the coastal area and river catchment of Dunmanus Bay. Bantry town accounted for almost 45% of this with a population of 3,348 with the remainder of the population living in rural areas of the catchment (National Census of Ireland 2011).

1.3.1 Classification and Analysis of Marine Sediment

As discussed in section 1.3, marine sediments originate from a wide variety of sources, including continental and ocean crust, microbes, plants and animals, chemical processes and outer space. However, it can be extremely difficult to identify the source of a particular deposit of marine sediment. Many factors can cause sediments to change from their original condition including, physical, chemical and biological transformations that occur after the sediment is formed. Various classification and analysis techniques are used to characterise sediments. *Descriptive classification* is based on a visual analysis of the texture and composition of a sediment sample. This is often the initial step in differentiating sediments. *Size classification*, based on visual, mechanical or laser-based sizing of sediments, helps
in understanding physical and chemical changes in sediments that occur during transportation and deposition. Genetic classification involves a more detailed description of the physical, chemical and biological properties of sediments. This should lead to a more detailed understanding as to how sediments are formed and deposited.

The composition of marine sediment includes naturally occurring major and trace elements acting as structural components of minerals. Important information on the origin of marine sediments is determined by their chemical and mineralogical composition and this information can be used to reconstruct the chemical and physical conditions of past environments and in some cases to recognize climatic events (Naimo et al, 2005). An example of this is the post-depositional mobilization of iron, manganese, barium and other elements as a result of redox reactions at the sediment-water interface linked to biological activity and sedimentation rate (Thomson et al., 1998). In comparison to deep-sea and deep-ocean sediments, the characteristics of marine sediments deposited on coastal areas (e.g. Dunmanus Bay) and on continental shelves are closely related to the geology and hydrography of the adjacent land areas as well as the local climate. As a result of this, a geochemical and/or a mineralogical study of these sediments can provide a valuable insight into regional hydrodynamics such as patterns of sediment transportation, deposition and weathering characteristics (Siddiqueie and Mallik, 1972; Moriarty, 1977; Shaw, 1978; Shaw and Bush, 1978; Gardner et al., 1980; Stein et al., 1994; Chauhan and Gujar, 1996; Lamy et al., 1998; Hillenbrand et al., 2003; Preda and Cox, 2004; Diju and Thamban, 2006; Bernárdez et al., 2011).
Coastal areas like bays and gulfs are among the most studied marine environments, due mainly to their environmental and socioeconomic importance. The primary objective of the majority of these studies is the estimation of abundance and distribution of sediment components (mainly major and trace chemical elements) which can indicate the sediments origin (McLaren et al., 1981; Ergin et al., 1996; Srisuksawad et al., 1997; Basaham and El-Sayed, 1998; Cho et al., 1999; Kim et al., 1999; Sirocko et al., 2000; Karageorgis et al., 2004; Preda and Cox, 2004; Fernandez et al., 2007). The identification of sediment sources and the distribution of sediment components provide useful information that can be used to assess the dynamics of a particular study area. For example, the vertical changes in sediment character can give an indication of changing sedimentation conditions over thousands of years (Sohlenius et al., 2001) while lateral changes in the character can be attributed to present oceanographic conditions (Leivuori and Niemisto, 1995; Brunskill et al., 2001). Numerous other studies also consider the mineral character of marine sediments, which can also help determine their sources and depositional conditions (e.g Bayhan et al., 2001; Jeong et al., 2004; Preda and Cox, 2004; Garcia-Rosales et al, 2011). To summarise, the classification and analysis of marine sediments is a complex process. Most studies employ a combination of analytical techniques which tend to complement one another and generate a wide range of results data.

1.3.2 Interpretation of Colours in Marine Sediment

The colour of marine sediment is dependent on a number of factors, including grain size, the chemical nature of the component minerals and the nature of the adsorbed material which occurs on the surface of the mineral grains. The specific
colour of muddy sediment is probably mainly influenced by the nature of the adsorbed material. Sediments containing very small particles, which have a large relative surface area have much greater powers of adsorption than sediments containing coarser material (Pantin, 1969). Sedimentologists have long interpreted the colour of marine sediments as a qualitative measurement on in-situ redox conditions (Tomlinson, 1916). Green or green-grey colours can be associated with reducing conditions (ferrous iron), while red or brown hues are attributed to an oxidised (ferric) environment (Lyle, 1983). Studies have shown that a brown (oxidised) sediment layer can often be found above green (reduced) sediments, especially in hemipelagic deposits (Bezrukov, 1960; Lynn and Bonatti, 1965). The thickness of this brown layer is hypothesized to be an indication of the amount of organic matter flux to the seabed and its rate of burial. If high rates of organic matter deposition occur, oxygen is rapidly consumed and the brown surface layer is anticipated to be thin or disappear. While at low rates of organic matter deposition or very slow sedimentation rates, the diffusion of oxygen into the sediments exceeds its consumption during the degradation of organic matter. As a result, the sediments remain brown throughout the length of the sediment column (Lyle 1983). Black hues in marine sediments are associated with pyrite formation. In anoxic environments pyrite can be formed as a result of organic matter degradation by sulphate-reducing bacteria (Schippers and Jørgensen, 2001). In bioturbated sediments, pyrite can be transported to the sediment surface where oxygen can chemically oxidise the metal sulphides (Luther et al., 1982; Thamdrup et al., 1994).

Bender et al, (1978) studied iron and manganese in the porewaters at the Manganese Nodule Project in the eastern tropical Pacific and they concluded that the
brown-green colour change was due to Fe (III) reduction. Pantin, (1969) studied the appearance and origin of colours in muddy marine sediments around New Zealand. His conclusions linked olive and green hues in sediment to adsorbed organic material and orange hues to the presence of ferric oxide or hydroxide, accompanied in some cases with manganese dioxide.

1.4 Hydrocarbon Seeps

In the marine environment, hydrocarbon seeps and hydrothermal vents are now known to be common and recognisable features that release fluids rich in methane and hydrogen sulphide (Campbell, 2006). It is estimated that between 6.6 – 19.5 teragrams of methane is released annually from the marine environment into the atmosphere (Judd et al., 2003). Since communities based on chemosynthetic carbon-fixation were first discovered almost three decades ago at seafloor cold hydrocarbon seeps (Paull et al., 1984) and hydrothermal vents (Lonsdale, 1977; Corliss et al., 1979), further investigations of the seabed have revealed numerous modern vent-seep locations that sustain various populations of metazoans and microbes. Hydrothermal vents and hydrocarbon seeps are known to exist worldwide, and can occur in most marine environments from shallow waters to the deep ocean, with seep characteristics ranging from diffuse seafloor venting to more focused gas escape (e.g. Miura et al., 1997; Bohrmann et al., 1999, 2002; Fujikura et al., 1999; Van Dover et al., 2001; Hovland et al 2002; Buenz et al., 2003, 2005; Edmonds et al., 2003; Judd, 2003; Buenz and Mienert, 2004). Geophysical data from many of these seafloor features show clear evidence of fluid seepage and venting e.g. mud volcanoes and
pockmarks (Hovland et al, 1997; Uenzelmann-Neben et al., 1997; Grave 2000; Gay et al., 2003, 2006a, b, 2007; Pilcher and Argent, 2007).

Typical deposits formed at hydrothermal vents include igneous rock formations and volcanic massive sulphide deposits. Typical hydrocarbon seep deposits include $^{13}$C-depleted authigenic carbonates, commonly with shelly biota, forming at or near the seafloor (Van Dover, 2000; Fujioka et al., 2002). At the bottom of the chemosynthetic food chain, the methane-and/or-sulphide rich fluids of vents and seeps are oxidised by symbiotic prokaryotes to produce biomass used by mega-invertebrates (Van Dover, 2000). Additionally, ecological distribution patterns at vent and seep sites are controlled by fluid flux rates and the availability of reduced chemical species in the water column or sedimentary pore waters (e.g. Van Dover, 2000; Sahling et al., 2002; Treude et al., 2003). Site analysis at seeps and gas hydrate locations have, for example, verified the importance of sulphate-dependent, anaerobic oxidation of methane (AOM) in authigenic carbonate formation (e.g. Elvert et al., 1999; Hinrichs et al., 1999; Thiel et al., 1999; Aharon, 2000; Boetius et al., 2000; Valentine, 2002; Treude et al., 2003). The formation of authigenic carbonate and barium sulphate in seep environments is the result of the microbially mediated process of AOM, or as a consequence of it (Ritger et al., 1987; Ferrell and Aharon, 1994; Fu et al., 1994; Aquilina et al., 1997; Nähr et al., 2000; Greinert et al., 2001). Authigenic minerals at hydrothermal vents form by the mixing of hot, metal-rich, reduced fluids with seaweed (Hannington et al., 1995). The physical characteristics of hydrothermal vents and hydrocarbon seep deposits can often provide evidence to their origin. Many authigenic precipitates are (1) isolated stratigraphically (2) exist in areas linked with syn-sedimentary faults or mud diapirs.
and (3) situated in geologic settings comparable to those of vent-seep environments today (e.g. Moore et al., 1986; Dubé, 1988; Campbell, 1992, 1995; Campbell et al., 1993, 2002; Little et al. 1998, 1999b). Hydrocarbon seepage (slow emission rate) and venting (fast emission rate) are generally characteristic of low-temperature, fluid expulsion systems of sedimentary basins (Aharon, 1994; Parnell, 2002) whose typical geological output have been termed chemoherm i.e. “a build up of chemical carbonates and calcareous skeletal debris of chemosymbiotic fauna whose carbon is primarily derived from microbial processes in domains of cold hydrocarbon venting and which possess anomalously negative carbon isotope composition relative to the seawater carbon pool” (Aharon, 1994). For seep-carbonates it is important to establish the length of time they are exposed to the seafloor environments because (1) shells can become incorporated in carbonate cements that formed during post-burial fluid flow and (2) erosion may reveal “chimneys” or other carbonate features that originally developed in the subsurface (Diaz-del-Rio et al., 2003; Paull et al., 2005). In hydrocarbon seep areas, with high levels of methane production, methane can migrate upward to form gas hydrates near the seafloor and/or can be released directly into the water column as seeps and flares (Merewether et al., 1985; Ginsburg et al., 1993; Hornafius et al., 1999). In sediments some of this rising methane becomes anaerobically oxidized in the sulphate reduction zone through microbially mediated AOM to produce $\text{HCO}_3^-$ . This accompanying increase in alkalinity drives carbonate precipitation in seepage areas at or near the seafloor (Paull et al., 1992, Ritger et al., 1987). However, during normal organic matter degradation the resulting admixture of carbon and seawater can result in a change in the $^{13}$C signal of the biogenic methane, shifting the $\delta^{13}$C values in the forming carbonates to those more typical of thermogenic methane. This indicates that the possibility of a wide range of
isotopic signatures is possible for the carbonate-carbon formed in marine sediments associated with methane seepage. The resulting deposits are generally classified as “methane derived carbonates” or seep carbonates (Campbell, 2006). It is important to remember that, during carbonate development in sediments in hydrocarbon seepage areas, the possibility exists for the mixing of carbon sources and origins. This can result in the masking of original conditions (Campbell et al., 2002). The most comprehensive way to understand and explain hydrocarbon seepage, and its effect on organisms and sediments, is through an integrated analytical approach (e.g. Campbell et al, 2002; Peckmann et al., 2002; Conti et al., 2004).

There is general consensus that marine pockmarks are seepage related, at least in their origin. This suggestion is consistent with the richer fauna that is found inhabiting pockmarks and seepage locations as compared to surrounding areas (Dando et al., 1991; Sibuet and Olu, 1988). In areas of the North Sea, gas seepage in pockmarks has been found to stimulate and increase local benthic production through a bacteria based food web (Dando et al., 1991; Hovland and Thomsen, 1997). In addition, gas hydrates in the pore space of pockmark sediments are often related to the gas hydrate stability conditions associated with that location (Chand and Minshull, 2003; Fichler et al., 2005). In contrast, chemical analysis to confirm that gas seepage and venting are definite contributing factors to pockmark formations have only been made in a few locations worldwide and the majority of this analysis data is from isolated pockmarks, rather than pockmark fields (Ussler et al., 2003). The occurrence and preservation of pockmarks in areas of specific seabed sediment types seems to suggest that their formation is possibly more closely related to the specific type of seabed sediment than the source path of fluid venting such as faults.
etc. (Hovland, 1981; Chand et al., 2008). There seems to be a number of mechanisms and conditions responsible for pockmark formations and while they are generally considered to be a phenomena caused by the escape of gas or fluid from the seabed/bedrock, at some stage mostly fine-grained sediment will be brought into suspension and transported away by currents. Thus, soft fine-grained sediment is often suggested as a necessary medium for the formation of pockmarks.

Hovland (2003) suggests two methods of proving fluid seepage through the seabed, either visually (by seeing bubbles or “shimmering water”) or by geochemical sampling and analysis. A visual fluid flow is normally called a macro-seep and one that cannot be easily seen but which can be determined geochemically, a micro-seep. In addition to this, there is indirect documentation where biology is used (bacterial mats etc.) to accurately determine a seep location on the seabed (Sassen et al., 1993). Usually such seeps, because they have a chemical signal, come under the micro-seep category (Hovland, 2005).

The pockmark field mapped in Dunmanus Bay contains over 60 pockmarks. Some of the pockmarks are up to 20 m in diameter and they range from 0.3 m to 0.8 m in depth. The pockmarks appear in clusters and seem to be parallel to one another although observing the entire pockmark field, as a whole, there is a distinct northeast-southwest orientation, with the two rock outcrops at either end (Szpak, 2012a; O’Reilly, 2013).
1.5 Marine Calcification

1.5.1 Calcium Carbonate

The behaviour of calcium in the marine environment is of significant interest because of the formation of biogenic and nonbiogenic calcium carbonate (CaCO$_3$), a process known as calcification, and its connection with the global carbon cycle (De LaRocha and DePaolo, 2000; Heuser et al., 2005). Calcium Carbonate, in various forms, is an important and often dominant component of marine sediments. The main source of carbonate minerals has shifted from abiotic precipitation to biogenic sources (i.e. those minerals that are actively precipitated from the sea water by organisms to form skeletal parts). These biogenic sources have subsequently shifted from being primarily shallow water benthic organisms to the present situation where small open ocean pelagic organisms dominate calcium carbonate formation. A significant amount of the calcium carbonate which is formed in marine environments is dissolved in the water column and in sediments through processes known collectively as diagenesis. This is the term used for all of the changes that a sediment undergoes after deposition and before the transition to metamorphism (Morse et al, 2007).

The presence of carbonate minerals in marine environments can be divided into those found in shallow water or photic zone (depths less than 200m) (e.g. Jørgensen, 1989; Jensen et al., 1992; Stakes et al., 1999; Peckmann et al., 2001; Kinnaman et al., 2010; Lavoie et al., 2010; O’Reilly et al. 2014) and in deep water (greater than 1km) environments (e.g. Ritger et al., 1987; von Rad et al., 1996; Chen et al., 2005; Feng...
et al., 2010; Crémière et al., 2012; Magalhães et al., 2012). The circumstances controlling the origins, mineralogy and diagenesis of carbonates in both these environments are very different. In shallow water environments, the sources and diagenesis of carbonates differ significantly between carbonate-rich and primarily siliclastic (detrital minerals such as clays and quartz sands) sediments. In deep water environments, carbonates predominantly originate from pelagic skeletal organisms, with coccolithophores (plants) being the most significant, followed by foraminifera (animals) (Archer, 1996).

The important role of Ca in biogeochemical processes is due to its chemical versatility which is based on its highly adaptable coordination geometry, its divalent charge, modest binding energies, fast reaction kinetics and its inertness in redox reactions (Williams, 1974). High Ca abundances can be an indication that sediments are of a natural origin (Salazar et al, 2004). As it is positively charged (cation) Ca is also active and mobile. It is a relatively large atom and its two electrons in the outer orbit tend to be lost resulting in the calcium cation $\text{Ca}^{++}$. Under certain conditions, these calcium cations can form bonds which vary in the strength in which they are held. Ionic Ca can be found in fresh and salt water. Interest in calcium and calcium carbonate formation and dissolution in the marine environment has increased due to the significant role these reactions have on the ocean’s response to the increasing partial pressure of carbon dioxide ($\text{pCO}_2$) in the atmosphere (e.g. Broecker and Takahashi, 1978; Opdyke and Walker, 1992; Archer and Maier-Reimer, 1994; Gehlen et al, 2005; Morse et al., 2007). Due to the combined effect of pressure increase and temperature decrease, the solubility of $\text{CaCO}_3$ increases with depth. In marine sediments, what happens to carbonate particles depends on the saturation rate
of bottom waters and thus carbonate solubility, rate of mixing, the \( \text{CaCO}_3 \) content of sediments, the metabolic activity and particle characteristics (i.e. specific surface and trace element content) (em.

(e.g. Emerson and Bender, 1981; Archer et al, 1989; Hales et al., 1994; Jahnke et al, 1994; Martin and Sayles, 1996; Jahnke et al., 1997; Mucci et al., 2000) In addition, the post-depositional dissolution of marine carbonates may affect the chemical and isotopic composition of biogenic carbonate particles such as foraminifera (Lohmann, 1995; McCorkle et al., 1995; Martin et al., 2000; Broecker and Clark, 2001, 2003).

1.5.2 Limestone

In some marine environments Ca reacts with dissolved \( \text{CO}_2 \) to form limestone. Most limestones form in shallow, calm, warm marine waters. Here organisms capable of forming \( \text{CaCO}_3 \) shells and skeletons can readily extract the required ingredients from ocean water. When these animals die their shells and skeletal material accumulate as sediment that can be lithified into limestone. This limestone, of biological origin, settles on the seafloor becoming part of sediments and new rock formations. Some limestones may also be formed by the direct precipitation of marine waters, although limestones formed this way are less abundant than biological ones (O’Donoghue, 1990).

1.5.3 Carbonate Minerals

Examples of Ca containing minerals on the seabed are calcite and aragonite, both polymorphs of \( \text{CaCO}_3 \). These minerals are also produced by various sea
organisms to make their shells, aragonite (pteropods) and calcite (foraminiferal and coccolithophorid). Although coccolithophorids are thought to dominate global CaCO₃ production (Westbroek et al., 1993), isotopic and elemental studies of foraminiferal shells are widely used to reconstruct past ocean circulation and chemistry (e.g. Boyle and Keighwin, 1982; Boyle, 1988, 1992; Curry et al., 1988; Duplessy et al., 1988; Lea and Boyle, 1989, 1990; Lea, 1993; Rosenthal and Boyle, 1993; Anderson and Archer, 2002).

The most basic requirement for the precipitation of these minerals is that the product of the concentrations of calcium (Ca²⁺) and carbonate ions (CO₃²⁻) exceeds the solubility product of calcite and aragonite respectively (Bosak, 2011). Temperature and pressure are a significant influence in the solubility of carbonate minerals. Solubility decreases with increasing temperatures and increases with increasing pressure. When a solution is in equilibrium with carbon dioxide the carbonate ions are determined by pH. In solutions that are under-saturated, such as modern seawater, biological activity generally controls the precipitation of CaCO₃ (Bosak and Newman, 2005). As the concentration of carbonate ions increases with increasing pH, the precipitation of calcium carbonate minerals will also increase with increasing pH. There are many microbial metabolic processes that can increase pH and/or the concentration of carbonate ions. These include, sulphate reduction in marine sediments (Visscher, 2000; Van Lith et al., 2003; Dupraz and Visscher, 2005), anaerobic oxidation of methane in conjunction with sulphate reduction in marine sediments (Reitner et al., 2005). Factors that inhibit the precipitation of calcium carbonate minerals include the absorption of various metabolites such as
sulphate, and organic materials onto the faces of the growing crystals (Teng et al., 1998; Plant and House, 2002; Bosak and Newman, 2005).

1.6 Methane Seeps and Carbonate Precipitation

Authigenic carbonate precipitation is one of the common outcomes in seep environments, these are associated with seabed features such as pockmarks, mud diapirs and mud volcanoes (Cangemi et al., 2010; Gontharet et al., 2007; Haas et al., 2010; Hovland et al., 2005). These authigenic carbonates are known to occur in sediments containing CH$_4$ hydrates and in sediments at or near the seabed over CH$_4$ hydrate deposits (Bohrmann et al., 1998; Aloisi et al., 2000; O’Reilly et al. 2014; Smith and Coffin., 2014). Referred to as Methane-Derived-Authigenic-Carbonates (MDAC) these carbonates are known to form carbonate structures and concretions on the seafloor (carbonate mounds, slabs, rocks etc.) in areas with a significant CH$_4$ flux (Greinert et al., 2001; Moore et al., 2004; Ussler and Paull., 2008). Carbonates in sediments can be formed as a result of the microbially-mediated oxidation of CH$_4$ and authogenic carbonates are regularly associated with faults that can facilitate the upward migration of fluids and CH$_4$ (Bohrmann et al., 1998; Rodriguez et al., 2000; Berelson et al., 2005). Carbonate in hydrate bearing sediments can be biogenic and/or authogenic carbonate derived from dissolved inorganic matter (DIC) in seawater or from DIC generated during the oxidation of organic matter, methane, or non-methane hydrocarbons (Formolo et al., 2004). In marine sediments containing or overlying a CH$_4$ hydrate, there is close affinity between gas hydrates, CH$_4$ flux, the anaerobic oxidation of methane (AOM), the oxidation of organic matter through sulphate reduction (SR), and authigenic carbonate mineralisation (Naehr et al., 2000;
The precipitation of authigenic carbonate minerals (calcite, aragonite, dolomite etc.) in such areas contribute in regulating the flux of CH$_4$ to the water column and atmosphere (Boetius and Suess, 2004). In cold seep and gas-hydrate influenced sediments authigenic carbonate minerals (calcite, aragonite, dolomite etc.) can precipitate from the oxidation of methane-rich fluids. In this process, carbonate precipitates as a secondary reaction of the oxidation of organic matter by sulphate reduction and/or AOM. The reactions for these can be presented as follows:

**Sulphate Reduction:**

$$2(\text{CH}_2\text{O})_n + \text{SO}_4^{2-} \rightarrow 2\text{HCO}_3^- + \text{H}_2\text{S} \quad \text{Eqn. (1.1)}$$

**Anaerobic Oxidation of Methane:**

$$\text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + \text{HS}^- + \text{H}_2\text{O} \quad \text{Eqn. (1.2)}$$

Given that aerobic oxidation promotes carbonate dissolution in surficial sediments through the lowering of porewater pH, the combined effect of the microbially-mediated diagenetic reactions above result in increased porewater alkalinity (generating bicarbonate). In the presence of seawater-derived cations (Ca$^{2+}$, Mg$^{2+}$) this can lead to the precipitation of authigenic carbonates (Chatterjee et al., 2011; Valentine, 2002; Smith and Coffin, 2014). The resulting reaction is as follows:

$$\text{Ca}^{2+} + \text{HCO}_3^- \rightarrow \text{H}^+ + \text{CaCO}_3 (s) \quad \text{Eqn. (1.3)}$$
In areas located over suspected hydrate deposits, high concentrations of authigenic carbonates can signify elevated rates of AOM. Carbonate precipitation can occur at or around the sulphate-methane interface (SMI) or through the sulphate-methane transition zone (SMTZ). The SMTZ can be an area of intense CH$_4$ oxidation and carbonate precipitation associated with CH$_4$ oxidation can commonly form discrete (mm size) concretions in hydrate bearing sediments (Borowski et al., 1999; Snyder et al., 2007; Chatterjee et al., 2011).

This study will specifically focus on the calcium and calcium carbonate component of the bulk sediment collected, to determine their concentrations and distribution patterns in the methane seep environment (pockmark field) confirmed to exist in Dunmanus Bay (Szpak, 2012a; O’Reilly, 2013). In the pockmark field there are no obvious visual indications of carbonate formation or methane-derived-authigenic-carbonates e.g. carbonate slabs, carbonate rocks or carbonate mounds etc. normally associated with hydrocarbon seeps. Thus analytical analysis of these sediments may provide a possible explanation for this and indicate what type of carbonate precipitation/dissolution mechanisms are taking place.

1.7 Gas Seepage and Pockmarks in Irish Waters

As well as Dunmanus Bay, gas seepage and pockmarks have been documented in other coastal areas in Irish Waters. These include the Malin Shelf, off the northeast coast of Ireland, where pockmarks and gas seepage have been recorded and studied (Szpak, 2012). Also, off the east coast, an active seepage at the Codling Fault Zone has been studied (O’Reilly, 2014).
1.8 Analytical Techniques for Inorganic Sediment Analysis

Marine sediments present a number of analytical problems. Often there is a limited quantity of sample to work with, so techniques favoured tend to be ones that are non-destructive and require little sample preparation. A typical marine sediment is a mixture of sediments from many and diverse sources, so a suitable analytical technique must be able to analyse both the major and minor components present in the sample. Also, because of the significant expense of sampling marine sediments, sampling expeditions tend to collect as many samples as possible. This results in a high number of samples to be tested so whatever analytical techniques are used must be able to accurately analyse a high volume of samples (Balsam et al., 2007).

The sampling procedures for collecting sediment samples often vary, depending on monitoring and analytical objectives, weather conditions etc. However to accurately compare studies and data analysis it is very important that harmonized sampling techniques and procedures are adhered to. Correct sample preparation, which includes separation of coarse material, homogenization and drying is a critical step in all sediment analysis.

One of the principal parameters used to characterise marine sediment is the qualitative and quantitative analysis of major elements (Ca, Fe, Mn, Mg, K, P, Na, Si, Ti, Al) and trace elements (in abundances > 1ppm; Ba, Ce, Co, Cr, Cu, Ga, La, Nb, Ni, Rb, Sc, Sr, Rh, U, V, Y, Zr, Zn). Appropriate analytical techniques include Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Inductively Coupled Plasma Optical (Atomic) Emission Spectroscopy (ICP-OES or ICP-AES) and X-ray Flouresence (XRF) (e.g. Bernick et
All these techniques have advantages and disadvantages including instrument availability, amount of sample available, number of samples to be tested, limit of detection, sensitivity and sample preparation requirements. In this study XRF, XRD and SEM were used to characterise the inorganic component of the marine sediment samples collected.

1.8.1 Particle Size Analysis

Particle size analysis is a fundamental yet very important physical property of sediments. It is considered a major factor that can influence the link between sediment composition and geochemical tendencies (Von Enyatten et al., 2012) and therefore provides important clues to sediment origin, transportation background and depositional conditions (Folk and Ward, 1957; Bui et al., 1990). Determining accurate classification in particle size distribution for natural geological samples, such as marine sediments, can be difficult. These sediments usually consist of a complex mixture of components with particles containing various shapes and materials such as organic matter and shell fragments etc. (Aloupi and Angelidis, al. 1995; Kalnicky and Singhvi, 2001; Radu and Diamond, 2009; El-taher, 2010; O’Reilly et al, 2012). In addition X-ray Diffraction (XRD) is widely used for bulk analysis of sediment composition and mineralogical characterisation (e.g. Grim, 1968; Brown and Brindley, 1980; Reynolds and Moore, 2007; O’Reilly et al., 2012) and Scanning Electron Microscopy (SEM) is used to study the surface, or near surface structure of bulk materials (Morse and Cornwell, 1987; Clayton and Pearse, 2007).
2001, Liaghati et al., 2003; Aloupi and Bouvy, 2008). However, obtaining accurate particle size analysis for marine sediments helps provide a greater understanding of the role of grain size in element concentration and distribution (Zaaboub et al., 2014). Trace elements and organic carbon are usually associated with fine-grained sediments because of their high surface to volume ratios and adsorption capacities (Burdige, 2006), while < 63µm particles are usually selected to monitor sediment contamination (Szava-Kovats, 2008). Grain size is an important factor when considering the variability and provenance of trace element concentrations in sediments (Forstner and Wittmann, 1981; Horowitz and Elrick, 1986, Cauwet, 1987; Ujevic et al., 2000). As grain size decreases, trace element concentrations tend to increase, reflecting variations in the physical and chemical dynamics affecting them (Forstner and Wittmann, 1981; Zaaboub et al., 2014).

Various techniques are used to determine grain size. These include, dry and wet sieving, sedimentation, and measurement by laser granulometer, x-ray sedigraph and Coulter counter (Blott and Pye, 2001). All these techniques involve the division of the sediment sample into a number of size fractions. This allows a grain sized distribution to be developed from the weight and volume percentage of sediment in each size fraction.

Many research results indicate that the chemical composition of sediment varies with grain size due to, multiple sources contributing mineralogically and texturally distinct grain sizes, mechanical weathering of rock fragments into finer components and chemical weathering of weak grains into products of alteration (Guagliandi et al., 2013). Spatial distribution and concentrations of elements in sediments have been
attributed, in part, to particle size (Jones and Bowser, 1978; Jenne et al., 1980; Förstner and Wittmann, 1981; Barbati and Bothner, 1993). Álvarez-Iglesias and Rubio (2007) investigated trace elements in shallow marine sediments from Ría de Vigo, Spain to determine sources, speciation and diagenesis. They observed a grain size effect in sediments where elements associated with fine-grained fractions, such as Al, V and Ni, correlated with the mud component of sediments. While elements such as Ca and Sr, with a biogenic provenance, were generally associated with coarse-grained fractions. Ohta and Imai (2011) used dried sieving techniques for particle size analysis as part of their investigation of multi-elements in coastal sea and stream sediments in the Island Arc Region of Japan. They determined that mineralogical compositions of coastal sediments vary with particle size and that this change can result in a change in chemical compositions. They concluded that the coarse sediments found in the marine environment contain quartz and calcareous shells, which enhance Si, Ca and Sr concentrations and deplete other elements. While consequently the concentrations of most elements increase with decreasing particle size. Zaaboub et al., (2014) investigated trace elements in different marine sediment fractions from the Gulf of Tunis, in the Central Mediterranean Sea. To determine particle size distribution they used a laser grain size meter. Their results indicated a significant correlation between particle size and type and concentration of trace elements. They concluded that the coarse sediment fraction had greater quartz enrichment and that finer particle sediment was richer in alkaline elements such as Na and K.
1.8.2 X-ray Fluorescence (XRF)

An X-ray Fluorescence (XRF) spectrometer is used for routine and relatively non-destructive chemical analysis of rocks, minerals, sediments and fluids. It is typically used to determine the inorganic chemical composition of a range of material types. XRF is fast and accurate and usually requires little sample preparation. It can also be used to determine the thickness and the composition of layers and coatings. Applications are extensive and include mining, mineralogy, geography and environmental analysis of water and waste materials along with metal, cement, oil, polymer, plastic and food industries (Brouwer, 2003).

In XRF, x-rays produced by a source irradiate a sample (Figure 1.8). Usually this source is an X-ray tube. When the elements are excited by an x-ray they can become ionised and if the energy of the radiation is enough to displace a tightly-held inner electron, the atom becomes unstable and an outer electron supersedes the missing inner electron. When this happens energy is released due to the increased binding energy of the inner electron orbital compared to the outer one. So therefore, in a particular element, the energy of the emitted photon is representative of the transition between specific orbitals and the resulting fluorescent x-rays can be used to detect abundances of elements present in a sample.

The elements present in the sample will emit fluorescent X-ray radiation with discrete energies (equivalent to colour for optical light) that are characteristic for these elements. By measuring the energies of the radiation emitted by the sample it is possible to determine which elements are present and by measuring the intensities of
the emitted energies it is possible to determine what concentration of each element is present in the sample.

Figure 1.8: Image outlining primary X-ray radiation (courtesy Thermo.com/nitcom)

Spectrometer systems can be divided into two main groups: energy dispersive systems (EDXRF) and wavelength dispersive systems (WDXRF). EDXRF spectrometers have a detector that is able to measure the different energies (wavelengths) of the characteristic radiation (x-rays) coming directly from the sample. The detector can separate the radiation from the sample into the radiation from the elements in the sample. This separation is called dispersion. WDXRF spectrometers use an analysing crystal to disperse the different energies. All radiation (x-rays) coming from the sample lands on the crystal. The crystal diffracts the different energies (wavelengths) into different directions, similar to a prism that disperses different colours into different directions (Brouwer, 2003). When the detector is placed at a certain angle, the intensity of the x-rays with a certain wavelength can be measured.
XRF as an analytical technique is limited to the analysis of relatively large homogenised samples (> 1 gram) and to materials for which compositionally similar, well characterised standards are available. However, with adequate sample amounts and good sample preparation techniques, XRF is especially well suited for rock and sediment analysis (including inorganic marine sediment) for bulk chemical analysis of major elements (Ca, Fe, Mn, Mg, K, P, Na, Si, Ti, Al) and trace elements (in abundances > 1ppm; Ba, Ce, Co, Cr, Cu, Ga, La, Nb, Ni, Rb, Sc, Sr, Rh, U, V, Y, Zr, Zn) (e.g Preda and Cox, 2004; Apeagyei et al., 2010; Hadler et al., 2011; Willershäuser et al., 2011; Rowe et al., 2012).

1.8.3 X-ray Diffraction (XRD)

X-ray Diffraction (XRD) is a non-destructive analytical technique used to identify and determine the crystalline structure of materials by determining their interplanar spacings. It has been of major importance in the natural sciences, since the first x-ray diffraction experiments were carried out on a single crystal in 1912. XRD provides a means of understanding the structure of materials on an atomic scale allowing the links between the crystal structure and the physical and chemical properties of the material to be established.

The fundamental principle of x-ray diffraction is based on Bragg’s Law (Bragg, 1913). This can be expressed as (Brown and Brindley, 1980):

\[ n \lambda = 2d \sin \theta \]  
Eqn. (1.4)

\( n = \) Order of interference (an integer value)
\( \lambda = \) Wavelength of radiation  
\( d = \) Interplanar distance  
\( \theta = \) Scattering Angle

This was derived by the English physicists Sir W.H. Bragg and his son Sir W.L. Bragg in 1913 to explain how the cleavage faces of crystals appear to reflect X-ray beams at certain angles of incidence. Bragg diffraction occurs when an electromagnetic radiation with a wavelength comparable to the interatomic spacing (distance between atomic planes) falls upon a crystalline structure and is then scattered in accordance to Bragg's law (Figure 1.9).

![Figure 1.9: When a monochromatic X-ray beam with wavelength \( \lambda \) is incident on lattice planes in a crystal at an angle \( \theta \), diffraction only occurs when the distance travelled by the rays reflected from successive planes differs by a complete number \( (n) \) of wavelengths. (Image Panalytical.com)](Image)

A diffraction pattern is collected by measuring the intensity of the scattered waves as a function of the scattering (Bragg) angle. Very strong intensity peaks are obtained in the diffraction pattern when the Bragg condition is satisfied (e.g KCl). A diffraction pattern consists of a series of reflected intensities versus the angular position (2\( \theta \)). Amorphous materials such as glasses, polymers and liquids do not have a long range...
order or a periodic network and therefore X-ray waves are scattered randomly as no
diffraction of the beam is possible. While in crystalline materials the interaction
gives rise to a diffraction pattern. The characteristics of the individual peak
(intensity, width etc...) will depend on experimental factors, defects in the perfect
lattice, differences in the strain in different grains and the size of the crystallites.

X-rays are produced from an X-ray tube by passing an electrical current into a
Copper anode filament (Cobalt, Molybdenum and other materials can be used as a
source). The interaction of X-rays with a crystalline solid produces a diffraction
pattern. Each pattern is unique for each material. This means that the same material
will always give the same reflections and a mixture of materials (e.g. a sediment
sample) each with its own specific structure will produce its own pattern
independently from the other. Most of the materials subjected to XRD analysis are
crystalline, i.e. they exhibit structural order with regular sets of crystal planes.

Identification is achieved by comparing the x-ray diffraction pattern (or
diffractogram) obtained from an unknown sample with an internationally recognised
database containing reference pattern for more than 70,000 phases (Panalytical.com).

Modern computer-controlled diffractometer systems use automatic routines to
measure, record and interpret the unique components in highly complex materials.
XRD can provide qualitative and quantitative analysis (Connolly, 2010). Qualitative
analysis usually involves the identification of a phase or phases in a sample by
comparison with “standard” patterns. This allows for a relative estimation of
proportions of different phases in multi-phase samples by comparing peak intensities
attributed to the identified phases. Quantitative analysis of diffraction data refers to
the determination of amounts of different phases in multi-phase samples.
Quantitative analysis can include the determination of particular characteristics of
single phases such as the precise determination of crystal structure and crystallite size and shape. A number of methods have been developed to use peak intensities for quantitative analysis of diffraction data these include The Absorption-Diffraction Method, Method of Standard Additions, Internal Standard Method, Reference Intensity Ratio Methods and Rietveld Method.

For X-ray diffraction analysis of soils and sediments, the Internal Standard Method and the Reference Intensity Ratio (RIR) method have been widely used for bulk mineralogical analysis including phase indentification and quantification (e.g. Chung, 1974; Kahle et al., 2002; Moros et al., 2003; Kim et al., 2006). This technique is outlined in the Materials and Methods Chapter.

1.8.4 Scanning Electron Microscope (SEM-EDS)

The scanning electron microscope (SEM) is primarily used to study the surface, or near surface, structure of bulk materials. The principle of operation of an SEM incorporates the use of a fine beam of electrons that scan across the surface of a specimen in synchronism with the spot of the display cathode X-ray tube (Figure 1.10). The electrons interact with the atoms in a sample and this produces signals that contain information about the samples surface topography, composition and electrical conductivity. The intensity of a chosen secondary signal from the specimen (i.e. secondary electrons) is monitored by a detector and the brightness cathode ray-tube (CRT) spot is controlled by an amplified version of the detected signal (Goldstein et al, 1981).
An Energy Dispersive X-ray analysis (EDX) detector is attached to the side of the SEM close to the specimen. EDX uses characteristic X-rays that are excited from the amount of specimen irradiated by the beam. The analysis region is defined by focusing the beam on a small area using scanning mode.
Electron microscopy can be used to determine the size and shape of clays (Grim, 1964). Scanning and Transmission electron microscopy can determine the mineralogy, microfabric and pore geometry of sediment and soil samples. Berti et al, (2006) used this analytical technique to analyse and characterise the microfabric and mineralogy of marine sediments taken from of the coast of French Guyana and from the Gulf of Mexico. Shillito et al, (2009) used the SEM to investigate the chemical and mineralogical variations in finely laminated ash based deposits.

In terms of the analysis of samples, including sediment samples, the SEM has many advantages over traditional microscopes. It has a large depth of field, which allows a larger portion of a sample to be in focus at one time. The SEM also has a much higher resolution, therefore more closely spaced specimens can be magnified at much higher levels. In addition, because the SEM uses electromagnets instead of lenses, there is significantly more control in the degree of magnification. These advantages, as well as the actual strikingly clear images, make the scanning electron microscope a very useful instrument.

1.9 Scope of this research

During the sampling expeditions to Dunmanus Bay in 2009 and 2011 numerous sediment samples were collected. These samples were collected from areas both within and outside the pockmark area (where methane seepage was confirmed) and were also collected throughout the rest of the Bay. To date other research on these samples has focused primarily on the organic component of these sediments, with specific emphasis on organic carbon cycling (Szpak, 2012; O’Reilly, 2013).
This research will focus broadly on the inorganic component of these samples with the specific scope of this thesis being (1) to investigate the influence of methane seepage on calcium and calcium carbonate concentrations and (2) to determine if methane seepage influences the concentration and distribution patterns of major and trace elements in the Bay. Specific analysis such as this should give a unique insight into the geochemical dynamics within the sediment.

The relative importance of calcium and calcium carbonate concentrations are being specifically investigated because in other locations around the world where methane-related pockmarks exist they are often, though not always, associated with obvious carbonate features such as mounds etc. These obvious carbonate features do not seem to occur in Dunmanus Bay so the analysis carried out in this research should provide an insight as to why this is the case. To investigate calcium and calcium carbonate concentrations, three 6m vibrocores were collected. One core was collected from within a pockmark, one from beside a pockmark but still in the gas seepage area and another core taken for comparison away from the pockmark field. Established analytical techniques such as PSA, XRF, XRD and SEM-EDS will be used to analyse these sediments. All results will be presented and discussed in Chapter 3.

In marine environments in particular, detailed geochemical mapping is important as it provides important information in relation to elemental concentrations and distribution. Scientific knowledge of these elemental concentrations and distribution patterns are useful as they can indicate sediment source, areas of natural resources and areas of contamination etc. The presence of the methane-related
pockmark field in Dunmanus Bay also provides a unique opportunity to evaluate its influence, if any, on elemental concentrations throughout the Bay. To determine elemental concentrations and distribution patterns for major elements (Ca, Fe, Ti, Sr) and trace elements (Ba, Mn, Zr, Sc, Rb) twenty-two surficial sediments were collected throughout the bay and within the pockmark field. These major and trace elements were selected for analysis so as to provide a comprehensive range of data and also because they were particularly suitable for detection by FP-XRF analysis. All the results will be presented and discussed in Chapter 4.
Chapter Two

Materials and Methods
2.0 Materials and Methods

2.1 Bathymetry

Bathymetric data for Dunmanus Bay was initially gathered in 2006 during a Tenix Lidar Survey (shallow water) onboard the *RV Celtic Explorer* (outer part of the Bay). However because of the low resolution of the data acquired during this survey the pockmark field was not detected.

In 2007, a second survey of the Bay was carried out. This multi-beam survey by the *RV Celtic Voyager* was undertaken as part of the INFOMAR program and it was during this survey that the pockmark field was discovered. In April 2009, the *RV Celtic Voyager* again surveyed the area and this time very high resolution data provided further insight into the morphology and distribution of the pockmarks (Szpak et al., 2009). This data allowed accurate sampling to take place and samples were collected in 2009 and 2011.

2.2 Sampling

In Dunmanus Bay sampling was carried out during two research expeditions to the area. In April 2009 the *RV Celtic Voyager* collected day grab, box core and gravity core samples from within the pockmarks themselves and from the surrounding area. In May 2011, the *RV Celtic Explorer* obtained three 6 metre vibrocore samples. An on-board GPS system logged exact location co-ordinates for each sample collected.
2.3 Sampling Methods

A wide range of methods exist for sampling marine sediment and these methods need to take into consideration, the sample character, the type of analysis needed, cost, time and vessel suitability. Grab sampling is a technique widely used to examine the surface sediment (from about 10-15cm deep) and allows the determination of horizontal sediment characteristics. Various grab samplers can be used depending on the type of sediment being sampled (soft or hard) and the amount of the sample required. Sediment corers, on the other hand, provide a vertical cross-section of the sediment column. Corers include piston corers, gravity corers, vibrocorers and multi-corers and depending on the technique used, can vary in length from 10cm to 30m. The advantage of using corer samplers instead of grab samplers is that the cores preserve the stratigraphy and reach a greater depth of penetration.

Sampling methods used for this project were a Day Grab sampler, a Gravity Corer and a Vibrocorer.

The Day Grab (Figure 2.1) sampler uses a frame to keep the grab level on the seabed and two trigger plates to activate the release. The jaws of the sampler are supported in an open mechanism, which will cause minimum downwash as it lands on the seabed and lead weights are added to ensure penetration into the seabed. On this sampling expedition the Day Grab was mostly reliable in areas where the sediments were soft and fine-grained. They didn’t perform as well in areas where sediments contained coarser sands and shells etc. The sediment samples for geochemical analysis, (XRD/XRF/SEM) were sub-sampled and labelled onboard the vessel and stored at 4°C. Table 2.1 lists and describes the samples collected using this method.
The Gravity Corer (Figure 2.2) uses gravity force to penetrate the seabed. This can be used with a free fall winch or a trigger mechanism. The corer consists of a large weight on top of a steel core barrel. The core barrel is lined with a plastic liner and core catcher. A core cutter is attached to the bottom of the core barrel and a check valve, which is used to retain the sample, is located at the top of the weight stand.

Figure 2.2: Schematic of a typical gravity corer
On this expedition the Gravity Corer was fitted with a 2m long barrel (Figure 2.3), its performance was average as even in very soft sediment a full 2m recovery was never achieved. The highest recovery was 1.3m (Sample GC-03) with an average recovery being 1.0m. The sediment for geochemical analysis samples were sub-sampled and labelled on-board the vessel and stored at 4°C. Table 2.2 lists and describes the samples collected using this method.

![Figure 2.3: Gravity-Corer. (a) Gravity-Corer being dropped to seabed (b) Corer being raised from seabed. (c) Core sample being removed. (d) Core after it has been split, sub-samples were taken here.](Photos: N. Coleman 2009)

The Vibrocorer uses pneumatic and electrically driven hammer drills and is designed to collect cylindrical cores in soft, cohesive sediments. It consists of a base which rests on the seabed, a motor that generates vibrations allowing a metal cylinder to penetrate the seabed. The metal cylinder is fitted with a plastic liner and the sample is collected in this. A standard size vibrocore will obtain an 8.6cm diameter core. The vibrocore used was a GeoResources 6000 model. Three core samples were obtained, one from inside a pockmark crater, one from nearby the pockmarks and one obtained away from the pockmark area. Again sediments for geochemical analysis were sub-sampled on board and stored at 4°C. Table 2.3 lists and describes the Vibrocore samples collected.
Table 2.1: List of samples collected in Dunmanus Bay using the Day Grab sampler.

<table>
<thead>
<tr>
<th>Sample Label</th>
<th>Station</th>
<th>Type</th>
<th>Instrument</th>
<th>Depth(m)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CV09-23-DG-014</td>
<td>14</td>
<td>Grab</td>
<td>Day Grab</td>
<td>42.1</td>
<td>Very smooth fine sandy mud. Sticky and very homogenous.</td>
</tr>
<tr>
<td>CV09-23-DG-025</td>
<td>25</td>
<td>Grab</td>
<td>Day Grab</td>
<td>39.7</td>
<td>Grey/green mud with some small consolidated fragments.</td>
</tr>
<tr>
<td>CV09-23-DG-028</td>
<td>28</td>
<td>Grab</td>
<td>Day Grab</td>
<td>39.7</td>
<td>Very fine sandy mud, sticky and stiff in composition.</td>
</tr>
<tr>
<td>CV09-23-DG-033</td>
<td>33</td>
<td>Grab</td>
<td>Day Grab</td>
<td>39.4</td>
<td>Sticky mud with some consolidated fragments. A fine sandy matrix within the sample.</td>
</tr>
<tr>
<td>CV09-23-DG-097</td>
<td>97</td>
<td>Grab</td>
<td>Day Grab</td>
<td>42.5</td>
<td>Fine-grained, homogeneous, dark greenish grey sand with a small silt/mud component.</td>
</tr>
<tr>
<td>CV09-23-DG-098</td>
<td>98</td>
<td>Grab</td>
<td>Day Grab</td>
<td>37.8</td>
<td>Fine mud with silt and some fine sand. Dark greenish grey, homogeneous with worms and some small shell fragments in sediment.</td>
</tr>
<tr>
<td>CV09-23-DG-099</td>
<td>99</td>
<td>Grab</td>
<td>Day Grab</td>
<td>32.2</td>
<td>Fine sand/silt with some mud. Homogeneous with some small shell fragments and dark green-grey colour. Also in faunal worms and brittle starfish present.</td>
</tr>
</tbody>
</table>
### Table 2.1: Day Grab Sample Log (continued)

<table>
<thead>
<tr>
<th>Sample Label</th>
<th>Station</th>
<th>Type</th>
<th>Grab</th>
<th>Depth(m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CV09-DG-100</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Instrument</td>
<td>Day Grab Lat Long</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Description</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mainly fine sand/silt with some small mud fraction. Homogeneous, dark green grey with some patches of colour change to dark/black. Infauna include urchins. Brittle starfish and worms with coarse starfish and worms with coarse sediment burrows. Contains whole and small shell.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample Label</th>
<th>Station</th>
<th>Type</th>
<th>Grab</th>
<th>Depth(m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CV09-DG-101</td>
<td>101</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Instrument</td>
<td>Day Grab Lat Long</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Description</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dark greenish gray colour mud with silt/fine sand. Shell fragments and worms present. Colour change 10cm down from surface.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample Label</th>
<th>Station</th>
<th>Type</th>
<th>Grab</th>
<th>Depth(m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CV09-DG-102</td>
<td>102</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Instrument</td>
<td>Day Grab Lat Long</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Description</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Medium to fine sand with a fine silt mud fraction and some coarser shell/pebbles. Dark greenish grey in colour with some dark/black and brown sections where colour changes</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample Label</th>
<th>Station</th>
<th>Type</th>
<th>Grab</th>
<th>Depth(m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CV09-DG-103</td>
<td>103</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Instrument</td>
<td>Day Grab Lat Long</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Description</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fine sand/silt sediment with mud fraction. Distinct colour change from green to brown approx 6 cm below the surface. Also has some small shell fragments and worms.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample Label</th>
<th>Station</th>
<th>Type</th>
<th>Grab</th>
<th>Depth(m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CV09-DG-128</td>
<td>128</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Instrument</td>
<td>Day Grab Lat Long</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Description</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mud with a large portion of fine sand/silt. Dark green in colour and very homogeneous. Also contains white shell fragments throughout.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample Label</th>
<th>Station</th>
<th>Type</th>
<th>Grab</th>
<th>Depth(m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CV09-DG-129</td>
<td>129</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Instrument</td>
<td>Day Grab Lat Long</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Description</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mud with fine silt/sand fraction and homogeneous. Dark greenish grey in colour and also contains white shell fragments.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2.2: List of samples collected in Dunmanus Bay using the Gravity Corer.

<table>
<thead>
<tr>
<th>Sample Label</th>
<th>Station</th>
<th>Type</th>
<th>Core</th>
<th>Instrument</th>
<th>Lat</th>
<th>Long</th>
</tr>
</thead>
<tbody>
<tr>
<td>CV09-23-GC-01</td>
<td>1</td>
<td>Core</td>
<td>Lat 51 33.6552' N Long 9 42.4416' W</td>
<td>Gravity Corer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Description</td>
<td></td>
<td></td>
<td>Sandy mud, dark green/grey in colour with shell occurrences in layers.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CV09-23-GC-03</td>
<td>2</td>
<td>Core</td>
<td>Lat 51 33.6220' N Long 9 42.6651' W</td>
<td>Gravity Corer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Description</td>
<td></td>
<td></td>
<td>Recovery: 1.3m. Dark green/grey in colour. Homogeneous mud with sandy 0.35cm, 0.9-95cm. Air pocket at 0.55cm.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CV09-23-GC-04</td>
<td>3</td>
<td>Core</td>
<td>Lat 51 33.6300' N Long 9 42.5849' W</td>
<td>Gravity Corer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Description</td>
<td></td>
<td></td>
<td>Recovery: 1.13m. Dark green/grey in colour. Shell occurrences in first 12cm and at layers at 1.0m, homogeneous mud enriched with sand at first and at 0.65-0.8cm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CV09-23-GC-09</td>
<td>-</td>
<td>Core</td>
<td>Lat</td>
<td>Gravity Corer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Description</td>
<td></td>
<td></td>
<td>Recovery: 0.95m. Dark green/grey in colour. Shell occurrences at 5-10cm, homogeneous mud with sandy layer at 0.5cm.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CV09-23-GC-10</td>
<td>-</td>
<td>Core</td>
<td>Lat 51 33.5114' N Long 9 42.8673' W</td>
<td>Gravity Corer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Description</td>
<td></td>
<td></td>
<td>Recovery: 1.0m. Dark green/grey in colour, homogeneous sandy mud.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CV09-23-GC-11</td>
<td>-</td>
<td>Core</td>
<td>Lat 51 33.7941' N Long 9 42.1240' W</td>
<td>Gravity Corer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Description</td>
<td></td>
<td></td>
<td>Recovery: 1.14m. Dark green/grey in colour, homogeneous sandy mud.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Table 2.3: List of samples collected in Dunmanus Bay using the Vibrocorers.**

<table>
<thead>
<tr>
<th>Sample Label</th>
<th>CE11-VC1</th>
<th>Station</th>
<th>VC1</th>
<th>Type</th>
<th>Core (6m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instrument</td>
<td>Vibrocore</td>
<td>Lat</td>
<td>N</td>
<td>Long</td>
<td>51° 33.5404’ N</td>
</tr>
<tr>
<td>Description</td>
<td>Mud/sandy mud in the top 3M and mainly sandy, with areas of gravel and cobbles in the remainder.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Length (cm)</td>
<td>575</td>
<td>Water Depth (m)</td>
<td>40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Location</td>
<td>Core taken from inside pockmark crater</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample Label</th>
<th>CE11-VC1</th>
<th>Station</th>
<th>VC2</th>
<th>Type</th>
<th>Core (6m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instrument</td>
<td>Vibrocore</td>
<td>Lat</td>
<td>N</td>
<td>Long</td>
<td>51° 33.5998’ N</td>
</tr>
<tr>
<td>Description</td>
<td>Similar to VC1 mud/sandy mud in the top 3M and mainly sandy, with areas of gravel and cobbles in the remainder.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Length</td>
<td>545</td>
<td>Water Depth (m)</td>
<td>43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Location</td>
<td>Core taken from outside the pockmark crater but in an area where seismics showed acoustic turbidity (i.e gas)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample Label</th>
<th>CE11-VC1</th>
<th>Station</th>
<th>VC87</th>
<th>Type</th>
<th>Core (6m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instrument</td>
<td>Vibrocore</td>
<td>Lat</td>
<td>N</td>
<td>Long</td>
<td>51° 33.0784’ N</td>
</tr>
<tr>
<td>Description</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Length</td>
<td>578</td>
<td>Water Depth (m)</td>
<td>41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Location</td>
<td>Core taken as a &quot;control&quot; sample. Taken from outside pockmark area and gas seepage zone.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 2.3 Analysis

#### 2.3.1 Analysis Strategy

Particle size analysis was carried out on all the samples to characterise sediment composition. Samples from the 6m vibrocores were analysed for calcium concentration using FP-XRF, Bench XRF (WDXRF) and SEM-EDS. XRD was used to determine the primary carbonate phase in the bulk sediment. The Reference
Intensity Ratio (RIR) method (using KCl as an internal standard) was used to qualitatively and semi-quantitatively determine (in weight percent) the main carbonate phase (e.g., \( \text{CaCO}_3 \)) in the sediment (Chung, 1974; Kahle et al., 2002; Moros et al., 2003; Kim et al., 2006).

All surficial samples collected, from 22 sampling stations, were analysed on a FP-XRF to determine levels of both major (Ca, Fe, Mn, and Ti) and trace (Sr, Ba, Mn, Zr, Sc and Rb) elements (Radu and Diamond 2009; Hadler et al., 2011; Willershäuser et al., 2011). FP-XRF results data generated (in parts per million) was mapped using Ocean Data View (ODV) software. These maps show elemental concentration and spatial distribution patterns throughout the Bay and pockmark field. Statistical analysis was also carried out on the FP-XRF results data to establish if there was a difference in element concentration medians between the pockmark field and the rest of the Bay.

2.3.2 Field Portable X-ray Fluorescence (FP-XRF)

Element concentrations were determined for every sample using a Field Portable Niton® XL3t 900 XRF Analyser. This Field Portable XRF (FP-XRF) can be used remotely in the field or in a laboratory environment. In this case, testing was done in the laboratory, with the FP-XRF fixed in a stationary test stand and enclosure. The samples were tested for 180 seconds and data was collected using Niton NDTr 6.5.2 software. This yielded the total content of major elements Ca, Fe, Mn and Ti, and trace elements Ba, Sr, Zr and Rb. Before and after every sample batch an internal calibration was performed to confirm instrument stability and
consistency. The instrument manufacturer specifies a resolution below 275eV and for all the internal calibrations done for this project all resolutions were between 170eV and 180eV. To assess the accuracy of the XRF, a set soil standards by NIST (NCSDC 73308 and GBW 07411) were run seven times as specified in EPA Method 6200. Using Microsoft Excel, linear regression for each set of results was calculated. The results were as follows:

NCSDC 73308 (low concentration): Regression slope of 0.97, $R^2 = 0.9469$

GBW 07411 (high concentration): Regression slope of 0.99, $R^2 = 0.9897$

All the samples were prepared, according to EPA Method 6200. Samples were weighed and dried in an air-circulating oven at 110°C from 6 to 12 hours. Samples were weighed after drying and then carefully ground with a mortar and pestle. They were then sieved at 250 micron and mounted in a sample cup (Niton Sample Cup 187-466 and XRF Mylar Chemplex # 256).

2.3.3 Bench X-ray Fluorescence (XRF)

Further analysis was done on the 6m vibrocore samples using a Philips PW1480/00 Sequential XRF Spectrometer. Run duration per sample was 2.5 minutes. Calibration standards for the analysis involved standard reference powders with certified oxide concentrations (BCS 319/1, BCS 389, AN 9, AN 10, AN 20). Samples were milled to attain particle size < 100μm and 1 part sample was mixed with 10 parts flux (Lithium Tetraborate). Samples were transferred to a furnace in a platinum crucible and heated at 1240°C for 15 minutes. It was then rotated to complete mixing and heated again for a further 5 minutes. The sample was then poured onto a pre-heated platinum plate to form a bead and allowed to cool to room
temperature. Results for element concentrations for Ca are given in their oxide form (CaO).

2.3.4 X-Ray Diffraction (XRD)

A PANalytical X-Pert XRD was used to carry out x-ray powder diffraction. Instrument settings were as follows: A Cu anode tube was used and voltage and current were set at 45kV and 35mA. Scan Mode was continuous and samples were mounted in spinning mode. Scan Axis was 2 Theta-Omega. Start angle was 2.0º and end angle was 80.0. Step size was 0.010º and time per step was 0.30s. Scan speed was 0.033º/s. Total run time was 39mins.

To determine the carbonate phase in the bulk sediment a randomly oriented powder mount was used for each sediment sample. The random orientation ensured that the incident X-rays had an equal chance of diffracting off any given crystal lattice face of the minerals in the sample. Samples were prepared according to USGS Laboratory Manual. They were dried at 110ºC for 6 hours, gently ground with a mortar and pestle and then sieved to 63µm (ASTM sieve no. 230). At this stage an Internal Standard (Potassium Chloride) was added to the sample in the following ratio: Sample (3): KCl (1). KCl is a very crystalline substance and its clear and defined intensities enable the use of the Reference Intensity Ratio (RIR) Method to calculate the main mineral phases in the sample. The RIR is the ratio between the integrated intensities of the peak of interest (CaCO₃) and that of a known standard (in this case KCl).
Therefore, for our CaCO$_3$ phase a calibration sample containing 50%KCl and 50% CaCO$_3$ was first run on the XRD.

Using the formula:

\[
\frac{I_\alpha}{I_{\text{KCl}}} = k \frac{C_\alpha}{C_{\text{KCl}}} \quad \text{Eqn. (2.1)}
\]

A Calibration Constant (k) is calculated. (k = 1.02 for CaCO$_3$). A calibration curve was also generated for different ratios of CaCO$_3$:KCl (Figure 2.4). Then running a sample (containing KCl as an internal standard with the ratio Sample:KCl (3:1) and using the above formula the unknown concentration level of a phase (in this case CaCO$_3$) in weight percent can be calculated.

![CaCO$_3$/KCl Calibration Curve](image)

*Figure 2.4: Graph showing calibration curve for varying ratios of CaCO$_3$ and KCl*
2.3.5 Scanning Electron Microscope (SEM-EDS)

A Hitachi Field Emission Scanning Electron Microscope, model Hitachi SU70, was used for further analysis of the 6 m vibrocore samples. Samples were dried at 110°C and sieved to 250µm. 0.25g of the sample was sprinkled onto a carbon sticky tab which was attached to a 15mm aluminium stub. This was then coated with gold for 20 seconds in an Emi Tech K550 sputter coater (this was done to make the samples conductive). The voltage used for the images varied from 3kV to 6kV. A 15mm working distance was used for all. The elemental analysis was carried out on an Oxford Energy Dispersive System. This was carried out at 20kV with a 15mm working distance.

2.3.6 Statistical Analysis of Results

Statistical analysis was done on the XRF results data from the surficial sediments to establish if there was a statistically significant difference in element concentrations between the pockmark field and the rest of the Bay. For this a non-parametric Mann-Whitney U Test was done on the results data. The Mann-Whitney U Test is a non-parametric test that is used to evaluate whether the medians on a test variable differ significantly between two groups from the same population and as it is a non-parametric test it does not assume any assumptions related to the distribution (Sheppard et al., 2012). In this study, the null hypothesis (H₀) is considered to be where there is no difference between element concentration distributions between the pockmark field and the rest of the bay. Consequently, if the null hypothesis is rejected, i.e. the p-value is below five percent (0.05), it is inferred that there is
significant difference between the two areas. Alternatively, if the null hypothesis is accepted (p > 0.05) then it is considered that there is no significant difference between the areas.

2.3.7 Spatial Distribution Map Template

Ocean Data View (ODV), specialist computer software, was used to generate the spatial distribution maps of Dunmanus Bay presented in this study. ODV is a software package for interactive exploration, objective analysis and visualization of oceanographic and geo-referenced data sets. ODV can display original data points or gridded fields based on the original data (Schlitzer, 2015). For the particle size spatial distribution maps the GPS data for each sampling station was entered into the software along with the percentage sand, clay etc. measured. Similarly, for the elemental maps, the GPS data for each sampling station was entered along with each element concentration measured. This way the required spatial distribution maps were generated. Barret et al (2012) used ODV software to map trace element composition of suspended matter in the North Atlantic Ocean, while Govin et al (2012) used ODV software to map major element distribution in Atlantic surface sediments in terms of terrigenous input and continental weathering.
Chapter Three

Influence of Methane Seepage on Calcium and Calcium Carbonate Concentrations in Shallow Water Marine Cores
3.0 Influence of Methane Seepage on Calcium and Calcium Carbonate Concentrations in Shallow Water Marine Cores

3.1 Introduction

To investigate the influence of methane seepage on calcium concentration and calcium carbonate dissolution and precipitation in marine sediments a number of factors have to be considered. These include, the rate of gas seepage (Luff et al., 2004), the CaCO$_3$ saturation state (Feely et al., 2004; Doney et al., 2009), the anaerobic oxidation of methane (Hovland, 2002; Smith and Coffin, 2014), sulphate reduction (Campbell et al., 2001), oxidation of organic matter (Emerson and Hedges, 2003; Smith and Coffin, 2014), local pH (Schneider et al., 1998; Morse et al., 2007), and the role of carbon dioxide (Feely et al., 2004). Either combined or individually these factors in conjunction with the physical composition of the sediment play a major role.

The calcium carbonate equilibrium in the marine environment is of particular importance wherever carbon dioxide is released into water by various processes and where carbonate minerals buffer the system by mechanisms of dissolution or precipitation. Carbon dioxide can originate from a gaseous exchange with the atmosphere or during the oxidation of organic matter. Either way this equilibrium controls the local pH value and this is an essential parameter is such environments in the outcome of calcium carbonate precipitation or dissolution (Schneider et al, 1998). The following series of chemical reactions govern seawater carbonate chemistry:
Once dissolved in seawater carbon dioxide gas reacts with water to form carbonic acid ($H_2CO_3$), which can then dissociate by losing hydrogen ions to form bicarbonate ($HCO_3^-$) and carbonate ions ($CO_3^{2-}$). Any increase in $CO_2$ to seawater will increase aqueous $CO_2$, bicarbonate and hydrogen ion concentrations. An increase in the hydrogen ion concentrations will lower pH. Carbonate ion concentration will subsequently reduce because of the increasing hydrogen ions (Andersson et al. 2007; Doney et al., 2009).

Calcium carbonate minerals are formed when aqueous $Ca^{2+}$ and $CO_3^{2-}$ react to form solid phase $CaCO_3$.

$$Ca^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \leftrightarrow CaCO_3_{(s)} \hspace{1cm} \log Ksp = 3.22 \hspace{1cm} \text{Eqn (3.2)}$$

Where $Ksp$ indicates the solubility product for the given calcium carbonate polymorph (Busenberg and Plummer, 1986). For carbonate minerals to precipitate the saturation state for that mineral must be reached. Calcite and aragonite are both recognised calcium carbonate minerals in marine environments (de Choudens-Sanchez and Gonzales, 2009). The saturation state ($\Omega$) for both calcite and aragonite are dependent on the concentration of the $CO_3^{2-}$ ions available in seawater (Feely et al., 2004) and is governed by the following equation:

$$\Omega_{(cal/arg)} = \frac{[Ca^{2+}][CO_3^{2-}]}{Ksp_{(cal/arg)}} \hspace{1cm} [\log Ksp_{(cal)} = -8.5][\log Ksp_{(arg)} = -8.3] \hspace{1cm} \text{Eqn. (3.3)}$$
Precipitation only occurs at a saturation state greater than unity (supersaturation). If the solution is less than unity (undersaturation), organisms will not be able to instigate mineral precipitation (Orr et al., 2005). Also in an environment that is in a saturation state of less than unity, the existing calcium carbonate minerals could become dissociated (Tyrrell, 2007). Saturation states are highest in shallow, warm tropical waters and lowest in cold high-latitude regions and at depth, where CaCO$_3$ solubility increases with decreasing temperature and increasing pressure (Feely et al., 2004).

The dissolution of calcium carbonate in the marine environment can be a complicated process. Dissolution can be governed by surface-controlled or transport controlled processes and is dependent on factors such as pH and saturation state (Morse et al., 2007). The extent to which metabolic CO$_2$ leads to CaCO$_3$ dissolution depends on a number of factors that will vary depending on different marine environments. These factors include the saturation state of the overlying water, the depth profile of organic carbon mineralisation rate, the C$_{org}$/CaCO$_3$ ratio of the particulate matter accumulating in the sediment and the dissolution dynamics of the CaCO$_3$ (Wenzhöfer et al., 2001).

In marine sediments many microbial metabolic processes can influence pH and/or the concentration of carbonate ions e.g. sulphate reduction (Visscher, 2000; Van Lith et al., 2003; Dupraz and Visscher, 2005), anaerobic oxidation of methane coupled with sulphate reduction (Reitner et al., 2005). Upward migration of CH$_4$-enriched fluids in seeps can produce HCO$_3$ as soon as the CH$_4$ enters the sulphate reduction zone and this has the potential to cause the precipitation of authigenic
carbonates (Gieskes et al., 2011). Pockmarks are regularly characterised by methane seeps which initiate the development of different chemosynthetic communities (Hovland and Judd, 1988; Menot et al., 2010; Olu et al., 2009). The CH$_4$ migrating through seeps could be oxidised by bacterial consortia or archea through the anaerobic oxidation of methane (e.g. Ruffine et al., 2013), this could provide the chemical components for authigenic carbonate precipitations (Peckmann et al., 2001; Greinert et al., 2002; Feng et al., 2009). There are a number of reasons that explain the absence of authigenic carbonate minerals in sediments from methane seeps. These include, inactivity or low methane seepage, low dissolved methane contents in migrating fluids, high bioturbation rates, high sedimentation rates and/or high fluid flow rates (Luff and Wallmann, 2003; Luff et al., 2004; Bayon et al., 2009).

The aim of this study is to investigate the influence of methane seepage on calcium and calcium carbonate concentrations in a shallow water marine environment. Three 6 meter Vibrocores were collected in the Bay (Figure 3.1). Two cores were taken from within the pockmark field. VC1 core was taken from inside a pockmark crater and VC2 core was taken from outside the pockmark crater but in an area where seismic data showed acoustic turbidity (i.e. gas). For comparison, a reference core, VC87, was taken from outside the pockmark area. Table 3.1 lists the cores and locations. In order to determine and compare carbonate concentrations between the three vibrocores, the bulk sediment, rather than the carbonate-free, opal-free and oxide-free fractions was analysed. Particle size analysis was carried out on cores from the gas seepage area (VC1 and VC2).
Sediments analysed on FP-XRF, SEM-EDS and Bench XRF showed that Ca was present in high concentrations across all samples collected. This is not surprising given that Ca is a major component in sandy and coarse-grained sediment samples (Ravasopoulos et al., 2011). XRD analysis indicated that CaCO$_3$ was the dominant carbonate phase (Figure 3.8). In addition to the above analysis, sub-samples from all vibrocores were analysed on FP-XRF, in a laboratory environment, for major elements Ca, Fe, Ti, and Sr and trace elements Ba, Mn, Zr, Sc and Rb. These results are not presented or discussed here in detail but for reference purposes they are listed in the Appendix 1.

Table 3.1: Vibrocore sampling location and description from Dunmanus Bay

<table>
<thead>
<tr>
<th>Sample</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Depth (m)</th>
<th>Length (cm)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>VC1</td>
<td>51.559</td>
<td>-9.713</td>
<td>40</td>
<td>575</td>
<td>Pockmark crater</td>
</tr>
<tr>
<td>VC2</td>
<td>51.6</td>
<td>-9.71</td>
<td>43</td>
<td>545</td>
<td>Pockmark vicinity</td>
</tr>
<tr>
<td>VC87</td>
<td>51.553</td>
<td>-9.7322</td>
<td>41</td>
<td>578</td>
<td>Control/Reference</td>
</tr>
</tbody>
</table>
Figure 3.1: Dunmanus Bay, Bantry Bay and catchment area with major structural features and index map with site location (top panel). The major fault in this area, the Dunmanus Fault crosses just north of the pockmark field with the minor Gortavallig Fault branching out just 250 m north-west from the pockmark field. Bottom panel shows 6 m vibrocore sampling location, VC1, VC2 and VC87.
3.2 Particle Size Analysis

Particle size analysis was carried out on VC1 and VC2 cores using laser granulometry (Malvern MS2000) for sediment fractions < 1000µm and dry sieving for fractions > 1000µm. Percentage per size class calculated using the MS2000 were converted to total sample percentages. PSA was not carried out on VC87, it contained mainly sand and did not contain the muddy stratum which was present in VC1 and VC2. Tables 3.2 and 3.3 show the PSA results.
Figure 3.2: Particle Size Analysis results data for VC1 (inside the pockmark)
(mbsf = metres below sea floor)
In VC1, sediments from 0 to 1.4 meters below sea floor (mbsf) were poorly sorted olive-grey-green clayey mud, with silt and clay averaging 74.2% and 15.7% respectively. From 1.4 to 1.6 mbsf sediments were characterised by very poorly sorted muddy sand (with shell fragments) to sandy mud, transforming to poorly sorted/very poorly sorted sandy mud to 3.0 mbsf. From 3.0 to 3.8 mbsf there was a gradual transition from sandy gravel to coarse gravel until about 4.0 mbsf. From 4.0 mbsf down to 5.35 mbsf sediments consisted mainly of well sorted sand. VC2
displayed a higher sand content and lower clay content and in general exhibited a more variable lithology in the first 2.0 mbsf compared to VC1. From 1.8 mbsf downward sediment type was broadly similar between VC1 and VC2. However, compared to both VC1 and VC2, the reference core VC87 displayed a more homogenous lithology down its 5.75 mbsf. In all 3 vibrocores, there was a distinctive gravel stratum at 4.0 mbsf and this has been identified as the source of the enhanced reflector in acoustic profiles. Sandy sediments (including gravels) are recognised to have enhanced permeability compared to mud (Wilson et al, 2008). Therefore it is probable that the occurrence of pockmarks in this area of the Bay is due to the lithology within the pockmark field and not the coarser-grained sediment types. Gas seepage (e.g. methane) via permeable strata and its subsequent accumulation in muddy layers and eventual expulsion via fluidisation of gas, water and sediment into the water column correlates with Judd and Hovland (1988) and is probably the most likely formation mechanism for pockmarks in Dunmanus Bay (Szpak, 2012a; O’Reilly, 2013).
3.3 FP- XRF Results

![Graphs showing calcium concentration (ppm) down the 6M Vibrocores. VC1 core taken from inside the pockmark crater. VC2 core taken from outside the pockmark crater but in an area where seismics showed acoustic turbidity (i.e. gas). VC87 is the reference core (mbsf = meters below seafloor).]

Figure 3.4: Calcium concentration (ppm) down the 6M Vibrocores. VC1 core taken from inside the pockmark crater. VC2 core taken from outside the pockmark crater but in an area where seismics showed acoustic turbidity (i.e. gas). VC87 is the reference core (mbsf = meters below seafloor)

FP-XRF results indicate that Ca was a dominant element in all three cores. However concentrations differed significantly between the control core and the two cores from the pockmark area. VC87 (reference core) had significantly higher
concentrations of Ca ranging from 256246 ppm at the seabed level of the core right down to 135570 ppm at the bottom of the core (5.75M down). In VC1 (inside pockmark) and VC2 (outside pockmark) Ca levels were lower than VC87. However all Ca concentrations decreased down the core. While Ca levels in VC87 dropped by approx. 50% from top of core (seabed level) to the bottom of the core, Ca levels in VC1 and VC2 drop by 73% and 76% respectively.
3.4 SEM-EDS Results

Ca concentrations were confirmed by SEM-EDS analyses. VC1 and VC2 downcore concentration patterns are similar to the XRF results. Ca concentrations decreased down the core of VC1 (inside pockmark) and VC2 (in pockmark area). In VC1, Ca concentration decreased from 44.25 wgt %, at seabed level (0-0.3M) to 1.66 wgt% at the bottom of the core (5.20-5.35M). In VC2, Ca concentrations decreased from 41.34 wgt%, at seabed level (0-0.3M) to 1.55 wgt% at the bottom of the core.
(4.92-5.22M). In VC87 (control core), Ca concentrations were overall higher (as also indicated in XRF results) and do not decrease as much down the core, as they do in VC1 and VC2. In VC87, the Ca level was 57.0 wgt% at seabed level (0-0.16M) and reduced down the core to 33.7 wgt% at the bottom of the core (5.70-5.75M).

3.5 Bench XRF Results

Bench XRF analysis confirmed Ca (expressed in its oxide form CaO) to be a dominant element. For CaO, in VC1, levels decreased from 17.8 % at seabed level
(0.15M) to 2.5% at the bottom of the core (5.28M). In VC2, CaO levels decreased from 18.6 %, at seabed level (0.15M) to 2.0 % at the bottom of the core (5.07M). In VC87 (the control core taken from outside pockmark area) CaO levels were higher overall and did not decrease as much down the core, as they did in VC1 and VC2. In VC87, the CaO level is 34.8 % at seabed level (0.08M) and reduced down the core to 15.2 % at the bottom of the core (5.73M).
3.6 XRD Results

XRD showed that quartz was the dominant mineral phase in the bulk sediment. CaCO₃ was the carbonate phase identified (Figure 3.8). CaCO₃ concentrations in VC1 and VC2 were similar from 0 to 0.5 mbsf. However concentrations in VC1 from 1.0 to 4.0 mbsf were higher (this corresponds to PSA description that there was a gradual transition from sandy gravel to coarse gravel until about 4.0 mbsf). In both
vibrocores CaCO₃ concentrations then gradually decreased down the cores. In VC87, the reference core, CaCO₃ levels increased down to the mid-point of the core (3.0 mbsf). Then levels reduced again down the core to <1.0 % at 6.0 mbsf.

Figure 3.8: An X-ray diffractogram of a typical sample analysed on XRD in this study. It identifies quartz (SiO₂) and calcium carbonate (CaCO₃) as the main peaks. The potassium chloride (KCl) peak is from the reference KCl powder added to the sample to allow the determination of the relative intensity ratio (RIR).
3.20 Discussion

In marine environments, hydrocarbon seeps and associated features like pockmarks etc. are a frequently observed phenomenon (Judd and Hovland, 2007; Haas et al., 2010, Ruffine et al., 2013). In these areas, where methane is the migrating gas, biogeochemical processes can be governed by the anaerobic oxidation of methane (AOM) in association with a combination of methane-oxidising archaea and sulphate-reducing bacteria (Boetius et al., 2000). This combination between anaerobic methane oxidising bacteria and sulphate-reducing bacteria is likely due to microbially mediated reactions that affect dissolved inorganic carbon equilibria and carbonate mineral stability (Aloisi et al., 2002). In certain environments this process can lead to an increase in carbonate alkalinity, inducing the precipitation (crystallisation) of carbonate minerals, and the generation of sulphide, which forms the substrate for sulphide-oxidising micro-organisms at the sediment-water interface of seeps. In addition to this, it is also thought that the oxidation of organic compounds via sulphate reduction can promote carbonate precipitation, because processes that lead to the generation of H₂S gas or result in pyrite formation tend to raise porewater pH (Curtis and Coleman, 1986; Curtis et al., 1986; Hovland et al., 1987). Therefore there seems to be a clear connection between carbonate precipitation and methane oxidation under an anoxic environment. Conversely, the oxidation of methane in oxygenated conditions should have the opposite effect in that pH should drop and conditions favourable to carbonate dissolution should prevail (Hovland et al., 1987; Aloisi et al., 2002).
In seeps a sufficient supply of migrating methane over a sustained time period seems to be a fundamental requirement for the precipitation of CaCO$_3$ (Judd 2001; Ussler et al., 2003). Under normal conditions methane migrates slowly upwards and this gives the sulphate-reducing bacteria adequate opportunity to consume the gas molecules. However, if the rate of supply of methane is greater than the rate of oxidation via sulphate reduction then some methane can survive and enter the zone of aerobic bacterial activity (Hovland et al., 1987). Usually methane-derived authigenic carbonates (MDAC) form as rock-like concretions when a carbonate precipitate cements the normal seabed sediment. This carbonate is usually high-magnesium calcite, aragonite or dolomite. Studies of the carbon isotopes involved in this process indicate that their source is methane rather than normal seawater or sediment porewater (Judd 2001).

In the pockmark field in Dunmanus Bay there is past evidence of input from dead and decaying biomass in sediments. During the CV09_23 Survey in 2009 we collected a boxcore sample from within a pockmark cluster. This sample had a strong and putrefying odour. Organic analysis of the sediment indicated that the sample was composed of a significant amount of fresh and decaying organic matter (kelp or seaweed) (Spzak 2012; O’Reilly 2013).

The three cores analysed in this study showed no obvious signs of carbonate precipitation such as concretions etc. Given that VC1 and VC2 in particular were collected from within the seep area pockmark field this is somewhat surprising but not unique. Ussler et al., (2003) while studying submarine pockmarks in Belfast Bay, Maine, reported no obvious authigenic carbonates in sediments analysed and they
concluded that this could be because the pockmarks may be inactive or a process different from gas seepage could have been responsible for the pockmark formation. In Dunmanus Bay, methane levels measured were low and this appears to be a major factor for the non-precipitation of authigenic carbonates. To facilitate the supersaturation of pore fluids with $\text{HCO}_3^-$, which usually results in the formation of MDAC, a sufficient supply of methane is required, coupled with anaerobic oxidation of methane (Hovland et al., 1987; Stakes et al., 1999; Mazzini et al., 2004; O’Reilly et al., 2013).

Considering the results for VC1, we know that the results for FP-XRF, SEM-EDS and Bench XRF show a gradual decrease in Ca concentration down the total length of the core. XRD results for CaCO$_3$ broadly follow a decreasing trend down the cores however its trend differed from the Ca results in the section of the core from 3 mbsf up to the seabed. This section of the core contained an organic layer mixed with a higher mud content. In this region of the core, specifically 1.5-2.0 mbsf, sediment consisted predominantly of mud and sandy mud, with horizontal cracking and numerous layers with shell hash and organic material. Average PSA data for this section of the core is 90% mud and 10% sand. The on-board description of the core sediment for this section (1.40 - 1.60 mbsf) describes a strong odour ($\text{H}_2\text{S}$) and it was the only part of the core that had an odour. It was also noted that shell fragments and whole bivalves were also present in the sediment at this section. This part of the core also corresponds with an increase in Fe concentration (see Appendix 1) which was measured by FP-XRF at 19551 ppm. In addition to this, other research done on the core identified spikes in $\text{H}_2\text{S}$ corresponding with this section of the core (O’Reilly, 2013). Increases in Fe or $\text{H}_2\text{S}$ can be indicative of
pyrite precipitation (Jenkins et al., 2011; Hovland, et al., 2007) but the colour of the sediment at this point, olive-green instead of grey/black does not support this. However, there was a colour change in the sediment above this section of the core. From 0.7 mbsf – 0.9 mbsf the sediment was dominated by black clayey mud and Fe concentrations remained high in this area at 16000 ppm so the possibility of some pyrite precipitation cannot be ruled out. SEM-EDS analysis of the sediment did not detect any obvious pyrite crystals. Pyrite precipitation is sometimes a prerequisite to carbonate precipitation because it can raise local pH and thus promote an alkaline environment (Hovland et al., 1987). Usually methane-derived authigenic carbonates occur in the presence of methane close to the boundary between oxic and anoxic sediments. Here sulphate originating from seawater is fully utilised, by sulphate-reducing bacteria and anaerobic methane-generating microbes exist. This region is known as the sulphate-methane transition zone (SMTZ) and it generally lies within a few metres of the seabed surface (Judd, 2001).

For VC1, the SMTZ is probably situated between 0 – 3 mbsf. Methane, although in low volumes, has been confirmed as the migrating gas in the pockmark field (Szpak, 2012a). In addition peaks in methane were identified between 1.4 and 2.0 mbsf, suggesting the possibility of methane production in situ as well as migrating from depth (O’Reilly, 2013). Peaks in total organic matter content between 1.4 and 2.0 mbsf suggest that organic matter degradation has a role in methane production (O’Reilly, 2013). In addition, sulphate profiles indicate an initial decrease down to around 1.5 mbsf before increasing again (Szpak 2102a; O’Reilly et al., 2011). In certain environments with sufficient gas supply this SMT zone can be an area of intense methane oxidation and carbonate precipitation (Borowski et al., 1999;
Bayon et al., 2005; Snyder et al., 2007; Chatterjee et al, 2011). This does not appear
to be the case here probably due to the low rate of supply of methane and as a result
it seems conditions that favour carbonate saturation are not reached.

For VC2, sediment characterisation down to 3.0 mbsf was predominantly
sandy mud, with horizontal cracking (at 0.50, 0.68 and 2.35 mbsf) and numerous
layers with shell fragments average PSA data for this section of the core is 65% mud
and 35% sand. Similar to VC1, the on-board description of the core sediment for this
section also described a strong odour (H$_2$S). This time it occurred in two sections of
the core at 0.50 mbsf and 0.68 mbsf. Here the odours do not correspond with an
increase in Fe concentration (Appendix 1). Downcore Fe concentrations were
generally lower in VC2 compared to VC1. However in VC2, at 3.0 mbsf, SEM-EDS
analysis did identify a well-developed framboidal pyrite (Figure 3.9) and here the
EDS spectra identified substantial peaks in sulphur and iron. FP-XRF analysis at this
section of the core measured a spike in iron concentration at 17284 ppm. Despite the SEM-EDS evidence of pyrite, there was no colour change to dark grey/black in the sediment which usually accompanies pyrite precipitation. Even though VC2 was not located in a pockmark like VC1 it was still located near the pockmark area where seismics confirm acoustic turbidity (i.e. gas). Again other research on these cores confirmed the presence of CH$_4$ in VC2 (O’Reilly, 2013) and with the presence of the mud strata and organic matter described in sediment descriptions, the SMT zone is probably located in the section of the core 0-3mbsf. But like VC1 there was no visual evidence of authigenic carbonate precipitation.

VC87, the reference core, collected away from the pockmark field displayed a more homogenous lithology down its 5.75 mbsf compared VC1 and VC2. The top of the core consisted almost totally of coarse-grained sand, the middle section of the core contained finer sand fractions but also contained a significant amount of fine
shell fragments. The bottom section of the core contained mainly fine sand. FP-XRF, SEM-EDS and Bench XRF all determined high Ca concentration from ~3.0 mbsf to the seabed. These Ca concentrations were considerably higher than VC1 and VC2. For the FP-XRF, Ca concentrations increased from 157624 ppm at 2.88 mbsf to 256246 ppm at 0.08 mbsf. For SEM-EDS analysis Ca increased from 37.57 wt% at 2.88 mbsf to 55.87 wt% at 0.8 mbsf. Bench XRF results show just an increase from 22.8% at 2.08 mbsf to 34.8% at 0.08 mbsf. Previous analysis on this core showed that CH\textsubscript{4} levels were negligible (Szpak 2012a; O’Reilly 2013). CaCO\textsubscript{3} levels in this core peaked at 3.0 mbsf. This peak coincided with the large quantity of shell fragments present in this section of the core. Thus, these shell fragments probably cause the increase in CaCO\textsubscript{3} content (Doney et al., 2008). They decreased from 3.0 mbsf to 0.08 mbsf to 6.63% at 0.08 mbsf. From ~ 3.0 mbsf in VC87 all Ca and CaCO\textsubscript{3} concentrations decreased down the core.

The low levels of methane in the seep area were also reflected by a benthic survey carried out in the Bay (Szpak et al., 2009). Usually seeps with methane venting are characterised by a number of different macroscopic and microscopic habitats (e.g Barry et al., 1996; Levin et al., 2003). Indeed carbonate-cemented crusts and concretions are often the end products of microbial chemosynthesis complex communities of methane-oxidising archaea and sulphur-oxidising bacteria thriving on the migrating methane (Neimann et al., 2005; Lavoie et al., 2010). The benthic survey of Dunmanus Bay shows that benthic communities are dominated by four common species, sea cucumber (Leptopentacta elongata), polychaete (Scalibregma inflatum), polychaete (Diplocirrus glaucus) and the brittlestar (Amphiura filiformis)
and overall show structures typical for around Ireland. Organisms usually associated with methane seepages were not observed (Szpak et al., 2009).

In addition to the low rate of supply of methane in the pockmark field there is another factor that needs to be taken into consideration for the non-precipitation of authigenic carbonates. In all three cores collected there was a distinct gravel layer detected at 3.5-4.0 mbsf. This gravel layer showed up in acoustic profiles of the bay (Figure 3.10). A prominent feature of sandy sediments (including gravel) is their high permeability which can enable pressure gradients to force a flow through pore spaces (Meysman et al., 2007). This resulting pore water flow could form a transport mechanism for various abiotic components (Webb and Theoder, 1968) and for biological particles such as bacteria and algae (Rusch and Huettel, 2000).

Figure 3.10: Profile image showing a transect across the Dunmanus Bay Pockmark Field and outlining the area of acoustic turbidity. The white arrows indicate where lateral migration of seawater (and gas) could be taking place via the permeable gravel layer.

Studies have shown that advective transport exerts considerable control on sediment biogeochemistry (e.g. Shum and Sundby, 1996), microbial ecology (e.g. de Beer et al., 2005), and solute transfer across the sediment-water interface (e.g. Huettel et al., 1998). Thus, there could be lateral migration of seawater (or gas) through this gravel
stratum approximately 4 mbsf in the Dunmanus Bay cores. This hypothesis is supported by organic analysis done on these sediments in other studies. These studies detected a rapid depletion of CH₄ and H₂S in sandy sediments and SO₄²⁻ profiles increase to seawater levels in VC2 from 1.6 mbsf downwards after initially decreasing (O’Reilly 2013). Analysis of a gravity core from the 2009 survey of the area also confirm SO₄²⁻ decreased in the first 1 mbsf before increasing (Szpak 2012a). This permeable sand and gravel layer could facilitate the reintroduction of seawater from depth (O’Reilly 2013). The advection of seawater through permeable sediments has been shown to have a large effect on rates of production and respiration in sediments (Janssen et al., 2005; Glud et al, 2008). It is also possible that this advection can influence the dynamics of carbonate precipitation and dissolution. CO₂ in seawater can change the overall composition of dissolved inorganic carbon species and lowers the pH. This can inhibit numerous biological processes, including marine calcification (Feely et al., 2004; García-Rosales, et al., 2011; Cyronak et al., 2013 and references therein). It is probable that this could be a major factor for the overall reduction of Ca and CaCO₃ with depth in all three cores.
In summary, the results from the cores analysed in this project indicate that the decrease in Ca with depth and the non-precipitation of CaCO₃ minerals seems to be governed by a number of factors (Figure 3.11). These include:

1. The low supply of methane migrating from depth, resulting in an insufficient quantity of the specific carbon isotope (¹³C) usually supplied by the migrating methane in vents and seeps and a requirement for the formation of methane-derived authigenic carbonates (Judd, 2001).

2. Microbial reactions in the sulphate-methane transition zone which prohibit the supersaturation of CaCO₃. The presence of H₂S in both VC1 and VC2 in approximately the first 3 mbsf and the confirmation of a pyrite framboid in VC2 indicate that various reactions are occurring (Hovland, 1987). However the rate of supply of methane is not sufficient to instigate these microbially mediated reactions.

<table>
<thead>
<tr>
<th>Depth (Meters below seafloor)</th>
<th>VC1</th>
<th>VC2</th>
<th>VC87</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>mud green/grey black</td>
<td>sandy mud dark grey</td>
<td>coarse sand</td>
</tr>
<tr>
<td>-2</td>
<td>sandy mud olive green/grey</td>
<td>muddy sand green-grey</td>
<td>sand</td>
</tr>
<tr>
<td>-3</td>
<td>muddy sand olive green/grey</td>
<td>sandy mud muddy sand green-grey</td>
<td>sand</td>
</tr>
<tr>
<td>-4</td>
<td>gravel/sand</td>
<td>lateral migration (seawater/gas)</td>
<td>gravel/sand</td>
</tr>
<tr>
<td>-5</td>
<td>sand</td>
<td>normal sand colour</td>
<td>sand</td>
</tr>
<tr>
<td>-6</td>
<td>sand</td>
<td>Reduced Ca &amp; CaCO₃ concentration</td>
<td>sand</td>
</tr>
</tbody>
</table>

Figure 3.11: Summary of downcore physical and chemical characteristics of vibrocores.
sufficiently to promote carbonate precipitation and specifically the precipitation of methane-derived authigenic carbonates (Aloisi et al., 2002).

(3) The existence and possible effect of the permeable gravel layer between 3.5-4.0 mbsf. This permeable gravel layer could enable the lateral migration of seawater (or gas) from depth. The rapid depletion of CH$_4$ and H$_2$S down the cores in VC1 and VC2 after 3 mbsf and the increasing SO$_4^{2-}$ down the core of VC2 (after initially decreasing) as determined in other studies (Szpak, 2012a; O’Reilly, 2013) and the decrease in Ca and CaCO$_3$ as determined in this study support this possibility. This influx of seawater (containing CO$_2$) could affect the dynamics of the CaCO$_3$ equilibrium, lower local pH and promote the dissolution of calcium carbonate rather than its precipitation (Feely et al., 2004).

Current pockmark studies include a wide range of scientific disciplines that report various aspects of seabed gas and fluid escape and the interconnections between geochemical, physical and ecological processes (Lavoie et al., 2010; Ruffine et al., 2013). Many studies indicate methane-related pockmarks with visual carbonate features (e.g. Mazzini et al., 2004; O’Reilly et al., 2013). While other research into methane-related pockmarks report no obvious carbonate features, primarily due to inactive or insufficient gas seepage (Ussler et al., 2003).

Future research work in Dunmanus Bay could focus on the common silicate mineral quartz (SiO$_2$) and its concentration and distribution patterns throughout the Bay and pockmark field. In marine environments SiO$_2$ is an important component as it is required for the development of various sea organisms like diatoms etc. In this
study SiO₂, as well as CaCO₃, was identified by XRD to be a major component of the sediments analysed and it would be interesting to evaluate in a future study if there was any correlation in SiO₂ concentration trends within the pockmark field, throughout the Bay and down the cores.

3.21 Conclusion

It is difficult to determine, with absolute certainty, the direct influence of methane seepage on Ca and CaCO₃ concentrations in Dunmanus Bay. This appears to be mainly due to the low rate of supply of methane migrating from depth which ultimately results in the lack of visual evidence of methane-derived authigenic carbonates. However, despite the low levels of migrating methane from depth, its influence and possible effect can be considered in broader terms when it is considered in conjunction with other factors in the Bay such as seabed morphology and sediment characteristics.

Particle size results and sediment characteristics for the gas seepage area (pockmark field) of the Bay show a clear stratification with depth, where fine-grained sediment is underlain by progressively coarser-grained strata. The occurrence of fine-grained sandy mud and mud appears to be specific to the pockmark field and this lithology may contribute to pockmark formation in this area and not in the rest of the Bay. Previous studies in relation to the organic component of sediments from this pockmark field confirm CH₄ migration from depth is occurring, as well as the possibility of CH₄ production in-situ. Although, the CH₄ levels measured are low, it is probable that this gas migration through permeable
strata and its subsequent accumulation in muddy layers and eventual expulsion through the seabed is the most likely reason for the pockmark features. Pockmarks in methane seepage areas are often associated with methane-derived authigenic carbonate precipitation (mainly calcite and aragonite) and precipitation of these minerals is usually accompanied by the appearance of seabed features such as carbonate concretions etc. This is not the case in this gas seepage area. The results show a general decrease in Ca concentrations with depth and indicate that no obvious precipitation of CaCO$_3$ minerals occurs. This is due to a combination of factors which include a low methane seepage rate, microbially mediated reactions in the sulphate-methane-transition-zone that affect the calcium carbonate equilibrium and the possibility of lateral migration of seawater (carrying CO$_2$) from depth through a permeable gravel layer located approximately 4 meters below the seafloor. The negligible levels of CH$_4$ in VC87, the reference core, and the characteristics of the core sediment suggest that Ca and CaCO$_3$ here are probably mostly of biogenic origin. In cores VC1 and VC2, which contain fine-grained sandy mud and mud (specific to the pockmark field) and organic matter, the presence of H$_2$S in approximately the first 3 mbsf and the confirmation of a pyrite frambooid in VC2 indicate that some microbial reactions are occurring. It is possible that a greater supply of migrating methane from depth could facilitate further reactions and create an environment more favourable to the precipitation of authigenic carbonates. Results from this project suggest that the methane seepage in Dunmanus Bay can be considered to be low and periodic and in terms of seep classification it could be called a micro-seep.
Chapter 4

Elemental Distribution and Concentration in Surficial Sediments
4.0 Elemental Distribution and Concentration in Surficial Sediments

4.1 Introduction

An understanding of the cycling of elements in coastal environments, such as bays and estuaries, requires knowledge of the distribution of these elements among sediment, water and biota. The spatial distribution and abundances of elements in each of these three components depends on (1) the chemical and physical nature of these elements as they are introduced into the specific coastal environment, (2) the chemical and physical conditions of the environment such as pH, temperature, salinity, tidal characteristics, geomorphology etc. and (3) the ability of these elements for biota accumulation or for adsorption on particulate matter (Cross et al., 1970). Coastal areas such as bays and gulfs are among the most studied marine environments. The main objective of the majority of these studies is to determine the abundance and distribution of sediment components such as, major and trace elements, which can help identify their source (Ergin et al., 1996; Srisuksawad et al., 1997; Basaham and El-Sayed, 1998; Cho et al., 1999; Kim et al., 1999; Sirocko et al., 2000; O’Reilly et al., 2014). Understanding elemental concentrations and distribution patterns in surficial marine sediments is important for interpreting sediment records. The geochemistry of these sediments is controlled by both the composition of the material initially deposited in the sediments and the chemical, biological or physical processes that affect this material after its deposition (Burdige, 2006). These processes are generally referred to as early diagenesis (Berner, 1980). Marine sediments are highly fractionated crustal materials and are generally supplied to the ocean from a number of different sources (Calvert, 1976). Most near shore
sediments are brought to the sea by the action of local rivers and their composition is largely influenced by the lithology of the catchment area (Karageorgis et al., 2004). Biogenic elements like Ca and Sr and lithogenic elements like Ti, Fe, Si and Al have been investigated in surface sediments in the Aegean Sea (Karageorgis et al., 2004). In addition, studies on the distribution of major elements (Ca, Fe, Al, Si, Ti, K) and their imprint on terrigenous input and continental weathering have been carried out in Atlantic surface sediments (Govin et al., 2012). Elemental variation patterns have also been studied in sediments in the South China Sea. Here some of the major elements, such as Al, Fe, K, Mn, Mg, and trace elements such as the alkali elements (Rb and Cs), the alkaline earth elements (such as Ba) and transition metals (such as Sc, V, Co, Cr, Zn) were studied (Wei et al., 2004). Elements, such as Fe and Mn have been investigated widely due to their redox-sensitive behaviour in aquatic environments (e.g. Mackereth, 1966; Wersin et al., 1991; Davison, 1993; Calvert and Pedersen, 2007; Och et al., 2012).

The distribution patterns of elements in marine sediments provide important information about seawater chemistry in the past, about erosion and weathering processes and about biogeochemical cycles (Schnetger et al., 2000; Calvert and Pedersen, 1993; Hild and Brumsack, 1998; Brumsack and Wehausen, 1999; Brumsack, 2006; Müller, 2012). In addition, marine sediments provide important information on past oceanographic and climatic changes, such as variations in biological productivity, the redox condition of bottom water, seawater and sediments, possible tectonic activity, wind strength and volcanic, hydrothermal, hydrogenous, aeolian and fluvial sources (Schnetger et al., 2000). The effect of seabed features like hydrocarbon seeps, hydrothermal vents, mud diapirs and pockmarks on sediment
geochemistry have been widely investigated (e.g. Hovland et al., 2002; Lackschewitz et al., 2005). Most often interpreted as fluid-escape features, marine pockmarks are well studied in areas with gas hydrates, regular tectonic activity, deltas and petroleum resources (Judd and Hovland, 2007). However, pockmarks also exist in marine environments which lack these characteristics and that currently exhibit minimal fluid venting (Ussler et al., 2003). The pockmark field in Dunmanus Bay lies in a northeast-southwest orientation and contains over 60 pockmarks, which are arranged in clusters. The pockmarks vary in size and depth with some measuring up to 20 m in diameter and up to 0.8 m in depth.

In this study, an integrated analytical approach is used to determine and map element abundances throughout Dunmanus Bay and include the pockmark field region within the Bay. Variations in sediment geochemistry will be determined and compared between all sampling stations and this will incorporate statistical analysis of the results data. 22 surficial sediment samples were collected in the Bay and these include day-grab samples, box core samples and the top sediment from a number of gravity core samples (Table 4.1).
### Table 4.1: List and location of surface sediments in Dunmanus Bay.

Stations in red are from within the pockmark field (seepage area). Stations in black are from the rest of the Bay.

<table>
<thead>
<tr>
<th>Station</th>
<th>Latitude</th>
<th>Longitude</th>
</tr>
</thead>
<tbody>
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<td>51.56092</td>
<td>-9.70736</td>
</tr>
<tr>
<td>3</td>
<td>51.56037</td>
<td>-9.71109</td>
</tr>
<tr>
<td>4</td>
<td>51.5605</td>
<td>-9.70975</td>
</tr>
<tr>
<td>9</td>
<td>51.5581</td>
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</tr>
<tr>
<td>11</td>
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<tr>
<td>37</td>
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</tr>
<tr>
<td>97</td>
<td>51.55292</td>
<td>-9.7371</td>
</tr>
<tr>
<td>98</td>
<td>51.56398</td>
<td>-9.69403</td>
</tr>
<tr>
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<td>-9.64751</td>
</tr>
<tr>
<td>129</td>
<td>51.58143</td>
<td>-9.62703</td>
</tr>
</tbody>
</table>

The existence of the pockmark field in Dunmanus Bay, gives the seabed here an additional anomaly that has to be taken into account when discussing and analysing these results i.e. does the presence of the pockmark field (hydrocarbon seep) in the Bay have an effect on the spatial distribution and abundance of elements? In addition, known facts specific to the bay have to be considered when reviewing results e.g. sediment composition, particle size, fluvial input, high rainfall and catchment geology. Taking these considerations into account, the distribution and concentration of major elements, Ca, Fe, Ti and Sr and trace elements Ba, Mn, Zr, Sc and Rb are presented and discussed. In order to determine and compare...
elemental concentrations from both within the pockmark field and throughout the bay, the bulk sediment, rather than the carbonate-free, opal-free and oxide-free fractions was analysed. Particle size analysis was carried out on the samples and then the samples were analysed for 9 elements in total, major elements (Ca, Fe, Ti, Mn) and minor elements (Sr, Ba, Zr, Sc, Rb) using a Field-Portable XRF, in a stable laboratory environment. Particle size and elemental spatial distribution maps were compiled using Ocean Data View software.

### 4.1.1 Particle Size Analysis

Particle size analysis results are presented in Table 4.2. Spatial distribution maps are shown in Figures 4.1, 4.2, 4.3 and 4.4.

<table>
<thead>
<tr>
<th>Station</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Clay (%) (&lt; 2µm)</th>
<th>Silt (%) (2-63µm)</th>
<th>Mud (%) (63-2000µm)</th>
<th>Sand (%) (63-2000µm)</th>
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</thead>
<tbody>
<tr>
<td>14</td>
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<td>62.1072418</td>
</tr>
</tbody>
</table>

*Table 4.2: Particle Size Analysis data for surface sample from Dunmanus Bay.*
Samples from the three day grab sampling stations in the inner part of the bay (#129, #103, #128) all consisted mainly of fine sand/silt with a mud fraction. In these stations, sand was the primary component (averaging 58.96%) with mud (clay + silt) making up the remainder at 41.04%. All samples contained some white shell fragments. #128 and #129 were both dark greenish in colour and very homogenous. #103 had a distinct colour change from green to brown approximately 6cm below the surface and also had some small shell fragments.

The next five day grab sampling stations, moving out westerly along the bay were stations #102, #101, #100, #99, #98. Here again sediment was characterised by mainly fine sand/silt with mud fractions. Stations #98, #99 and #100 were dark green/grey in colour, homogenous, with some small shell fragments. Station #101 was also dark green/grey in colour with shell fragments. There was a colour change to brown approximately 10cm below the surface. Station #102 was dark green/grey on colour with some dark/black and brown sections. It contained some coarser shells and some pebbles. All stations, except #101 and #98, showed a high sand content (above 70%). In contrast, #101 and #98 predominantly consisted of mud (59.85%) with the percentage sand as low as 40.15%. The next six surface sampling stations were taken in the pockmark area. These were day grab stations #14, #25, #28, #30, #32, #33. Here all samples were dominated by mud and were sticky and stiff in composition with a fine sand fraction. This physical description was supported by the PSA results. In these stations the percentage mud (clay + silt) are all in excess of 80%, with values peaking at #14 at 90.14%. The percentage sand in all samples was below 20%. Samples were predominantly green/grey in colour. In station #30 there was a visible redox layer in the sample with some black globules of organic matter.
Station #37, a box core sample, was also collected in the pockmark area. It contained 88% mud (clay + silt) and 12% sand. It was greenish/grey in colour with no blackness and contained a mixture of shell fragments which were present in the first 10-12cm. Finally, station #97 was in the outer part of the bay and away from the pockmark area. Here sediment was fine-grained, homogenous, dark greenish/grey sand with a small silt/mud component. In contrast to the pockmark area sediments, fine sand dominated at 92.49% with mud (clay + silt) making up the remainder 7.51%. In summary, the PSA results of surface sediments in Dunmanus Bay range from a predominantly fine sand composition with a mud fraction from the inner bay outwards to sediments dominated by a high percentage of mud/silt and sand only making up the minor fraction. Therefore sediment composition is almost reversed in the pockmark area. Then moving out westerly to the outer bay area the sediments revert to a predominantly high sand percentage and a lower mud fraction.

Figure 4.1: ODV map showing the distribution pattern for Mud (%) in the Bay.
Figure 4.2: ODV map showing the distribution pattern for clay (%) in the Bay.

Figure 4.3: ODV map showing the distribution pattern for silt (%) in the Bay.
In addition to the day grab and box core samples discussed above, there were six additional surface sediments analysed for elemental composition. These were six gravity cores (GC#01, GC#03, GC#04, GC#09, GC#10 and GC#11) from which the elemental results of the top core sediment is included in the results presented in this section. The gravity cores were not analysed for particle size but a physical description is included here. GC#01 contained sandy mud, was dark green/grey in colour with shell fragments. GC#03 contained homogenous sandy mud and was dark green/grey in colour. GC#04 contained homogeneous mud enriched with sand and dark green/grey in colour. It also contained shell fragments. GC#09 was dark green/grey in colour with shell fragments. It was homogeneous mud with a sandy layer. GC#10 was homogeneous sandy mud and dark green/grey in colour. GC#11 was dark green/grey in colour with homogeneous sandy mud.
4.1.2 Calcium

In marine environments Ca can react with dissolved CO$_2$ to form limestone. This limestone settles on the seafloor becoming part of new rock formations. Examples of Ca containing minerals on the seabed are calcite and aragonite, both polymorphs of CaCO$_3$. These minerals are also produced by various sea organisms to make their shells, aragonite (pteropods) and calcite (foraminiferal and coccolithophorid). Although coccolithophorids are thought to dominate global CaCO$_3$ production (Westbroek et al., 1993), isotopic and elemental studies of foraminiferal shells are widely used to reconstruct past ocean circulation and chemistry (e.g. Boyle and Keighwin, 1982; Boyle, 1988, 1992; Curry et al., 1988; Duplessy et al., 1988; Lea and Boyle, 1989, 1990; Lea, 1993; Rosenthal and Boyle, 1993; Anderson and Archer, 2002). Ca primarily represents the carbonate of sediment (Peterson et al., 2000; Bozzano et al., 2002). The Earth’s crust has a Ca concentration of 41,000 ppm (McGowen et al., 1979).

![Figure 4.5: ODV map showing Ca concentration and distribution patterns.](image)

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XRF results confirmed that Ca was present in high concentration in all surface samples analysed. Figure 4.5 shows Ca distribution pattern for the Bay. Ca concentration among the sampling stations in the inner Bay area, #129, #128, #103 all display varied Ca concentration levels. The innermost station, #129, had a value of 117782 ppm. There was an increase at the next station, #128, to 150630 ppm and a further increase at the next station, #103, to 189380 ppm. Indeed, of all the surface sediments analysed this was the highest Ca value. #103 was located close to the southern landmass of the Bay and it was also from the more shallow sampling station at 26.2 m. The next three sampling stations, #102, #100 and #101 all again had varying Ca concentrations. Stations #102 and #101 had concentrations of 134901 ppm and 147116 ppm respectively. In contrast, #100 had a low value of 108224 ppm. This was the lowest concentration of Ca in the inner part of the bay. Station #100 was located in the mid-point of the bay equidistant between the northern and southern landmasses. The next two stations, #99 and #98, had high Ca concentrations. #99 measured 178385 ppm and #98 186527 ppm. Sampling station #11, was located just outside the pockmark field and had a Ca concentration of 159957 ppm. Ca concentration in sediments collected from sampling stations within the pockmark field were relatively consistent and were as follows: #09 (190409 ppm), #10 (154133 ppm), #03 (152789 ppm), #14 (150886 ppm), #04 (157176 ppm), #33 (161599 ppm), #25 155724 ppm), #28 (159373 ppm), #37 (156315 ppm), #30 (158251 ppm), #32 (153938 ppm) and #01 (159268). Sampling station #97 was the most westerly station and located in the outer part of the Bay. Of the total surface sediments analysed, this station had the lowest Ca concentration of the entire Bay.
with a Ca concentration of 106824. This station was located away from the pockmark field and was the deepest surface sediment collected at 42.4 m.

Overall the Ca distribution patterns of higher Ca concentration were similar throughout the Bay and within the pockmark field. The high Ca abundances in the Bay are primarily due to a combination of both biogenic origin and the underlying alluvial fill in the Bay. The main exception to this was station #97 which was located in the outer Bay. The Ca concentration range within the pockmark field was 150856 – 190410 ppm and the range for the rest of the Bay was 106824 – 189380 ppm. Ca concentrations could be further enriched in certain parts of the bay by shell production/fragments (McGowen et al, 1979). Station #97, as mentioned, had the lowest Ca concentration (106824 ppm) this station was located in the outer part of the Bay. The PSA for this station indicated that the sediment was dominated by higher sand content (92.5%). Studies done on surface sediments in Matagorda Bay in Texas had Ca concentrations of 10,000 – 50,000 ppm (McGowen et., al 1979) and in Dublin Bay and the Western Irish Sea recent studies determined concentration ranges 48000 - 168000 ppm (Bauer 2012).

4.1.3 Iron

In shallow-marine sediments, post-depositional chemical reactions involving Fe play a significant role in determining the types of minerals that precipitate in these environments. Variations in Fe concentration create contrasting chemical environments which can produce distinctive mineral compounds (Taylor and Macqueker, 2011). Fe is considered a major lithogenic element and is the second
most dominant component in all surface samples analysed. Fe abundances in natural environments are influenced by redox potential. Iron oxides tend to remain as insoluble oxides at high redox potential in well-oxygenated waters. Dissolved Fe is precipitated hydrogenously in oxygenated sediments and the higher the redox potential the more likely they could be precipitated (Berner, 1971). Therefore it is possible that high Fe concentration in sediments could indicate aerobic conditions during deposition (Quinby-Hunt et al., 1988). An important role is played by iron oxides/hydroxides in the oxic environment by scavenging heavy metals (Waldichuk, 1985; Arakel and Hongjun, 1992). Fe is also principally associated with silt-clay fractions since clay minerals tend to carry more Fe than sand grains (Dolenec et al., 1998). Fe concentration in the Earth’s crust is 56000ppm (McGowen et al., 1979).

Figure 4.6: ODV map showing Fe concentration and distribution patterns.

Figure 4.6 shows Fe distribution patterns in the Bay. Fe concentrations for the four sampling stations located in the inner area of the Bay were as follows: #129 (8860
ppm), #103 (11561 ppm), #128 (11854 ppm) and #102 (9706 ppm). The next two sampling stations #99 and #100 had Fe concentrations of 10342 ppm and 7675 ppm respectively. Station #100 had the lowest Fe concentration of all the surface samples analysed, however #101 located nearby and just north of #100 had more than double Fe concentration levels at 16959 ppm. Reviewing the physical description of these sediment samples, both primarily consisted of fine sand/silt with a mud fraction, however #100 had some patches of colour change from green/grey to dark/black. This could indicate the presence of pyrite. All sediments from within the pockmark field showed relatively high and consistent Fe concentrations: #09 (13242 ppm), #10 (17835 ppm), #03 (118310 ppm), #14 (18922 ppm), #04 (17102 ppm), #33 (15888 ppm), #25 (17707 ppm), #28 (16841 ppm), #37 (17393 ppm), #30 (17833 ppm), #32 (18008 ppm) and #01 (16999 ppm). Sampling station #11, located just outside and to the north-west of the pockmark field had an Fe concentration of 17070 ppm. Iron distribution in the Bay doesn’t appear to be restricted to sediment type e.g. the highest concentration, #97 had an Fe concentration of 22581 ppm and #100 the lowest concentration of 7675 ppm yet they both had similar percentages of clay, silt and sand. In the bay there were parallel distributions patterns for Fe, Mn and Ti e.g. Station #97 had highest concentration of all three (Fe=22581ppm, Mn=447ppm, Ti=3868ppm). Studies done on trace element geochemistry on sediments from Punnakkayal Estuary, Tamil Nadu, India, measured Fe concentrations on the sea floor of 69180 ppm (Muralidharan and Ramasamy, 2014) and in Dublin Bay and the Western Irish Sea studies determined an Fe abundances range of 5400 – 12000 ppm (Bauer, 2012).
4.1.4 Titanium

Ti is considered a major lithogenic element and in studies of the marine environment, Ti is generally used to estimate the abundance of terrestrial materials (in particular the detrital components) in sediments (Murray and Leinen, 1996; Wei et al., 2003). Ti is released from primary minerals during chemical weathering but it is normally precipitated before being transported from the area of weathering (Nesbitt and Markovics, 1997). As a result of this, in weathering terms, it is considered a conservative element (Yan et al., 2007). Ti is also known to be concentrated in phyllosilicates (Condie et al., 1992) and is relatively immobile during various sedimentary processes and thus it can represent the source rocks (McLennan et al., 1993). Ti enrichment has been documented in silt and clay size fractions in granitic rocks in Spain (Taboada et al., 2006) and in archaean rocks in Canada (Fralich and Kronberg, 1997). Ti concentration in the Earth’s crust is 5700 ppm (McGowen et al., 1979).
Figure 4.7 shows Ti distribution pattern for the Bay. Sampling stations at the inner part of the Bay #129 and #128 had similar levels of Ti concentrations of 2797 ppm and 2860 ppm respectively. The next station #103 Ti concentrations fell to 2281 ppm. For the next three stations moving out the bay Ti concentrations were 2928 ppm for #102, 2958 ppm for #101 and 2641 ppm for #100. There was a significant drop at the next station #99 when concentrations fell to 2146 ppm and this was the lowest Ti concentration of all the surficial sediments. At the next station #98, Ti levels remained low at 2357 ppm. Ti concentrations within the pockmark field were relatively consistent. Station #10 at the southern part of the pockmark field had a high Ti concentration at 3165 ppm. Station #01 at the eastern side of the pockmark field had a Ti concentration of 3665 ppm. The remaining sampling stations in the pockmark field had concentrations as follows: #09 (2457 ppm), #03 (2967 ppm), #14
(2931), #04 (2893), #33 (2910 ppm), #25 (2899 ppm), #28 (2866 ppm), #37 (2845 ppm), #32 (2829), #30 (2834). Station #11, which was located nearby, but away from the pockmark field, had a lower Ti concentration of 2656 ppm. Station #97, located in the outer part of the Bay had the highest Ti concentration of all the surface sediments at 3868 ppm. In summary, Ti concentrations throughout the Bay were consistent. Measurements from sampling stations within the pockmark field were similar to those in the rest of the Bay. The two stations that differed from the rest were #103 with a Ti concentration of 2281 ppm and #97 which had the highest concentration of the whole Bay. Ti distribution patterns were similar to those of Fe and Mn. In the Bay, Ti concentrations were relatively consistent in all sediments and probably represent terrigenous materials, source rocks along with sand and mud. Studies done on surface sediments in Matagorda Bay in Texas had Ti concentrations of 3,000 – 5,000 ppm (McGowen et., al 1979) and in Dublin Bay and the Western Irish Sea recent studies determined Ti concentration range of 7 – 1800 ppm (Bauer, 2012). Further studies done on surface sediments in Jarrett Bay, North Carolina measured Ti concentrations of 3000 ppm (Berryhill, 1972).

4.1.5 Strontium

Sr is very similar chemically to heavier alkali earth elements Ca and Ba. In Bay environments Sr, like Ca, is closely associated with shell material (McGowen et al., 1979). It is common in limestone although the Sr/Ca ratio in the majority of limestone is as low as 1:1000 (Kulp et al., 1952). High levels of Sr can be associated with Ba minerals like barite. Sr is strongly associated with Ca and can be indicative of calcareous rock especially in association with Sr, Mg and Ba. Sr is easily
mobilized during weathering, especially in oxidising acid environments, and is incorporated in clay minerals and fixed to organic matter. It is estimated that approximately 80% of Sr entering the marine environment from rivers is derived from the weathering of carbonate and sulphate minerals and the remainder derived from silicates (Brass 1976). In marine sediment Sr is primarily present as a result of natural rather than anthropogenic processes (Prohic et al., 1995). Sr concentration of the Earth’s crust is given as 375 ppm (McGowen et al., 1979).

Figure 4.8: ODV map showing Sr concentration and distribution patterns.

Figure 4.8 shows Sr distribution pattern in the Bay. Sr enrichments were consistently higher in and around the pockmark field, with a range from 634 ppm to 685 ppm. The stations measured as follows: #09 (746 ppm), #10 (653 ppm), #3 (648 ppm), #14 (656 ppm), #04 (651 ppm), #33 (634 ppm), #25 (662 ppm), #28 (656 ppm), #37 (659 ppm), #30 (685 ppm), #32 (656 ppm) and #01 (664 ppm). Station #11, which was
located nearby, but away from the pockmark field, had a lower Sr concentration of 675 ppm. In the rest of the Bay there was considerable variation in Sr distribution. Starting with the three inner sampling, stations #129 had a relatively low concentration of 266 ppm. At the next station, #128, Sr concentration increased to 409 ppm, and increased further at the next station #103, where concentrations increased to 645 ppm. Moving out the Bay to the next three stations concentration levels also varied. Station #102 had a concentration of 303 ppm and #101 measured 551 ppm, however #100 had the lowest Sr concentration in the whole Bay at 205 ppm. At the next two stations #99 and #98 concentrations increased again with concentrations of 565 ppm for #99 and 695 ppm for #98. Station #97, located in the outer part of the bay, had a Sr concentration of 360 ppm. In the Bay, Sr had a much lower concentration but followed a similar distribution pattern to Ca. This link between Sr and Ca can be due to the geochemical similarities of the two elements (Shankar et al., 1987). For example, Station #09 had the highest Ca concentration (190410 ppm) and the highest Sr concentration (746 ppm) and Station #97 had the lowest Ca level (106824 ppm) and one of the lower Sr concentrations (360 ppm). In fine-grained sediments analysed in Morphoe Bay, Cyprus Ca and Sr concentrations decreased from the outer Bay to near-shore by almost 50%. Ca and Sr concentrations in Dunmanus Bay would not fully reflect this and although proximity to the landmass and local rock formations do seem to affect concentrations on some stations e.g. Station #103 was located in the inner bay but it had high concentrations of Ca (189380 ppm) and Sr (645 ppm). This station though was located close to the southern landmass so it is possible that this could be a factor. In the pockmark field Sr was relatively and consistently high, with a range from 634 – 664 ppm, this is possibly due to its potential link with carbonate minerals where Sr can substitute for
Ca (Shankar et al., 1987). Studies done near Serres, France determined Sr concentrations ranges of 300 – 650 ppm in surface sediments (Müller et al., 2012). In the Adriatic Sea Sr concentrations of 410 – 888 ppm were measured in surficial sediments (Dolenec et al., 1998). In Dublin Bay and the Western Irish Sea, recent studies measured a Sr concentration range of 48 - 263 ppm (Bauer, 2012).

### 4.1.6 Barium

In marine sediments, fluctuations in the accumulation rate of Ba are considered to be an indication of variations in marine biological productivity through time. However, using Ba as a proxy for paleoproductivity partly relies on it being preserved in the sediment in a predictable and consistent way (McManus et al., 1998). In sedimentary solid phases Ba has been proposed as a proxy for both modern oceanographic processes (Bishop, 1988; Dehairs et al., 1991, 1992; Dymond et al., 1992) and paleoceanographic conditions (Schmitz, 1987; Lea and Boyle, 1989, 1990; Elderfield, 1990; Dymond et al., 1982; François et al., 1995). Other studies also suggest that marine barite (BaSO$_4$), the principal Ba-containing solid phase, could potentially be used to record seawater strontium isotopic compositions or patterns of rare earth element accumulations (Guichard et al., 1979; Paytan et al., 1993; Paytan, 1995). To confidently interpret the sedimentary concentration and distribution of Ba in the marine environment a more comprehensive understanding of its geochemistry, especially during early diagenesis, is required (McManus et al., 1998). It is associated with various particulate phases in the water column and in marine sediments (e.g. carbonates, organic matter, opal, ferromanganese, oxyhydroxides, terrestrial silicates and other detrital material, and barite (Dehairs et al., 1980,
Dymond et al., 1992; Schroeder et al., 1997; Gonneea and Payton, 2006). Ba concentrations in marine sediments can correlate with a variety of terrigenous, biogenic and oxide phases, which include CaCO$_3$, opal, excess Fe and terrigenous material (Schroeder et al., 1997). Some studies have tried to determine Ba concentrations within phase fractions of biogenic material (CaCO$_3$, opal and organic matter) and ferromanganese oxyhydroxides. Results from these studies suggested Ba concentrations in carbonates contain 30 ppm to 200 ppm (Lea and Boyle, 1989; Dehairs et al., 1980), in opal ~ 120 ppm (Dehairs et al., 1980), in organic matter ~ 60 ppm (Martin and Knauer, 1969; Riley and Roth, 1971) and in ferromanganese oxyhydroxides ~ 1000 – 2000 ppm (Dymond et al., 1984). Ba concentrations in the Earth’s crust are recorded at 425 ppm (McGowen et al., 1979).

Figure 4.9: ODV map showing Ba concentration and distribution.

Figure 4.9 shows Ba distribution pattern for the Bay. Commencing with the two stations at the inner part of the Bay #129 and #128, Ba concentrations were relatively
high with 311 ppm for #129 and #128 measured 332 ppm. Concentrations were lower at the next two stations #102 (293 ppm) and #103 (249 ppm). Concentration levels increased again for the next four stations as follows: #101 (353 ppm), #100 (320 ppm), #99 (331 ppm) and #98 342 ppm. Ba concentrations from sampling stations within the pockmark field remained high. There was a minor drop in concentrations on the western side of the pockmark field at stations #4 (302 ppm), #14 (308 ppm), #03 (310 ppm), #37 (309 ppm) and #25 (311 ppm). Concentrations increased at stations on the eastern side of the pockmark field at stations #28 (318 ppm), #33 (353 ppm), #32 (360 ppm) and #01 (324 ppm) and increased again at stations #09 (359 ppm) and #10 (340 ppm). Sampling station #11, located nearby but away from the pockmark field had a Ba concentration of 322 ppm. Sampling station #97, located in the outer part of the Bay had the lowest Ba level in the entire Bay, with a concentration level of just 61 ppm. Naturally occurring Ba has long associations with the Dunmanus Bay area. Barite was mined nearby until 1920 (Hallissy, 1923). In Dublin Bay and the Western Irish Sea, recent studies measured a Ba concentration range of 1 – 67 ppm (Bauer, 2012). Studies done near Serres, France measured Sr concentrations ranges of 40 - 170 ppm in surface sediments (Müller et al., 2012). In the Adriatic Sea Ba concentrations of 40 - 170 ppm were measured in surficial sediments (Dolenec et al., 1998).

4.1.7 Manganese

Mn is considered one of the most mobile elements during early diagenesis, due primarily to its redox chemistry (Karageorgis et al., 2004). Under oxic water environments Mn occurs as insoluble Mn(II) and Mn(IV) oxides, while in anoxic
environments it occurs as Mn(II) in the dissolved phase (Calvert and Pedersen, 1993). Under oxic bottom water conditions or near the freshwater-seawater interface Mn can precipitate in the form of Mn oxide/hydroxides. While in suboxic and anoxic conditions Mn$^{2+}$ diffuses upward in the sediment column (Calvert, 1976; Salomons and Förstner, 1984; Thomson et al., 1986; Shankar et al., 1987; Schnetger et al., 2000). Like Fe, Mn is one of the most extensively studied trace elements in marine sediments (e.g. Shaw et al., 1990; Calvert and Pedersen, 1993; Hild and Brumsack, 1998; Schnetger et al., 2000; Beck et al., 2008). Mn is mainly delivered to the ocean by physical weathering, erosion of rocks and by aeolian and fluvial transport (Müller, 2012). Mn concentrations in the Earth’s crust are recorded at 425 ppm (McGowen et al., 1979).

Figure 4.10: ODV map showing Mn concentration and distribution.

Figure 4.10 shows Mn distribution pattern for the Bay. Mn concentrations in the six inner sampling stations measured relatively low values: #129 (115 ppm), #128 (180 ppm), #103 (192 ppm), #102 (150 ppm), #100 (135 ppm) and #99 (178 ppm). There
was a slight increase at the next station #98 where a concentration of 222 ppm was measured. Within the pockmark field Mn concentrations were consistent: #09 (187 ppm), #10 (260 ppm), #3 (262 ppm), #14 (286 ppm), #04 (294 ppm), #33 (257 ppm), #25 (243 ppm), #28 (240 ppm), #37 (269 ppm), #30 (270 ppm), #32 (257 ppm) and #01 (664 ppm). Station #11, which was located nearby, but away from the pockmark field, had a lower Mn concentration of 235 ppm. Given the abundances measured the Mn concentrations are probably naturally occurring, with slight variances at different stations dependent on its relationship with the other elements and minerals present.

Station #97 located at the outer Bay area had by far the highest Mn concentration of all the surface sediments analysed, with a concentration of 447 ppm. Here also Fe concentrations were the highest in the bay at 22581 ppm. Under certain conditions a close correlation between Mn and Fe can result in ferromanganese (Burdige, 1993). This ferromanganese, in the form of iron-manganese nodules, is widely distributed in the marine environment with some areas having a particularly high abundance. The metal ratio between Mn and Fe in most igneous rocks is generally given in the range 0.015 – 0.02 (Salminen, 1998). Studies in the Gulf of Cadiz calculated at a range 0.07 – 0.25 (Gonzales et al., 2009). At station #97 this ratio between Mn and Fe was 0.02 which could suggest that the sediment here (which was dominated by 92.5% sand) originates from silica from igneous rocks. Studies done near Serres, France determined Mn concentrations ranges of 410 - 660 ppm in surface sediments (Müller et al., 2012). In the Adriatic Sea Mn concentrations of 530 - 3800 ppm were measured in surficial sediments (Dolenec et al., 1998). In Dublin Bay and the Western Irish Sea, studies measured a Mn concentration range of 150 – 621 ppm (Bauer, 2012). Studies done on trace element geochemistry on sediments from
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Punnakkayal Estuary, Tamil Nadu, India, measured Mn concentrations on the sea floor of 339 ppm (Muralidharan and Ramasamy, 2014).

4.1.8 Zirconium

Zr is considered a conservative trace element and tends to be concentrated in sands in bay environments. Little study has been done on the behaviour of Zr in the marine environment although in principle it should provide important information on geochemical cycling (Donat and Bruland, 1995; Suhas et al., 2012). Obvious sources of Zr are Zr-bearing minerals either derived from continental sources through sediments or from basaltic ocean-floor rocks (Godfrey et al., 1996). These Zr-bearing minerals like zircon (ZrSO$_4$) are acknowledged to be resistant to weathering. It is therefore used as a reference element in elemental ratios to monitor the characteristics of other elements during chemical weathering (Yan et al., 2007). Zr concentrations in the Earth’s crust are recorded at 165 ppm (McGowen et al., 1979).

Figure 4.11: ODV map showing Zr concentration and distribution.
Figure 4.11 shows Zr distribution pattern for the Bay. The inner sample station in the Bay #129 had one of the lowest Zr concentrations at 153 ppm. There was a marginal increase in concentrations for the next two stations: #103 (193 ppm) and #102 (196 ppm). At the next sampling station, #128, which was located just north of #102 and #103, there was an increase in Zr concentration to 266 ppm. There was a variation in concentrations among the next three stations: #101 (312 ppm), #100 (166 ppm), #99 (193). The next station #98 had the highest Zr concentration of all surface sediments analysed at 321 ppm. Sampling stations from within the pockmark field also show variation in distribution patterns. Stations #10, #33 and #28 had slightly higher concentrations: #10 (318 ppm), #33 (319ppm) and #28 (331 ppm). The remaining stations concentrations were as follows: #09 (267 ppm), #03 (277 ppm), #14 (250 ppm), #04 (240 ppm), #37 (287 ppm), #25 (286 ppm), #30 (270 ppm), #32 (246 ppm) and #01 (258 ppm). Station #11, which was located nearby, but away from the pockmark field, had a Zr concentration of 277 ppm. Station #97, located at the outer Bay area, had a Zr concentration of 271 ppm.

Zr appears in all sediment types measured and fluctuations in abundances at these concentrations are probably due to natural variations within the composition of the sediment. Zr measured in this range is generally in sand, sandy mud and muddy sand (McGowen et al., 1979). Studies done near Serres, France determined Zr concentrations ranges of 16 - 120 ppm in surface sediments (Müller et al., 2012). In the Adriatic Sea Zr concentrations of between 20 - 50 ppm were measured in surficial sediments (Dolenec et al., 1998). In Dublin Bay and the Western Irish Sea, recent studies measured a Zr concentration range of 18 – 860 ppm (Bauer, 2012).
4.1.9 Scandium

Sc is considered a transition-trace-heavy metal. It is part of group 3 in the periodic table and has one naturally occurring isotope ($^{45}$Sc). Its geochemistry is significantly different from the heavier group 3 members and it rarely forms minerals in which it is the primary component. Sc concentrations in sea-water are very low (Bruland, 1983) and in marine sediments they are mostly bonded to terrestrial materials. Biogenic/non-biogenic scavenged Sc may also be present in pelagic sediments (Goldberg and Arrhenius, 1958). Sc can be strongly related to the catchment geology and higher concentrations can be found in near-shore sediments (Dolenec et al., 1998).

![Figure 4.12: ODV map showing Sc concentration and distribution](image)

Figure 4.12 shows Sc distribution pattern for the Bay. Sc concentration in the inner Bay sampling station #129 was measured at 101 ppm. At the next two stations #103
and #128 there were increases in concentration to 174 ppm and 167 ppm respectively. The next three stations, #102, #100 and #99, all had zero concentrations for Sc. Station #101, located to the north of these three stations had a concentration of 187 ppm and the next station in the Bay, #98, had a concentration of 162 ppm. Sediments measured from sampling stations within the pockmark field all had consistently high concentrations except for stations #33 (161 ppm) and #14 (178 ppm). The remaining stations had greater abundances: #09 (101 ppm), #10 (221 ppm), #03 (206 ppm), #04 (200 ppm), #25 (223 ppm), #28 (231 ppm), #37 (204 ppm), #30 (216 ppm), #32 (230 ppm) and #01 (241 ppm). Station #11, which was located nearby, but away from the pockmark field, had a lower Sc concentration of 204 ppm. At sampling station #97 no Sc was detected. Overall Sc distribution and concentration patterns throughout the bay varied. Concentrations were marginally higher in sediments taken from the pockmark field and this could probably be due to the higher clay content in these samples as Sc has a tendency to associate with clay. Studies undertaken in Serres, France determined Sc concentrations ranges of 2 - 12 ppm in surface sediments (Müller et al., 2012). In the Adriatic Sea Sc concentrations of between 6 - 12 ppm were measured in surficial sediments (Dolenec et al., 1998). In Dublin Bay and the Western Irish Sea, recent studies measured a Sc concentration range of 0 – 145 ppm (Bauer, 2012).

### 4.1.10 Rubidium

Rb is a trace element and a member of the alkali metal group 1 of the periodic table. It has two naturally occurring isotopes ($^{85}$Rb and $^{87}$Rb) and its chemical properties are similar to the other members of the alkali metal group. It does not form
any mineral of its own, but exists in several common minerals such as mica, K-feldspar and clays in which it is a replacement for potassium (Wedepohl, 1970). Rb is relatively rare with a crustal abundance of 78 ppm and elemental abundances in metalliferous ocean sediment of 16 ppm (Fyfe, 1999).

![Figure 4.13: ODV map showing Rb concentration and distribution](image)

Figure 4.13 shows the Rb distribution pattern for the Bay. Among the first four sampling stations in the inner Bay, station #128 had the greater Rb enrichment at 57 ppm. The remaining three stations had similar concentrations: #129 (49 ppm), #103 (51 ppm) and #102 (46 ppm). The next four sampling stations, which were located centrally in the Bay, showed varying concentrations: #100 (31 ppm), #99 (42 ppm), #101 (75 ppm) and #98 (56 ppm). Rb concentrations from sampling stations within the pockmark field were marginally higher, particularly in sediments from stations to the north and west of the pockmark field: #03 (88 ppm), #14 (96 ppm), #25 86
(ppm), #28 (81 ppm), #37 (85 ppm), #32 (89 ppm) and #30 (86 ppm). The remaining stations within the pockmark field had the following concentrations: #10 (83 ppm), #04 (83 ppm), #33 (75 ppm), #09 (55 ppm) and station #01 (81 ppm). Station #11, which was located nearby, but away from the pockmark field, had an Rb concentration of 81 ppm. Station #97 located at the outer Bay area had a concentration of 74 ppm. Rb is a relatively rare element and its distribution and concentration patterns throughout the bay vary. Like Sc, Rb concentrations are marginally higher is sediments taken from the pockmark field and this could due to the higher clay content in these samples. Studies undertaken in Serres, France determined Rb concentration ranges of 9 - 98 ppm in surface sediments (Müller et al., 2012). In Dublin Bay and the Western Irish Sea, recent studies measured a Rb concentration range of 13 – 47 ppm (Bauer, 2012).

4.2 Statistical Analysis of the Results Data

To evaluate the significant difference of elemental concentrations, if any, between the pockmark field (area of methane seepage) and the rest of the Bay, statistical analysis was done on the XRF results data from all the twenty-two surficial sediment samples. For this a non-parametric Mann-Whitney U Test was done on the results data (Table 4.3). This test was used to evaluate whether the medians of element concentrations differed significantly between the pockmark field and the rest of the Bay.
The statistical analysis indicated that there was no significant difference between medians in the pockmark field and the rest of the bay for Ca, Ti, Ba and Zr. Statistical analysis showed that there was significant concentration differences between the two areas for Fe, Sr, Mn, Sc and Rb.

### 4.3 Discussion

Marine sediments consist of highly fractionated crustal materials brought to the ocean from a number of different sources (Calvert, 1976). The composition of near-shore sediments in particular is largely determined by the lithology of the adjoining catchment area (Karageorgis et al., 2004). Specific factors influencing elemental concentration and spatial distribution patterns in coastal areas include, element transfer from land to sea, particle size effects, transportation effect of coastal sediments by ocean currents and tidal flows, early diagenetic processes,

<table>
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<th>Element</th>
<th>P-value</th>
<th>Median (ppm) Pockmark Field</th>
<th>Median (ppm) Rest of Bay</th>
<th>Difference between areas</th>
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<td>53.63</td>
<td>significantly different</td>
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</table>

*Table 4.3: A summary of statistical analysis results comparing element concentration medians between the Pockmark Field (seepage area) and the Rest of the Bay using a non-parametric Mann-Whitney U Test (Statistical Consulting Unit, UL)*
weathering/erosion of underlying rocks, biogenic components such as shell fragments etc. and contamination caused by human activity (Ohta and Imai, 2011).

Old Red Sandstone and limestone are the dominant rock types in the Dunmanus Bay area (Naylor 1975). The soils in the local catchment area include podzols, brown podzolics, gleys, lithosols and to a lesser extent peat. Podzols are formed by the leaching of nutrients from the surface and is usually accompanied by the translocation of finer particles to subsurface layers. Brown podzolics are similar to podsols and are formed under the podzolisation process. Gleys are soils with poor drainage mainly due to a high clay content and are associated with shale and sandstone. Lithosols are thin stony soils usually overlying solid or shattered bedrock and are found in coastal areas. Peats are characterised by high organic matter content (Fay et al., 2007). There is high rainfall in this region along the southwest coast of Ireland. The mean annual rainfall is in excess of 2000mm (Met Eireann 1981-2010). Particle size analyses and sediment characteristics for the Bay indicate sediments are mainly sands mixed with finer fractions, with the pockmark area having a higher mud/clay fraction.

4.4 Major Elements

The major element geochemistry in sediments is often used to determine origin because they tend to reflect the source rock composition (Al-Juboury and Al-Hadidy, 2009; Armstrong-Altrin et al., 2015). The major elements analysed in this study were calcium, iron, titanium and strontium. Statistical analysis of the XRF results for these major elements indicated that for Ca and Ti there was no significant difference between element concentrations medians in the pockmark field compared
Ca was determined to be a main component in the surficial sediments analysed. It was high throughout the bay with a range of 106824 – 190410 ppm. In terms of spatial distribution, there appeared to be no strong link between Ca concentrations and particle size or sediment type. Statistical analysis of the results data indicated that there was no significant difference in concentrations between the pockmark field and the rest of the Bay (Table 4.3). The median concentration among sampling stations within the pockmark field was 156745 ppm, with station #9 in the pockmark field having the highest total at 190410 ppm. This could be due to an association with various minerals in the finer silt/clay. The median Ca concentration for the rest of the Bay was 148873 ppm. Concentrations of Ca especially in shallow water coastal areas are usually considerably higher than the adjoining catchment landmass due to the higher contents of biogenic materials like shells etc. Due to these high levels of calcareous materials it is sometimes difficult to determine the actual terrigenous input in Ca input in coastal sediments (Ohta and Imai, 2011). Ca concentrations measured in the soils of the local catchment area are less than 3000 ppm and in this region these levels in soils are usually associated with Old Red Sandstones (Fay et al., 2007), so the high Ca abundances in the marine sediments appear to be highly influenced the biogenic input.

XRF results data also indicated that Fe was present in high concentrations in all samples analysed. It was high throughout the bay with a range of 7675 – 22581 ppm. Fe concentrations measured in the soils of the local catchment area range from
15000 – 25000 ppm and these levels in soils are usually associated with fine sandstones and shales (Fay et al., 2007). In terms of spatial distribution trends, Fe concentrations generally increased from the near-shore towards the outer Bay and were associated with all sediment type. Statistical analysis of the results data indicated that there was significant difference in Fe concentrations between the pockmark field and the rest of the Bay (Table 4.3). The median concentration among sampling stations within the pockmark field was 17550 ppm while the median Fe concentration for the rest of the Bay was 11707 ppm. This could be due to an association with the finer particles in the sediments from the pockmark area which had higher concentrations of clay and silt. Sediments in the rest of the Bay had a higher sand content. In their study of bottom sediments in Matagorda Bay in Texas, McGowen et al (1979) determined that higher Fe concentrations occurred almost exclusively in mud dominated areas of the Bay. Similarly, Rubio et al (2000) while researching the geochemistry of major and trace elements on sediments in the Ria de Vigo in Spain determined a greater Fe enrichment in muddy sediments compared to sandy sediments. Station #97 in the outer Bay had the highest Fe and Mn concentrations (22581 ppm and 447 ppm respectively) and it also had the highest sand content (92%). If Fe and Mn concentrations are higher in coarse and medium sands it can suggest the presence of Fe-Mn oxides. In addition Fe$^{2+}$ is easily oxidised in water and can precipitate on coarse-grains (Ohta and Imai, 2011).

Ti was present in consistent concentrations throughout the Bay and pockmark field with a range of 2146 – 3868 ppm. Statistical analysis for Ti indicated that there was no significant difference in concentrations between the pockmark field and the rest of the Bay (Table 4.3). The median Fe concentration among sampling stations
within the pockmark field was 2880 ppm and the median concentration in the rest of the Bay was 2726 ppm. Ti concentrations measured in the soils of the local catchment area range from 2500 – 3250 ppm which is above average (Fay et al., 2007). In terms of spatial distribution in the Bay, there appeared to be no obvious trends between Ti concentrations and particle size or sediment type, it was present in sand, muddy sand and sandy mud. Ti concentrations in seawater are very low (Bruland, 1983) and in marine sediments it exists mainly bonded to terrestrial materials (Goldberg and Arrhenius, 1958). Ti did have a positive correlation with Fe and Mn. Ti is a very immobile element and in the marine environment is considered to be an indicator of the terrigenous contribution in sediments (Wei et al., 2003) and its concentration could be governed by the adsorption capacity of other elements possibly Fe or Mn (McGowen et al., 1979; Karageorgis et al., 1996). Ti is usually retained in sediments due to its low solubility and its ability to be incorporated by clay minerals (Neal, 2002). Ti levels are consistent with concentrations measured in soils of the catchment area and so are probably representative of regional concentrations.

Sr concentrations had a range of 206 – 746 ppm throughout the Bay and pockmark field. In terms of spatial distribution patterns, there appeared to be no strong link between Sr concentrations and particle size or sediment type. Higher Sr concentration values though do seem to follow similar distribution patterns as Ca. These trends in Ca and Sr tend to be due to their geochemical similarities (Shankar et al., 1987) and this correlation could indicate that the majority of Sr in sediments could occur in a carbonate lattice (Lepland, 2001). Statistical analysis indicated that there was significant difference in concentrations between the pockmark field and the
rest of the Bay (Table 4.3). The median concentration among sampling stations within the pockmark field was 656 ppm, with station #9 in the pockmark field having the highest total at 746 ppm. The median Sr concentration for the rest of the Bay was 480 ppm. Sr is known to be present in seawater and to exist in marine algae and mollusc shells (Turekian, 1964; Bowen, 1956). Sr distribution can also be controlled by the presence of biogenic carbonate minerals that make up the shells of foraminifera and coccoliths (Stueber, 1978; Calvert et al., 1993; Rubio et al., 2000). The Sr concentration ranges in Dunmanus Bay are similar to concentrations measured in studies in Serres, France (Müller, 2012) and in the Adriatic Sea (Dolenec et al., 1998). In deep-sea cores analysed by Turekian (1964) a Sr range of 93 – 475 ppm was measured in sediment samples containing less the 20% CaCO₃. We know from the top core samples of the vibrocores that samples in Dunmanus Bay contain ~ 20% CaCO₃ thus the near-shore samples analysed in Dunmanus Bay appear to have higher Sr concentrations. Sr concentration in soils in the local catchment area are low with a range from 30 – 45 ppm (Fay et al., 2007).

4.5 Trace Elements

In marine sediments trace elements are supplied from terrestrial sources such as rivers and streams, drainage from adjacent landmass, biological activity within the ocean and from ocean bottom waters (Müller, 2012). Concentrations of these elements reflect the range of activity of chemical, oceanographic and sedimentary controls as to their origins, distribution and removal from the ocean (Calvert and Pederson, 1993). Particle size, carbonate content and organic matter content are important factors which control the concentration and distribution of trace metals in
sediments (Rubio et al., 2000). Due in part to the high specific surface of smaller particles fine-grained sediments tend to have relatively high metal contents. This enrichment is mainly the result of surface adsorption and ionic attraction (McCave, 1984; Horowitz and Elrick, 1987). Trace elements may be incorporated into minerals by, sorption onto growing crystal surfaces, impurities such as fluid or mineral inclusions or by solid-solution substitution for a major element that is an essential structural constituent (i.e. lattice component) of the mineral (McIntire, 1964; Sun and Hanson, 1975; Banner, 1995). The trace elements analysed in this study were Ba, Mn, Zr, Sc and Rb. Statistical analysis of the XRF results for these elements indicated that for Ba and Zr there was no significant difference between element concentrations medians in the pockmark field compared to the rest of the Bay while statistical analysis also indicated that there was a significant difference between the two areas for Mn, Sc and Rb (Table 4.3).

Except for station #97 (61 ppm), Ba was present in relatively consistent concentrations throughout the Bay and pockmark field with a range of 293 ppm – 359 ppm. Statistical analysis indicated that there was no significant difference in concentrations between the pockmark field and the rest of the Bay (Table 4.3). The median concentration among sampling stations within the pockmark field was 314 ppm while the median concentration in the rest of the Bay was 321 ppm. Ba concentrations measured in the soils of the local catchment area are in a range of 325 – 400 ppm for the southern landmass of the Bay and 250 – 325 on the northern landmass and on a national level the surrounding catchment area of the Bay has a high concentration of Ba (Fay et al., 2007). In terms of spatial distribution in the Bay itself, there appears to be no obvious trends between Ba concentrations and particle
size or sediment type. Loring (1979) looked at metal baseline levels in sediment in the Bay of Fundy (UK). He looked at Ba concentrations in terms of grain size and measured Ba concentrations as follows on sand (300 ppm), muddy sand (290 ppm), very muddy sand (310 ppm), sandy mud (350 ppm) and mud (400). The average Ba concentrations for the Bay of Fundy were 310 ppm. He concluded that Ba showed only slight variation with grain size. Sediments concentrations for Ba in Dunmanus Bay are similar to regional concentrations measured in soils.

There were some variations in Mn concentrations throughout the Bay and pockmark field with a range of 115 – 447 ppm. This was confirmed by statistical analysis which indicated that there was significant difference in concentrations between the pockmark field and the rest of the Bay (Table 4.3). The median concentration among sampling stations within the pockmark field was 259 ppm and the median concentration in the rest of the Bay was 186 ppm. Mn concentrations measured in the soils of the local catchment area are in a range of 500 – 1100 ppm (Fay et al., 2007). In terms of spatial distribution, Mn concentrations appears to be associated with all sediment type and there was a positive correlation with Fe and Ti. The increased Mn concentrations in the pockmark field are probably due to an increased association with the finer particles in these sediments. Early diagenetic processes and organic matter can elevate Mn concentrations in sediments dominated by silt and clay fractions (Ohta and Imai, 2011). Mn is primarily delivered to marine environments by external sources such as physical weathering, erosion of rocks and by fluvial and aeolian transport which all lead to increased Mn concentrations in surface waters (Müller, 2012). Other sources for Mn input include remobilisation of Mn from sediments and hydrothermal flux. The high solubility of Mn$^{2+}$ from
sediments deposited under reducing conditions may result in Mn being depleted in the sediments if incorporation into carbonate minerals does not occur (Hild and Brumsack, 1998). Mn redox cycling can play an important role in trace-metal enrichment in suboxic-anoxic environments because it can initiate or accelerate the transfer of trace elements from seawater to sediments and can also trigger the diagenetic remobilisation of trace elements within the sediment (Morford and Emerson, 1999; Tribovillard et al., 2006). Station #97 had the highest Mn concentration at 447 ppm, which also had the highest Fe concentration. If Fe and Mn concentrations are higher in coarse and medium sands it can indicate the presence of Fe-Mn oxides. In addition Mn$^{2+}$ and Fe$^{2+}$ are easily oxidised in water and can precipitate on coarse grains. Mn can be enriched in both coarse sand and very fine sediments containing silt and clay (Ohta and Imai, 2011). Rubio et al (2000) while researching the geochemistry of major and trace elements in sediments in the Ria de Vigo in Spain found Mn to be marginally more enriched in muddy sediments compared to sandy sediments.

Zr was present in reasonably consistent concentrations throughout the Bay and pockmark field, though with some variation between some stations. The overall range was between 153 – 331 ppm. Statistical analysis indicated that there was no significant difference in concentrations between the pockmark field and the rest of the Bay (Table 4.3). The median concentration among sampling stations within the pockmark field was 273 ppm and the median concentration in the rest of the Bay was 231 ppm. Spatial distribution patterns showed a slight tendency towards an association with finer particles. For example, station #28 in the pockmark field had a concentration of 331 ppm. Sediment characteristic for this station showed a high silt
and clay concentration at 82%, with sand making up the remaining 18%. Weathering and erosion processes provide the major source of metals in seawater and this is probably the major source of Zr in seawater (Pettke et al., 2002). Random distribution of Zr that does not seem to correlate with any major elements can indicate its occurrence in accessory minerals, such as in detrital zircon crystals (Lepland, 2001). However, the resistance of the mineral zircon, if present, to physical and chemical weathering and adsorption onto particle surfaces results in very low levels of Zr in seawater (e.g Suhas et al., 2012 and references therein). There is little knowledge regarding the processes affecting the distribution of Zr during authigenic mineral phase formation and their soluble salts in sediments. This is due to the presence of a wide variety of detrital minerals associated with authigenic phases such as Mg-rich calcite, dolomite and soluble salts. Identifying the mechanisms that allow the accumulation of Zr in sediments would require a detailed knowledge of the mineralogical composition present as well as knowledge of the microbial activity taking place (Censi et al., 2014).

Statistical analysis for Sc indicated that there was significant difference in concentrations between the pockmark field and the rest of the Bay (Table 4.3). The median concentration among sampling stations within the pockmark field was 211 ppm and the median concentration in the rest of the Bay is 140 ppm. Outside the pockmark field concentrations were not consistent with some stations indicating no Sc present. Spatial distribution patterns showed a definite tendency towards an association with the finer particle sediments in the pockmark field. Sc concentrations measured in the soils of the local catchment area are in a range of 8 – 10 ppm and these levels in soils are usually associated with sandstones and shales (Fay et al.,
Sc concentration in seawater is very low (Bruland, 1983) and it is proposed that Sc is mostly bonded to terrestrial materials in marine sediments (Goldberg and Arrhenius, 1958). Boust and Mauviel (1984), studied near surface sediments in deep water on the Cape Verde abyssal plain, NE Atlantic and associated an Sc enrichment with finer particles in sediments which contained less quartz. Sc is regarded as a highly compatible element and it seems not to favour any specific minerals in clastic sediments (Taylor and McLennon, 1985).

Rb was present in relatively consistent concentrations throughout the Bay and pockmark field with a range of 31 – 96 ppm. Statistical analysis indicated that there was significant difference in concentrations between the pockmark field and the rest of the Bay (Table 4.3). The median concentration among sampling stations within the pockmark field was 84 ppm and the median concentration in the rest of the Bay was 54 ppm. Rb concentrations were generally higher in the pockmark field with spatial distribution patterns displaying a definite tendency towards an association with the finer particles in the sediments here. Rb and K are closely linked in most types of marine sediment. The marginal increase in Rb in the pockmark field could be because it is possible that Rb can substitute for K is some clay minerals (Wedepohl, 1970; Bazzi, 2014). Rb concentrations measured in the soils of the local catchment area range from of 60 – 80 ppm on the northern landmass of the Bay and range from 80 – 100 pm in the southern landmass and these levels in soils are usually associated with sandstones and shales (Fay et al., 2007).

The analytical techniques used in this study, specifically XRF could also be used to analyse sediments located in bays in areas of high human population and
industrial activity. Coastal areas, especially inner bays, are often severely damaged by anthropogenic activities when large amounts of trace metals enter coastal environments every year as contaminants from anthropogenic-related processes such as untreated industrial wastewater, sewage effluent, mining and surface run-off etc. Analytical techniques like XRF and SEM-EDS could determine levels of concentration of various trace metals which could provide an insight into the level of contamination of a specific coastal environment, as well as possibly determining the major source of contamination. XRF can identify heavy metals such as lead, copper, iron etc. Results data of heavy metal concentrations measured could provide import geochemical information which could be used to identify and monitor contamination levels (Rubio, et al., 2000; Álvarez-Iglesias and Rubio, 2007).

4.6 Conclusion

This study of the distribution and concentration of major and trace elements in surficial sediments from Dunmanus Bay show that these elements are strongly influenced by the geology of the catchment area and biogenic components in the sea. Their concentration and distribution patterns may be further influenced by morphological characteristics of the seabed, local hydrological conditions and anthropogenic impact. Particle size analyses and sediment type from the Bay indicate sediments are mainly sands mixed with finer fractions, with a higher concentration of silt and clay in sediments from the pockmark field. The concentration and spatial distribution patterns of major elements (Ca, Fe, Ti, Sr) and trace elements (Ba, Mn, Zr, Sc, Rb) suggest that all were associated with all sediment types. Levels of concentration of Fe, Ti and Ba were broadly similar to levels in the soils in the
surrounding landmass. Ca concentrations were high throughout the Bay, suggesting a large biogenic influence in the sediment. Sr followed similar trends to Ca. Seawater contains high levels of Sr and also Sr can be a component of shell fragments. Mn was lower in the surficial sediments compared to regional soil concentration. The influence of methane seepage (pockmark field) on the concentration and distribution patterns of major and trace elements is specifically addressed in the statistical analysis results. Statistical analysis indicated that there was no significant difference in elemental concentrations between medians in the pockmark field and the rest of the Bay for Ca, Ti, Ba and Zr. Statistical analysis confirmed that there was significant difference in elemental concentrations between the two areas for Fe, Sr, Mn, Sc and Rb and this seems to indicate an association of these elements with the finer particles in sediments from the pockmark field.
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### Appendix 1

#### Vibrocore Downcore FP-XRF Results

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<th>VC2</th>
<th>VC87</th>
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<td>15563.25 (± 232.13 )</td>
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<td>259.46 (± 49.40)</td>
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<td>26.06 (± 2.75)</td>
<td>56.26 (± 4.20)</td>
<td>30.19 (± 3.07)</td>
</tr>
</tbody>
</table>